

Heavy metal geochemistry of contaminated fenland soils in NW England

By:

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Abstract

The use of peri-urban fenlands for agriculture using urban waste as manurial treatments is increasingly common worldwide, particularly in developing countries. The risk to human health from the use of these contaminated materials for crop production has been studied using two historically contaminated fenlands in NW England. The GBASE survey carried out by the British Geological Survey identified two areas of metal contaminated fenland; west of Manchester (Chat Moss) and north of Liverpool (Halsall Moss). The two areas are used for arable agriculture, and current demand for locally sourced food is increasing pressure on farmers to move to vegetable horticulture. The effect of the metal contamination on the soils and crops is of key importance to monitor any risk to the food chain.

Historical research identified the two mossland areas as contaminated with urban wastes, Halsall Moss contaminated with urban organic wastes such as manure and Chat Moss contaminated with urban organic and mineral wastes. Waste disposal on Chat Moss was carried out by the Manchester Corporation to dispose of city waste and generate farmland from the peat. During the drainage up to 1.92 Mt of waste was incorporated into the soil, representing 38% of the topsoil today.

Profiles of contaminated and control sites on Chat Moss and a contaminated site on Halsall Moss were collected, with pH, organic matter content and trace metal content measured. Trace metal content was elevated over subsoil levels in the topsoil of all sites, for example arsenic showed topsoil concentrations of 45 mg kg^{-1} in the most contaminated site (CM-3) compared to 3 mg kg^{-1} in the subsoil. The elevation of

trace metals in the historically uncontaminated sites indicated possible atmospheric deposition of metals at the control site. Contamination levels were found to be less than originally identified in the GBASE survey, possibly due to differing sample preparation methods and survey size. The GBASE survey measured an average lead concentration in contaminated sites of 1985 mg kg^{-1} compared to 378 mg kg^{-1} measured by the current study. Arsenic and cadmium concentrations exceeded Soil Guideline Values in the most contaminated site, 43 mg kg^{-1} and 1.8 mg kg^{-1} respectively, but all other metals were within guideline limits. Halsall Moss was found to be less contaminated than Chat Moss, due to the mainly organic nature of the waste disposed at Halsall Moss.

The mobility and fractionation of the contamination at the most contaminated site on Chat Moss were studied to understand the behaviour of the metals and assess potential risk to ecological or human health. Using sequential extractions, most metals were identified as hosted by organic, Fe/Mn oxide or residual phases. There was no difference observed in fractionation between control and contaminated sites, indicating that soil properties such as organic matter and Fe/Mn oxide content were more important in controlling fractionation than the source of metals. A comparison of Chat Moss with three soils of known contamination history also identified soil properties as key in controlling fractionation.

Lability of Pb in the contaminated Chat Moss soil was assessed using ^{204}Pb stable isotope dilution, it was found that 65% of lead was labile. This was the highest out of the four soils studied, and again most likely controlled by soil properties such as organic matter content and pH. The impact of flooding events on the Chat Moss

soils was assessed, and it was found that under redox conditions of ~ 200 mV, large quantities of arsenic, lead, molybdenum and manganese were released to soil solution, and drinking water limits for these metals were violated, for example As solution concentration reached $308 \mu\text{g L}^{-1}$ and the drinking water limit is $10 \mu\text{g L}^{-1}$. Environmental quality standards for freshwater were also violated by arsenic, copper, lead and zinc showing potential ecological hazard under these reducing conditions, with lead concentrations reaching $137 \mu\text{g L}^{-1}$ in contrast to the environmental quality standard of $4 - 20 \mu\text{g L}^{-1}$.

The effect of soil contamination on vegetables grown on Chat Moss was also investigated, EU limits for Cd were exceeded by lettuce and onion, and EU limits for Pb were exceeded by parsley, carrot, radish and onion. Hazard Quotients used to assess the impact of plant contamination in the context of human intake showed that only cadmium and molybdenum were potentially hazardous. Thus it is not recommended to grow lettuce (high Cd), parsley, cabbage, radish and onion (all high molybdenum) at contaminated sites on Chat Moss. To minimise risk, conducting liming to raise the pH and immobilise the metals could be used, and careful selection of cultivars that do not accumulate metals is recommended.

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DEDICATION

I dedicate this to my husband Brian.

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Chapter 1: General Introduction

1.1 Project background

Peri-urban agriculture is commonly used worldwide as a foodsource. The proximity to urban centres often results in contamination of the soil and plant materials. A major source of contaminants is the use of urban wastes as soil improving materials, a practice which was common in past years in the UK. Developing countries are increasingly using urban wastes as manurial materials, and through the study of historically contaminated regions in the UK implications of peri-urban agriculture to human health can begin to be assessed. The areas of Chat and Halsall Moss in the north west of England were mapped in the 1980's by the British Geological Survey as part of the National Geochemical Baseline Survey of the Environment (GBASE) project. This ongoing project aims to map the geochemistry of soils, stream waters and stream sediments in Britain. The soil survey, mapping on a 2 km grid with one aggregate sample per grid square, identified apparently elevated levels of heavy metals in the soils of Chat and Halsall Mosses (Figure 1.1). The samples comprised stream sediments and topsoil. The handling and processing protocol for the samples was developed from earlier protocols for stream sediment sampling. Once collected, samples were air-dried and sieved to 150 μm (Breward, 2003), before digestions and analysis for trace element content.

Highly localised hotspots of several trace elements (shown as white areas in Figure 1.1) were identified on both mosses, and combined with the peri-urban location of the sites there was interest in a further more detailed examination of the apparent

hotspots. The GBASE survey shows the potential spatial variability in the trace elements, but nothing was known of the depth profile, or the nature of the contamination. The origin of the contamination was also of interest, as preliminary research highlighted urban wastes were incorporated into the mosses during land drainage and improvement schemes. This mirrors practices still occurring today in many areas of the world, and by studying the long-term impact of urban waste incorporation into Chat and Halsall mosses the potential impact of these practices on the long term health and fertility of soils can be better understood. This study therefore investigated the historic metal contamination of the two mosses, as well as thoroughly assessing the soil properties such as pH, organic matter content, and metal properties such as fractionation and solubility. This was combined to study plant uptake of metals in respect to modern farming practices.

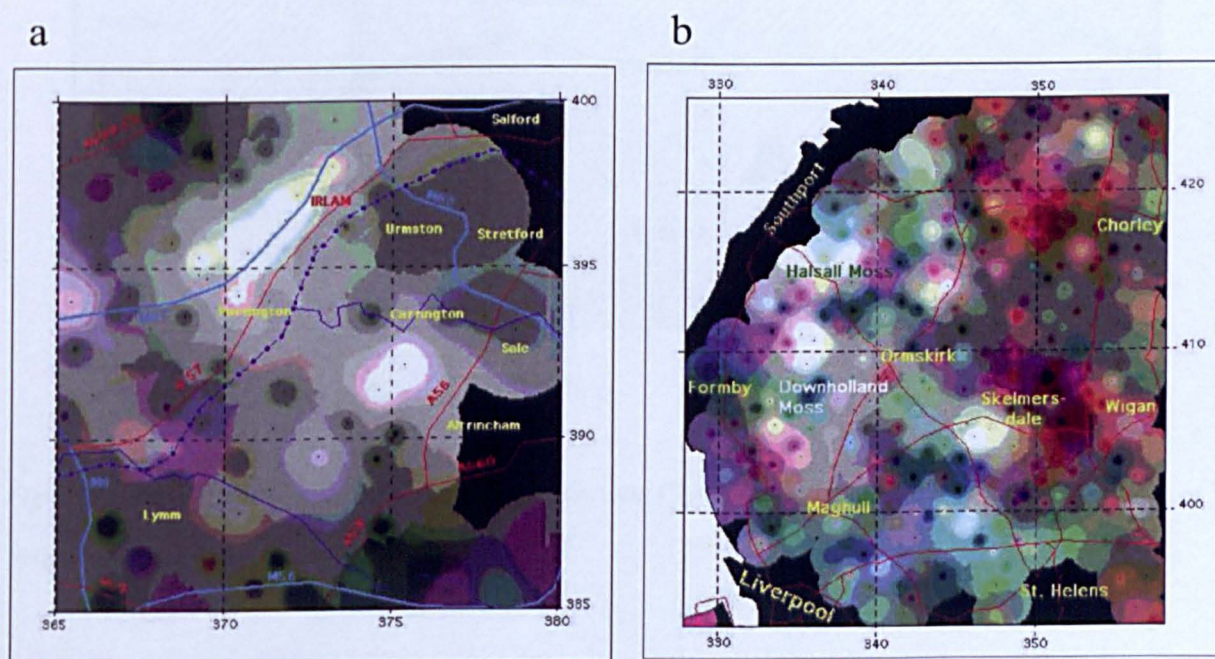


Figure 1.1: Geochemical three component maps of Chat (a) and Halsall (b) Mosses. Each element is shown as a different colour (Pb = green, Cu = red and Zn = blue). Where levels of all three elements are elevated at the same location these colours are merged to give a white colour. Images courtesy of N. Breward.

1.2 Incorporation of urban waste into the mosses.

1.2.1 Chat Moss

Chat Moss is an area of reclaimed peat mossland situated to the west of Manchester (Figure 1.2). The peat forms a low plateau lying 2.5 – 5.0 m above the surrounding landscape (Hall *et al.*, 1995), and 20 m above sea level.

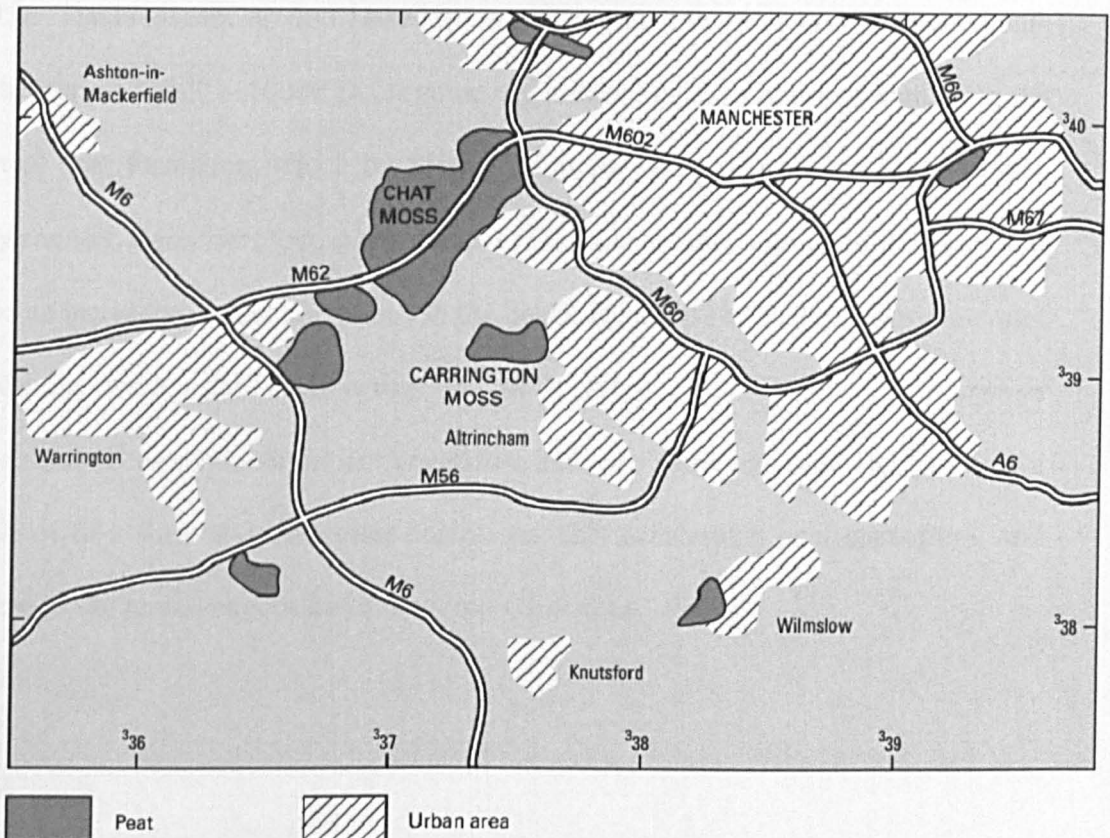


Figure 1.2: Peat deposits surrounding Manchester showing Chat and Carrington Moss, mapped from British Geological Survey DigMap 50K.

The area was reclaimed during the late 19th Century for food production and today arable farming remains the predominant land use, with wheat, potatoes and vegetables being the main crops. In some areas peat extraction takes place. The drainage ditches originally created during reclamation remain visible (Plate 1.1).

1.2.1.1 Geology and evolution of the moss

The bedrock of the entire Chat Moss area is comprised of Permo-Triassic sandstone and mudstone of the Sherwood Sandstone and Mercia Mudstone groups. The basin can be dated to 12000 BC using radiometric dating of the earliest mineral deposits of Upper Boulder Clay derived from the glaciation which affected the area, and left glacial outwash sands and gravels deposited over Boulder Clay terraces (Hall *et al.*, 1995). The landscape around 12000 BC was dominated by birch and pine woodland. In the period 10500 – 10000 BC organic deposition began in hollows, signalling the start of peat formation, which by 8500 – 7500 BC was widespread. Brushwoods, *Polytrichum*, *Aulacomnium palustre* and *Eriophorum* species dominate the peat, and indicate increasingly wet conditions in the basin. By 6000 BC true ombotrophic mire conditions were established across the moss (Hall *et al.*, 1995). *Sphagnum imbricatum* became the dominant vegetation between 1700 and 1400 BC, possibly a result of to a shift to even wetter conditions, that accelerated peat deposition, and increased the lateral expansion of the moss (Hall *et al.*, 1995).



Plate 1.1: Drainage ditch along the perimeter of a ploughed field.

1.2.1.2 Drainage and reclamation

Census data from the early 19th Century shows that the population of Manchester rapidly increased from 75,000 to 303,000 over a period of fifty years (<http://www.manchester2002-uk.com/history/victorian/Victorian1.html>) (Figure 1.3), increasing the demand for locally sourced food and land on which to produce it.

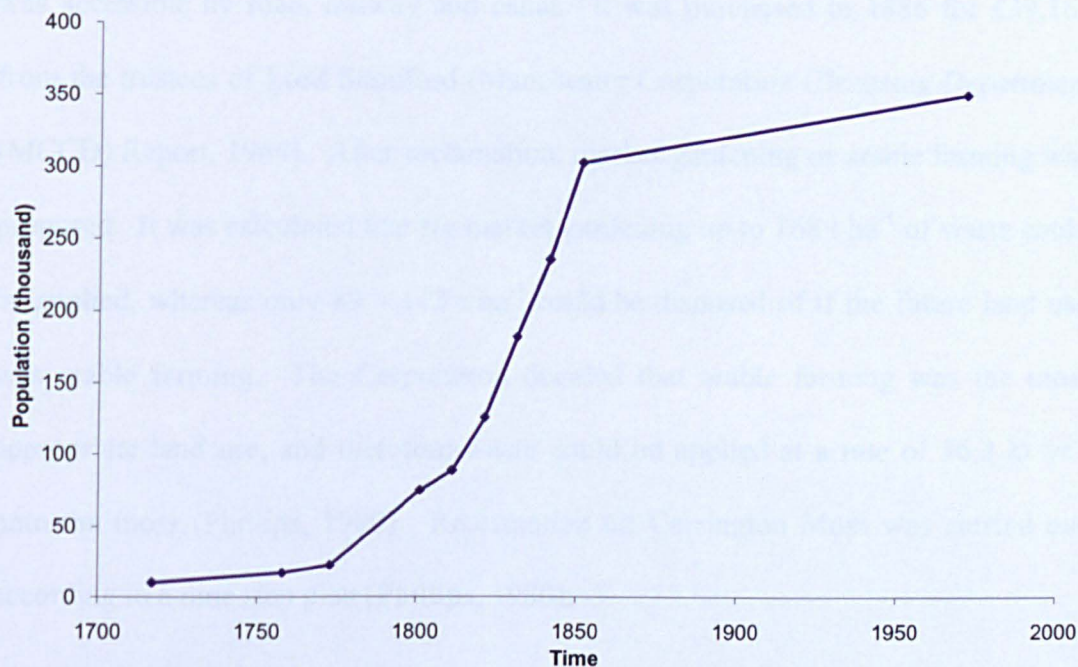


Figure 1.3: Recorded population increase in Manchester between 1700 and 1971, census information.

Increasingly large volumes of waste were being generated, the traditional disposal method was becoming unsustainable. In 1883 it was recommended by the cleansing superintendent for Manchester, Henry Whiley, that city refuse should be sent daily to a “location distant from the city” (Phillips, 1980). It was proposed that the dual problems of waste disposal and the demand for agricultural land could be solved by reclaiming the local peat bogs using the waste as a bulking-up material and agricultural manure as the bogs were drained. When looking for a suitable site for reclamation and waste disposal, the requirement was for a large area of land close to

the city and preferably with good transport links. Five locations were considered as suitable trial sites; Astley, Barton, Carrington, Irlam and Worsley Mosses (Phillips, 1980).

Carrington Moss, to the south of Chat Moss, was chosen for the reclamation trial as it was accessible by road, railway and canal. It was purchased in 1886 for £39,165 from the trustees of Lord Stamford (Manchester Corporation Cleansing Department (MCCD) Report, 1964). After reclamation, market gardening or arable farming was proposed. It was calculated that for market gardening up to 168 t ha^{-1} of waste could be applied, whereas only $89 - 112 \text{ t ha}^{-1}$ could be disposed of if the future land use was arable farming. The Corporation decided that arable farming was the most appropriate land use, and therefore waste could be applied at a rate of 36.2 kt yr^{-1} onto the moss (Phillips, 1980). Reclamation on Carrington Moss was carried out according to a nine step plan (Phillips, 1980);

1. A central east-to-west road was built across the moss.
2. Subsidiary roads were built at 90° to the central road.
3. A $2 \frac{1}{2}$ gauge railway was built across the moss to transport refuse onto the site.
4. Rectangular fields of 3.2 ha were constructed.
5. Each field was subdivided into four 0.81 ha plots with open drains 1.22 m deep.
6. Each 0.81 ha plot was drained by split drains 3.66 m apart.
7. In fields adjoining roads, open drains 1.8 – 2.7 m deep were dug (Plate 1.2).

8. Once sufficiently drained the land was cultivated and refuse added at a rate of 134 t ha^{-1} . This is greater than the original estimate of waste application, suggesting that the original estimate was inaccurate.
9. A rotation was established in which potatoes were planted for two years, oats for one year, with clover and rye grass in the fourth and fifth years.

Between 1886 and 1890, the area of uncultivated land on Carrington Moss halved from 243 ha to 121 ha, and by 1899 the reclamation was complete with the entire moss under cultivation. A total of 58 kt of refuse had been disposed of, representing 17% of all waste produced in Manchester during this period (Phillips, 1980).



Plate 1.2: Construction of open drains using traditional peat cutting methods circa 1887. (Courtesy of the collection of Dr Phillips).

Successful reclamation at Carrington prompted the purchase in 1895 of Chat Moss by the Cleansing Committee from Sir Humphrey de Trafford for £138,969. A recent survey had shown that 58% (568 ha) of the Chat Moss estate was in an “uninhabitable” condition and suitable for reclamation (MCCD Report, 1964).

Reclamation commenced in 1899, and by 1906 the area of uncultivated moss had fallen from 304 ha to just 20 ha. A total of 611 kt of refuse was incorporated into Chat Moss between 1900 and 1910 (16% of Manchester's waste). Waste disposal also continued at Carrington Moss during this period, accounting for a further 6% of Manchester's waste. By 1964, a total of 3.1 Mt of waste had been incorporated into both mosses, 61% of which was disposed of on Chat Moss (MCCD Report, 1964).

1.2.1.3 Waste disposal practices

Manchester's waste was collected and taken to depots close to the river Irwell. From there it was transported by barge along the Manchester Ship Canal or the river to wharves at Irlam or Carrington (MCCD Report, 1964) (Plate 1.3). At the wharf waste was loaded onto railway wagons (Plate 1.4) and transported out onto the moss. Waste was then incorporated during the drainage process before cultivation commenced. Initial cultivation was by hand as the land was too boggy for horses, but as the soil dried out, the use of horse and plough became possible (Phillips, 1980).

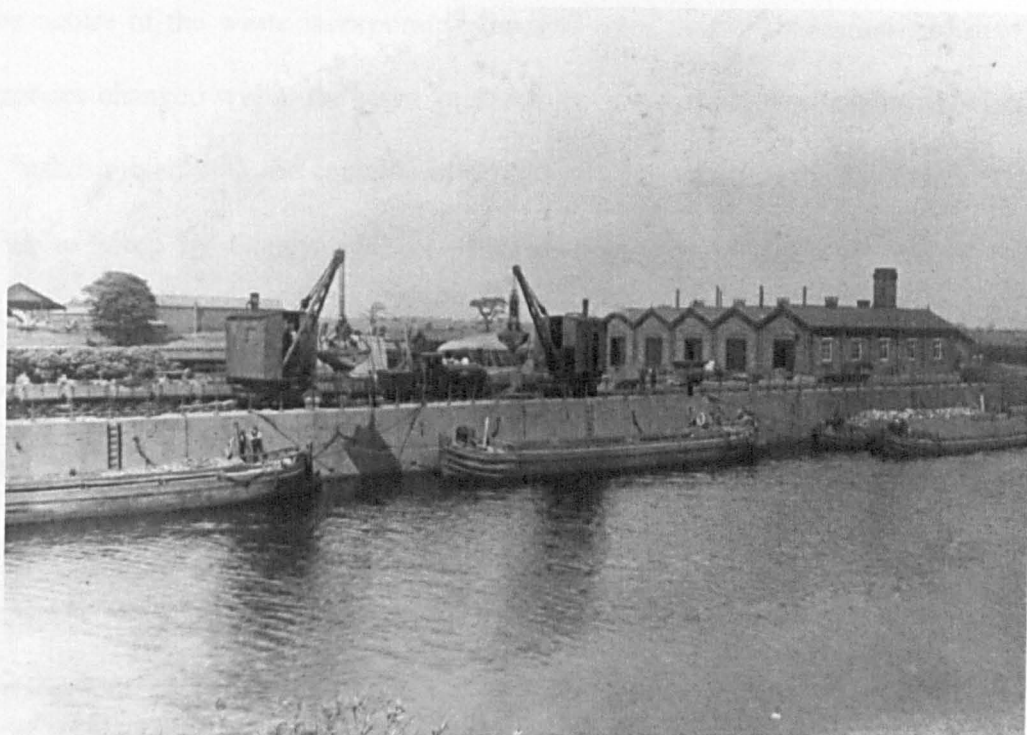


Plate 1.3: Refuse being bulk-loaded onto barges ready for shipment to the mosses (circa 1900) (courtesy of the collection of Dr Phillips).

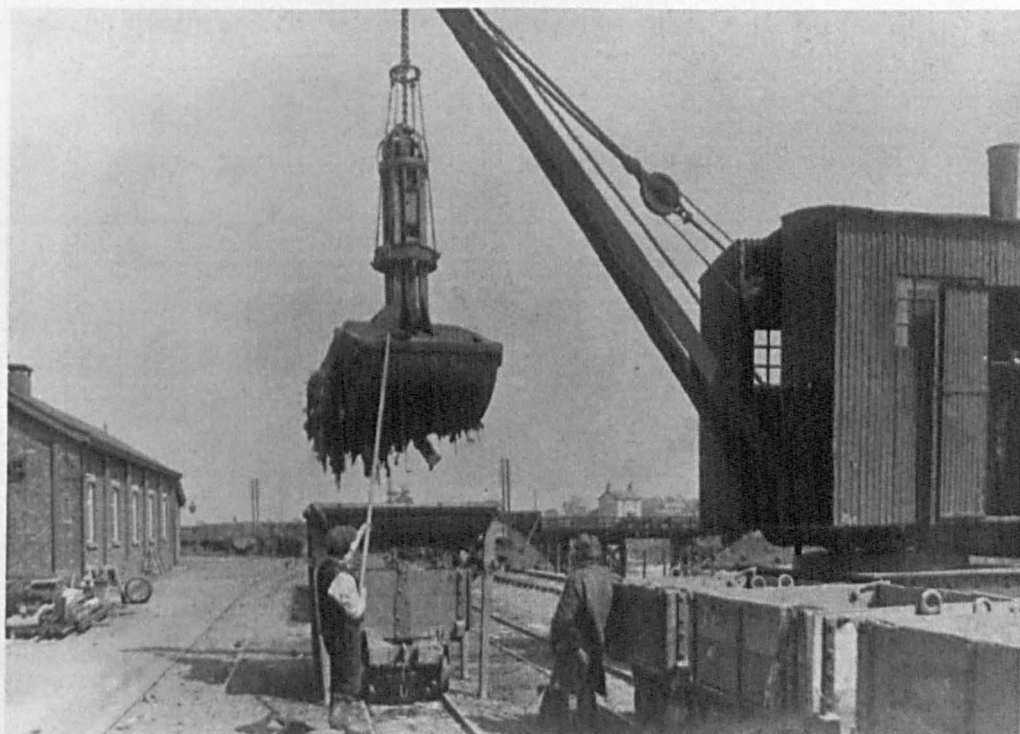


Plate 1.4: Waste being transferred from barges to railway wagons before transportation onto the moss (circa 1900) (courtesy of the collection of Dr Phillips)

The nature of the waste incorporated changed over time as sanitation and disposal practices changed within the city. In 1886, the main waste was ‘nightsoil’, defined as “ashes mixed with the contents of privies and the scrapings of the streets” (Holt, 1795 as cited by Coney, 1995). The quantity and composition of the waste incorporated into Chat Moss between 1900 and 1964 is given in Table 1.1. It was not recorded whether this was dry weight or wet weight, however the collection of waste at depots would have allowed water to drain from the waste, so it is likely to be a mixed source of dry and wet weight. Nightsoil was the dominant constituent of the waste between 1900 and 1914. After 1915 nightsoil production declined with the development of household toilet systems, and the dominant waste until ~1935 became privy midden and ashbin contents. By 1940 waste disposal at Chat Moss was reduced to mainly slaughterhouse refuse and lairage (slaughterhouse) manure as the sewage system and city tips were handling most other waste forms.

Table 1.1: Quantity and nature of refuse deposition at Chat Moss (MCCD report, 1964)

Waste material (t)	1900-1914	1915-1922	1923-1935	1936-1939	1940-1964
Night-soil	384,375	40,463	0	0	4,365
Sweepings	230,717	35,848	108,804	26,912	0
Privy midden and ashbin content	62,949	180,476	280,013	5,664	0
Garbage	20,961	10,532	38,476	10,388	0
Stable manure	3,221	2,133	92	0	0
Clinkers	102,301	36,964	77,571	21,174	508
Town’s manure	0	0	104,609	39,649	0
Dust	0	0	18,176	2,827	0
Slaughterhouse refuse	0	0	0	0	67,678
Lairage manure	0	0	0	0	6,517

Privy midden, ashbin contents, nightsoil and street sweepings comprised 71% of all the waste disposed on Chat Moss (Figure 1.4); a mixture of organic (nightsoil) and mineral wastes (street sweepings, ashbin contents). The total amount of waste

incorporated into Chat Moss exceeded that being disposed of on Carrington Moss within 15 years of waste disposal commencing at Chat Moss. (Figures 1.5 and 1.6).

1.2.2 Halsall Moss

Halsall Moss is a region of reclaimed peat moss to the north of Liverpool (Figure 1.7), and covers an area approximately three times that of Chat Moss. It is made up of many small mosses in basins separated by blown sand and till deposits, whereas Chat Moss region is one large moss and basin (Figure 1.2). The region is today used for arable farming with wheat and vegetables, especially potatoes, being the main crops.

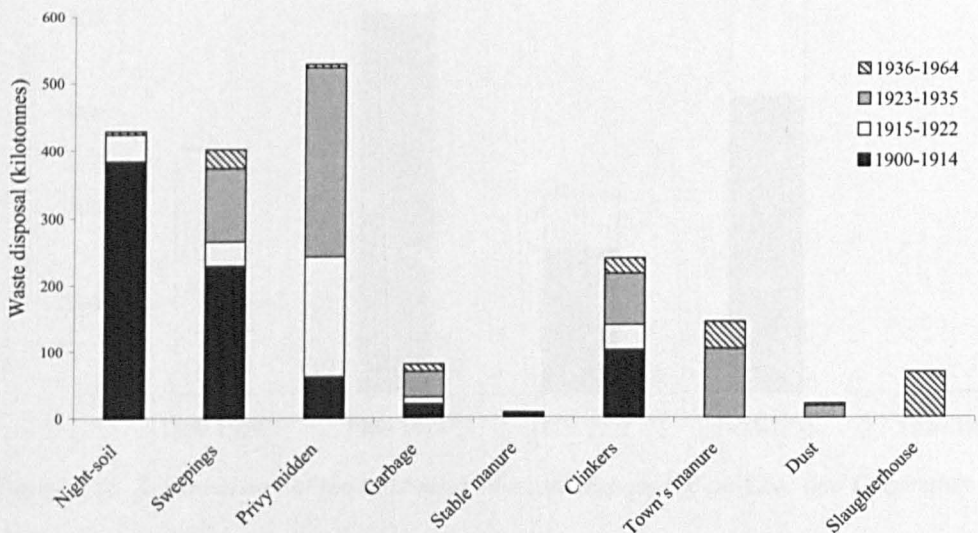


Figure 1.4: Weight of waste by type incorporated into Chat Moss between 1900 and 1964 (MCCD report, 1964)

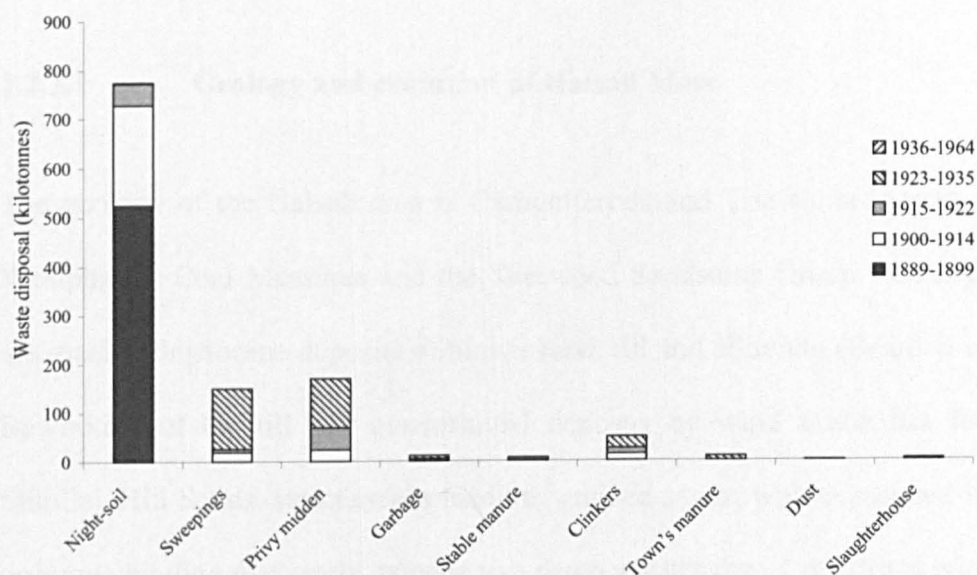


Figure 1.5: Weight of waste by type incorporated into Carrington Moss between 1889 and 1964 (MCCD report, 1964)

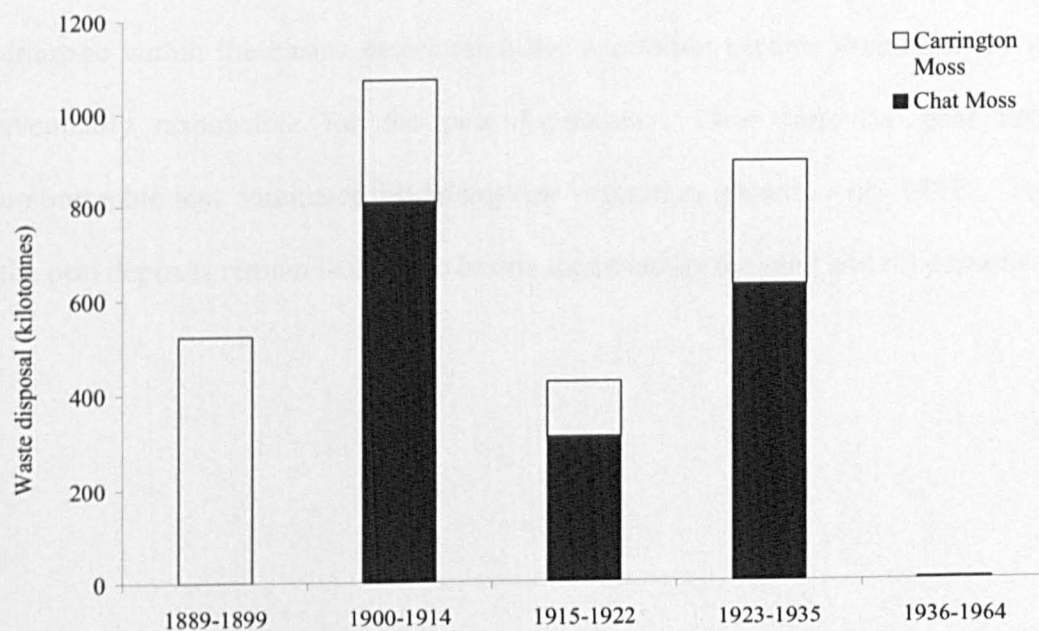


Figure 1.6: A comparison of the total mass of waste disposed of on Chat and Carrington Mosses in the period 1889 to 1964 (MCCD report, 1964)

1.2.2.1 Geology and evolution of Halsall Moss

The geology of the Halsall area is Carboniferous and Triassic sediments including Westphalian Coal Measures and the Sherwood Sandstone Group. Overlying these are glacial Pleistocene deposits of blown sand, till and alluvium (Beard *et al.*, 1987). Reworking of the till and glaciofluvial deposits by wind action has formed the Shirdley Hill Sands, structureless medium grained sands, with occasional iron oxide or humic binding that rarely extends to a depth greater than 1 m (Beard *et al.*, 1987). In basins within the sands, marine silts and clays (the Downholland Silt) were deposited. The original vegetation growing on this silt was trees and shrubs, but as drainage within the basins deteriorated the vegetation became dominated by reeds eventually responsible for the peat formation. Over time the peat became ombotrophic and dominated by *Sphagnum* vegetation (Beard *et al.*, 1987). Today, the peat deposits remain isolated in basins separated by the sand and till deposits.

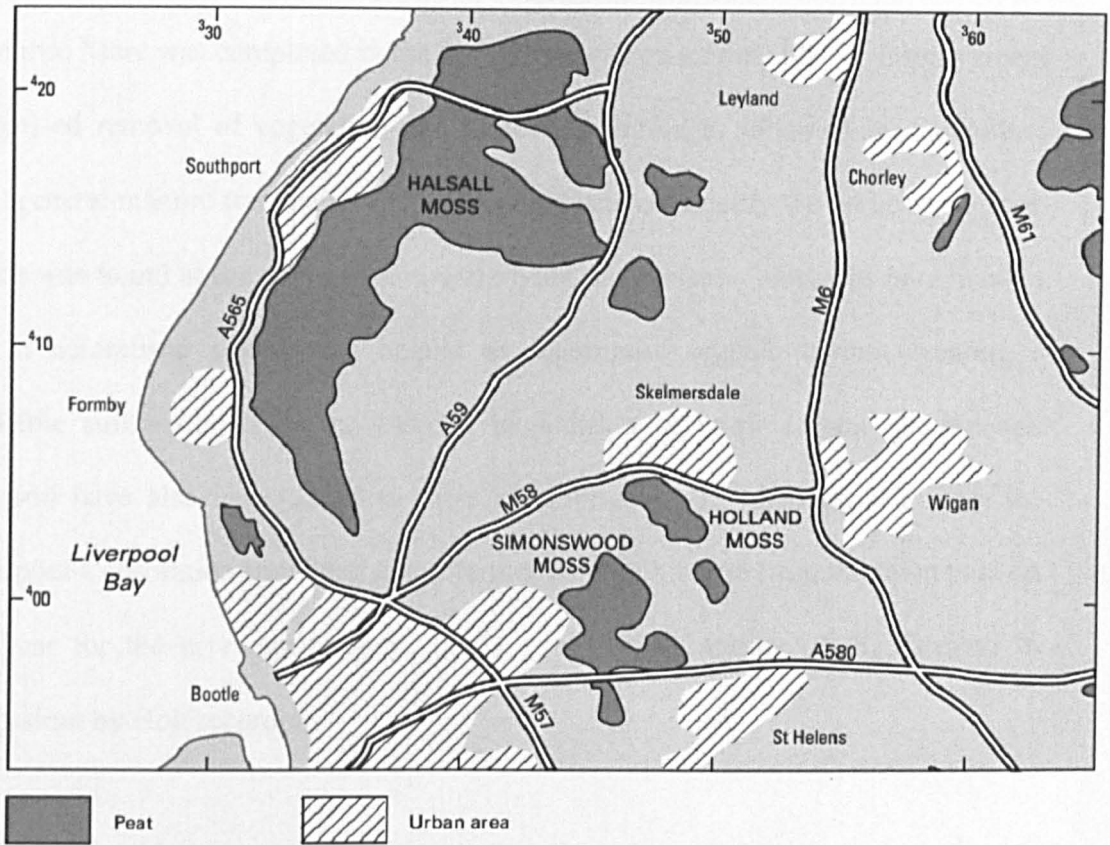


Figure 1.7: Peat deposits of the Halsall Moss region, mapped from British Geological Survey DigMap 50K.

1.2.2.2 History of waste disposal on Halsall Moss

Drainage and reclamation of the Halsall region was piecemeal compared to the organised approaches taken at Chat and Carrington (Section 1.2.2.2). Individual farmers improved their land with field drains (Rosbottom, 1987) to provide land on which to grow fresh produce to supply to the city of Liverpool. The resulting peaty podzol soils became known as “black-tops” and are found mainly around Ormskirk (Taylor, 1967). It has been recorded that by 1750 Tarlescough and Burscough Mosses in the north of the Halsall region were partially improved (Hale & Coney,

2005), and that the area surrounding Burscough remained marshy until the drainage of Martin Mere was completed in the 19th Century (Rosbottom, 1987). Improvement comprised removal of vegetation and increasing drainage, followed by cultivation and ‘general manure treatment’. This treatment was commonly the addition of marl, which was found at the edges of and underlying the mosses. Marl was beneficial in that it neutralised acidity and helped to decompose organic matter, creating a workable soil texture (Taylor, 1949). In addition to marl, animal manure and nightsoil have also been added to these soils since 1571, when records from the Liverpool Corporation show that every farmer who took waste from the town paid 6d per year for the privilege (Coney, 1995). In 1795, a survey of the farming in Lancashire by Holt recorded;

“in the memory of a worthy and experienced farmer who only died in the present year, that the first load of nightsoil brought from Liverpool towards the north was by his father, who was paid for carting away this nuisance and throwing into the river Mersey. The good effects upon the land which experience has proven dung to have, have caused it, at this period, to be sold at an advanced price, and carted to a considerable distance.” (Coney, 1995).

Nightsoil was therefore recognised as a suitable manure in the 18th century, and several farm leases from the 1790’s state that all manure, dung and compost from the farm must be laid on the land, and that the tenant must annually spread onto the holding “19 good cartloads of Liverpool dung” (Coney, 1995), further highlighting the importance of this manure. For every load of hay or straw sold off the farm, it was often required by the tenant farmer to purchase and bring back one cartload of

dung. In the 18th and 19th centuries, many farm leases contained clauses requiring two thirds of the sale of hay or straw to be expended;

“in the purchase of good natural or artificial manures to be bestowed on the premises” (Hale & Coney, 2005).

By 1845, the Liverpool Corporation was earning £1,150 per annum from the sale of town refuse, compared to only £800 earned by the Manchester Corporation for the same period (Swarbrick, 1993), where reclamation was still in its infancy.

Addition of manure to the soils of the Halsall region continued until the 1930's, when improved sanitation meant that the supply of town waste diminished (Clarke, 1990). The waste from Liverpool was less industrial in origin than that from Manchester, and restricted to nightsoil, blubber from the whaling industry and towns refuse such as soot, ashes and rags. The duration of disposal was also much longer than that on Chat Moss, lasting nearly 400 years compared to 150 years. The addition of these wastes to Chat and Halsall Mosses were likely to affect the trace metal content of the topsoils, which would also affect metal content of foodstuffs grown on the mosses, therefore an understanding of the behaviour of the metals within the soil is important.

1.3 Trace elements in soils

1.3.1 Trace element fractionation in soils

1.3.1.1 Sources of trace elements in soils

Anthropogenic activities have increased concentrations of trace elements in soils, as a result of industrialisation. Alloway (1989) defines seven categories of trace element additions to soils: atmospheric pollution from motor vehicles, combustion of fossil fuels, agricultural fertilisers and pesticides, organic manures including sewage sludge, disposal of urban and industrial wastes, metallurgical industries, and mining and smelting of non-ferrous metals.

Pollution from motor vehicles was a significant source of lead between the 1920s and 1990s as a result of addition of anti-knocking agents tetra ethyl Pb (TEL) and tetra methyl Pb (TML) to petrol. Pb contamination from vehicle exhaust emissions is observed in remote regions including the Scottish highlands (Farmer *et al.*, 2002) and peat bogs in the Swiss Alps (Weiss *et al.*, 1999a). Most industrialised countries have since the 1990s phased out leaded petrol because of concerns about the neurotoxicity of Pb. Today therefore, TEL and TML are no longer significant contributors of Pb to the environment except perhaps through redistribution of urban and roadside topsoil dust.

Coal combustion has been a significant source of trace elements (e.g. Pb, As, Cd, Ni, Se and Zn) in the UK since medieval times. In a study of UK coals, Farmer *et al.*, (1999) found an average Pb content of 18.9 mg kg⁻¹, with Scottish and Irish coals typically having twice the lead content of those from England and Wales. Coal

combustion represents 20% of anthropogenic arsenic release. Average coal consumption in the UK since 1700 is shown in Figure 1.8, with maximum coal combustion (150-200 Mt a⁻¹) between 1910 and 1970. Levels of these elements can be seen to increase significantly from 1750, the start of the Industrial Revolution.

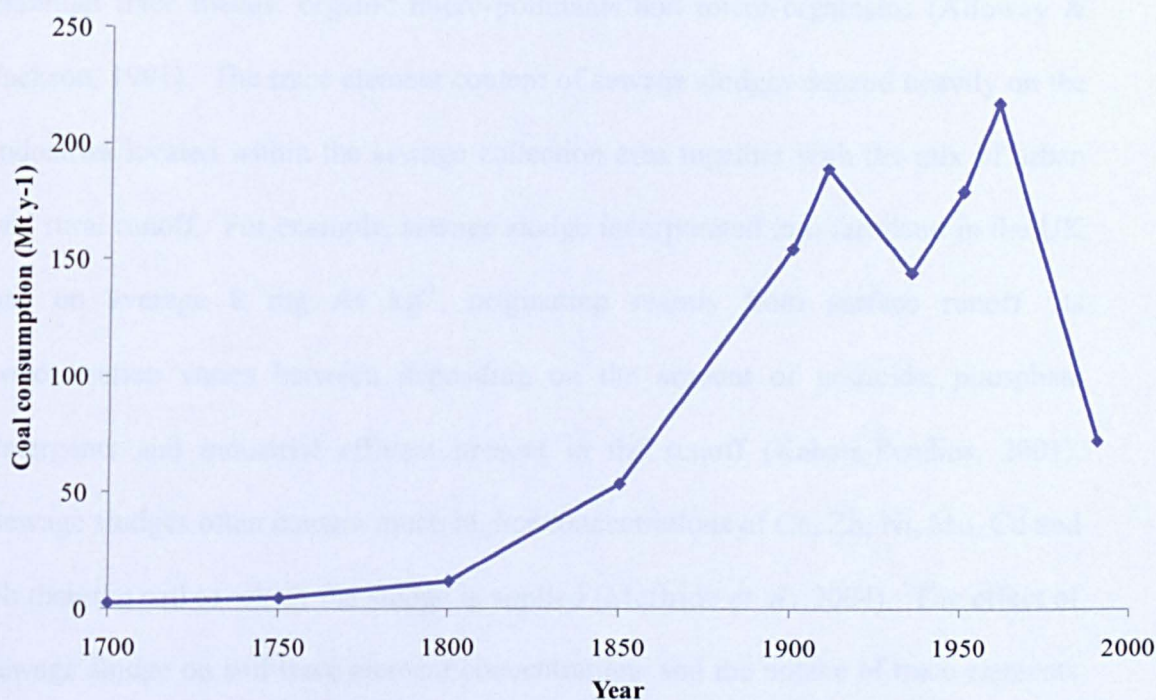


Figure 1.8: Coal consumption in the UK between 1700 and 1990. After Farmer et al., (1999)

Agricultural chemicals, including fertilisers and pesticides, have been widely used in the UK, although their use is now increasingly controlled by legislation. Arsenic was a common constituent of pesticides for over 100 years, and its worldwide use is estimated as 36,000 t As yr⁻¹ (Alloway 1989). Phosphatic fertilisers represent the most common source of Cd to agricultural soils, with Cu, Mn, Co, Ni, Se, Cr and Zn also present in agrochemicals.

Organic manures and sewage sludges have been used in the UK as soil amendments and fertilizers for hundreds of years, with manures and nightsoil having been used in

the Halsall region for 400 years (Sections 1.2.1.3 and 1.2.2.2). Sewage sludge is defined as the insoluble residue from waste water treatment after aerobic or anaerobic digestion. It typically comprises 60% organic matter, 5% CaO, 3% N, 2% P₂O₅, 1.5% MgO, and 0.5% K₂O, plus variable levels of micronutrients and non-essential trace metals, organic micro-pollutants and micro-organisms (Alloway & Jackson, 1991). The trace element content of sewage sludges depend heavily on the industries located within the sewage collection area together with the mix of urban and rural runoff. For example, sewage sludge incorporated into farmland in the UK has on average 8 mg As kg⁻¹, originating mainly from surface runoff. Its concentration varies between depending on the amount of pesticide, phosphate detergents and industrial effluent present in the runoff (Kabata-Pendias, 2001). Sewage sludges often contain much higher concentrations of Cu, Zn, Ni, Mo, Cd and Pb than the soil to which the sludge is applied (McBride *et al.*, 2004). The effect of sewage sludge on soil trace element concentrations and the uptake of trace elements by crops are therefore active areas of ongoing research (see e.g. Speir *et al.*, 2003, Alloway and Jackson, 1991, McBride *et al.*, 2004, Griffiths *et al.*, 2005, Qureshi *et al.*, 2004).

In the UK DEFRA imposes statutory limits on the concentrations of potentially toxic elements (PTEs) in topsoil that will receive sewage sludge, they also stipulate the annual amount of sludge that can be applied to a soil (Table 1.2).

Table 1.2: Permissible levels of potentially toxic elements (PTEs) contained in sewage sludge (adapted from the Code of Good Agricultural Practice for the protection of soil, MAFF, 1998)

Soil pH	Maximum permissible concentrations of potentially toxic elements (mg kg ⁻¹)			
	pH 5.0 – 5.5	pH 5.5 – 6.0	pH 6.0 – 7.0	pH >7.0
Zinc	200	200	200	300
Copper	80	100	135	200
Nickel	50	60	75	110
Soil pH 5.0 and above				
Cadmium	3			
Lead	300			
Mercury	1			
Chromium	400			
Molybdenum	4			
Selenium	3			
Arsenic	50			

Exceptions to these limits are permitted where a site (farm) has been historically used for disposal of sewage sludge by a water company. Such ‘dedicated sites’ are run under licence from DEFRA and controls are exercised over, for example, the end-use of farm produce (e.g. animal consumption only) and a soil liming policy employed. In addition, periodic geochemical surveys of the site may be required.

The source of trace elements can influence the subsequent behaviour of an element within a soil. In sewage sludge amended soils there is typically a high organic matter content, and phosphate concentration, which can help to immobilise elements added with the sludge. Iron and manganese oxides within the sludge can also bind with the sludge-borne metals (Alloway & Jackson, 1991).

Waste disposal, metallurgical and mining industries can all act as point sources of trace elements at high concentrations, but they are limited in their extent of spatial distribution. Lead, zinc, copper, arsenic and cadmium are commonly present at high levels and the release of As during the smelting of Cu ores represents the largest single anthropogenic input of As into the environment (Kabata-Pendias, 2001). Contamination from tailings, minespoil and smelter waste is usually in the form of the original ore, e.g. sulphide or oxide minerals. Trace elements in these forms are resistant to mobilisation and are often very stable in the soil environment into which the processed spoil is introduced.

1.3.1.2 Fractionation of trace elements in soils

Trace elements in soils are commonly divided into five fractions: exchangeable, carbonate, bound to organic matter, bound to Fe/Mn hydrous oxides and 'residual' – those contained within primary minerals or occluded within resistant mineral fractions (Lo & Yang, 1998). These fractions are typically operationally defined through sequential extraction procedures (see Section 1.3.2.1). The forms in which trace elements are present in a soil governs the mobility and solubility of the elements. For example, metal carbonates dissolve under acidic conditions whereas 'residual' trace elements are resistant to mobilisation under most soil conditions (see Section 1.3.1.3). The association of trace elements with soil components has been widely studied, and some typical associations have been noted, for example the high affinity of humus for Cu and the strong sorption of Co to Mn oxides (Kabata-Pendias, 2001).

1.3.1.3 The effect of soil characteristics on trace element fractionation

1.3.1.3.1 Soil pH

Soil pH is regarded as one of the most important factors controlling trace element mobility. Soils with low pH have increased trace element mobility. Rothwell *et al.*, (2005) observed that trace elements present in peatland soils are remobilised in the low pH soil solutions, and acidic groundwater increases dissolved trace element concentrations in streams draining the peats. Agricultural soil pH is modified by the addition of lime to raise the pH and this will immobilise some trace elements. Alloway & Jackson (1991) suggest that manipulation of pH is the most effective way to control the bioavailability of trace elements in sewage sludge amended soils. This concept is enshrined in the strict liming policy imposed on dedicated sludge disposal sites under DEFRA licence, the published pH ranges for trace element concentrations in soils controlled by the UK Sludge (use in agriculture) Regulations (1987), and the Environmental Agency CLEA risk assessment model.

Not all metals and metalloids exhibit increase solubility at lower pH. For example, molybdate becomes less soluble in acidic solution, and arsenate (AsO_4^{3-}) adsorbs more strongly to Fe -oxides at low pH (Hartley *et al.*, 2004). Cationic trace element solubility can also increase with pH due to complexation with soluble organic matter (humic and fulvic acids), which themselves become more soluble at higher pH (Qureshi *et al.*, 2004). Pb concentration in soil increases with increasing pH as Pb is strongly complexed with soluble organic matter (Ahlberg *et al.*, 2006). The effect of pH on Cd solubility is complex. Podar & Ramsey (2005) observed that Cd concentration in soil solution followed a 'U-shaped' pattern, with a decrease in

solubility between pH 5 and 7, and an increase between pH 7 and 8, highlighting the variable relationship with pH that Cd can have. Trace element behaviour is therefore controlled by a combination of adsorption onto Fe/Mn oxide and complexation with organic matter. At high pH values, dissolved organic matter becomes increasingly ionized, allowing for increase binding of trace elements, increasing the overall solubility of metals (Kalbitz & Wennrich, 1998). It has also been shown that oxide surfaces change from being positively charged at low pH to negatively charged at high pH, enabling increased adsorption of metal cations at high pH (Hartley *et al.*, 2004).

1.3.1.3.2 Soil organic matter content

Soil organic matter has a large adsorption capacity for trace elements (Alloway & Jackson, 1991, Ahlberg *et al.*, 2006). Grybos *et al.*, (2007) demonstrated that under reducing conditions, organic matter can act as an important sink for trace elements. As soil pH increases carboxyl groups progressively ionize and humus becomes more negatively charged, increasing the adsorptive capacity for trace element cations. Increased negative charge on mineral surfaces at high pH also means that mineral surfaces and organic matter repel each other more strongly, releasing organic matter and any bound metals into the soil solution. Grybos *et al.*, (2007) in a soil incubation experiment found that the kinetics of trace element release closely followed the release of dissolved organic matter, confirming soluble organic matter as an important trace element sink.

Strong complexation of trace elements with a soluble organic ligand will reduce sorption. Organic ligands that complex strongly with soil mineral surfaces, or exist in an independent flocculated state, can however increase ternary soil-ligand-metal complexes, and so reduce the solubility of metals. Schwab *et al.*, (2005) showed that adsorption of organic anions to soil particles increases the negative charge on the soil surfaces, and therefore increase the trace element adsorption capacity of soil. This has also been reported by Alloway & Jackson (1991) in a study of soils amended by sewage sludge, they found that the large organic matter content of sewage sludge increased the metal carrying capacity of the soil. The overall impact of organic matter on metal mobility therefore depends upon the balance between metal sorption by organic matter, adsorption onto mineral surfaces and also on the distribution of organic ligands between the solid and solution phases (Schwab *et al.*, 2005).

1.3.1.3.3 Soil redox potential

In surface soils, redox potential is controlled by rainfall, bioactivity and land use whereas in the vadose zone fluctuations in the water table are the dominant control (Ma & Dong, 2004). Changes in redox potential can affect trace element mobility as a result of changes in oxidation state, and the reduction of Fe and Mn hydrous oxides, which commonly contain trace metals within the matrix of the oxide, and so the reduction or dissolution of these oxides will release trace elements to the soil solution (Ma & Dong, 2004). Charlatchka & Cambier (1999) demonstrated that changes in pH and redox conditions have the greatest affect on the chemistry of trace element behaviour in soils, and that alternating aerobic / anaerobic conditions leads to pH and redox changes that affect the regulation of trace element speciation (See

Section 1.4.3). Typically pH rises as redox potential falls, acting to minimise trace element mobility. In experiments at constant pH where redox was reduced greater Fe/Mn and trace element solubilisation occurred demonstrating the importance of redox alone in controlling trace element mobility (Charlatchka & Cambier, 1999). Reducing conditions often develop in waterlogged soils, leading to changes in trace element solubility, even for elements that do not normally exist in different oxidation states (Contin *et al.*, 2007) because their solubility is controlled by bacterially-mediated dissolution of Fe/Mn oxyhydroxides which, as they dissolve, release sorbed ions into solution (Grybos *et al.*, 2007). Ma & Dong (2004) demonstrated the importance of Fe/Mn oxides in controlling trace element solubility under reducing conditions in a redox-controlled suspension experiment - Pb, Cd and Zn concentration increased in the soil solution as the concentration of Fe(II) increased and redox potential decreased. Under reducing conditions however, reductive Fe dissolution can expose previously unavailable sorption sites, temporarily increasing sorption capacity (Ma & Dong, 2004). Reduction of Fe(II) on hydroxide surfaces can also increase specific surface area again temporarily increasing adsorption capacity (Contin *et al.*, 2007).

1.3.1.3.4 Soil texture

Soil texture is less important than pH, redox potential and organic matter content in controlling trace element mobility, but it can influence trace element partitioning between the solid and solution phase. For example, Qureshi *et al.*, (2003) report that metals in ionic form have the greatest mobility in acidic coarse textured soils. Qureshi *et al.*, (2004) also found that for a given pH, mobility of Ni, Cd and Zn was

greater in a fine sandy loam soil than in a silt loam soil, indicating that soil texture can influence the mobility of these metals.

1.3.2 Measuring trace element fractionation in soils

1.3.2.1 Sequential extraction procedures (SEPs)

Sequential extraction procedures (SEPs) were first developed in the 1970's (Tessier *et al.*, 1979). It was recognised that the total trace element content of a soil was inadequate to assess the potential risks or impacts of trace contaminants. It was hoped that partitioning trace elements into functional fractions would provide information about the fractionation and biological or physico-chemical availability of the elements in contaminated soils. Partitioning is carried out by the application of a series of extractants which release trace elements hosted in different soil fractions. The various stages of the SEP are then used to assign operationally defined fractions to the trace elements.

Since the publication of the original method by Tessier *et al.*, (1979), sequential extractions have become widely used to identify the fractionation of metals and metalloids in a range of soils and sediments. The number of papers published since 1973 using a keyword search of “sequential extraction” and “soil”, with the results checked for relevance is shown in Figure 1.9, which indicates increasing interest in soil trace element fractionation, possibly boosted in the late 1990s following

recommendation of a “standard” method by the Bureau Communautaire de Références (BCR).

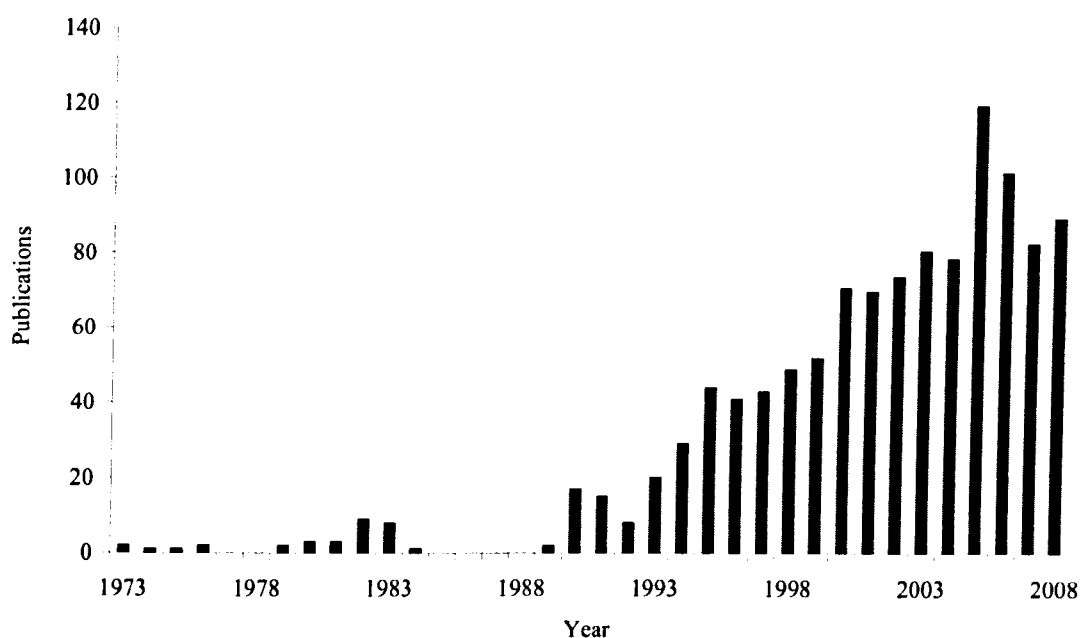


Figure 1.9: Number of publications per year using sequential extractions methods to determine trace element fractionation in soils. The keywords used in the search were “sequential extraction” and “soil” for work published between 1973 –and 2008.

Two sequential extraction schemes are now widely recognised; the 5-step “Tessier” and the 4-step “BCR” (Standards, Measurements and Testing Program of the European Commission) schemes (Table 1.3). The BCR method was developed to provide a standardised method which could be used for reference materials, combating problems of reproducibility and quality assurance (Ho & Evans, 2000). Using acid-stabilised reagents, or pH adjustment (to between 1.5 - 2.0) it was hoped that re-adsorption of trace elements onto solid phases during extraction would be reduced (Kim & McBride, 2006). This method differentiates between acid-extractable, reducible and oxidisable fractions, whereas the Tessier method includes

an additional step for extracting ‘exchangeable metal’ separately from the ‘carbonate bound fraction’ (Table 1.3).

Table 1.3: A comparison of the extraction steps used in the “Tessier” and “BCR” schemes.

Fraction	Tessier scheme		BCR scheme	
Extractable	F1	1 M MgCl ₂ , pH 7	F1	0.11 M acetic acid
Carbonate bound	F2	1 M NaOAc, pH 5		
Fe/Mn oxide bound	F3	0.04 M NH ₂ OH.HCl in 25% HOAc, pH 2	F2	0.5 M NH ₂ OH.HCl in 0.01 M HNO ₃ , pH 2
Organic matter / sulphide bound	F4	30% H ₂ O ₂ , pH 2 (HNO ₃) 0.8 M NH ₄ OAc in HNO ₃	F3	30% H ₂ O ₂ , pH 2 (HNO ₃) 1 M NH ₄ OAc, pH 2 (HNO ₃)
Residual	F5	HF, HClO ₄	F4	HNO ₃ , HCl

It is widely recognised that there are limitations to both the Tessier and BCR SEPs. In particular, it is accepted that trace elements can only be ascribed to ‘operationally defined’ fractions, defined by Alloway & Jackson (1991) as “identifying element phase or forms by the use of specific reagents”. This means that the choice of reagent influences the extent of metal extraction in each step of the SEP. Lo & Yang (1998) report the main limitations to SEPs as (i) limited selectivity of extractants, (ii) redistribution of trace elements during extraction, and (iii) the deficiency of reagent dose if the trace element content is too high. Many other authors report that redistribution and lack of specificity are the main shortcomings of SEPs and must be

taken into consideration when carrying out extractions (Young *et al.*, 2006; Kim & McBride, 2006; Lo & Yang, 1998; Ho & Evans, 2000; Raksasataya *et al.*, 1996). Young *et al.*, (2006) report that redistribution of trace elements can arise from undissolved residues of trace element rich phases released in subsequent extractions, or any extraction which increases the trace element ion activity in solution or changes solution pH. Ho & Evans (2000) found with the BCR scheme that 20-30% acid-extractable Cd and Zn was scavenged from the reducible phase, resulting in a net increase in the acid-extractable fraction and an underestimate of the metal fraction assumed to be bound to Fe/Mn hydrous oxides. Raksasataya *et al.*, (1996) observed substantial redistribution of Pb with both the BCR and Tessier methods studied using synthetic and spiked natural soils. Re-distribution and lack of specificity are inherent to SEPs, and reproducibility is affected by any changes to the schemes, such as the reagent used, concentration, pH, reaction time, temperature, soil-to-solution ratio, suspension mixing speed or the order in which extractions are carried out (Kim & McBride, 2006).

Nevertheless, SEPs do have proven applications in the study of trace element fractionation in soils. Lo & Yang (1998) suggested that the Tessier scheme provides qualitative analysis of the fractionation of trace elements in soils and Ho & Evans (2000) report that the operational speciation of trace elements can provide useful information on element partitioning. Provided limitations are taken into account, useful information about trace element fractionation in soils can be produced which, when combined with other analyses such as plant uptake studies or isotope dilution, can produce valid information on trace element mobility and contribute to risk assessment studies.

1.3.2.2 Measuring trace element ‘lability’ using isotopic dilution

The ‘labile’ trace element pool in soil can be defined as the quantity of an element which is able to exchange between the solid and solution phase. For example, Wolf *et al.*, (1986) stated that labile phosphate is the quantity of soil P in rapid equilibrium with solution P plus the amount of P in soil solution. Alongside definitions relating to chemical ‘reactivity’ in soil, trace element lability has also been associated with the concept of ‘bioavailability’ to plants and micro-organisms. Thus, Lopez & Graham (1972) refer to the amount of ‘available’ nutrients as the labile pool. Measuring the degree to which an (added) isotope can mix with the native elements, the process of ‘isotope dilution’, can be used to quantify this labile pool. Experimentally, this involves changing the isotopic composition of an element in a soil suspension by adding a known amount (a spike) of a stable or radio-isotope of that element. After a period of equilibration, the specific activity (for radio-isotopes) or isotopic abundance (for stable isotopes) of the spike isotope in solution is determined (Equation 1.1).

$$\frac{\text{spike } M_{\text{solution}}}{M_{\text{solution}}} = \frac{\text{spike } M_{\text{total}}}{M_{\text{labile}}} \quad (1.1)$$

It is important to keep the concentration of the spike small relative to the native soil pool to avoid chemically altering the system being studied. In this respect radio-isotopes have an advantage over stable isotopes in that they are not naturally present in the soil and so can be added at extremely low concentrations while still providing a viable assay. With stable isotopes, it is important to find a balance between a low enough spike concentration to avoid altering the system, and a large enough

concentration to cause a measurable change in isotopic abundance of the spike isotope.

The early uses of isotope dilution were for studying the behaviour of plant micronutrients using radio-isotope spikes. Lopez & Graham (1972) studied the lability of Mn, Fe, Zn, Co and Cu using the radio-isotopes ^{60}Co , ^{54}Mn , ^{59}Fe and ^{65}Zn . Wolf *et al.*, (1986) used the radio-isotope ^{32}P to measure the lability of P. The authors reported several difficulties in measuring labile P. In soils that had a high P fixation capacity, they believed that a proportion of ^{32}P added to the soil was irreversibly fixed and prevented from undergoing exchange with the ^{31}P on the soil surface. As a result, equilibrium was not achieved and measurement of labile P would result in an overestimate. Also, in soils where the solution P concentration is low, the increased difficulty in measuring P will contribute to inaccuracy in lability measurements. Problems such as 'irreversible' fixation of the spike or low soil trace element content are common to all isotope dilution measurements, and must be considered when designing isotopic exchange experiments.

Radio-isotopes have been widely applied to the measurement of soil metal lability where suitable isotopes are available. For example, Nakhone and Young, (1993) measured labile Cd using the radio-isotope ^{109}Cd , and Young *et al.*, (2000) measured the lability of Cd and Zn using ^{109}Cd and ^{65}Zn . For some metals, such as Pb however, suitable radio-isotopes are not available. In recent years as ICP-MS technology has become more widespread the use of stable isotopes has become more viable. In the last 12 years, stable isotope dilution has been used to measure the

lability of Cd (Ahnstrom & Parker, 2001, Ayoub *et al.*, 2003), Zn (Ayoub *et al.*, 2003), Pb (Degryse *et al.*, 2007; Tongtavee *et al.*, 2005) and Cu (Nolan *et al.*, 2004).

When using stable isotopes, the added isotope spike will be present naturally in the sample. The change in ratio of the spike isotope to a second isotope must therefore be recorded to quantify the extent of isotopic dilution of the added spike and hence the isotopic exchangeability of the metal in the soil. For example, Degryse *et al.*, (2007) used ^{208}Pb to measure the labile pool of Pb by measuring the $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio and the changes caused by the spike over the period of equilibration.

Many of the limitations to measuring isotopic exchangeability are common to both stable and radio-isotope dilution. This includes the effect of the post-spike equilibration period and the potential for gradual fixation of the spiked isotope into non-available sites within the soil. Ahnstrom & Parker (2001) measured the change in $^{111}\text{Cd}:^{110}\text{Cd}$ ratio over the isotopic equilibration period, and found that the ratio gradually decreased with time after the addition of the ^{111}Cd spike. Ayoub *et al.*, (2003) found that a spike of ^{111}Cd equilibrated with the labile Cd pool after 70 hours, but a ^{67}Zn spike did not fully equilibrate with the labile Zn pool. The authors found that there was a gradual decline in the enrichment of the soil solution due to the movement of ^{67}Zn into non-isotopically exchangeable sites, highlighting the potential problem of fixation of the spike. The length of the post-spike equilibration period can therefore affect the measurement of lability due to time-dependent processes that can cause fixation of the spike isotope. These processes will vary between different soils and metals, and so a standard equilibration period has been the subject of some disagreement in the literature.

When carrying out stable isotope dilution measurements, it is important to add sufficient spike to cause a measurable change in isotope ratios, but to keep the quantity of spike chemically insignificant to avoid changes in the partitioning of the element being studied. Ahnstrom & Parker (2001) added spike equivalent to 1% of the total Cd content. Ayoub *et al.*, (2003) aimed to create a measurable change in the Cd and Zn ratios by adding enough spike to change the $^{114}\text{Cd}/^{111}\text{Cd}$ ratio from 2.22 to 1.96, and the $^{66}\text{Zn}/^{67}\text{Zn}$ ratio from 6.76 to 6.10. The amount of Cd and Zn added was based on the amount of Cd and Zn extracted by 0.43 M CH_3COOH , used to estimate 'available' Cd and Zn.

As well as experimental variables affecting the measurement of lability, instrumental variables can also affect the results. Nolan *et al.*, (2004) investigated the effects of instrument performance of quadrupole ICP-MS on the measurement of Cu lability and noted that the precision and accuracy of isotope measurements can be significantly affected by signal stability, polyatomic spectral mass interferences and mass discrimination. The authors found that mass discrimination caused by the 'space-charge effect' (Nelms, 2005) is an important limitation for isotope ratio measurements. As lighter ions are deflected more than heavy ions, there is a differential loss of transmission through the ion lens system. Therefore the ratio of measured 'counts per second (cps)' for two isotopes will differ from their true isotopic ratio. The mass bias must be corrected for in order to calculate the isotopic abundance of the target isotopes. This can be done using a 'mass discrimination factor' (K-factor), which is the quotient of the true isotopic ratio divided by the measured cps ratio for an isotopic reference standard. Nolan *et al.*, (2004) use the reference standard NIST 976, run after every 4 samples, to continuously update the

mass discrimination factor and thereby correct the reported isotopic cps ratios for the samples. The results of the study showed good agreement between stable and radio-isotope dilution of Cu using a quadrupole ICP-MS in standard mode, suggesting that the mass discrimination correction is effective and the instrumental variables are not detrimental to the measurement of Cu lability.

In this investigation the lability of Pb in soils collected from Chat Moss was measured to further understand the behaviour of Pb and develop risk assessments for lead transfer into vegetables on Chat Moss. Additionally a suite of soils with other sources of Pb contamination (e.g. minespoil and roadside soils) will be investigated for comparison. The details of this work are described fully in chapter 4 section 4.4.

1.3.2.3 Source apportionment of Pb from relative isotopic abundance

Source apportionment using Pb isotope fractionation is based on the identification of isotopic reservoirs of Pb within the crust, which are related to the age of the rocks and the original U, Th and Pb content. Once a rock that does not contain U or Th has crystallised, its Pb isotopic ratio is set. If this rock is ore or coal-bearing, these will have the same isotopic ratio as the original rock. This ratio will be unique to the rock in question, allowing Pb to be traced back to its source. Lead is the final stable isotope resulting from the radioactive decay of ^{235}U , ^{238}U and ^{232}Th (Figure 1.10). ^{204}Pb is the only non-radiogenic lead isotope and so its abundance is unchanged since the Earth formed.

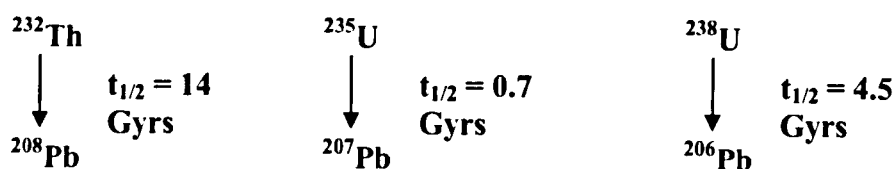


Figure 1.10: Simplified decay series of U and Th to produce Pb.

Over time, because of its shorter half-life, the amount of ^{235}U relative to ^{238}U has decreased, and the production of ^{206}Pb from ^{238}U became the main source of new Pb in geological materials. This has the consequence that geologically old materials are enriched in ^{207}Pb relative to ^{206}Pb , whereas geologically young materials are lower in ^{207}Pb relative to ^{206}Pb (Table 1.4). ^{232}Th is the main radioactive isotope of Th. Thorium only decays to ^{208}Pb , which has therefore resulted in the larger abundance of ^{208}Pb relative to the other Pb isotopes, as Th is more abundant than U in the solar system. Measured in cosmic abundance units (atoms per 10^6 atoms of Si), Th has an abundance of 3.35×10^{-2} whereas U has an abundance of 9.00×10^{-3} , a quarter of Th.

Table 1.4: Average relative isotopic abundance of lead isotopes.

Lead isotope	Relative abundance (%)
^{204}Pb	1.4
^{206}Pb	24.1
^{207}Pb	22.1
^{208}Pb	52.4

Source apportionment of anthropogenic Pb, such as Pb ore, coal and petrol-derived lead, using lead isotopes has been extensively studied on a range of materials

including soils, peat cores and mosses (e.g. Bacon *et al.*, 1996; 2006; Farmer *et al.*, 2005; Weiss *et al.*, 1999a; 1999b). The number of published papers containing the keywords “lead isotopes” and “anthropogenic” are shown in Figure 1.11, and reflects increasing activity and interest in this area since 1990. The trend shown probably reflects, to some degree, the increasing availability of ICP-MS to the scientific community.

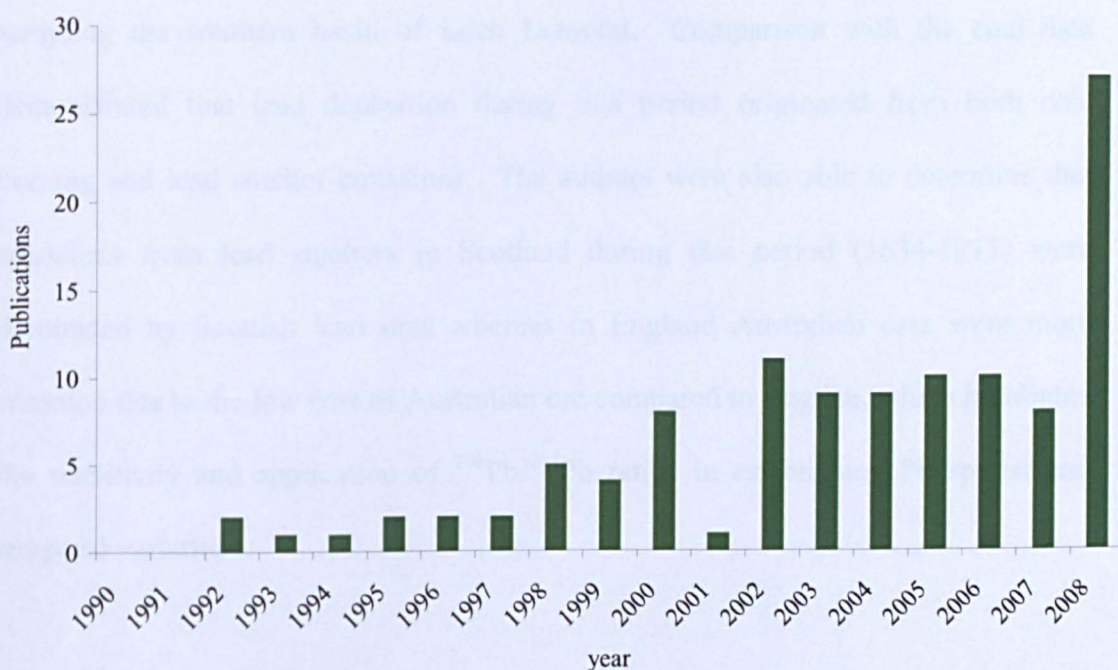


Figure 1.11: Number of publications per year investigating anthropogenic influences on Pb isotopes. Results shown are from a Web of Science keyword search for “lead isotope” AND “anthropogenic” for the period 1990 - 2008.

Ault *et al.*, (1970) used $^{206}\text{Pb}/^{204}\text{Pb}$ ratios to discriminate between sources of Pb contamination in roadside grasses, tree cores and soils. With the development of ICP-MS however, Bacon *et al.*, (1996) demonstrated that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio varies most within environmental media and is the most suitable ratio for source

discrimination. Typical $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for a range of common environmental contaminants are shown in Table 1.5.

Farmer *et al.*, (1999) measured $^{206}\text{Pb}/^{207}\text{Pb}$ in coals and observed discrete ranges depending upon source (Table 1.5). They calculated the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of atmospheric Pb deposition for the period 1634 – 1817 to be 1.178 ± 0.006 based on sampling the southern basin of Loch Lomond. Comparison with the coal data demonstrated that lead deposition during this period originated from both coal burning and lead smelter emissions. The authors were also able to determine that emissions from lead smelters in Scotland during this period (1634-1817) were dominated by Scottish lead ores whereas in England Australian ores were more common due to the low cost of Australian ore compared to English, which highlights the sensitivity and application of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in establishing Pb spatial and temporal variations.

A clear petrol-derived $^{206}\text{Pb}/^{207}\text{Pb}$ signature has been observed in many study locations, including Canadian roadside grasses (Li, 2006) and Swiss peat bogs (Weiss *et al.*, 1999a), demonstrating that, even in remote areas, petrol-derived Pb can form a recognisable part of atmospheric pollution. Lead isotope studies can be used to demonstrate the depth of penetration of (aerially deposited) anthropogenic Pb in soils (Farmer *et al.*, 2005) and, combined with sequential extractions, enable identification of the soil fractions that host anthropogenic Pb (Bacon and Hewitt, 2005).

Table 1.5: Common lead isotope ranges for lead ore, coal and lead additives to petrol.

Source of lead	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	Reference
<i>Coal:</i>				
Durham	1.185	2.066	2.449	Farmer <i>et al.</i> , (1999)
Yorkshire /Nottinghamshire	1.1865	2.0762	2.4643	
Derbyshire	1.181	2.0795	2.455	
North Wales	1.177	2.099	2.47	Farmer <i>et al.</i> , (2005)
South Wales	1.1808	2.0794	2.456	
Scotland	1.1812	2.0282	2.4790	
Ireland	1.1998	2.0447	2.4503	
<i>Lead ore:</i>				
Welsh ore	1.16-1.18			McGill <i>et al.</i> , (2003)
Irish ore	1.15-1.17			Farmer <i>et al.</i> , (2005)
Pennine ore	1.17-1.19			
Scottish ore	1.170			
Australian ore	1.04			
<i>Petrol-derived lead:</i>				
Alkyl Pb additives from Australian ore	1.09			Farmer <i>et al.</i> , (2005)
Tetra-alkyl additives from Australian and Columbian lead	1.06-1.09			Farmer <i>et al.</i> , (1999)
Airborne particulate Paris (1980's)	1.09-1.11			Semlami <i>et al.</i> , (2004)
<i>Natural lead:</i>				
Preanthropogenic aerosols and Upper Continental Crust	1.19-1.22			Weiss <i>et al.</i> , (1999a)

The likely source of Pb contamination at Chat Moss will be determined in this investigation through measurement of lead isotope ratios, and using the data in Table 1.5 and Figure 1.12 for comparison, as well as the suite of soils used in the isotope dilution study (see chapter 4).

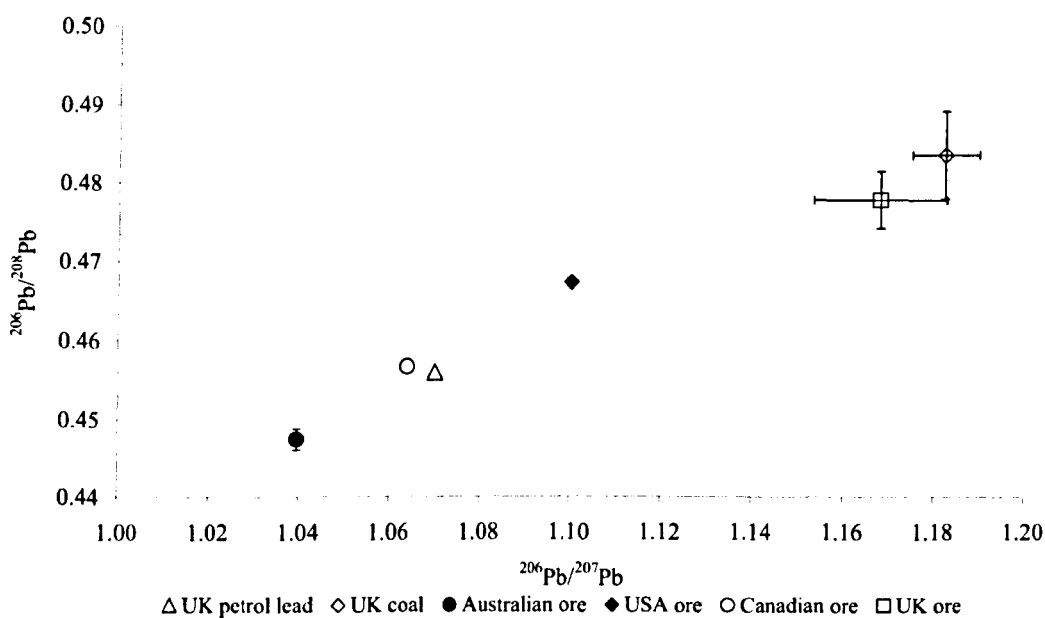


Figure 1.12: Typical ranges of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{207}\text{Pb}$ for common anthropogenic lead sources, error bars show standard deviation.

1.4 Trace element uptake by vegetable crops

1.4.1 Factors affecting the rate of uptake of trace elements from contaminated soils

The rate of uptake of trace element by plants from contaminated soils is controlled by many factors including soil pH and organic matter content, and plant characteristics including species and rate of growth. Uptake of trace elements can occur through the diffusion of water including soluble elements into plant cells, or the trace elements can be taken up by active transport across the plasma membrane

of cells (Yoon *et al.*, 2006). For example, active uptake of arsenate occurs through phosphate uptake channels (Clemens, 2006) and for arsenite, the silicic uptake channels are used (Ma *et al.*, 2008). Sulphate uptake channels can also transport Se across the plasma membrane, and Cd^{2+} can be taken up through Fe^{2+} , Ca^{2+} and Zn^{2+} transport pathways (Clemens, 2006).

Soil pH is regarded as one of the most important soil characteristics controlling plant uptake of metals (Alloway & Jackson, 1991), and as pH becomes more acidic trace elements become typically more available for plant uptake. In a study of vegetables grown in contaminated soils, Kachenko & Singh (2006) found increased plant uptake of trace elements in the contaminated soils, which they attributed to increased soil acidity (pH 6.65 – 6.22) increasing the availability of trace elements for uptake. Anton & Mathe-Gaspar (2005) state that soil pH and temperature are the most important controls on trace element uptake. The authors found that at high temperature and low pH the Cd and Zn content within the plant shoot was significantly increased, and that soil pH is an important factor influencing the availability of Cd and Zn in plants.

Whilst soil pH is important in controlling trace element solubility (Section 1.3.1.3), with acidic soil pH promoting solubility of many trace elements, this does not translate directly to bioavailability. It has been shown that at lower pH, whilst the concentration of metal ions in solution is greater, the concentration of protons in solution is also greater, and this can result in competition for absorption sites on the plant roots, meaning that increased solubility may not result in increased plant uptake of the metal ions. The effect of this competition has been shown by Hough *et al.*,

(2005), who modelled the uptake of Cd and Zn by grass plants and the effect of pH using the Free Ion Activity Model (FIAM). This model incorporates the activity of the ion in solution and the activity of protons in solution to model the competition between these ions for the absorption sites on roots. It was found that whilst pH correlated well with uptake of Cd and Zn, the best correlation was seen when competition between the metal ion and protons was included within the model, with a 20% increase in the account of variation of metal uptake by the grass with competition between the metal ion and protons compared to using pH as the model parameter.

The use of pH as a predictor of trace element uptake by plants may be effective at high pH values, but at acidic pH values it becomes less effective. This can be seen in the case of the UK guideline values for Cd in soil (SGV) (Environment Agency, 2002a), which are pH dependent. The predicted uptake of Cd by green vegetables calculated using Equation (1.2), taken from the SGV, with an assumed soil Cd content of 1.00 mg kg^{-1} is shown in Figure 1.13 CF is the soil-to-plant concentration factor for leafy vegetables ($\mu\text{g g}^{-1}$ DW plant over $\mu\text{g g}^{-1}$ DW soil), pH is the soil pH.

$$\ln(\text{CF}) = 11.206 - (1.634 \times \text{pH}) \quad (1.2)$$

The model predicts Cd plant content of 100 mg kg^{-1} at a pH of 4, which is unrealistic for a soil Cd content of 1.00 mg kg^{-1} , however in the neutral to basic pH range, the predicted Cd uptake is more realistic and the model used in the SGV may be applicable at higher pH but not in the acid pH range. However in the latest version

of the SGV (Environment Agency, 2009a), the uptake of Cd by plants is predicted by a soil-to-plant transfer factor with no effect of pH.

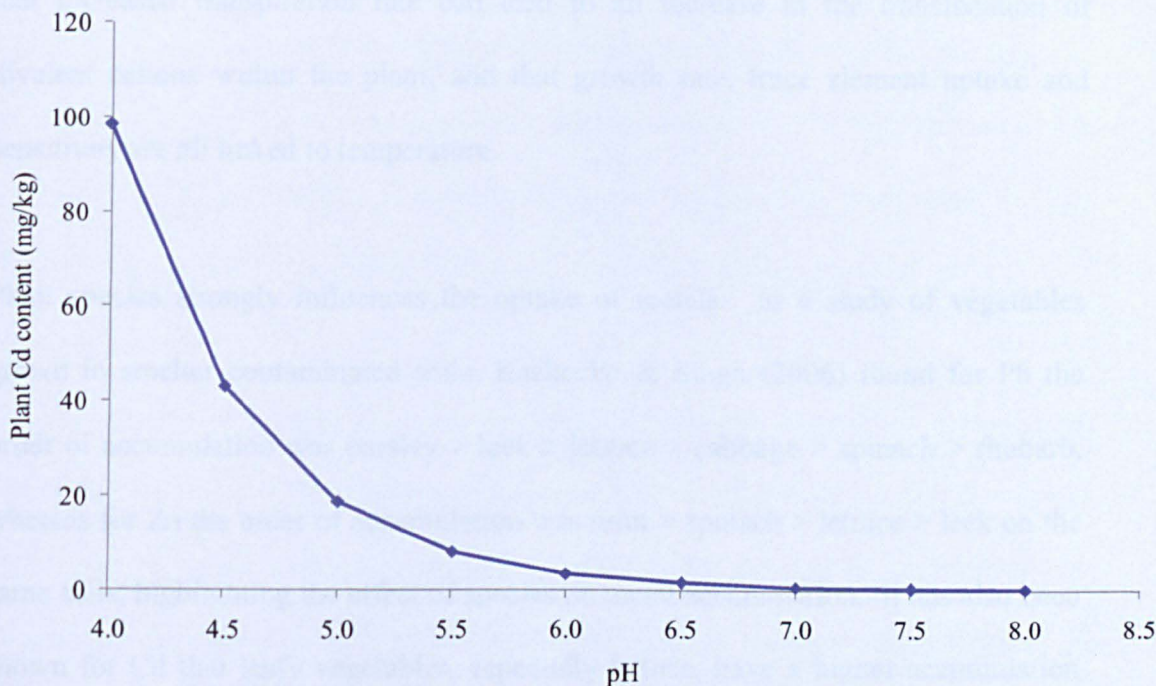


Figure 1.13: Predicted response of plant Cd uptake to pH, calculated using the CLEA model (Enviroment Agency, 2002a).

Dissolved organic carbon (DOC) content in the soil can also affect plant uptake, with increased DOC causing an increase in bioavailability through the formation of organo-metallic complexes (Kidd *et al.*, 2007). Plants secrete low molecular weight organic compounds that act as metal chelators to aid metal uptake (Clemens, 2006), and complexation of trace metals with root exudates can either increase or decrease the bioavailability of the metals depending on the solubility of the exudates, with citrate and oxalate able to form soluble complexes with Cu and Zn (Zhao *et al.*, 2007). If there is a large proportion of insoluble organic matter there will be reduced bioavailability of metals, due to complexation, as observed in sewage sludge

amended soils (Speir *et al.*, 2003). The solubility of organic matter is also pH dependent (see section 1.3.1.3) and so the influence of these two soil factors on metal uptake by plants cannot be easily separated. Anton & Mathe-Gaspar (2005) showed that increased transpiration rate can lead to an increase in the translocation of divalent cations within the plant, and that growth rate, trace element uptake and sensitivity are all linked to temperature.

Plant species strongly influences the uptake of metals. In a study of vegetables grown in smelter contaminated soils, Kachecko & Singh (2006) found for Pb the order of accumulation was parsley > leek > lettuce > cabbage > spinach > rhubarb, whereas for Zn the order of accumulation was mint > spinach > lettuce > leek on the same soils, highlighting the effect of species on metal accumulation. It has also been shown for Cd that leafy vegetables, especially lettuce, have a higher accumulation than root vegetables (Podar & Ramsey, 2005).

When predicting uptake of heavy metals by plants for risk assessment purposes, pH, activity of the metal ion in solution, DOC and plant species would seem to be the most influential factors and so any model that would predict potential risk from metal uptake must include these factors. Total soil metal content will also influence the rate of uptake of metals as it will control the size of the pool of bioavailable metals, but a large total metal content does not lead to a large bioavailable metal content, and so all the factors need to be considered before risk can be assessed.

1.4.2 Assessing risk to human health using Hazard Quotients

There are four pathways through which humans can be at risk from the intake of potentially toxic elements. These are ingestion of contaminated soil particles, ingestion of plants grown on contaminated soils, inhalation of contaminated dust and vapours and absorption of the contaminant through the skin. The main pathways are the ingestion of plants grown on contaminated soils and exposure to soil dust, and the ingestion of contaminated plants will be considered in this investigation.

The level of risk posed by trace element uptake into vegetables growing in contaminated soils can be assessed using Hazard Quotients (HQ). Hazard Quotients are derived from the metal content of the vegetable, the average daily intake of the vegetable, body weight and a reference dose of the metal which is the average daily dose at which the metal intake will not be harmful (Equation 1.3, Datta & Young, 2005).

$$HQ = \frac{M_{\text{plant}} \times ADI \times \text{fresh weight conversion}}{RfD \times \text{Average body weight}} \quad (1.3)$$

M_{plant} = metal content of edible portion of vegetable (mg kg^{-1})

ADI = Average daily intake of vegetable (kg d^{-1})

RfD = dose at which metals are not harmful ($\text{mg kg}^{-1} \text{d}^{-1}$)

Reference doses are often taken from the USEPA IRIS (Integrated Risk Information System) database (Qishlaqi *et al.*, 2008), and a selection can be seen in Table 1.6. There is assumed to be no risk from consumption of ‘contaminated vegetables’ if the

Hazard Quotient (HQ) is less than 1. If the HQ is greater than 1 then a health risk exists (Chary *et al.*, 2008; Qishlaqi *et al.*, 2008; Datta & Young, 2005).

Table 1.6: Reference doses taken from IRIS for selected metals.

Metal	Reference Dose (mg kg⁻¹ d⁻¹)
Zn	0.3
Cd	0.001
Ni	0.02

Hazard Quotients are element specific and so can give a realistic assessment of the intake of various elements from a single vegetable plant. In a study of vegetables grown in sewage irrigated soils in India, the Hazard Quotients were found to vary from 0.002 for Ni to 5.3 for Zn for different vegetables (Chary *et al.*, 2008). Using this approach, an estimate of the risk posed by a trace element can be made and will be used to assess the risk to human health from vegetables grown on historically contaminated soils on Chat Moss (see section 6.5).

1.5 Aims and rationale

1.5.1 Establish the nature and extent of contamination at Chat and Halsall Mosses

The aim of this project was to establish the spatial variability of contamination at Chat and Halsall Mosses, and the level of contamination at these sites. The source(s) of contamination were also be investigated. Levels of trace elements found at Chat and Halsall Mosses were related to original GBASE data to investigate the validity of the data when looking at field-scale contamination rather than a regional scale. Trace element levels were studied through ICP-MS analysis of soil samples (Chapter 3.1.3.3), and spatial variability was investigated using Portable XRF field studies (Chapter 3.2).

1.5.2 Investigate the reactivity of the contamination on the mosses

Once contaminant concentrations had been established, the reactivity of the individual trace elements was studied. This included determining the speciation and solubility of the main contaminants using sequential extractions (Chapter 4.3) and stable isotope dilution (Chapter 4.4). The development of ^{204}Pb stable isotope dilution was a key step in this process. The influence of flooding events on metal solubility was also investigated (Chapter 5).

1.5.3 Assess bioavailability of trace elements

The bioavailability of the trace element for plant uptake in vegetable plants was assessed using information determined for metal reactivity and pot trials (Chapter 6).

This was important for the Chat and Halsall Moss areas because although current land use is arable farming, a change to market gardening has been proposed. The impact of potential climatic variations on the trace element bioavailability will also be assessed. Element reactivity and bioavailability information was used to estimate risk to human health from consumption of vegetables grown on Chat and Halsall Moss using Hazard Quotients (Chapter 6.4).

Chapter 2: General materials and methods

Characterisation of the soils and contamination on Chat and Halsall Mosses was carried out using a range of methods, including pH and Eh measurement on soil slurries, organic matter determination through loss on ignition, and total metal content measurement carried out on soil solutions prepared through HF-HNO₃-HClO₄ digests. Measurements of lead isotope ratios on soil solutions were also carried out using ICP-MS. Scanning Electron Microscopy was also used to characterise the contamination artifacts within the soil.

2.1 Site selection, sampling method and soil preparation

Sites were chosen for sampling on Chat Moss and Halsall Moss based on the original BGS G-BASE data (Section 1.1), with the intention to sample arable sites with relatively large concentrations of trace metals. A range of sites were selected and letters to landowners were sent to request permission to sample. Once access had been granted four sites on Chat Moss and one on Halsall Moss were sampled. This strategy resulted in the selection of sites that were not sufficiently representative of the entire moss, but this was all that was possible with the limited site access. It was intended to sample contamination hotspots identified by the GBASE survey, however difficulties in locating landowners and obtaining permission to sample limited the sampling options. In order to carry out fully representative sampling, adaptive sampling using kriging could have been employed. This would involve an initial sampling phase followed by kriging to interpolate the trace element concentrations in unsampled sites. An assessment could then be carried out of the

risk of wrongly estimating trace metal concentrations of the unsampled sites using kriging, with sites at high risk being visited for additional sampling. This multi-phase sampling process has been used to map contamination levels in Taiwan, and was shown to be more successful than random sampling (Juang *et al.*, 2005). Three of the sites on Chat Moss were located within the historically contaminated region which showed elevated heavy metal concentrations in the GBASE data, and one was located outside the area used for urban waste disposal, but within the moorland, and so was selected as a control area which had been drained and improved but had not received any waste amendment. This was supported by the GBASE data which did not show elevated heavy metal concentrations at this location. The site chosen for sampling on Halsall Moss was shown to have elevated heavy metal concentrations based on the GBASE survey. However due to the piecemeal nature of the historical waste disposal on Halsall Moss (Section 1.2.2.2) it could not be confirmed that this was a contaminated area before the sampling visit. Table 2.1 shows a list of site codes and brief descriptions.

Samples from sites CM-1 and CM-12 were collected on 19th December 2005 and samples from sites CM-3 and CM-9 were collected on 8th February 2006. Further samples were collected from CM-3 in a second sampling visit in 10th August 2006. At each site three auger borings were taken in a triangular pattern, with approximately 10 m between each core. Samples were taken every 10 cm down the auger core, with the surface sample taken from 0 to 20 cm. Samples were collected to a depth of 110 cm, unless the water table or underlying soil was reached. These samples were used to determine total metal content, LOI and pH to characterise the vertical distribution of the waste material and soil conditions.

Table 2.1: Site codes and descriptions of sample sites

Site Code	Grid Reference	Soil Classification	Description	Land Use	Geology
CM-1	SJ 697 983	Altcar Association – amorphous peat	Control site, drained but no waste amendment. Peat soil.	Arable farm	Permo-Triassic sandstone
CM-3	SJ 752 967	Altcar Association – amorphous peat	Contaminated site with waste amendment. Peat soil.	Arable farm	Permo-Triassic sandstone
CM-12	SJ 685 957	Altcar Association – amorphous peat	Contaminated site with waste amendment. Peat soil.	Arable farm	Permo-Triassic sandstone
CM-9	SJ 742 905	Downholland Association – loamy sand to sandy loam	Contaminated site with waste amendment. Sandy soil.	Equestrian smallholding	Permo-Triassic sandstone
HM-1	SD 453 050	Sollom / Astley Hall Association – peaty sand, loamy sand, sandy loam	Contaminated site with waste amendment. Sandy soil.	Arable farm	Carboniferous and Triassic sandstones

At the second sampling visit to CM-3, nine auger borings were collected at random intervals across a 90 m by 90 m sample grid set up for a portable XRF survey, with samples collected from 0 to 20 cm depth and subsequently every 10 cm. Bulk topsoil samples (c. 100 kg) were also collected from the top 40 cm of the soil surface for plant trials. At site HM-1, samples were collected on 7th November 2007, and three cores were collected in the same manner as the samples on Chat Moss.

All depth profile soil samples were air-dried and gently crushed and sieved to < 2 mm to break up aggregates and remove unwanted material such as plant debris and stones. Samples were stored in air-tight plastic bags prior to analysis. The bulk topsoil collected from CM-3 was air-dried and sieved to 6 mm to remove stones and large aggregates before storing for use in vegetable pot trials (Chapter 6).

2.2 Soil pH

Soil pH was measured on the 2 mm sieved air-dried soil samples. Approximately 5 g soil was mixed with 20 ml deionised water in a 42 ml Oak Ridge polycarbonate centrifuge tube. The soil-water suspension was shaken on an end-over-end shaker for 30 minutes to equilibrate and the pH measured on the resulting slurry. pH was measured using a Hanna pH 209 pH meter, after calibration with pH 7.00 (Na_2HPO_4 and KH_2PO_4) and pH 4.01 (KH phthalate) buffers. Replicate samples from each site were measured to provide an estimate of the combined sampling and analysis error; no (pseudo)replication of discrete samples was undertaken.

2.3 Soil redox potential

Redox potential was measured on soil slurries using a Jenway 3010 pH meter with a combined platinum and Ag-AgCl reference electrode. In order to measure redox potential, a reference Eh must first be measured. This is done by measuring the Eh value recorded for a saturated quinhydrone suspension in pH 4.01 and pH 7.00 buffers. The measured values of potential (E_{meas}) are then subtracted from the known redox potentials (Eh) for quinhydrone at those pH values and averaged to give the potential of the reference electrode (E_{ref}). This value is then added to the measured redox potentials for samples (E_{meas}) to give the true redox potential (Eh).

2.4 Organic matter content

Organic matter content was estimated on 2 mm sieved air dried soil samples using 'Loss on Ignition' (Rowell, 1994). Approximately 5 g soil was weighed into ceramic crucibles, which were then oven-dried at 105°C overnight to drive off any moisture.

The oven-dried samples were then ignited in a muffle furnace at 550°C for 8 hours and ashed. Once cool the crucibles were weighed, and loss on ignition (LOI) determined gravimetrically. This method was selected as being the most parsimonious, as extremely precise measurement of organic matter content was not necessary, and at the high organic matter content of these soils the LOI method was sufficiently precise.

2.5 Preparation of samples for total trace metal analysis

2.5.1 Preparation of soil samples for total trace metal analysis

Subsamples (10-20 g) of the 2 mm sieved air-dried soil samples were milled using a Retsch PM400 ball mill to a fine powder. Approximately 250 mg of this finely ground material was digested in a PFA beaker with 4 ml HNO₃ (Trace element grade; Fisher Scientific, UK) and digested on a Teflon-coated graphite block digester (Analysco, UK) heated in a stepwise fashion to 80°C. After this stage, 2.5 ml HF, 2 ml HNO₃ and 1 ml HClO₄ (all trace element grade) were added to each beaker and digestion was carried out with stepped heating to 160°C. Once this stage was complete, a further 2.5 ml HNO₃ (trace element grade) and 2.5 ml MilliQ water (18.3 MΩ) was added and heated to 50°C for 30 minutes. The final solution was then made up to 50 ml in plastic volumetric flasks using MilliQ water (18.3 MΩ) and then decanted and stored unrefrigerated in 30 ml universal sample bottles (5% HNO₃). Prior to analysis each sample was diluted with MilliQ water to a 1/10 dilution factor using a compudil – D auto diluter (Hook and Tucker Instruments).

2.5.2 Plant preparation for total trace metal analysis

Once harvested, plant samples were washed with deionised water and oven-dried at 40°C until dry. The samples were then finely ground using a Retsch ZM 200 centrifugal plant mill fitted with a 0.5 mm titanium sieve to avoid Fe and Cr contamination. Two hundred milligrams of the finely ground plant material was placed in a Teflon vessel and 6 ml HNO₃ (trace element grade) was added. Samples were digested with microwave heating in an Anton Paar multiwave fitted with a 48 place carousel. Digested samples were diluted to 20 ml with MilliQ water (18.3 MΩ) and stored for analysis. Prior to analysis samples were diluted with MilliQ water (18.3 MΩ) using a dilution factor of 1/10 with a compudil – D auto diluter (Hook and Tucker Instruments).

2.6 Measurement of total metal content by ICP-MS

Total metal content for soil and plant samples was determined using ICPMS (*Thermo-Fisher Scientific X-Series^{II}*) with a 'hexapole collision cell' (7% hydrogen in helium) upstream of the analytical quadrupole. Samples were introduced from a covered autosampler (*Cetac ASX-520* with 4 x 60-place sample racks) through a concentric glass venturi nebuliser (*Thermo-Fisher Scientific*; 1 mL min⁻¹). Internal standards were introduced to the sample stream via a T-piece and included Sc (100 ng mL⁻¹), Rh (20 ng mL⁻¹) and Ir (10 ng mL⁻¹) in 2% trace element grade HNO₃. External multi-element calibration standards (*Claritas-PPT grade CLMS-2* from *Certiprep/Fisher*) included Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V and Zn, all in the preferred range of 0 – 100 µg L⁻¹. Sample processing was undertaken using Plasmalab

software (version 2.5.4; *Thermo-Fisher Scientific*) set to employ separate calibration blocks and internal cross-calibration where required. For each digestion batch data was corrected using two blank digestions and quality control was assessed with two samples of a reference material for each data run (NIST 2711 Montana Soil or NIST 1573a Tomato Leaves). If the reference material data was not within 5% of certified values then the entire batch of data was discarded. All elemental concentrations were converted to mg kg^{-1} (equation 2.1)

$$C_{\text{soil}} = \frac{(C_{\text{sol}} - C_{\text{blank}}) \times \text{Vol}}{W_{\text{soil}}} \quad (2.1)$$

Where C_{soil} is the elemental concentration (mg kg^{-1}) in the soil sample; C_{sol} and C_{blank} are the concentrations ($\mu\text{g L}^{-1}$) in the soil and blank digests, corrected for dilution, Vol is the digest volume (50 mL) and W_{soil} is the mass of soil digested (c. 200 mg). The same equation was used to calculate elemental concentration in the plant material.

2.7 Measurement of lead isotope ratios by ICP-MS

Lead isotope ratio analysis was undertaken using ICP-MS (*Thermo-Fisher Scientific X-Series^{II}*), in standard mode, on total trace element digests (Chapter 2.5.1). The lead isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb were measured, as well as ^{202}Hg to correct for ^{204}Hg . The isotopes ^{202}Hg and ^{204}Pb were measured with a dwell time of 10 ms, and ^{206}Pb , ^{207}Pb and ^{208}Pb were measured with a low quadrupole ‘dwell time’ of 2.5 ms. Maximum and minimum quadrupole ‘settle times’ were set to 1000 μS , and 10 – 15 runs were used for each sample. The objectives of these settings are to minimize

errors from plasma noise between the individual isotope measurements which limits the accuracy and precision of single collector quadrupole instruments compared to multi-collector magnetic sector ICPs. Samples were introduced from a covered autosampler (*Cetac ASX-520* with 4 x 60-place sample racks) through a concentric glass venturi nebuliser (*Thermo-Fisher Scientific*; 1 mL min⁻¹). No internal standard or calibration standards were used. However a range of concentrations of the standard NIST 981 (8, 16, 24, 32 and 41 µg L⁻¹) were measured at the beginning of each analysis run to correct for 'dead time'. This is a correction factor which allows for the inoperability of the detector immediately following a pulse counting event and thereby ensures no loss of sensitivity as concentration of analyte increases (Nelms *et al.*, 2001; Nelms, 2005; pp 131). The correct dead time setting is that which gives the same isotope ratios, regardless of Pb concentration. The diluted NIST 981 samples were also used to correct for mass discrimination. After every 6 samples, one NIST 981 sample was analysed, and a correction factor ('K factor') was calculated from the deviation from the known Pb isotope ratios in NIST 981 to correct for mass bias and signal drift throughout the analysis (Nelms, 2005; pp 164).

Chapter 3: Characterisation of sites

3.1 Soil profile description and analysis

3.1.1 Introduction

This chapter describes the characterisation of soil from selected sites on Chat and Halsall Mosses, focussing on variation in pH, organic matter content and trace metal concentrations as a consequence of waste disposal. Sites were selected from the GBASE survey, conducted by the BGS, to cover a range of contamination loadings from highly contaminated to background levels. Full descriptions of the sampling strategy and the sites can be found in Chapter 2.1; photographs of the sites are shown in Plates 3.1A and 3.1B.

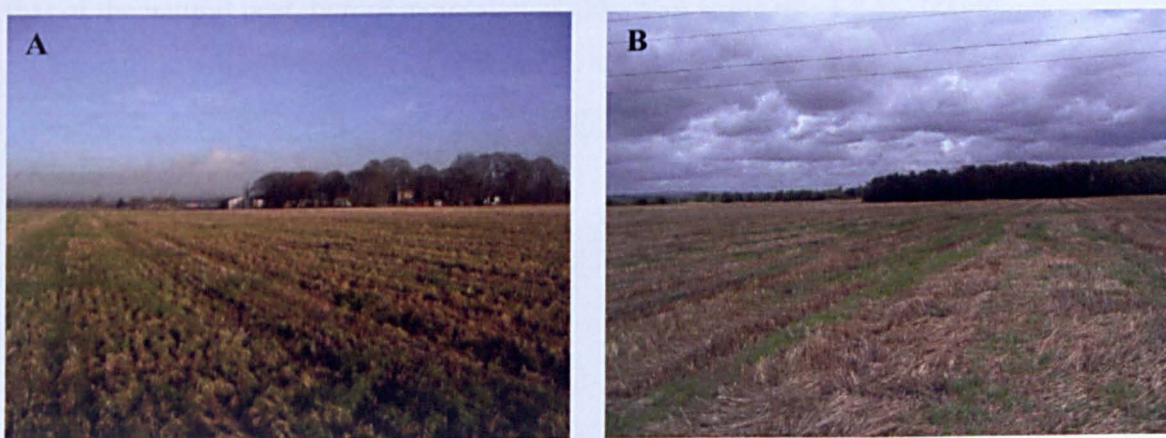


Plate 3.1: Control site CM-1 on Chat Moss (A), Contaminated site CM-3 on Chat Moss (B)

3.1.2 Materials and Methods

Soil sampling and preparation, and determinations of soil pH, organic matter content and trace metal concentrations were carried out as described in Chapter 2.

3.1.3 Results and Discussion

3.1.3.1 Variation in soil pH with depth

Soil pH profiles for the four sites sampled on Chat Moss exhibited distinct, and different, profiles (Figure 3.1), although sites CM-3 and CM-12 showed the same soil profile. At the control site on Chat Moss (CM-1; Plate 3.1A), where there was no recorded history or field evidence of waste disposal, the pH value of the topsoil was ~5.1; this gradually decreased below 30 cm to pH 4.4 in the peat (at 50 cm depth) where it remained virtually constant down to a depth of 110 cm. At the site subject to waste-amendment (CM-3; Plate 3.1B) pH remained at ~ 6.3 from the surface to a depth of 50 cm, the depth of the topsoil effectively created by historic waste disposal. Below this, pH dropped sharply to a value of ~4.3, consistent with that of the natural peat, before increasing slightly to a value of ~4.8 at 100 cm.

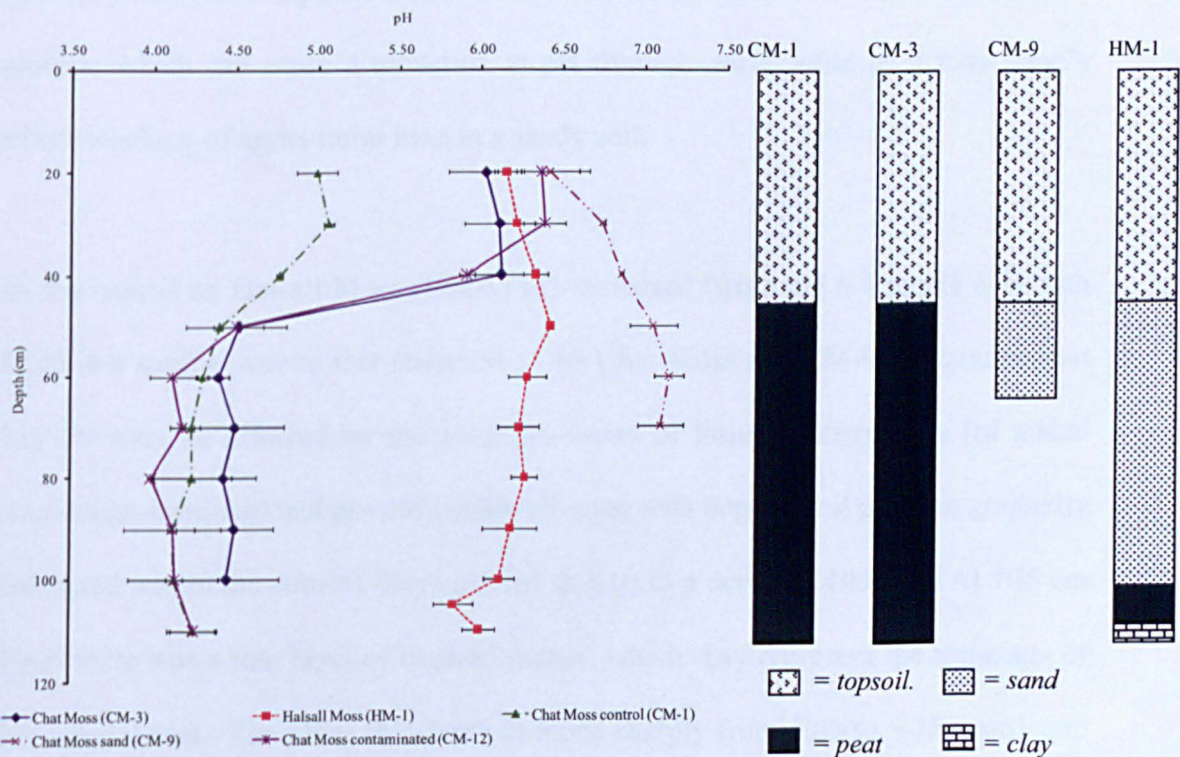


Figure 3.1: pH and soil profiles for Chat and Halsall Mosses, error bars show standard error of three replicates.

The high pH value in the waste-amended topsoil (CM-3 and CM-12) is likely to be a consequence of agricultural liming but there may also be an influence of the historic incorporation of iron and steel foundry waste and coal ash which will have contained carbonates, oxides and silicates, with the oxides and carbonates potentially contributing to a higher pH than seen in the control site. The slight increase in pH between 20 cm and 30 cm is probably caused by migration of lime to this depth. Ploughing to a depth of 20 cm aerates the topsoil, allowing increased oxidation of organic matter and ammonium which also acts to reduce the pH.

The pH profile at site CM-9 reflects the absence of peat at depth and the presence of a sandy sub-soil. Soil pH value at the surface was 6.5, optimum for nutrient availability (Soffe, 2003), increasing to 7.2 in the sandy subsoil. The lower pH at the surface of this site compared to the subsoil may be the result of ammonium fertiliser addition which can cause a reduction in pH through nitrification or it may simply reflect leaching of agricultural lime in a sandy soil.

In the topsoil on Halsall Moss (HM-1) pH increased (from pH 6.1 to pH 6.4) with depth in a similar way to that observed at the Chat Moss site CM-9, suggesting that this site may be affected by the same processes of liming, nitrification (of added ammonium fertilizer) and possibly redox changes with depth. Soil pH then gradually decreased within the subsoil (from pH 6.4 to 6.0) to a depth of 105 cm. At 105 cm depth there was a thin layer of organic matter, which may represent the remnants of the original peat. The pH at this depth dropped sharply from 6.00 to 5.75, consistent with the occurrence of an organic layer, before rising back to pH 6.00 in the clay

layer below. The gradual decrease in pH observed between 50 cm and 100 cm may be the result of migration of organic matter through the sandy subsoil prior to accumulation at 105 cm above the impermeable clay layer. Black lenses of organic material were observed in the soil profile and were more frequent as depth increased.

3.1.3.2 Variation in loss on ignition (LOI) with soil depth

The distribution of organic matter (measured as LOI) within the soil profile varied between the five sites (Figure 3.2). The control site on Chat Moss (CM-1) had undergone the least reclamation and was closest to the original moorland, and had an organic matter content of 70% in the topsoil which increased to 95% in the peat subsoil at 40 – 50 cm. The CM-1 (control site) profile was indicative of the original reclamation of the moss and showed the consequent loss of organic matter resulting from drainage and oxidation of the soil. The organic matter content was constant within the (mixed) plough layer, but then increased steadily from 30 to 50 cm, where it reached a maximum and thereafter was constant (90-95%) with depth. From field observations, the nature of the organic matter also changed with depth, with well humified material in the topsoil and fibrous raw peat at greater depth, typical of the Chat Moss moorland.

In comparison with the control site (CM-1), the two contaminated sites examined on Chat Moss (CM-3 and CM-12) had lower organic matter contents in the topsoil but similar values for LOI in the peat subsoil below 50 cm. The smaller organic matter contents in the topsoil partly reflect the cultivation effects seen at the control site and, additionally, the inclusion of inorganic waste materials into the moss during

reclamation on sites CM-3 and CM-12. This waste contained several forms of mineral waste such as furnace slag and domestic coal ash, which have reduced the organic matter content of the topsoil to less than 60% compared to >70% at the control site (CM-1).

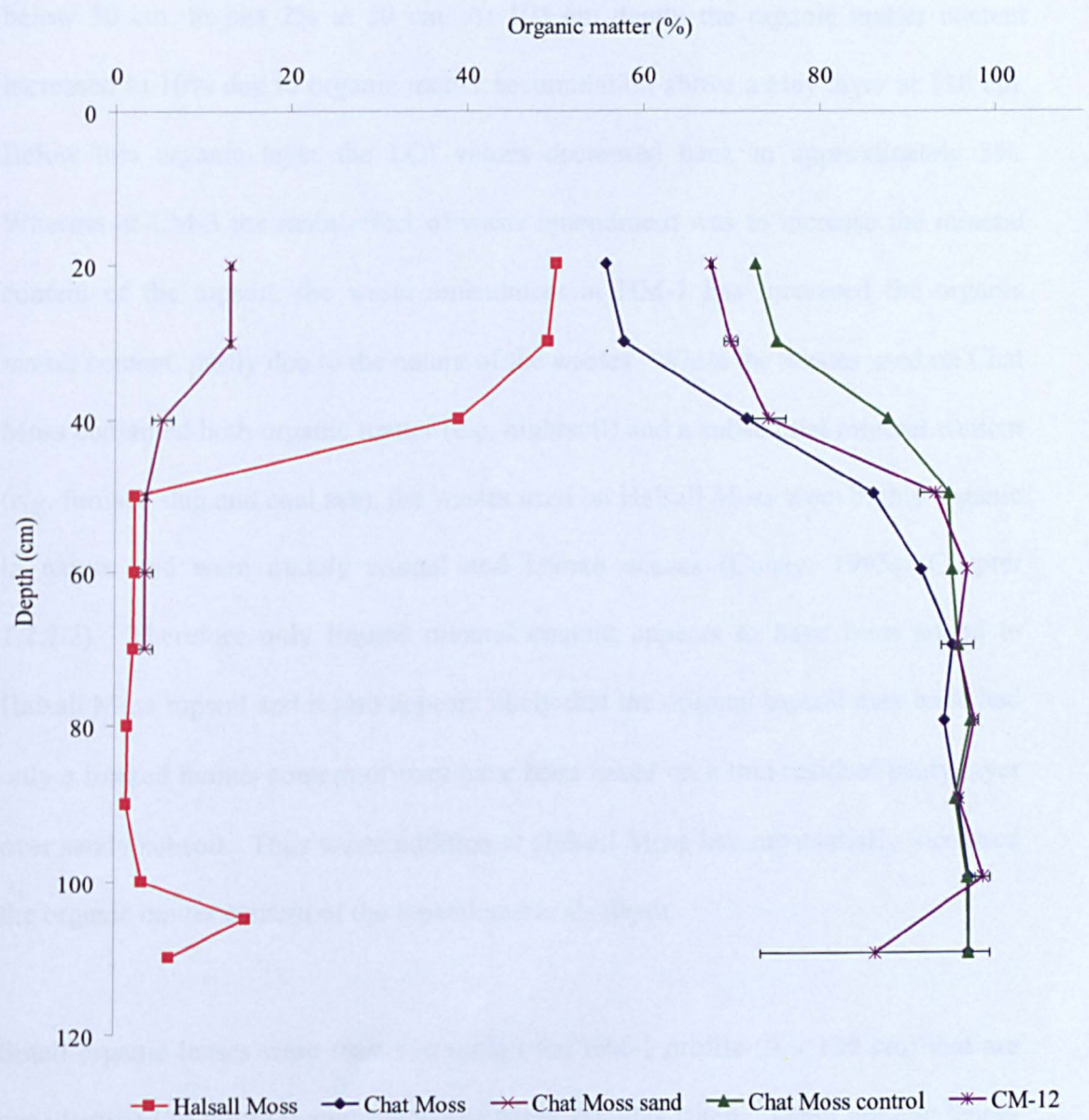


Figure 3.2: Organic matter profiles as a function of depth for sites Chat Moss (CM-3), Chat Moss control (CM-1) Chat Moss contaminated (CM-12), Chat Moss sand (CM-9) and Halsall Moss (HM-1). Error bars show standard error of three replicates.

At Halsall Moss (HM-1), the organic matter profile differed markedly from those found at Chat Moss, partly because the parent materials at the two locations are dissimilar (Section 3.1.1). The organic matter content of the topsoil (c. 50%) was similar in magnitude to that of the Chat Moss soils. However, LOI declined steeply below 30 cm, to just 2% at 50 cm. At 105 cm depth, the organic matter content increased to 10% due to organic matter accumulation above a clay layer at 110 cm. Below this organic layer the LOI values decreased back to approximately 5%. Whereas at CM-3 the main effect of waste amendment was to increase the mineral content of the topsoil, the waste amendment at HM-1 has increased the organic matter content, partly due to the nature of the wastes. While the wastes used on Chat Moss contained both organic matter (e.g. nightsoil) and a substantial mineral content (e.g. furnace slag and coal ash), the wastes used on Halsall Moss were highly organic in nature and were mainly animal and human wastes (Coney, 1995) (Chapter 1.2.2.2). Therefore only limited mineral content appears to have been added to Halsall Moss topsoil and it also appears likely that the original topsoil may have had only a limited humus content or may have been based on a thin residual peaty layer over sandy subsoil. Thus waste addition at Halsall Moss has substantially increased the organic matter content of the topsoil and/or its depth.

Small organic lenses were observed within the HM-1 profile (0 – 120 cm) that are not identified in the LOI analysis of the auger samples taken. These organic lenses were also observed by the Soil Survey of England and Wales (Beard *et al.*, 1987); they were thought to be secondary accumulation of leached humus acids rather than a buried palaeosol.

At Chat Moss, the large, well humified organic matter content to 40 cm depth, coupled with the circumneutral pH values of an agricultural topsoil should mean that cationic trace metals are strongly held. In addition, trace metals leaching in complexed form with soluble organic acids will pass into an acidic subsoil (Section 3.1.3.1) which should cause flocculation of humic acids. Leaching of trace metals would then only occur with dissociation of the flocculated complex and the low adsorption capacity of the acidic, poorly humified peat could accentuate this. However the presence of sulphide in the anaerobic layers of the Chat Moss peat (discussed further in Chapter 5) may cause secondary precipitation of some metals. Overall the risk to groundwater may be quite small at the contaminated Chat Moss sites such as CM-3.

At Halsall Moss, the elevated organic matter content in the topsoil combined with increase in pH towards the base of the topsoil (Chapter 3.1.3.1) may help solubilise metals that are complexed with the organic matter. Below the topsoil the sandy texture of the soil is likely to facilitate leaching of humic and fulvic acids and so it may be possible for metals moving in complexed form, originating from the topsoil, to reach drainage outlets or the groundwater. Nevertheless, the decrease in pH seen in the subsoil at the Halsall Moss site will reduce the solubility of mobilized organic matter and encourage flocculation of the organic acids, which may be the origin of the thin organic lenses seen in field observations.

The rapid pH change at the boundary between the topsoil and native peat seen at Chat Moss is particularly interesting because it may represent a zone where metals

present in the waste materials are mobilised as a result of the lower pH (Qureshi *et al.*, 2004; Rothwell *et al.*, 2005; Alloway & Jackson, 1991; Charlatchka & Cambier, 2000). Decreasing redox potential can result in increased pH (Grybos *et al.*, 2007) and may be the cause of the slight pH rise observed in the peat as a function of depth or distance from the oxidation front. The boundary of the peat with the topsoil will be the most oxygenated region of the peat. Although metals are less mobile in aerobic mineral soils (Charlatchka & Cambier, 2000) due to adsorption on Fe/Mn hydrous oxides, this is unlikely to apply in organic soils and the low pH associated with this redox boundary would be expected to increase solubility of free metal ions.

The mobility of metals in the soils examined is likely to be controlled by a combination of factors, especially considering the important role of humus in peaty soils and the potential for anaerobic conditions within the soil profile. Acidic conditions will reduce the negative charge on humus, increase the positive charge on hydrous oxides, and thereby encourage free metal ion mobility in the soil solution. However, high pH values can also encourage metal mobility through the dissolution of molecular and colloidal organic matter (humic and fulvic acids) with which metals may be complexed (Grybos *et al.*, 2007; Schwab *et al.*, 2005). The net effect of pH change is therefore difficult to predict but will depend largely on the strength of metal binding: strongly bound Cu is likely to be mobilized with humus acids at high pH whereas more weakly bound Cd will be more soluble at low pH as free Cd²⁺ ions. The mobility of metals in Chat Moss soils will be further discussed in Chapters 4 and 5.

3.1.3.3 Variation in trace metal concentration with soil depth

3.1.3.3.1 Group 2 metals: Ca, Sr, Ba

Both contaminated sites CM-3 and HM-1 were enriched with Ca in the top 40 cm, with the concentrations dropping sharply at 40-50 cm to background levels within the underlying soil (Table 3.2 and Figure 3.3). Data for Ca is only available for sites CM-3 (Chat Moss) and HM-1 (Halsall Moss).

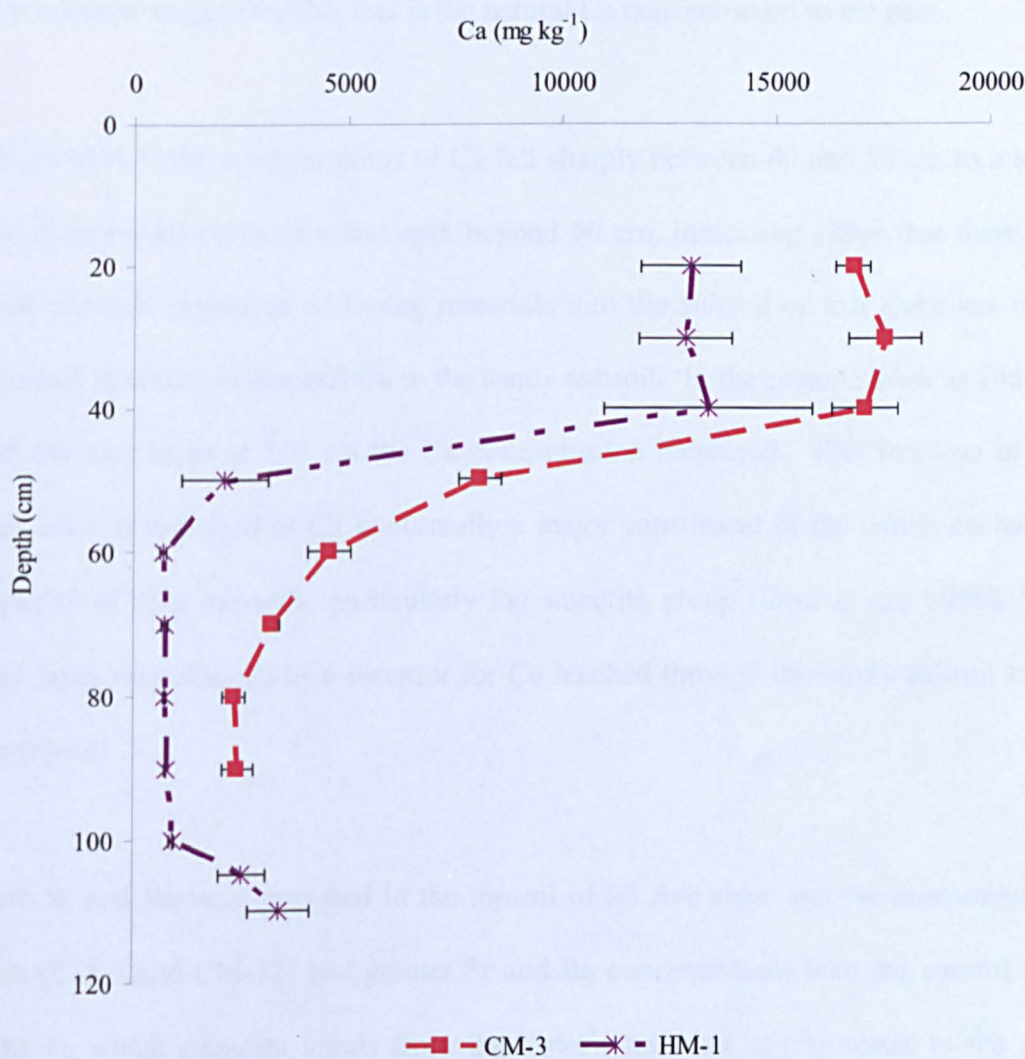


Figure 3.3: Average concentrations of Ca within the soil profiles of sites CM-3 (contaminated Chat Moss) and site HM-1 (contaminated Halsall Moss). Error bars show standard error of three replicates.

It is likely that this enrichment in the topsoil was caused by a combination of liming and the addition of waste materials to the soil, especially in the case of CM-3 where it is known that Ca-rich materials such as steel furnace waste have been incorporated into the soil. Concentrations of Ca in the peat subsoil of CM-3 decreased more gradually between 50 and 80 cm, possibly due to the migration of Ca into the subsoil from the topsoil, which may be encouraged by the pH decrease seen at the topsoil/subsoil boundary (Section 3.1.1.1). The concentration between 80 and 90 cm was constant suggesting that this is the natural Ca concentration in the peat.

At site HM-1, the concentrations of Ca fell sharply between 40 and 50 cm to a level which remained constant with depth beyond 60 cm, indicating either that there has been minimal migration of liming materials into the subsoil or that there has been minimal retention of leached Ca in the sandy subsoil. In the organic layer at 105 cm and the clay layer at 110 cm the Ca concentration increased. This increase in the clay layer is expected as Ca is normally a major constituent of the cation exchange capacity of clay minerals, particularly the smectite group (Deer *et al.*, 1996). The clay layer may also act as a receptor for Ca leached through the sandy subsoil from the topsoil.

Both Sr and Ba were enriched in the topsoil of all five sites, and the contaminated sites (CM-3 and CM-12) had greater Sr and Ba concentrations than the control site (CM-1), which suggests inputs from the historic addition of city waste to the soil (Table 3.2 and Figures 3.4 and 3.5).

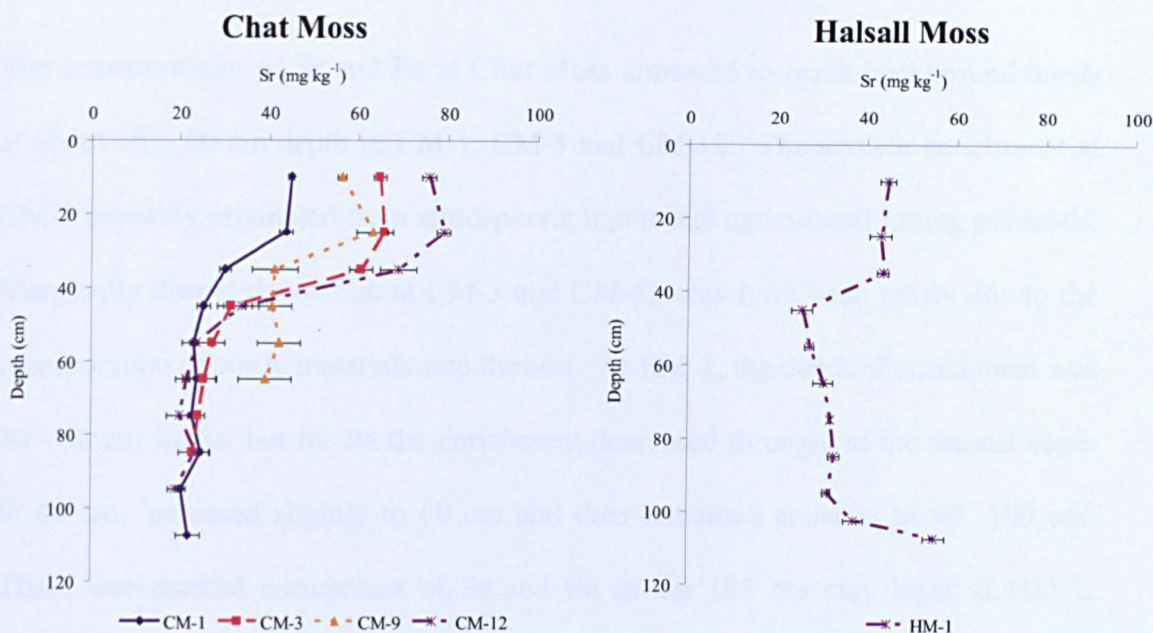


Figure 3.4: Average concentrations of Sr within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

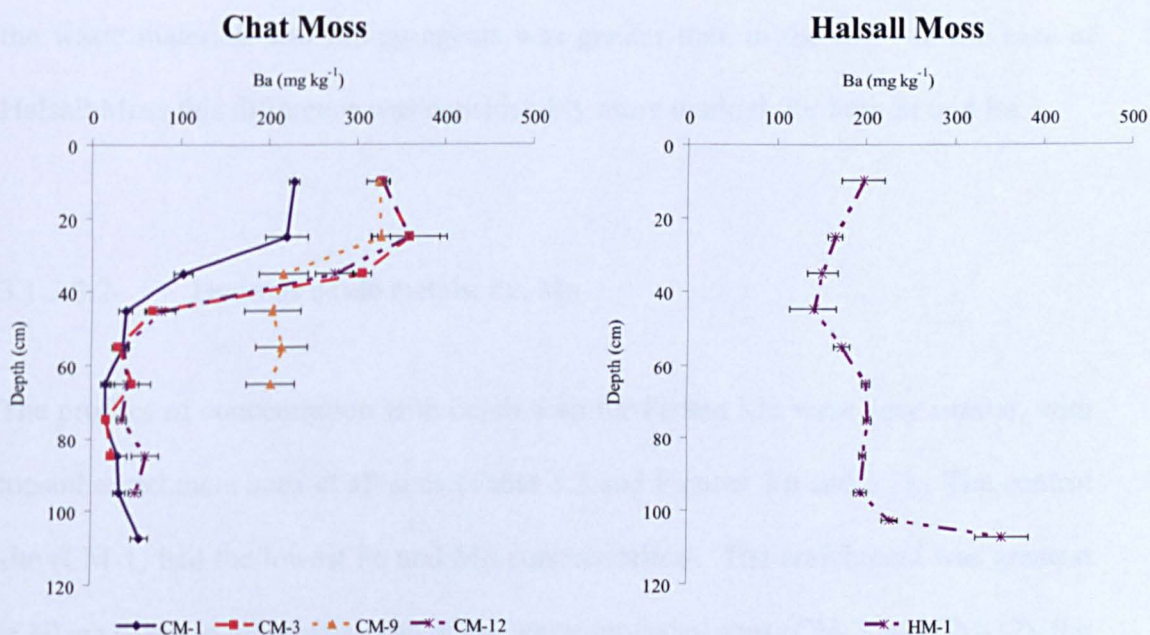


Figure 3.5: Average concentrations of Ba within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

The concentrations of Sr and Ba at Chat Moss appeared to reach background levels at about 50 – 60 cm depth in CM-1, CM-3 and CM-12. The surface enrichment at CM-1 probably originated from atmospheric inputs and agricultural liming materials. Marginally deeper deposition at CM-3 and CM-12 may have been partly due to the incorporation of waste materials into the soil. At HM-1, the depth of enrichment was 30 - 40 cm for Sr, but for Ba the enrichment decreased throughout the topsoil depth to 40 cm, increased slightly to 60 cm and then remained constant to 90 -100 cm. There was marked enrichment of Sr and Ba in the 105 cm clay layer at HM-1, suggesting retention on cation exchange sites in 2:1 alumino-silicates (Deer *et al.*, 1996).

The profiles for Ca, Sr and Ba were broadly similar in Chat Moss but the degree of surface enrichment in Sr was considerably less suggesting that the ratio of Ca:Sr in the waste materials and liming agents was greater than in the soil. In the case of Halsall Moss this difference was considerably more marked, for both Sr and Ba.

3.1.3.3.2 Hydrous oxide metals: Fe, Mn

The profiles of concentration with depth seen for Fe and Mn were very similar, with topsoil enrichment seen at all sites (Table 3.2 and Figures 3.6 and 3.7). The control site (CM-1) had the lowest Fe and Mn concentrations. The enrichment was greatest at 30 cm depth in all profiles, but at the waste-amended sites (CM-3 and CM-12), the enrichment again extended to 50 cm depth. This shows that waste disposal has enriched the contaminated sites with various forms of Fe and Mn; this is further discussed in a Scanning Electron Microscopy study (Section 4.2.3). From the

historical records, it can be seen that foundry waste such as ash and slag materials formed a large component of the waste deposited on Chat Moss (Section 1.2.1.3), and so it would be expected that iron oxides would form part of the waste material incorporated into the topsoil.

The concentrations of Fe and Mn were very low in the topsoil of HM-1, as was the degree of enrichment of Fe relative to the subsoil. This agrees with the historical records which showed that the waste deposited at Halsall Moss was dominated by animal manures, as compared with the industrial wastes employed at Chat Moss. Again, a large degree of Fe enrichment was seen in the clay layer at HM-1, which may represent octahedrally substituted Fe(II) in, for example, smectite minerals (Deer *et al.*, 1996) or could simply arise from colloidal association of Fe hydrous oxide minerals with alumino-silicates.

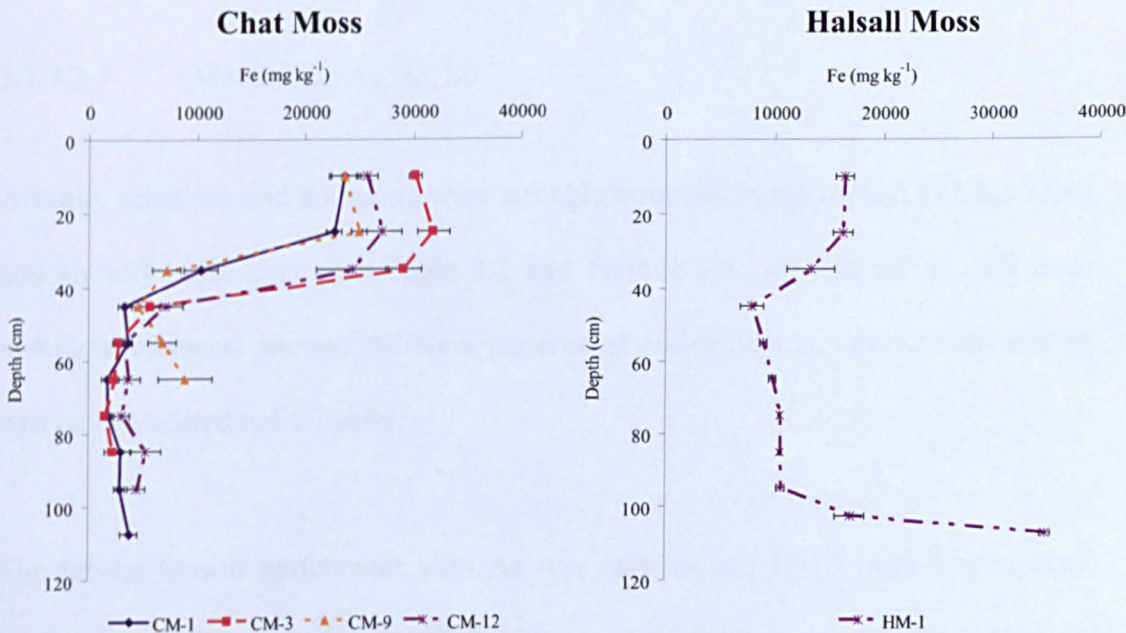


Figure 3.6: Average concentrations of Fe within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

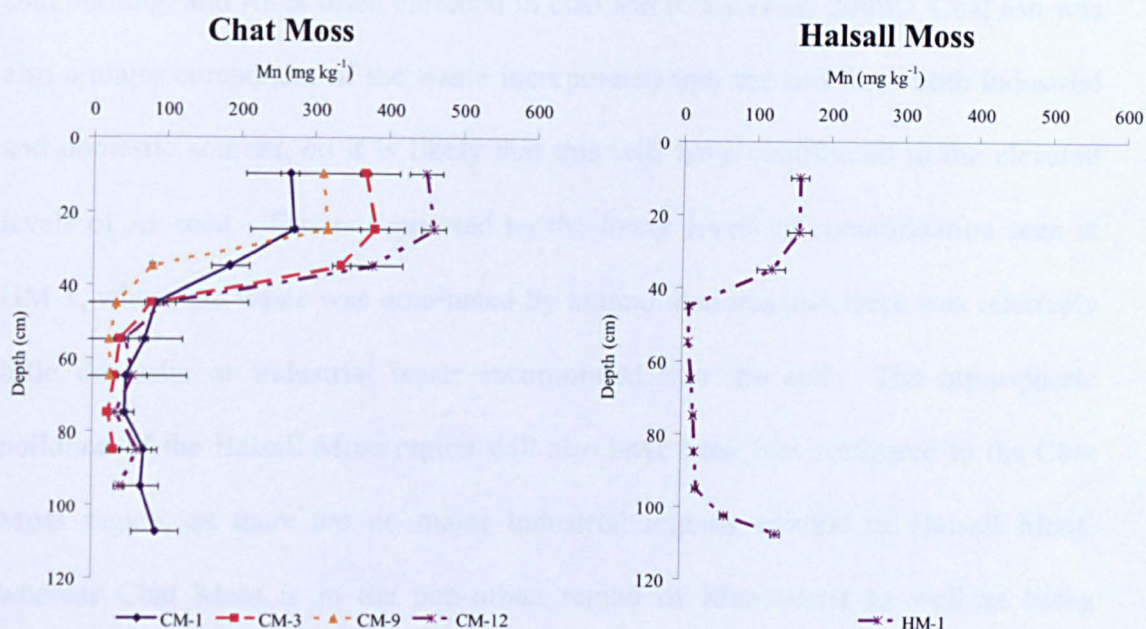


Figure 3.7: Average concentrations of Mn within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

3.1.3.3.3 Metalloids: As, Se, Sb

Arsenic, selenium and antimony were strongly enriched in the topsoil of Chat Moss and Halsall Moss sites (see Table 3.2 and Figures 3.8, 3.9 and 3.10). All three metalloid elements showed different patterns of enrichment across the sites and so will be considered individually.

The lowest topsoil enrichment with As was seen in site HM-1 with intermediate levels in sites CM-1, CM-9 and CM -12 and substantially greater concentrations in site CM-3 (Figure 3.8), and site CM-3 was the only site to exceed the Soil Guideline Values for As levels in allotments (43 mg kg⁻¹) (Environment Agency, 2009b). One of the dominant sources of atmospheric pollution in the Manchester region has been

coal burning, and As is often enriched in coal ash (Cloy *et al.*; 2009). Coal ash was also a major component of the waste incorporated into the soil from both industrial and domestic sources, so it is likely that this will have contributed to the elevated levels of As seen. This is supported by the lower levels of contamination seen at HM-1, where the waste was dominated by animal manures and there was relatively little domestic or industrial waste incorporated into the soil. The atmospheric pollution of the Halsall Moss region will also have been less compared to the Chat Moss region, as there are no major industrial regions upwind of Halsall Moss, whereas Chat Moss is in the peri-urban region of Manchester as well as being downwind of the Pennine ore field and smelting region.

Arsenic concentrations in the subsoils of all five sites were very low and the boundary between the topsoil and subsoil appears quite sharp. In the case of site CM-3, the topsoil had approximately ten times the As concentration seen in the subsoil. This may indicate that there had been little downward movement of As from the topsoil and that As is not mobile in the waste-amended topsoils, even at the highest concentrations (c. 45 mg kg⁻¹). It is unlikely that the As was present as As(III) in aerobic topsoils amended with combustion wastes and more likely that the As was strongly held as arsenate bound to Fe hydrous oxides, or unreduced sedimentary ores associated with furnace waste. Alternatively, there may have been significant mobilization of As from the topsoil but the organic subsoil was unable to retain leached arsenate. In the anaerobic peat layer the As(V) is likely to be reduced to the even less strongly bound arsenite form. However at sites CM-1 and CM-9 there was a gradual decrease in As concentration between 30 and 50 cm, which is

below the depth of the topsoil, suggesting that there was some mobility of As in the topsoil and that it had moved beyond the depth of the original waste incorporation.

Selenium showed the lowest topsoil enrichment in HM-1 followed by CM-9; soils CM-1, CM-3 and CM-12 all had the same levels of enrichment in the topsoil (Figure 3.9). Thus, a comparison of CM-1 and CM-3 suggests that waste amendment has not substantially changed the Se status of the Chat Moss soils. The Soil Guideline Value for Se in allotment soils (120 mg kg^{-1}) was not exceeded in any soils investigated. The depth of enrichment was broadly the same as seen for As. There was little evidence for movement and retention in subsoil; the subsoil Se concentrations were similar across all sites. Selenium may be present in organic form in humus (Kabata-Pendias, 2001) and the large increase in organic matter in the subsoil may be acting to immobilise Se in this layer. However, in the clay layer at HM-1, there was a large enrichment of Se to the same level of that seen in the topsoil. This may suggest leaching of selenite through the sandy matrix of the subsoil and retention on the Fe hydrous oxides in the clay layer.

Antimony showed enrichment above background in the CM-3 topsoil (over CM-1) suggesting inputs in the waste material. The depth of enrichment followed the same pattern as As and Se, with 50 cm depth of enrichment seen at CM-3, CM-12 and HM-1, and 30 cm seen at CM-1 and CM-9 (Figure 3.10). As seen for As, the subsoil concentrations of Sb were very small in all five sites. There was negligible enrichment of Sb seen in the clay layer at HM-1. The Sb in the topsoil may have originated from atmospheric deposition and coal ash disposal as Sb has a similar behaviour to As in that it is concentrated in coals (Kabata-Pendias, 2001). Although

concentrations in CM-3 were greater than in the Chat Moss control site (CM-1), the Sb concentrations in topsoil were similar for sites CM-3, CM-12 and HM-1. Given the known differences in the degree of industrial activity and the nature of the wastes used in Chat and Halsall Mosses this suggests that inputs of Sb from waste have been quite small.

3.1.3.3.4 Trace metals: V, Cr, Co, Ni, Cu, Zn, Mo, Cd, Sn, Cs, Pb, Bi

Topsoil enrichment was seen across the five sites for all the trace metals except Cu and Mo at HM-1, which showed no enrichment above the levels seen in the subsoil (see Table 3.2 and Figure 3.3). The concentration of trace metals in the topsoil was highest in the waste amended sites on Chat Moss (CM-3 and CM-12) and lowest in the control site (CM-1) and in CM-9. The concentrations seen in the Halsall Moss topsoil (HM-1) were always equal to or less than those of CM-1 and CM-9 and was dominated by animal manures, and there has been relatively little atmospheric pollution on Halsall Moss compared to Chat Moss.

The depth of the contamination for all the trace metals followed the pattern seen before, of slightly deeper contamination at the sites that received waste amendment (CM-3, CM-12 and HM-1) compared to the sites which probably only received atmospheric inputs and normal agricultural amendments (CM-1 and CM-9). The subsoil concentrations across all five sites were similar for all the remaining trace metals. However, V, Ni, Cr, Cs, and Co underwent an increase in concentrations in the clay layer of HM-1. Large variability was seen in the profiles of some trace metals (Ni, Cd, Zn, Sn, Pb) which most likely represents the variability of waste

disposal across the the sites, as the greatest error was seen in the two sites known to have received waste (CM-3 and CM-12), indicating an uneven distribution of contamination.

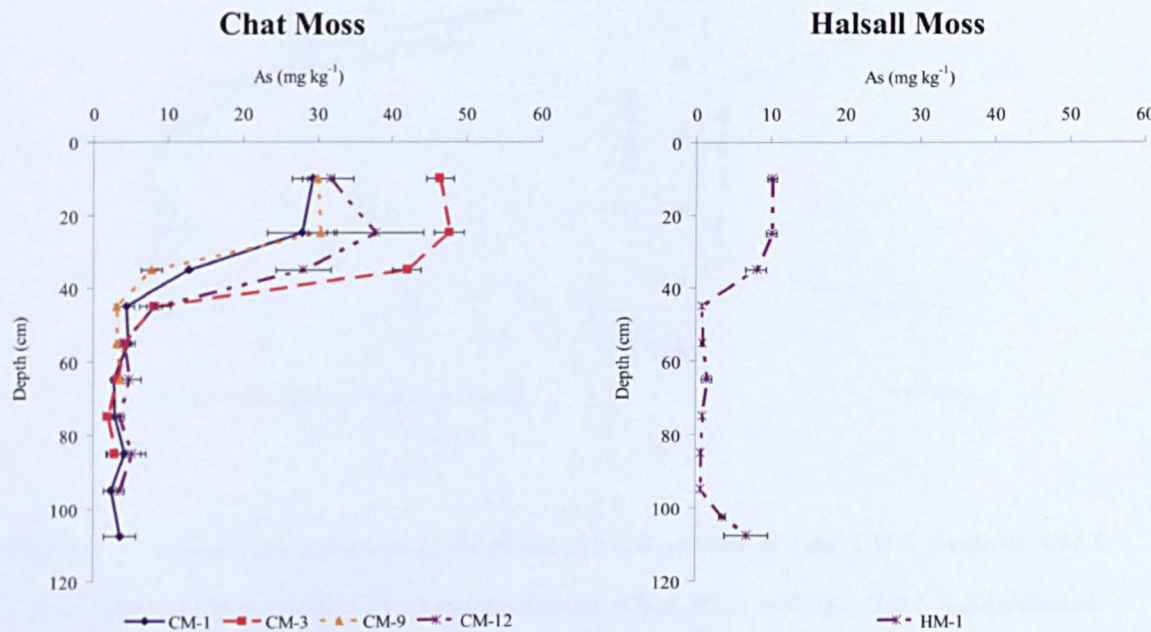


Figure 3.8: Average concentrations of As within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

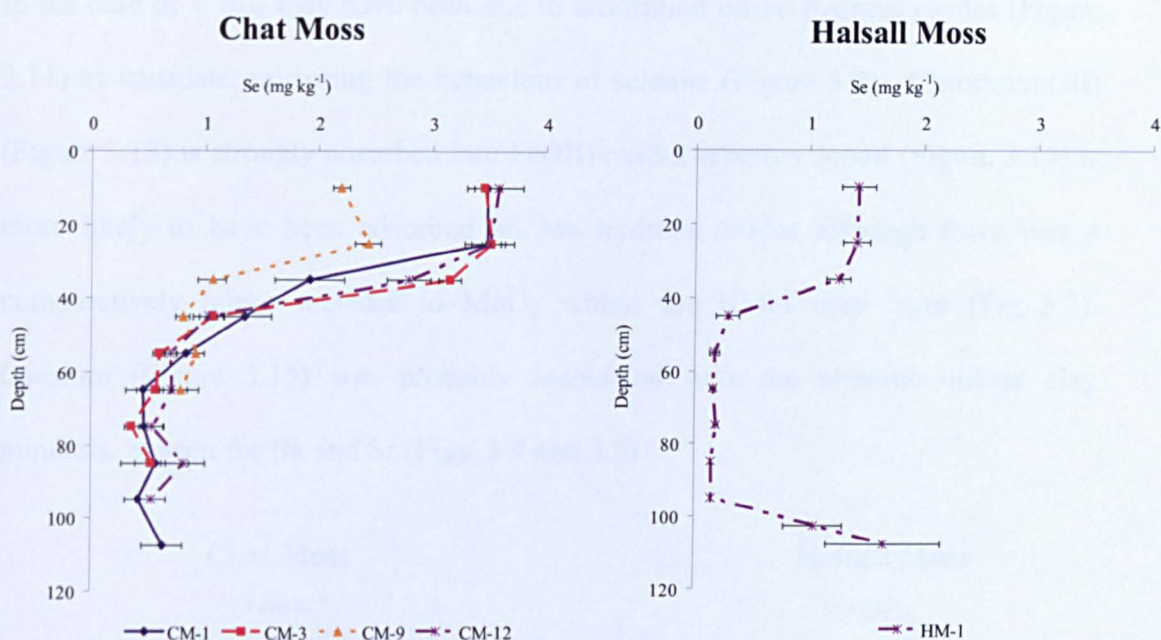


Figure 3.9: Average concentrations of Se within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

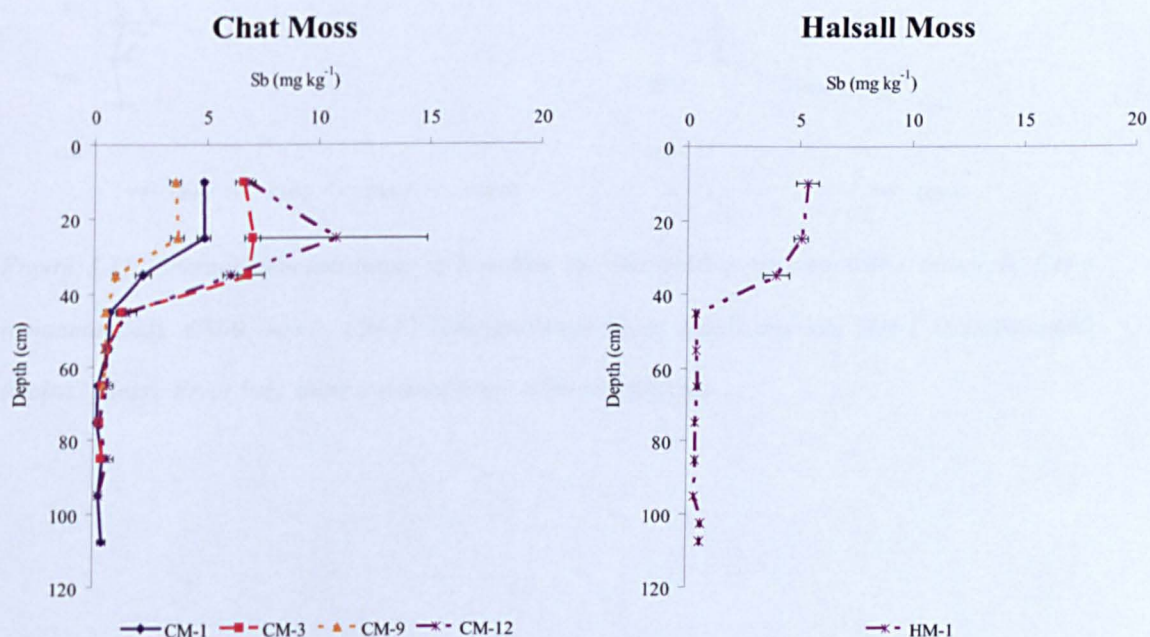


Figure 3.10: Average concentrations of Sb within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

In the case of V this may have been due to adsorption on Fe hydrous oxides (Figure 3.11) as vanadate, mirroring the behaviour of selenite (Figure 3.9). Chromium(III) (Figure 3.13) is strongly adsorbed into Fe(III) oxides whereas cobalt (Figure 3.14) is more likely to have been adsorbed on Mn hydrous oxides although there was a comparatively minor increase in MnO₂ within the HM-1 clay layer (Fig 3.7). Caesium (Figure 3.15) was probably associated with the aluminosilicate clay minerals, as seen for Ba and Sr (Figs. 3.4 and 3.5).

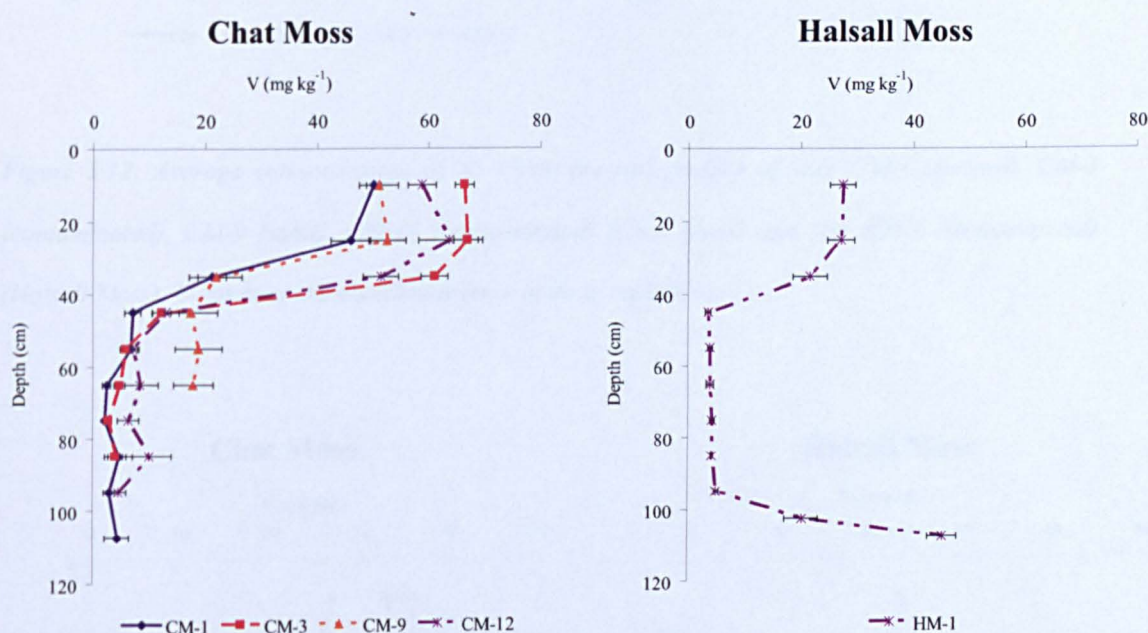


Figure 3.11: Average concentrations of V within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

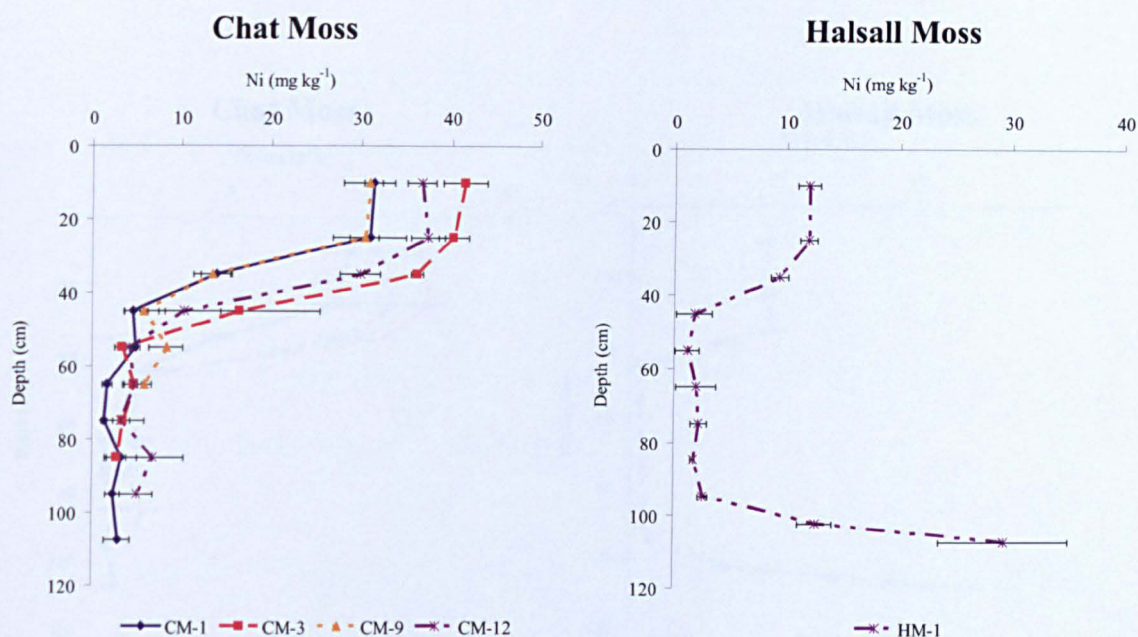


Figure 3.12: Average concentrations of Ni within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

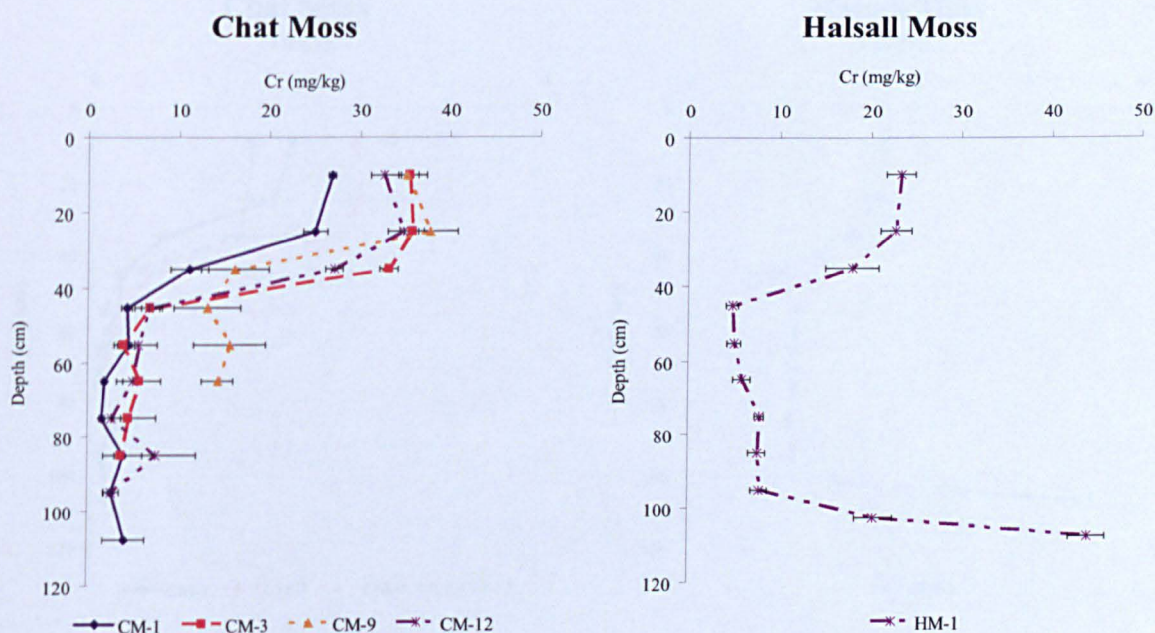


Figure 3.13: Average concentrations of Cr within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

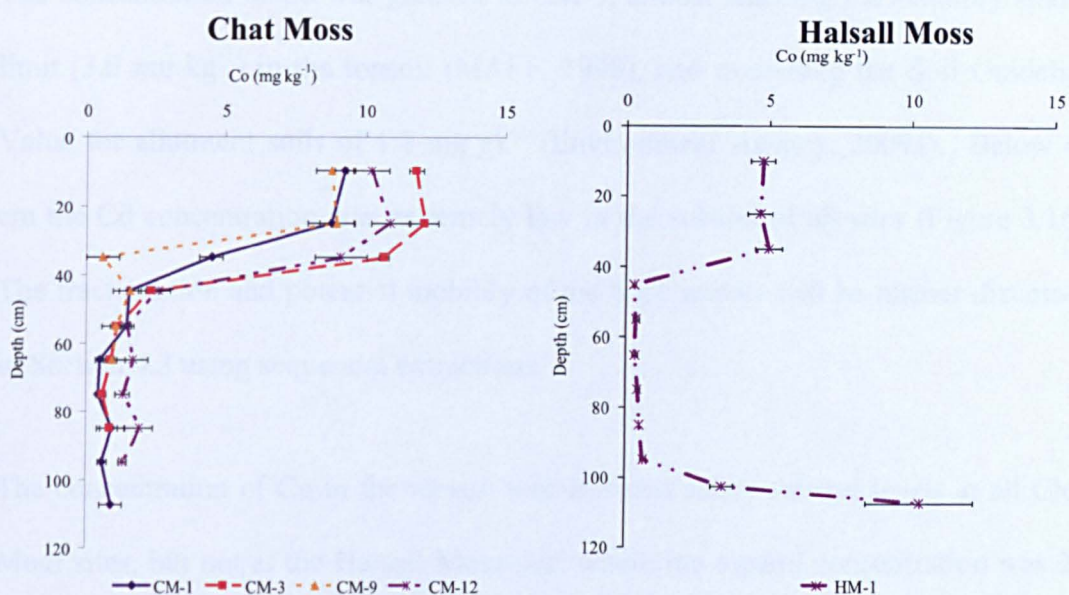


Figure 3.14: Average concentrations of Co within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

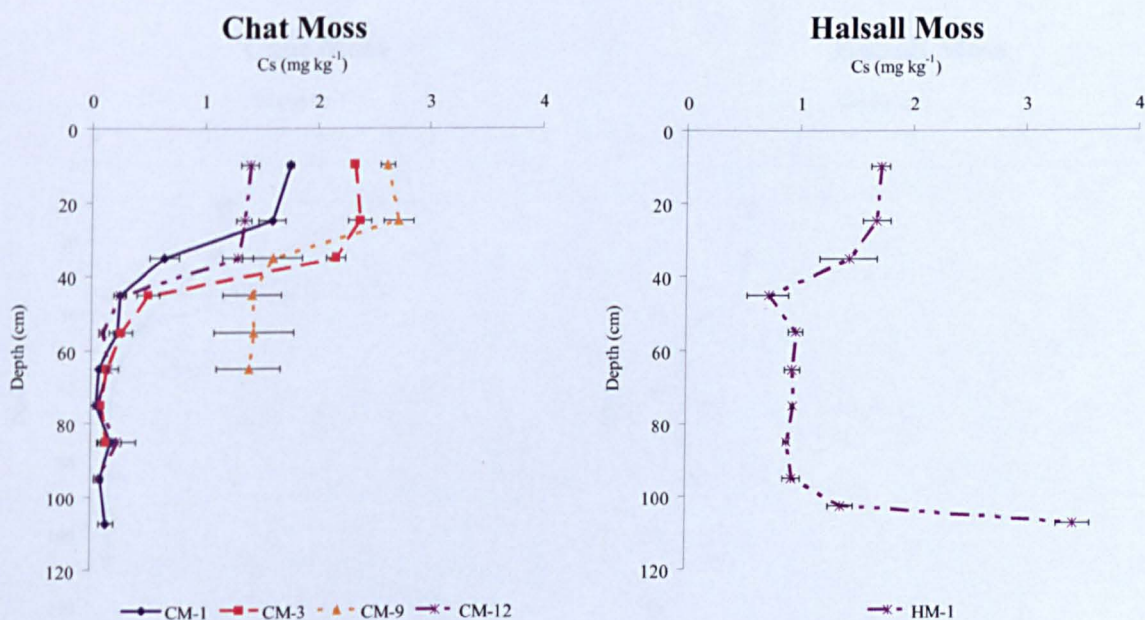


Figure 3.15: Average concentrations of Cs within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

The concentration of Cd was greatest in CM-3, almost reaching the statutory sludge limit (3.0 mg kg^{-1}) in the topsoil (MAFF, 1998), and exceeding the Soil Guideline Value for allotment soils of 1.8 mg kg^{-1} (Environment Agency, 2009a). Below 40 cm the Cd concentration was extremely low in the subsoil of all sites (Figure 3.16). The fractionation and potential mobility of the trace metals will be further discussed in Section 4.3 using sequential extractions.

The concentration of Cu in the topsoil was elevated above subsoil levels at all Chat Moss sites, but not at the Halsall Moss site, where the topsoil concentration was 27 mg kg^{-1} compared to the subsoil concentration of 34 mg kg^{-1} (Figure 3.17). Sites CM-3 and CM-12 showed the highest levels of Cu in the topsoil ($150 - 177 \text{ mg kg}^{-1}$) and the greatest depth of enrichment over background. Sites CM-1 and CM-9 had lower and similar Cu concentrations ($80 - 85 \text{ mg kg}^{-1}$).

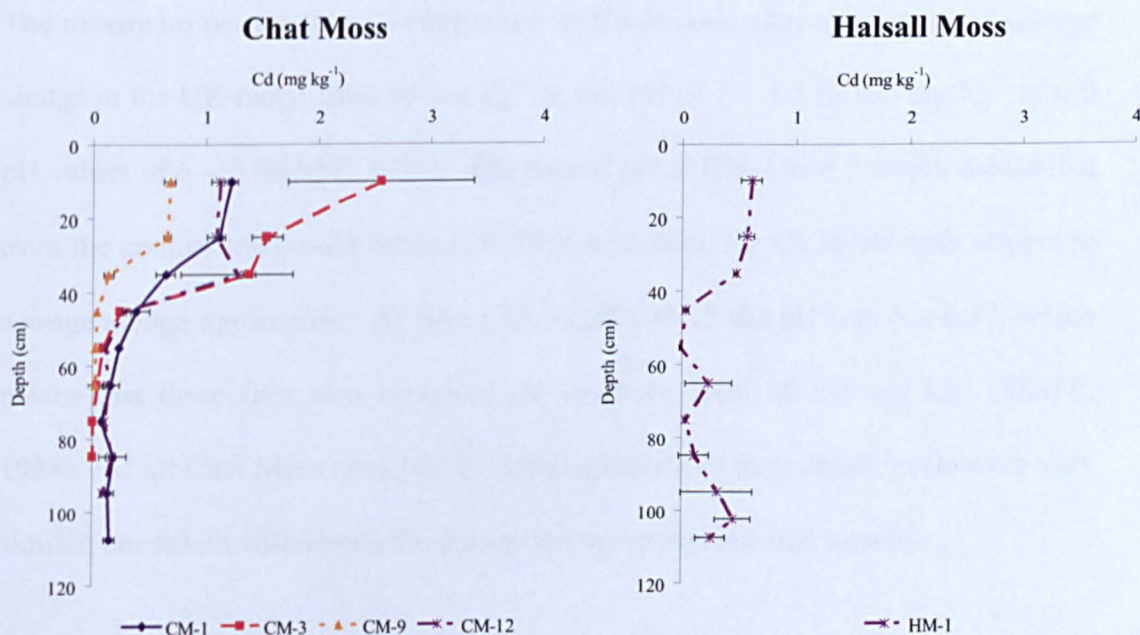


Figure 3.16: Average concentrations of Cd within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

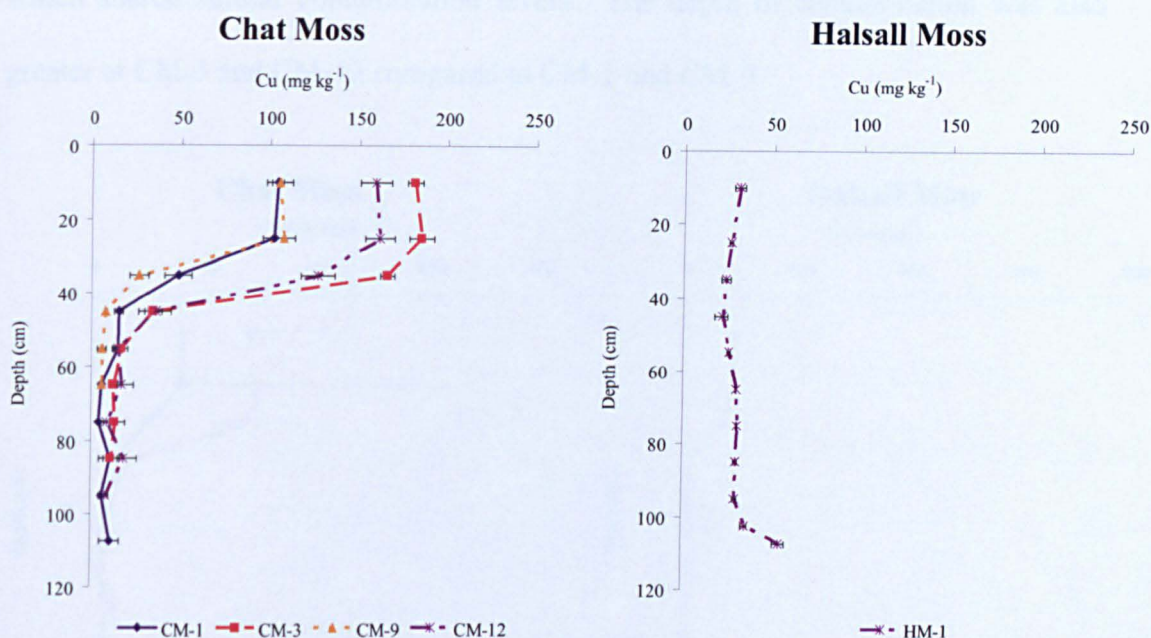


Figure 3.17: Average concentrations of Cu within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

The maximum permissible concentrations of Cu in soils after application of sewage sludge in the UK range from 80 mg kg⁻¹ at soil pH of 5 – 5.5 to 135 mg kg⁻¹ at soil pH values of 6 – 7 (MAFF, 1998). The topsoil pH at CM-1 was 5 which means that even the control site would exceed DEFRA guidelines for Cu levels with respect to sewage sludge application. At sites CM-3 and CM-12 the pH was 6 – 6.37, which means that these sites also exceeded the statutory level of 135 mg kg⁻¹ (MAFF, 1998). At all Chat Moss sites, the Cu concentrations in the subsoil levels were very similar, consistent with strong Cu adsorption in the organic-rich topsoils.

Zinc topsoil concentrations were elevated above the subsoil levels at all sites on Chat Moss and Halsall Moss (Figure 3.18). A similar pattern to that of Cu was observed, with CM-3 and CM-12 having significantly higher Zn levels than CM-1 and CM-9,

which shared similar contamination levels. The depth of contamination was also greater at CM-3 and CM-12 compared to CM-1 and CM-9.

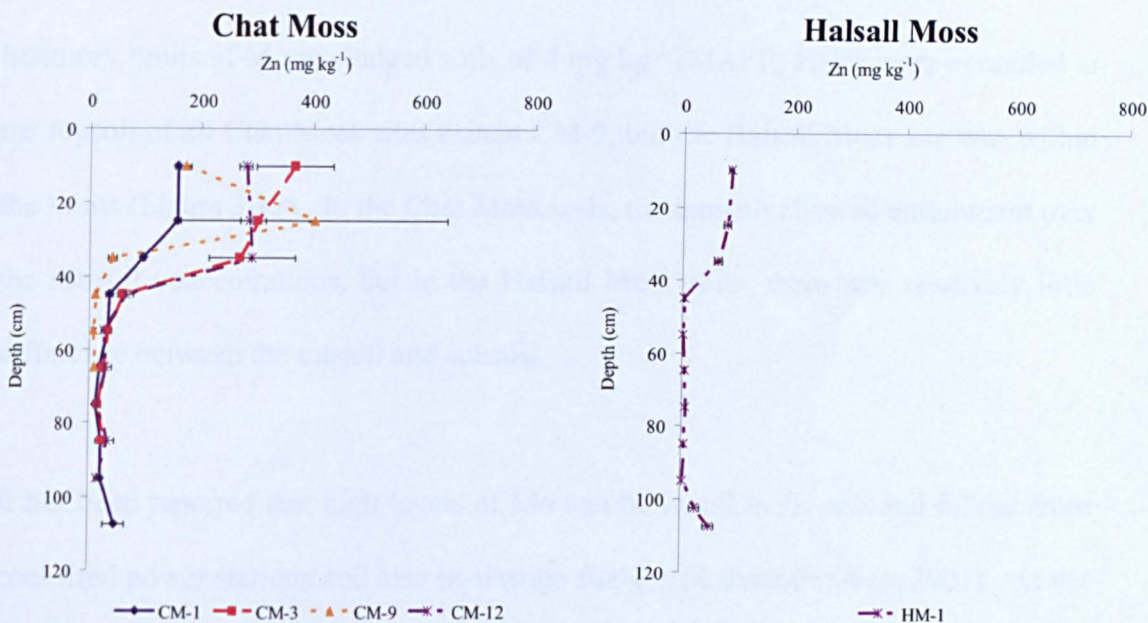


Figure 3.18: Average concentrations of Zn within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

When comparing the Zn topsoil concentrations with the MAFF guidelines for soil receiving sewage sludge (MAFF, 1998), it can be seen that concentrations at the waste-amended sites CM-3 and CM-12 exceed the guideline levels of 200 mg kg⁻¹ but CM-1 and CM-9 were broadly within guideline levels. Concentrations of Zn were lowest at HM-1 (76 mg kg⁻¹), but the subsoil levels of Zn showed a different profile to the Chat Moss sites, with a sharp decrease at the topsoil-subsoil boundary but a slight increase in Zn concentration at the subsoil-clay boundary. Zinc can be mobile in soils but is held strongly by clay and organic matter (Kabata-Pendias, 2001), so again the profile at HM-1 may indicate metal migration down through the sandy layer to the clay and organic layer at the base of the soil profile where the Zn is adsorbed. The subsoil levels at Chat Moss are all very similar, and very low,

suggesting either no substantial movement of Zn down the soil profile or poor retention of mobilized Zn in the acidic fibrous peat subsoil.

Statutory limits of Mo in sludged soils of 4 mg kg^{-1} (MAFF, 1998) were exceeded in the topsoil of all Chat Moss sites except CM-9, but the Halsall Moss site was within the limits (Figure 3.19). In the Chat Moss soils, the topsoils showed enrichment over the subsoil concentrations, but in the Halsall Moss soils, there was relatively little difference between the topsoil and subsoil.

It has been reported that high levels of Mo can be found in fly-ash and fallout from coal fired power stations and also in sewage sludges (Kabata-Pendias, 2001). At the Chat Moss sites, waste incorporated into the soil included coal and fly-ash, as well as human wastes and sewage materials, all of which may have caused the elevated Mo concentrations seen in the topsoils. At Halsall Moss, the waste material was mainly animal manures, which may explain the lower levels of Mo seen in these soils. Again there was no evidence for migration of Mo into the subsoil at Chat Moss or no evidence of retention of leached Mo.

Tin showed elevation in the topsoil compared to the subsoil at the Chat and Halsall Moss sites, although the topsoil concentrations were considerably greater in the Chat Moss sites than the Halsall Moss site (Figure 3.20). Tin concentrations in the Chat Moss sites range from 8 mg kg^{-1} (CM-1) to 20 mg kg^{-1} (CM-3 and CM-12), and Sn concentration in the Halsall Moss topsoil was only 4 mg kg^{-1} . At all sites there was a sharp decrease in Sn concentration in the subsoil to 1 mg kg^{-1} or less, although there was a slight increase at the base of the Halsall Moss profile in the organic and clay layer.

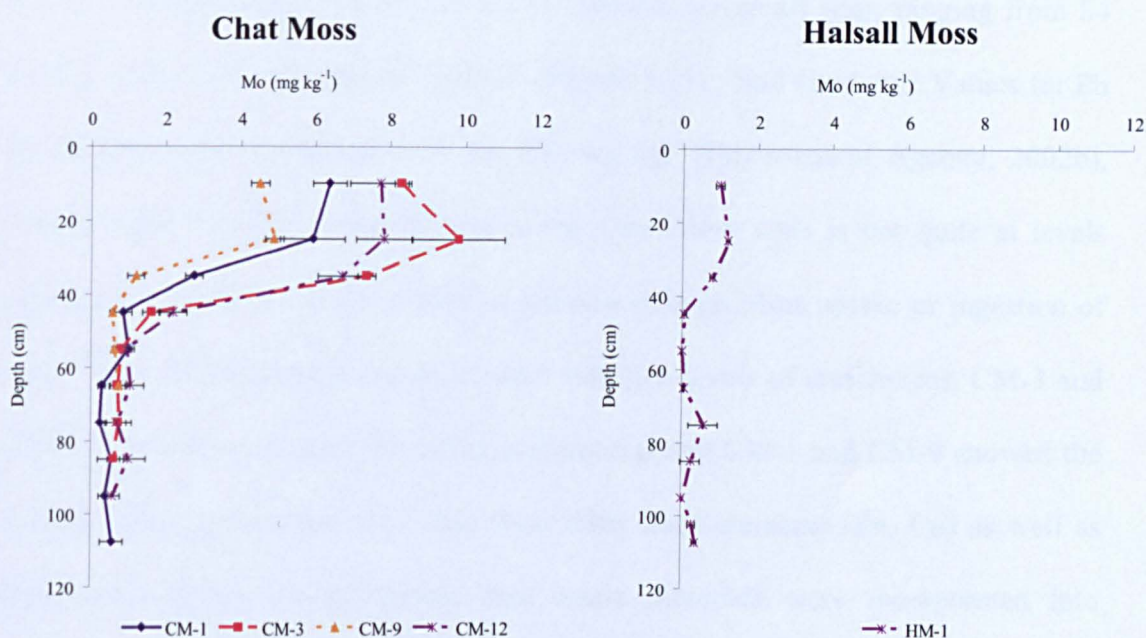


Figure 3.19: Average concentrations of Mo within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

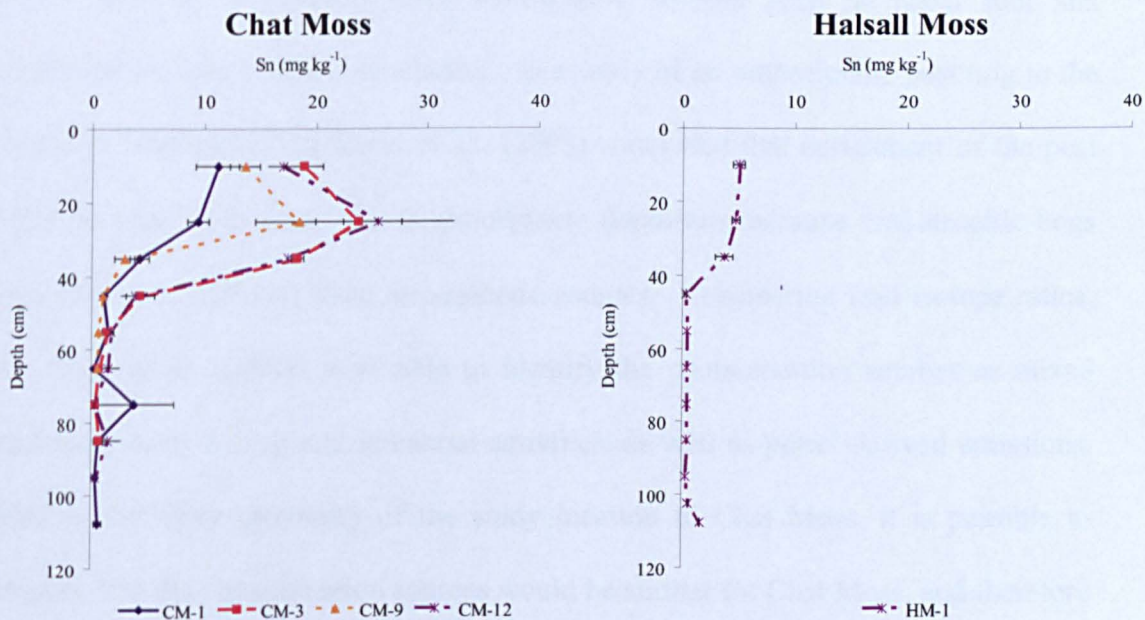


Figure 3.20: Average concentrations of Sn within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

Topsoil concentrations of Pb were highly variable across all sites, ranging from 84 mg kg⁻¹ (HM-1) to 406 mg kg⁻¹ (CM-3) (Figure 3.21). Soil Guideline Values for Pb in allotment and residential soils are 450 mg kg⁻¹ (Environment Agency, 2002b), which shows that the contamination in the Chat Moss soils is not quite at levels which are considered to be harmful to humans through plant uptake or ingestion of soil. The Chat Moss sites can be divided into two levels of enrichment; CM-3 and CM-12 showed the highest Pb soil concentrations and CM-1 and CM-9 showed the lowest. This corresponds with data from other trace elements (Zn, Cu) as well as historical research which showed that waste materials were incorporated into reclaimed soil at the sites CM-3 and CM-9, whereas there is no evidence for waste incorporation at CM-1 or CM-9. This indicates that waste incorporated into the soil during reclamation has contributed to the elevated levels of Pb in the contaminated sites (CM-3, CM-12), with the elevated topsoil Pb concentrations seen in CM-1 and CM-9 possibly originating from atmospheric sources such as fossil fuel and industrial emissions from Manchester. In a study of an ombotrophic peat bog to the south of Manchester, Le Roux *et al.*, (2003) concluded that enrichment of the peat with Pb must have been due to atmospheric deposition because ombotrophic bogs can only gain nutrients from atmospheric sources. Considering lead isotope ratios, Le Roux *et al.*, (2003) were able to identify the contamination sources as mixed pollution from mining and industrial activities, as well as petrol-derived emissions. Due to the close proximity of the study location to Chat Moss, it is possible to assume that the contamination sources would be similar for Chat Moss, and therefore that atmospheric pollution probably contributed to the elevated trace elements seen in 'uncontaminated' topsoils at CM-1 and CM-9 sites. Further discussion of the contamination sources at Chat and Halsall Mosses can be found in Chapter 4.1.

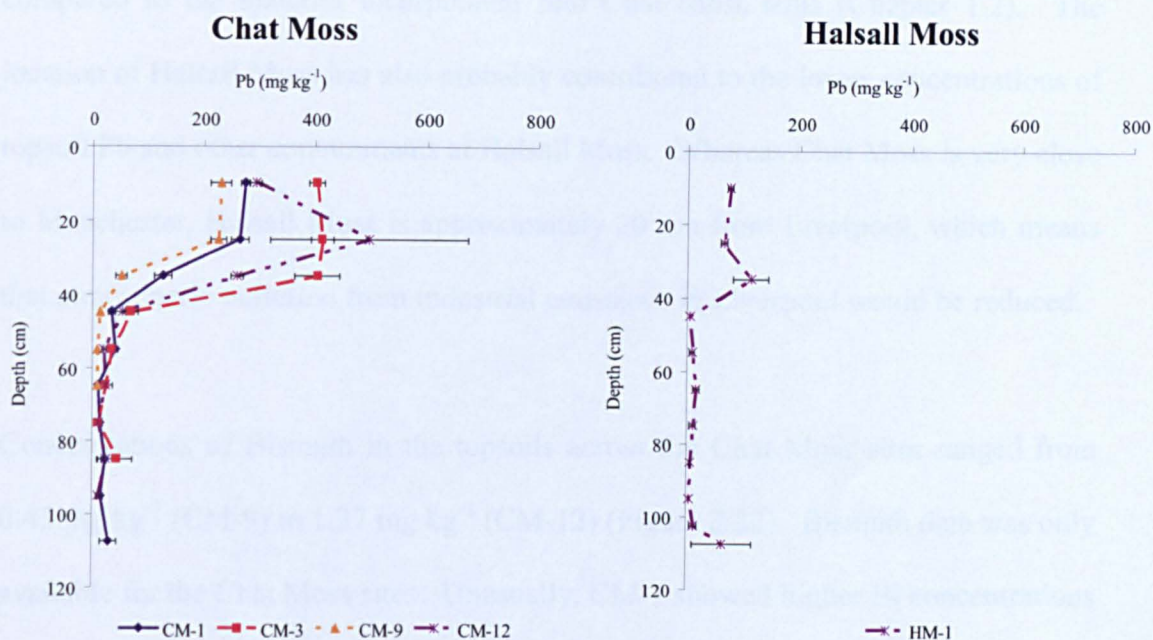


Figure 3.21: Average concentrations of Pb within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), CM-12 (contaminated) (Chat Moss) and site HM-1 (contaminated) (Halsall Moss). Error bars show standard error of three replicates.

The subsoil Pb concentrations at all four Chat Moss sites were very similar, and most likely represent a background uncontaminated Pb concentration. There was no evidence of migration of Pb from the topsoil and its subsequent retention within the subsoil. Lead is generally considered to be an extremely immobile element in soil, strongly bound to soil organic matter and Fe hydrous oxides (Morin *et al.*, 1999). Mobility and reactivity of Pb in the Chat Moss soils will be further discussed further in Chapter 4.4.

Halsall Moss showed the lowest concentration of Pb in the topsoil, although subsoil concentrations were consistent with those measured at Chat Moss. Again this reflects what is known about the nature of the waste incorporated into Halsall Moss

compared to the material incorporated into Chat Moss soils (Chapter 1.2). The location of Halsall Moss has also probably contributed to the lower concentrations of topsoil Pb and other contaminants at Halsall Moss. Whereas Chat Moss is very close to Manchester, Halsall Moss is approximately 20 km from Liverpool, which means that atmospheric pollution from industrial emissions in Liverpool would be reduced.

Concentrations of Bismuth in the topsoils across the Chat Moss sites ranged from 0.43 mg kg⁻¹ (CM-9) to 1.37 mg kg⁻¹ (CM-12) (Figure 3.22). Bismuth data was only available for the Chat Moss sites. Unusually, CM-1 showed higher Bi concentrations than CM-3, suggesting that historic waste disposal has not been a significant source of Bi. Bismuth can accumulate in coals, but atmospheric deposition of volatilised Bi may be the main source in these soils, rather than coal ash from the waste. In a study of arable soils in Scotland, a mean Bi concentration of 0.25 mg kg⁻¹ was found (Kabata-Pendias, 2001), which is significantly lower than the data collected for the Chat Moss topsoils, but slightly higher than the concentration found in the subsoils below 50 cm. Again, this indicates that coal burning in Manchester has caused accumulation of Bi from atmospheric deposition in the Chat Moss soils. Subsoil concentrations ranged from 0.01 mg kg⁻¹ (CM-9) to 0.13 mg kg⁻¹ (CM-12) and there was no evidence for migration and accumulation of Bi down the soil profile, with subsoil concentrations being consistent with depth at each site.

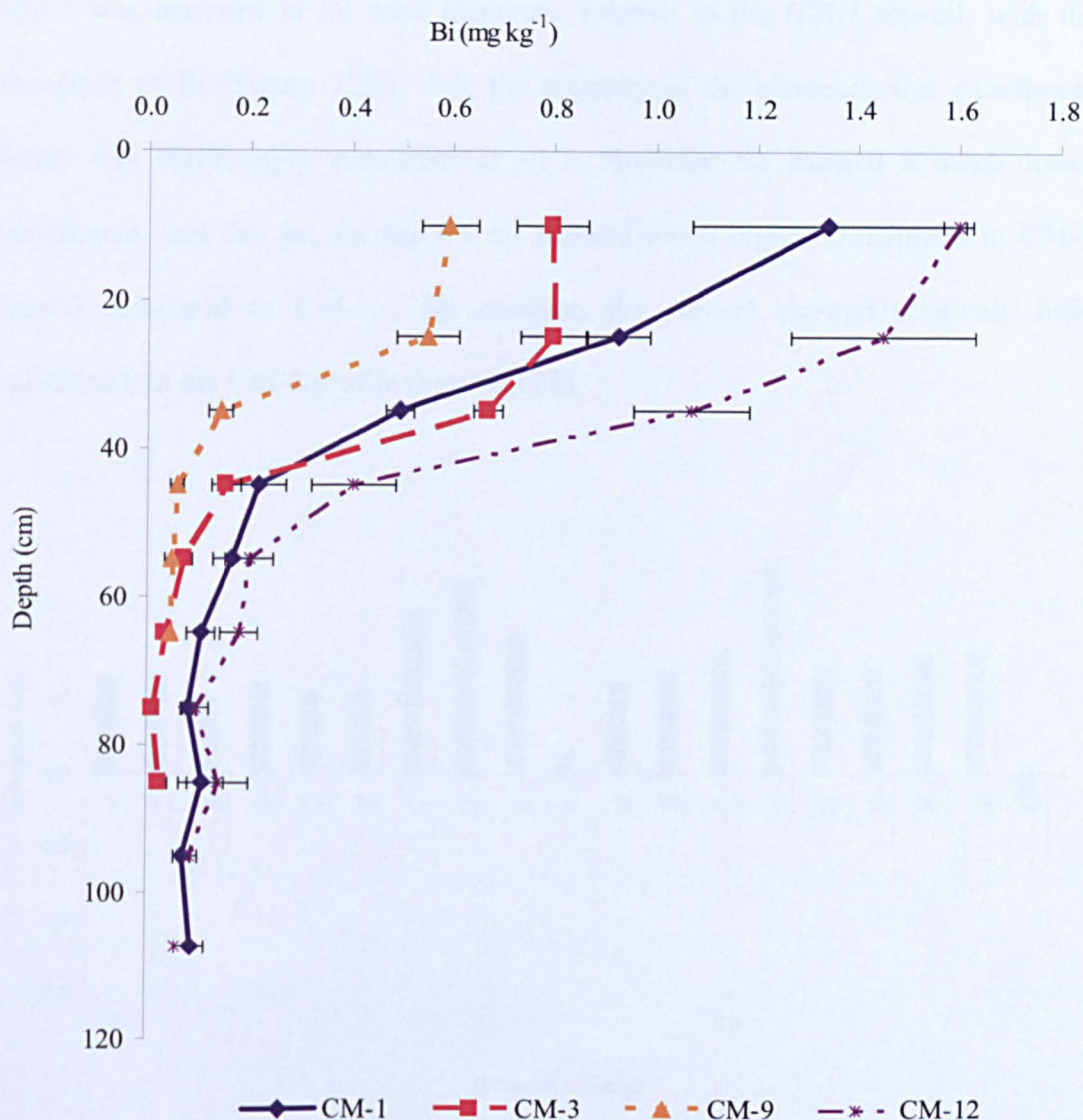


Figure 3.22: Average concentrations of Bi within the soil profiles of sites CM-1 (control), CM-3 (contaminated), CM-9 (sand), and CM-12 (contaminated) (Chat Moss). Error bars show standard error of three replicates.

Enrichment Factors were calculated by dividing the average topsoil concentration from CM-3 (contaminated) by the average topsoil concentrations of CM-1 (control) and then normalising to 0, so that a positive value shows enrichment of CM-3 over CM-1, and a negative value shows enrichment of CM-1 over CM-3. When the topsoil (0 cm – 40 cm) and subsoil (50 cm – 110 cm) averages for sites CM-1 (control) and CM-3 (contaminated) were considered, it was seen that the topsoil at

CM-3 was enriched in all trace elements, relative to the CM-1 topsoil, with the exception of Bi (Figure 3.23). For the majority of the elements, this enrichment factor was surprisingly consistent at ~1.7. However Se showed a much lower enrichment, and Sn, As, Zn and Cu all showed much higher enrichment in CM-3 topsoil compared to CM-1. By contrast, the subsoil showed relatively little enrichment in the CM-3 profile (Figure 3.23).

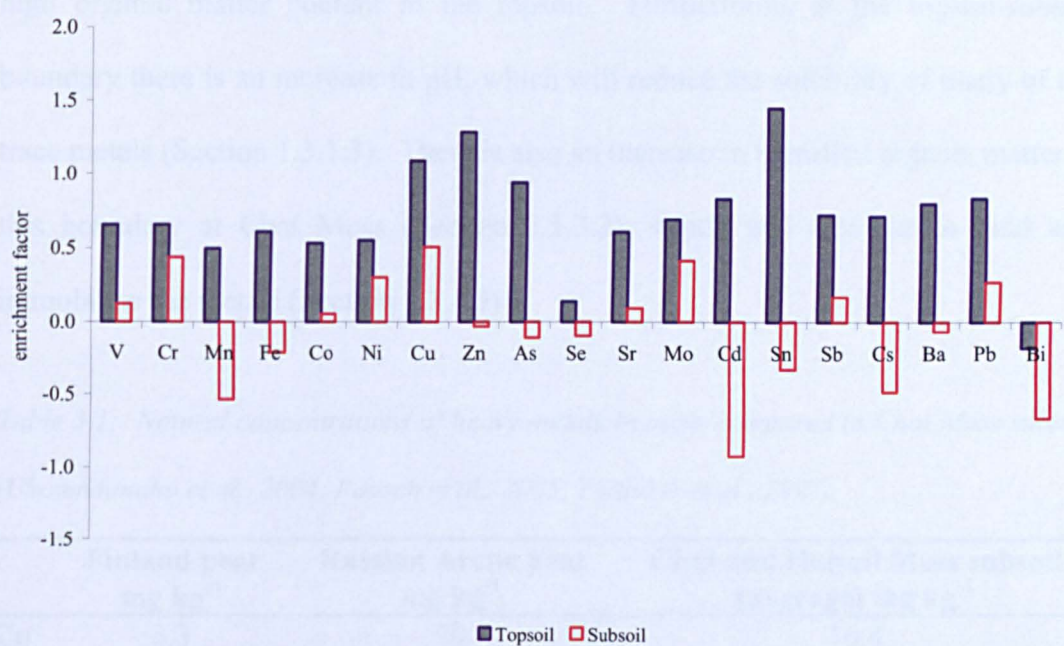


Figure 3.23: Enrichment factors of CM-3 topsoil and subsoil compared to CM-1. Positive number shows enrichment in CM-3 relative to CM-1, negative number shows depletion in CM-3 relative to CM-1

The concentration of trace metals seen in the subsoil are similar to those reported for pristine peats in Finland and the Arctic Circle. Metal concentrations of topsoil from an uncontaminated peat in Finland, (Ukonmaanaho *et al.*, 2004; Rausch *et al.*, 2005) are seen in Table 3.1, along with metal concentrations in a pristine peat from the Russian Arctic circle (Zhulidov *et al.*, 1997), and the corresponding metal concentrations for the subsoil of the four Chat Moss sites (average of all four sites).

The metal concentrations seen in the subsoil at Chat and Halsall Moss are within the ranges reported for peats that have not been affected by anthropogenic processes or pollution (Table 3.1). This either supports the suggestion that metals have not moved out of the topsoil at either Chat or Halsall Mosses or it indicates that the acidic fibrous peat substrate has a low retention capacity. The low mobility of the metals down the soil profile is most likely due to a combination of the circumneutral pH and high organic matter content in the topsoil. Furthermore, at the topsoil-subsoil boundary there is an increase in pH, which will reduce the solubility of many of the trace metals (Section 1.3.1.3). There is also an increase in humified organic matter at this boundary at Chat Moss (Section 3.1.3.2), which will also act to bind and immobilise the metals (Section 1.3.1.3).

Table 3.1: Natural concentrations of heavy metals in peats compared to Chat Moss subsoil (Ukonmaanaho et al., 2004; Rausch et al., 2005; Zhulidov et al., 1997).

	Finland peat mg kg⁻¹	Russian Arctic peat mg kg⁻¹	Chat and Halsall Moss subsoil (average) mg kg⁻¹
Cu	3.3	20	16.4
Pb	11.3	6.2	22.4
Ni	2.5		5.53
Zn	32.4	35	22.2
As	2.6		3.51
Co	0.3		1.37
Cd	0.5	0.17	0.122

Table 3.2: Topsoil and subsoil element concentrations for Chat and Halsall Moss sites.

	CM-1 (mg kg ⁻¹)		CM-3 (mg kg ⁻¹)		CM-9 (mg kg ⁻¹)		CM-12 (mg kg ⁻¹)		HM-1 (mg kg ⁻¹)	
	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
Ca	-	-	17100	4200	-	-	-	-	13100	1490
Sr	39.6	22.7	63.6	24.8	53.6	1.89	74.6	21.7	43.7	35.2
Ba	184	30.8	331	28.8	289	9.13	320	53.7	172	222
Fe	18900	2820	30400	2230	18600	470	25700	3940	15300	14600
Mn	242	63.7	362	29.7	236	6.60	429	43.6	145	37.4
As	23.4	3.45	45.4	3.07	22.8	0.75	32.5	3.87	9.46	2.20
Se	2.96	0.563	3.38	0.509	1.90	0.0943	3.29	0.669	1.37	0.502
Sb	3.96	0.350	6.83	0.409	2.73	0.0965	7.90	0.411	4.80	0.476
V	39.2	3.93	64.8	4.41	41.8	0.939	57.9	6.82	25.4	12.5
Cr	21.1	3.09	34.8	4.44	29.7	1.75	31.6	4.43	21.4	14.1
Co	7.50	0.802	11.5	0.846	6.11	0.200	10.1	1.43	4.82	2.29
Ni	25.4	2.71	39.3	3.54	24.9	1.31	34.6	4.40	11.1	7.37
Cu	85.0	8.86	178	13.4	80.0	3.94	150	12.4	27.0	33.6
Zn	137	26.3	313	25.5	205	5.96	286	22.7	75.9	14.2
Mo	5.02	0.515	8.50	0.728	3.54	0.213	7.43	0.755	1.00	0.217
Cd	1.00	0.161	1.83	0.0333	0.493	0.0285	1.16	0.117	0.548	0.197
Sn	8.30	1.21	20.4	0.817	11.7	0.279	20.1	1.01	4.48	0.590
Cs	1.33	0.127	2.29	0.159	2.31	0.0474	1.35	0.158	1.61	1.36
Pb	221	22.8	407	28.9	169	11.3	350	17.4	84.3	17.6
Bi	0.922	0.104	0.756	0.0345	0.429	0.0126	1.37	0.127	-	-

3.2 Spatial variability of trace element concentrations in topsoil (Portable XRF survey)

3.2.1 Introduction

To assess the spatial variability of the metal content of the soil surface, on a field-scale, a portable X-Ray Fluorescence analyser was used to map the contamination of a single field in an area of Chat Moss with a known history of waste disposal: the CM-3 site. The purpose of this was to assess the extent to which the historic application of waste to the fields and subsequent cultivation activities had evenly distributed the waste across the field. A secondary consideration was to determine whether sampling topsoil or soil profiles in a relatively limited area of a field could provide a reasonable representation of the whole area. By using Field Portable XRF (FP-XRF), it was possible to quickly measure contamination levels across a field grid without having to destructively remove samples.

FP-XRF was developed to provide rapid assessments of contamination levels *in situ* with little or no sample preparation required. Measurements can be taken on undisturbed soil, but it is often recommended to remove large stones, twigs and other obstructing materials. The soil should then be smoothed down to give the best contact surface with the instrument for the most accurate measurement. A Niton XLt analyzer (Thermo Scientific) instrument was used, which could analyse multiple elements over a range of environmental levels

3.2.2 Survey design

Before using the FP-XRF at Chat Moss, a test was carried out to assess the accuracy of the instrument by measuring the Pb and Zn content of soil plots with known trace metal concentrations. The topsoil plots (0.25 m x 0.25 m x 30 cm depth) were constructed using soil, contaminated with sewage sludge, imported to the University of Nottingham farm from a sewage processing farm in the East Midlands run by Severn Trent Water Ltd. The plots were arranged in four blocks of 10 contrasting soils, intended to cover a range of metal concentrations. They were established in 2003 as part of a 'phytoremediation' project at the Sutton Bonington campus of the University of Nottingham. The Pb and Zn concentrations in the soil plots had been previously measured, by Aqua-Regia digestion and Atomic Absorption Spectroscopy (AAS). The results of the comparison with FP-XRF in this initial test are presented in Section 3.2.3.

The survey of the field on Chat Moss was carried out at site CM-3, which had the highest contamination levels as seen in the initial GBASE survey and in the first sampling (Section 3.1.3.3). A 90 m x 90 m grid was set up with measurements taken every 10 m across the grid, resulting in a total of 100 measurement points at the corner of each 10 m x 10 m grid square (Figure 3.24). At nine randomly selected locations across the grid topsoil samples were collected and analysed, following acid digestion, by ICP-MS (Chapter 2.5.1 and 2.6) for comparison with the FP-XRF data. At each data collection point, the FP-XRF was used with a 30 second scan, pressed against the soil surface which had been cleared of large stones and vegetation and smoothed over. The FP-XRF data was then correlated with the ICP-MS data to assess the validity of this *in-situ* method on the highly organic Chat Moss soils.

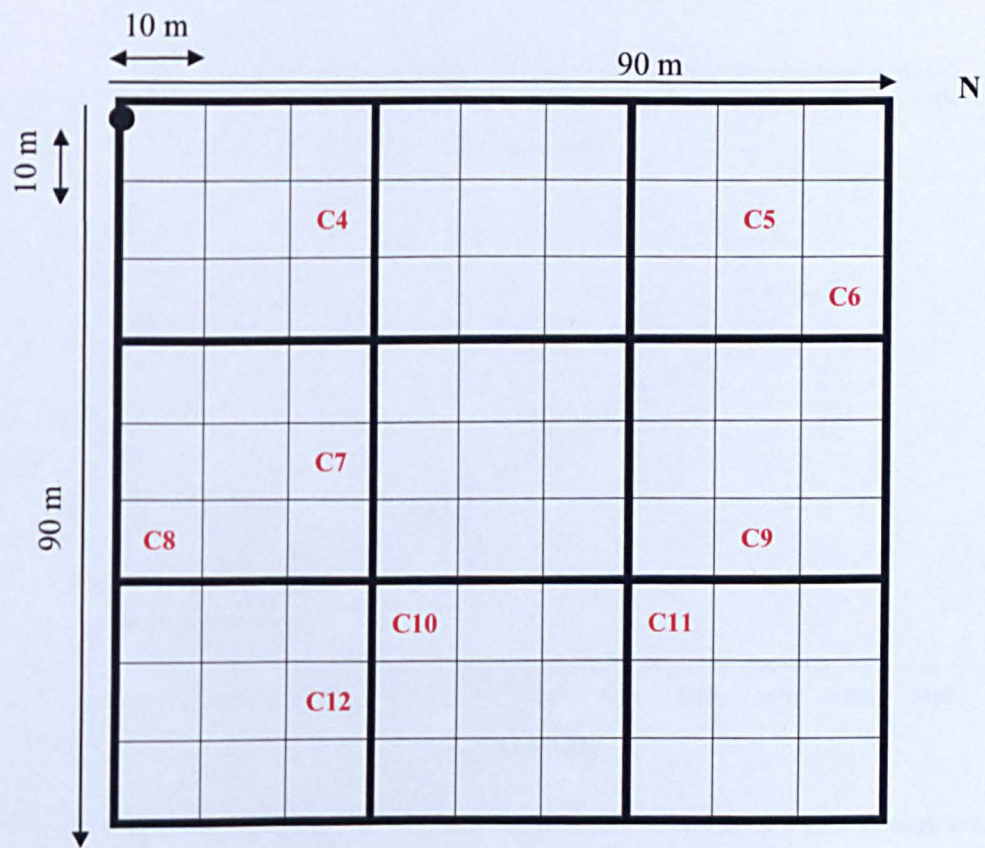


Figure 3.24: FP-XRF sample grid at site CM-3, with core sites marked by C4 – C12.

3.2.3 Pre-survey test results

The results of the pre-survey test can be seen in Figure 3.25. There was good agreement between the topsoil metal concentrations, measured by acid digestion and AAS, and the FP-XRF data collected in the field for both Pb and Zn, with r^2 values of 0.987 for Zn and 0.896 for Pb. On the basis of these results it was determined that the FP-XRF field survey of Chat Moss was viable.

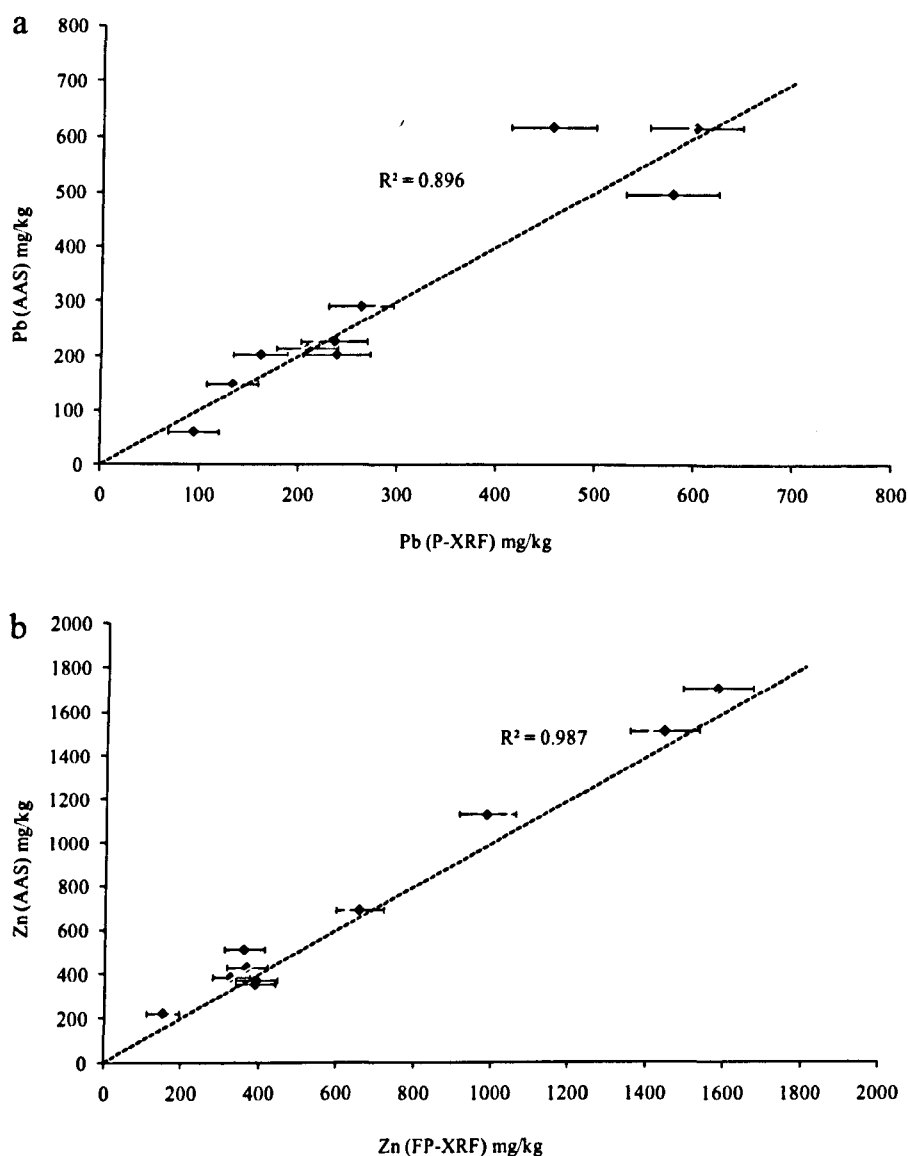


Figure 3.25: Metal concentrations of Pb (a) and Zn (b) in 10 topsoil plots from a sewage treatment farm in the East Midlands: P-XRF data plotted against metal concentration previously measured by acid digestion and AAS (S. Young, unpublished data), broken line shown is the 1:1 relation.

3.2.4 Chat Moss survey results and discussion

The elements analysed by FP-XRF in the field were Sr, Rb, As, Pb, Zn, Cu, Co, Fe, Mn, Cr, V, Ti and Ca. The averages across the grid are given in Table 3.3, along with the detection limits for the instrument. The lower limits of detection are taken from a pressed powder pellet in a geological matrix; for in-situ field use, it is likely that these detection limits will be higher because scans were taken of the smoothed soil surface.

Table 3.3: Arithmetic average trace element concentrations in topsoils at the Chat Moss site CM-3 and detection limits for FP-XRF

	Chat Moss average (mg kg ⁻¹)	Detection limits (mg kg ⁻¹)
Sr	64 ± 1.4	4.0
Rb	27 ± 0.2	3.2
As	46 ± 1.8	5.6
Zn	368 ± 69.1	19.1
Cu	181 ± 4.5	28.3
Co	Below detection	192
Fe	30000 ± 1091	31.1
Mn	368 ± 7.0	33.0
Cr	35 ± 1.0	21.1
V	66 ± 1.7	28.0
Pb	403 ± 14.1	10.8

The results from the FP-XRF were correlated with the samples collected at locations C4-C12 across the sampling grid (Figure 3.24) which were analysed by ICP-MS following soil digestion (Chapter 2.5.1 and 2.6) (Figure 3.26 – 3.38).

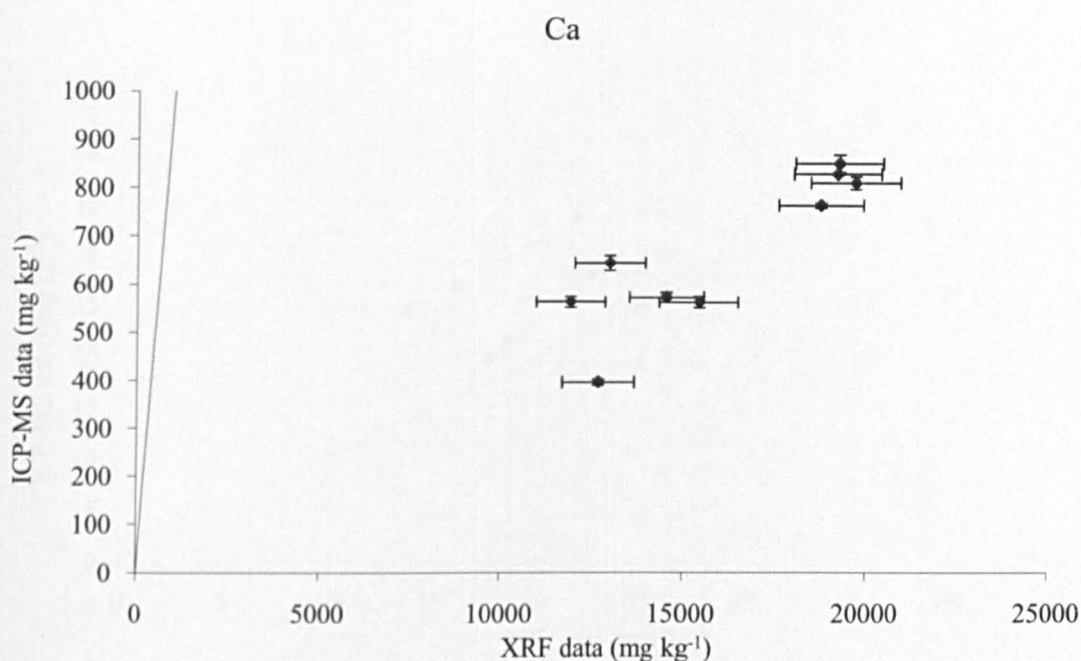


Figure 3.26: Correlation graphs for Ca concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

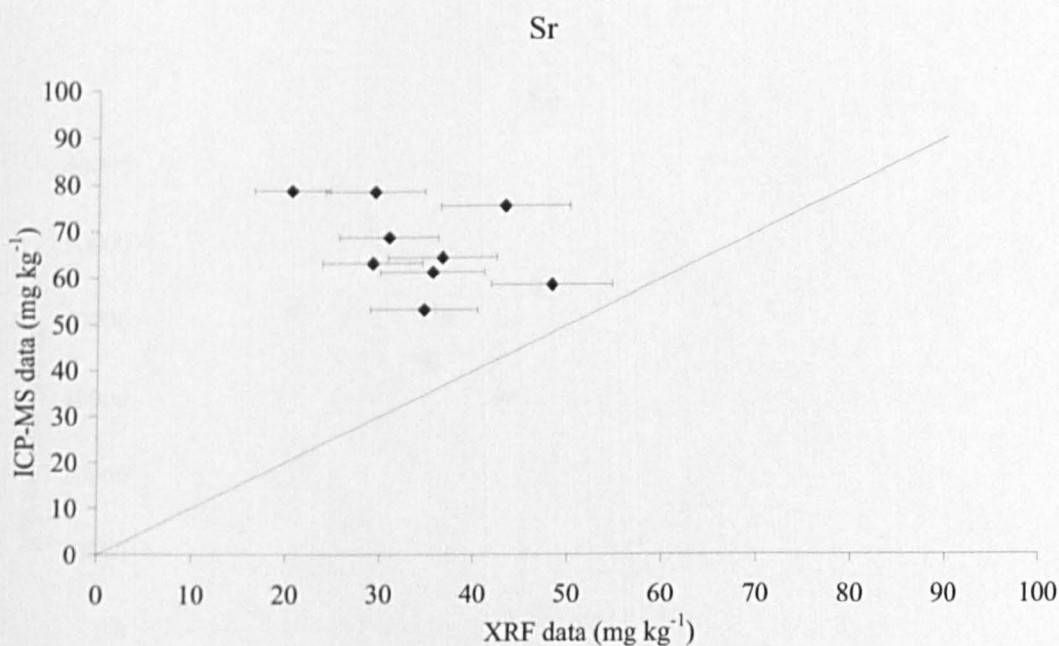


Figure 3.27: Correlation graphs for Sr concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

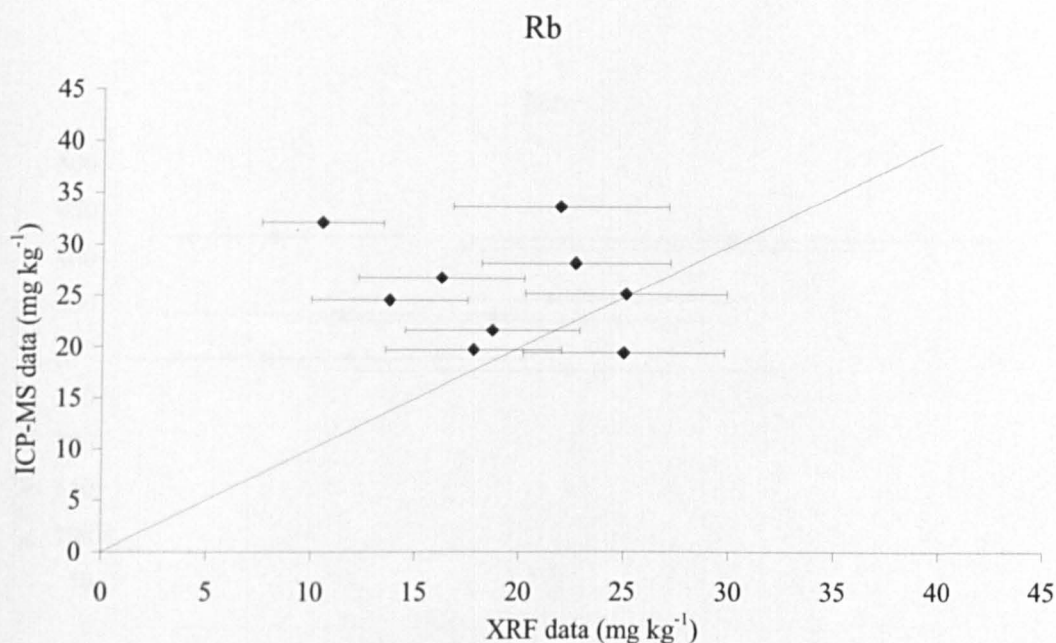


Figure 3.28: Correlation graphs for Rb concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

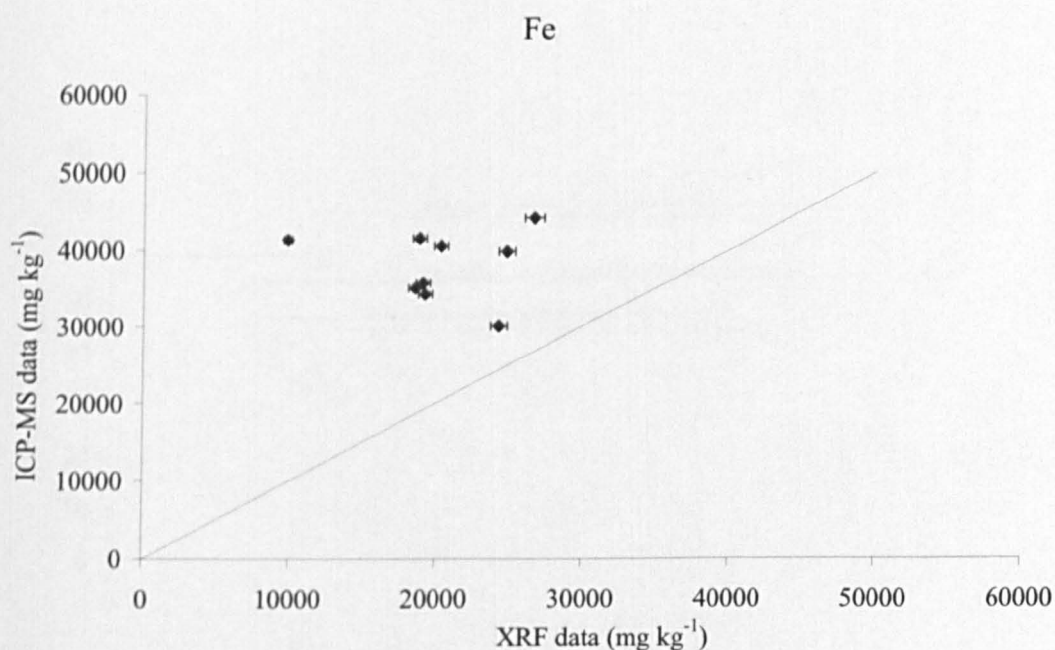


Figure 3.29: Correlation graphs for Fe concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

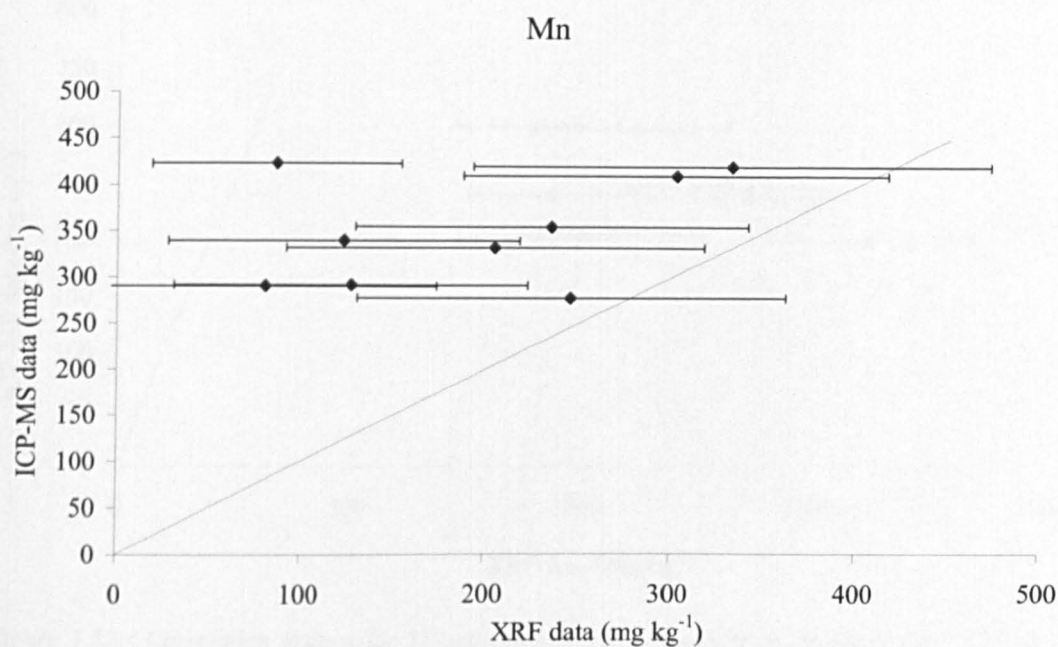


Figure 3.30: Correlation graphs for Mn concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

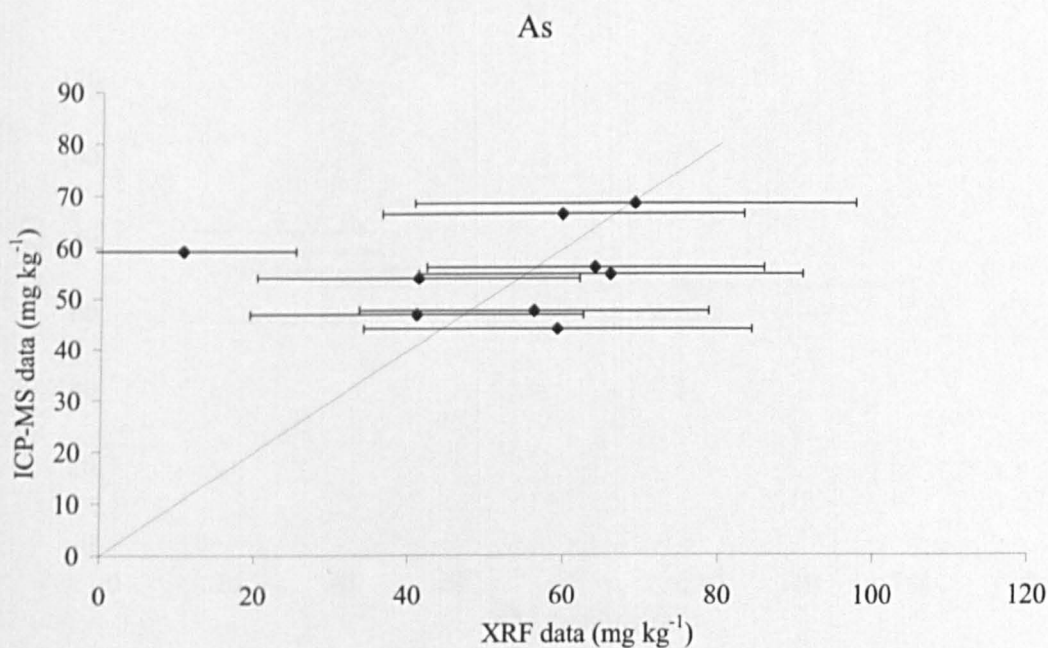


Figure 3.31: Correlation graphs for As concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

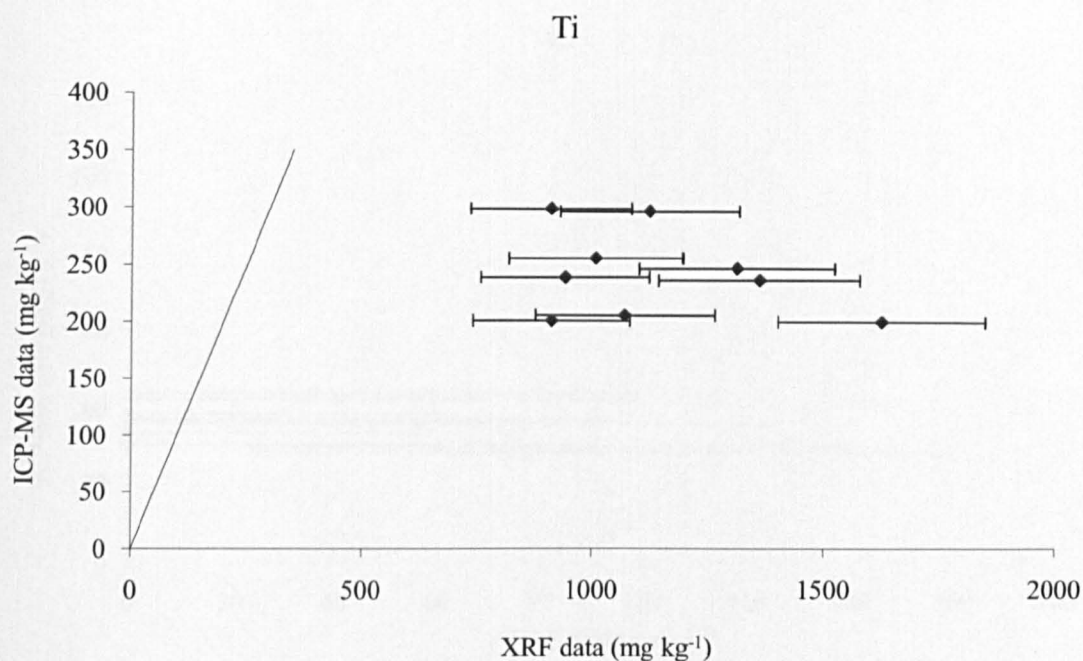


Figure 3.32: Correlation graphs for Ti concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

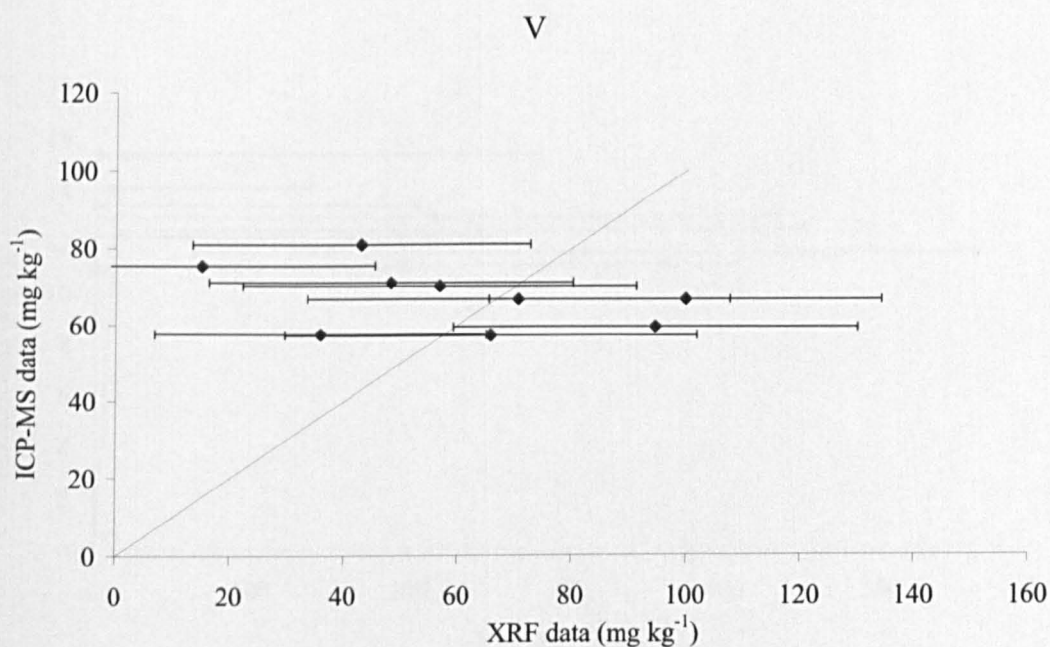


Figure 3.33: Correlation graphs for V concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

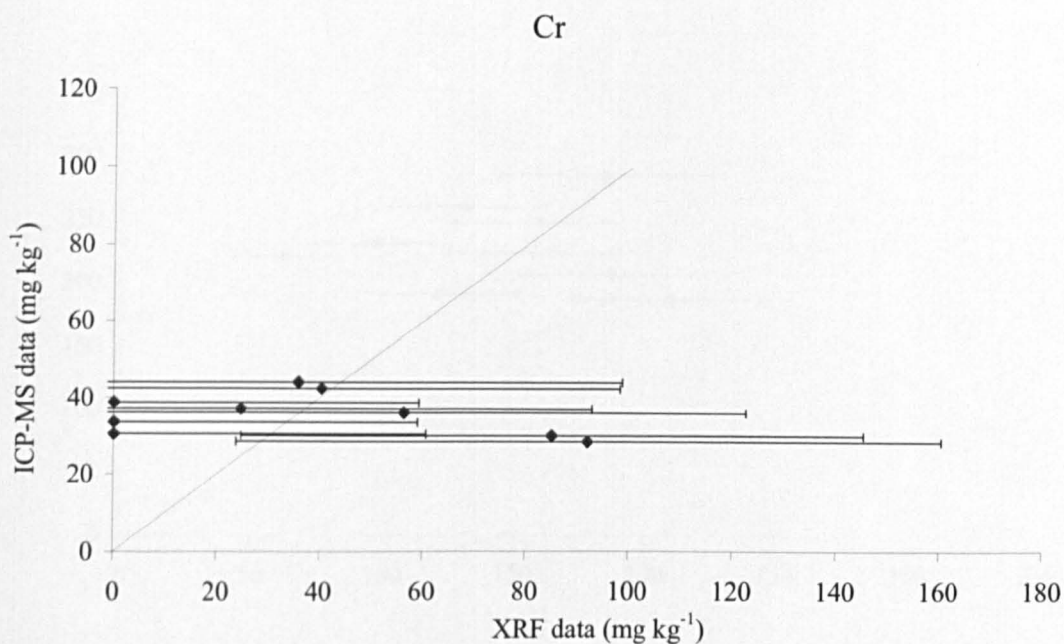


Figure 3.34: Correlation graphs for Cr concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

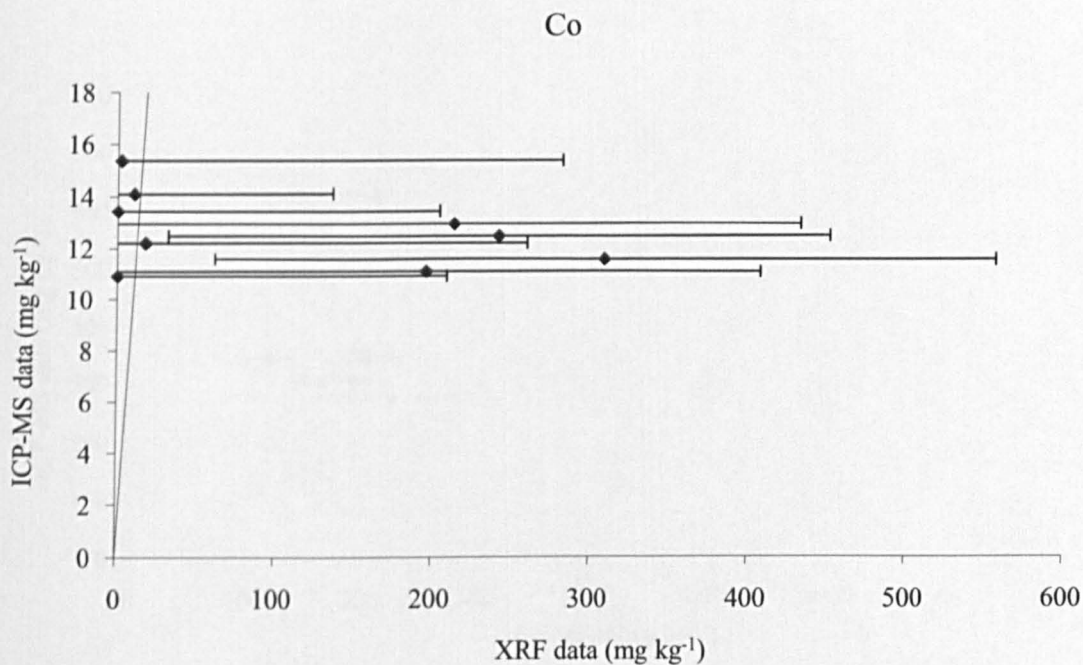


Figure 3.35: Correlation graphs for Co concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

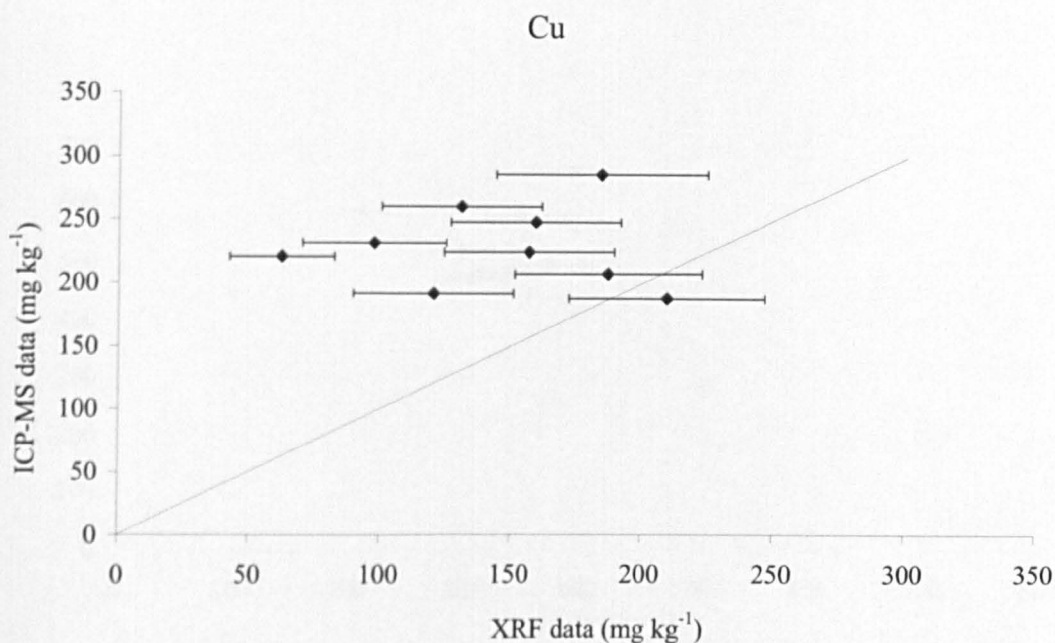


Figure 3.36: Correlation graphs for Cu concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

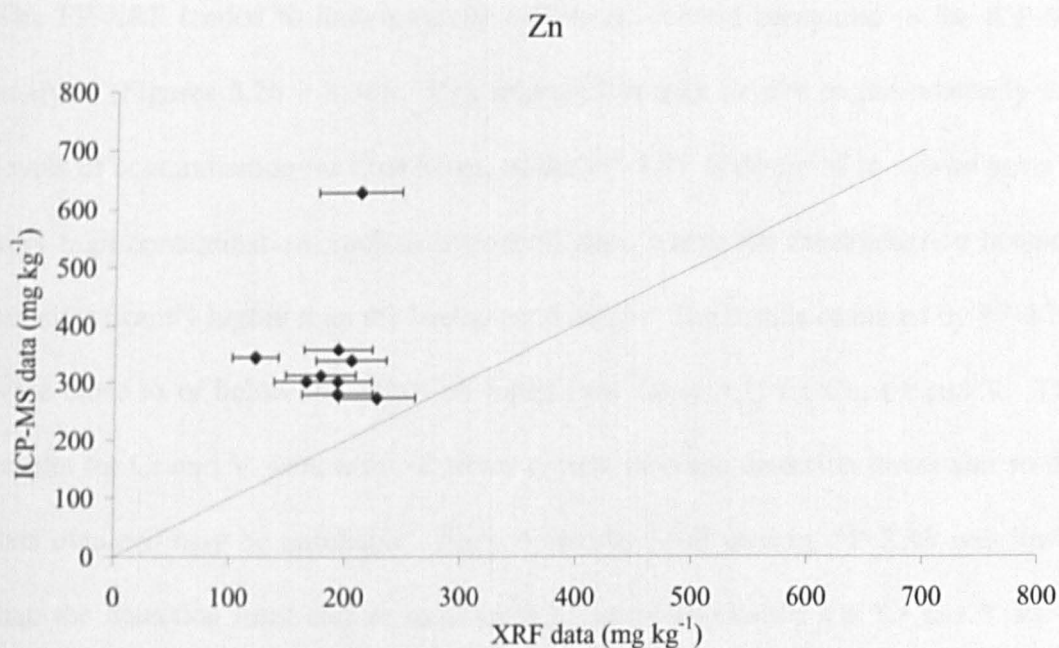


Figure 3.37: Correlation graphs for Zn concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

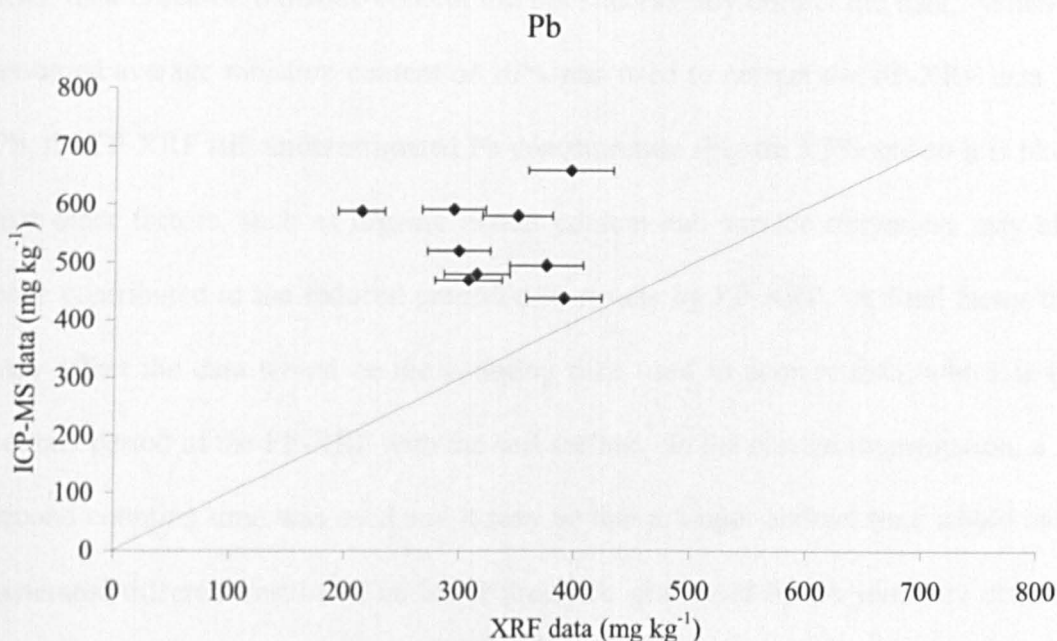


Figure 3.38: Correlation graphs for Pb concentrations in topsoils from locations C4 – C12 at the Chat Moss site CM-3 (Figure 3.24) determined by acid digestion and ICP-MS and FP-XRF data. Solid line is the 1:1 relation. Error bars show standard error.

The FP-XRF tended to underestimate soil metal content compared to the ICP-MS analysis (Figures 3.26 – 3.38). This imprecision may be due to the relatively low levels of contamination on Chat Moss, as the FP-XRF is designed to survey areas of very high contamination, such as minespoil sites, where the contamination hotspots are significantly higher than the background levels. The results obtained by FP-XRF were close to or below the detection limits (see Table 3.3) for Co, Cr and V. The results for Cr and V were only ~2 times greater than the detection limits and so the data obtained may be unreliable. For Co, the data collected by FP-XRF was lower than the detection limit and so must be considered unreliable; Co, Cr and V show some of the worst correlations. It has been shown by other authors that moisture content, surface roughness and organic matter content can all affect the readings given by FP-XRF (Ge *et al.*, 2005). However, a correction factor applied to the FP-

XRF data based on moisture content did not successfully correct the data. When an assumed average moisture content of 10% was used to correct the FP-XRF data for Pb, the FP-XRF still underestimated Pb concentration (Figure 3.39) and so it is likely that other factors, such as organic matter content and surface roughness may also have contributed to the reduced precision in results by FP-XRF. A final factor that may affect the data would be the counting time used to acquire data, which is the contact period of the FP-XRF with the soil surface. In the current investigation, a 30 second counting time was used and it may be that a longer contact time would have generated different results. The lower precision generated by the moisture content, organic matter content, surface roughness and counting time do not explain the consistent bias toward underestimation by the FP-XRF, and in the scope of the current investigation this is currently unexplained. Ca content was greatly overestimated by FP-XRF compared to the ICP-MS data. This is a combination of the fact that calibration of the FP-XRF was only carried out for trace elements and not major elements such as Ca, as well as possible spectral interferences, for example it has been reported that the Sn $L\beta$ line can be an interference on the Ca $K\alpha$ line (Ferret *et al.*, 2003).

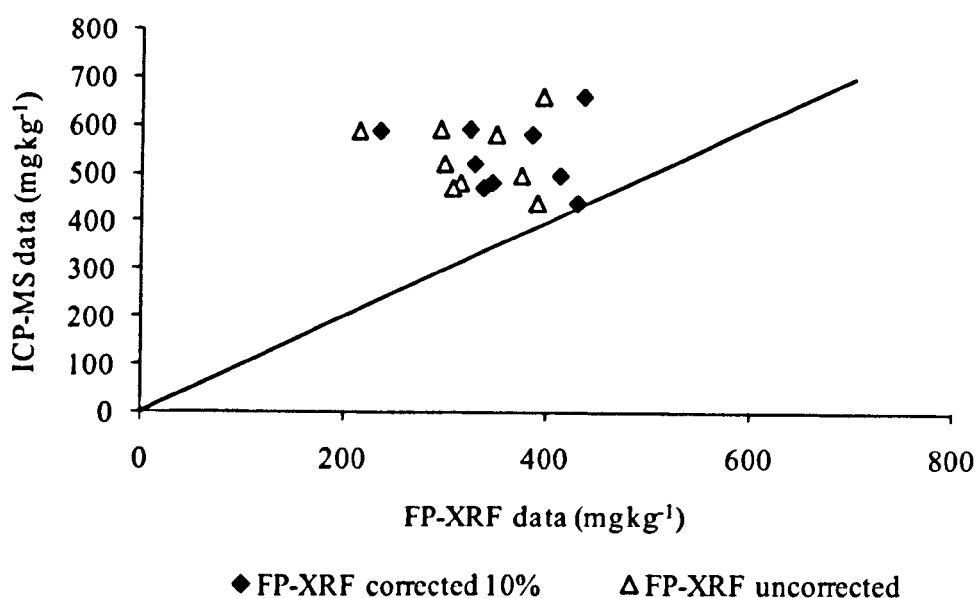


Figure 3.39: Concentrations of Pb in topsoil from locations C4 – C12 at the Chat Moss site CM-3 determined by acid digestion and ICP-MS and FP-XRF data; the FP-XRF data was corrected for an assumed soil moisture content of 10%. The solid line is the 1:1 relation.

Whilst the FP-XRF data is consistently lower than the ICP-MS data, the factors causing the variation (moisture content, organic matter content) should be reasonably consistent across the field. On this basis, it should still be reasonable to use the FP-XRF data to show the approximate variation in total metal content across the field grid (Figure 3.24). A geochemical map of the site is shown in Figure 3.40 with Pb concentration classified into three groups: low, medium and high.

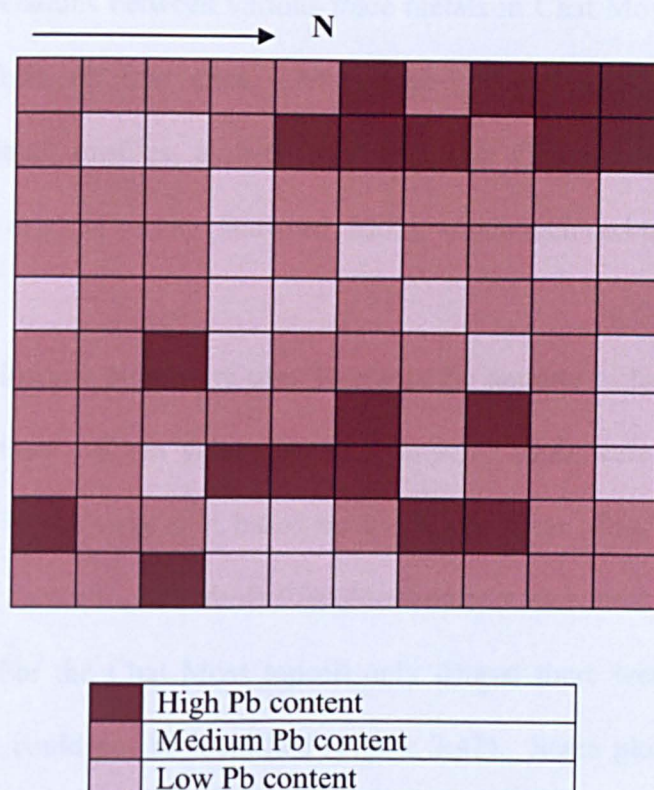


Figure 3.40: Distribution of Pb concentration in topsoil across the field site (Figure 3.24) based on FP-XRF data

There is a substantial variation in Pb content across the field, with no obvious pattern to the variation but with two broad areas, in the top right and bottom middle, with Pb concentrations in excess of 450 mg kg^{-1} (Figure 3.40).

3.3 Geochemical association of trace metals

Principle Component Analysis (PCA) is often used to study the relationship between a large number of variables which may have a wide numerical range (Halim *et al.*, 2009). PCA can show the number of factors affecting a dataset using scree plots as well as identifying relationships between elements through cluster analysis and dendrograms. Principle Component Analysis and Cluster Analysis were used to

investigate associations between various trace metals in Chat Moss soils. The Chat Moss dataset from all four sites (CM-1, CM-3, CM-9 and CM-12) was used including the depth profiles, as well as the British Geological Survey G-BASE dataset from the original survey (Breward, 2003), which included topsoil data only.

Scree plots and loading plots were used to assess the number of factors affecting the data in each dataset. Eigen values above 2 in scree plots were considered to be significant, and in the scree plot based on the whole Chat Moss dataset, only one highly dominant factor for the whole Chat Moss dataset was seen, most likely depth (Figure 3.41). For the Chat Moss topsoil only dataset there were 2 main factors found, but these could not be identified (Figure 3.42). Scree plots of the GBASE data suggested 3 dominant factors affecting element association in the contaminated sites, and only 2 dominant factors at the uncontaminated sites (Figures 3.43 and 3.44).

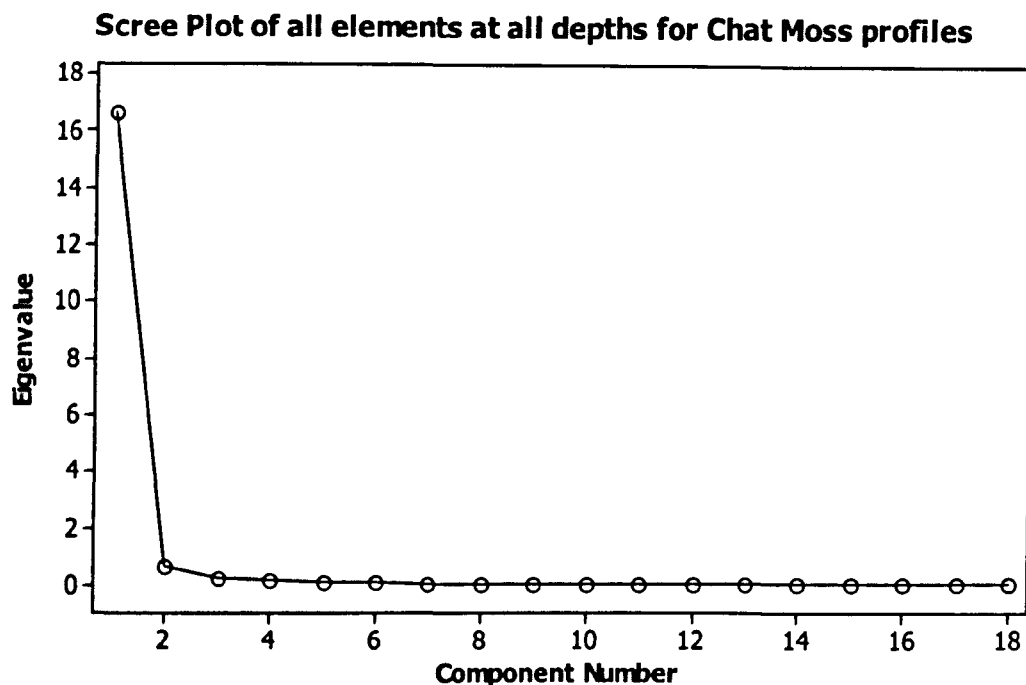


Figure 3.41: Principal Component Analysis of all elemental data at all depths for the Chat Moss soils (CM-1, CM-3, CM-9 and CM-12): Scree plot, number of data points = 45.

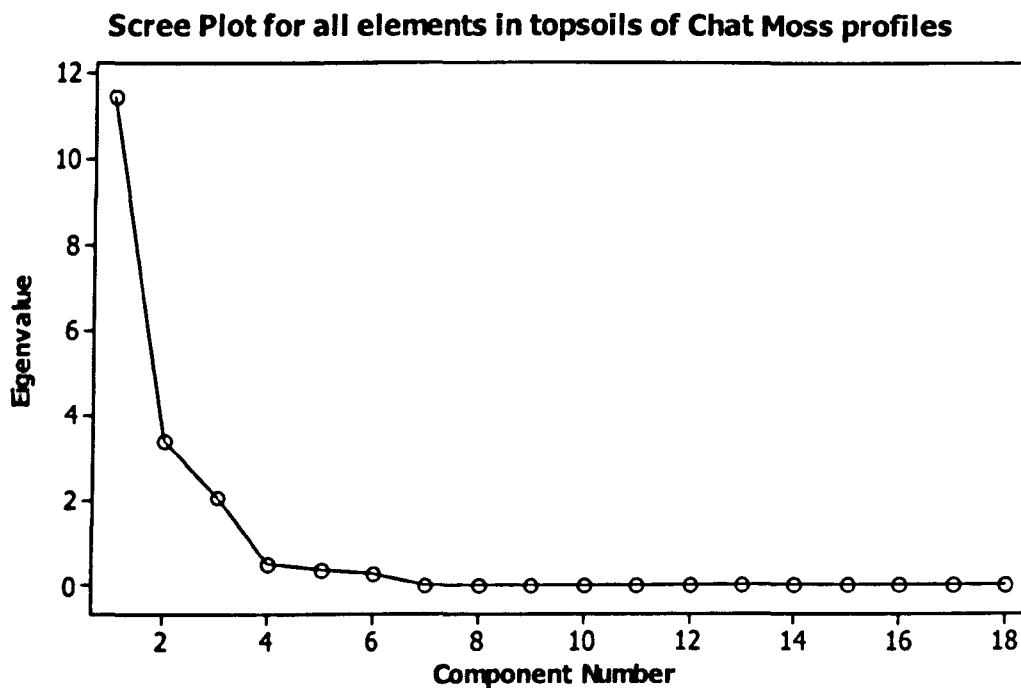


Figure 3.42: Principal Component Analysis of all elemental data in topsoils of the Chat Moss soils (CM-1, CM-3, CM-9 and CM-12): Scree plot, number of data points = 8.

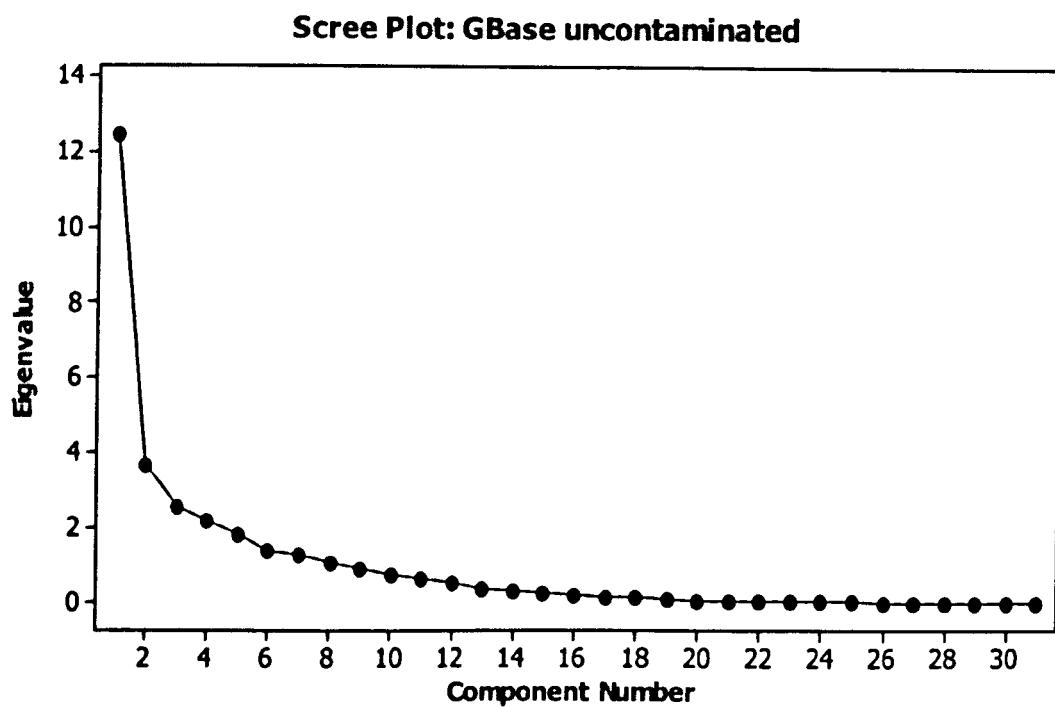


Figure 3.43: Principal Component Analysis of uncontaminated data from GBASE dataset Pb < 300 mg kg⁻¹: Scree plot, number of data points = 32.

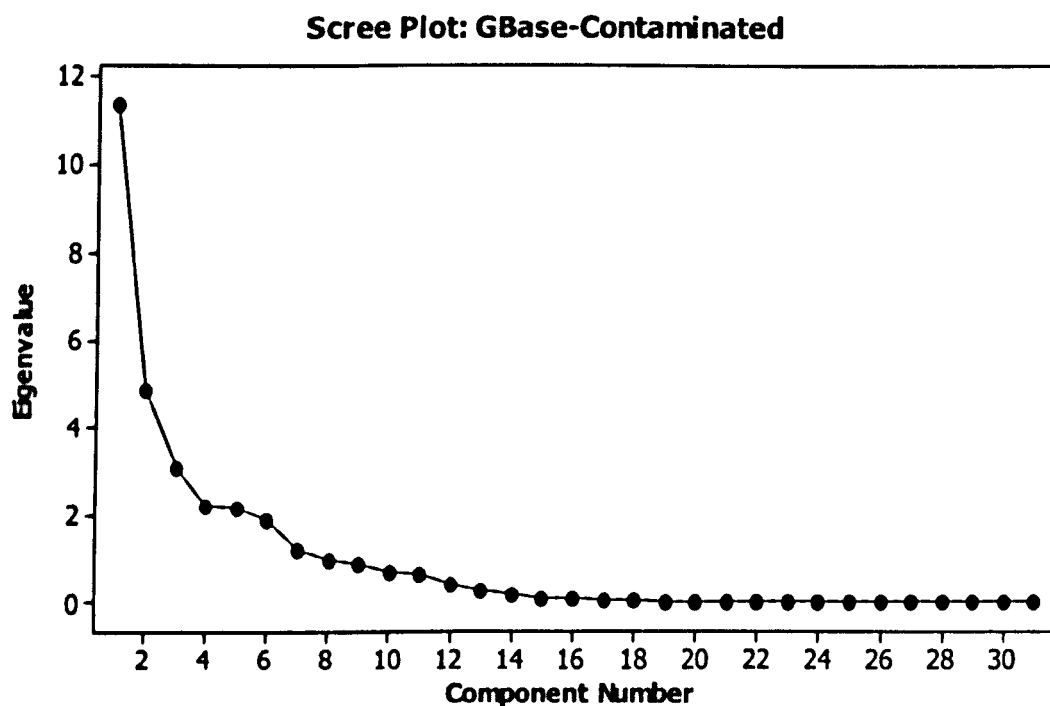


Figure 3.44: Principal Component Analysis of contaminated data from GBASE dataset Pb > 300 mg kg⁻¹: Scree plot, number of data points = 20.

Loading plots showed that the first factor affecting both the contaminated and uncontaminated sites using the GBASE data may be sand/clay content, or grain size, but the second and third factors cannot be identified (Figures 3.45 and 3.46). Loading plots of the contaminated and uncontaminated datasets broadly showed the same grouping (Figures 3.45 and 3.46). The observation that the Zr, Si and Ti group was at one end of the axis and clay components such as Rb and K are at the other end suggests that the first component may be a mineralogical component. In the contaminated loading plot, a more complex picture was observed than the uncontaminated loading plot, probably due to the complex history of the contaminated sites.

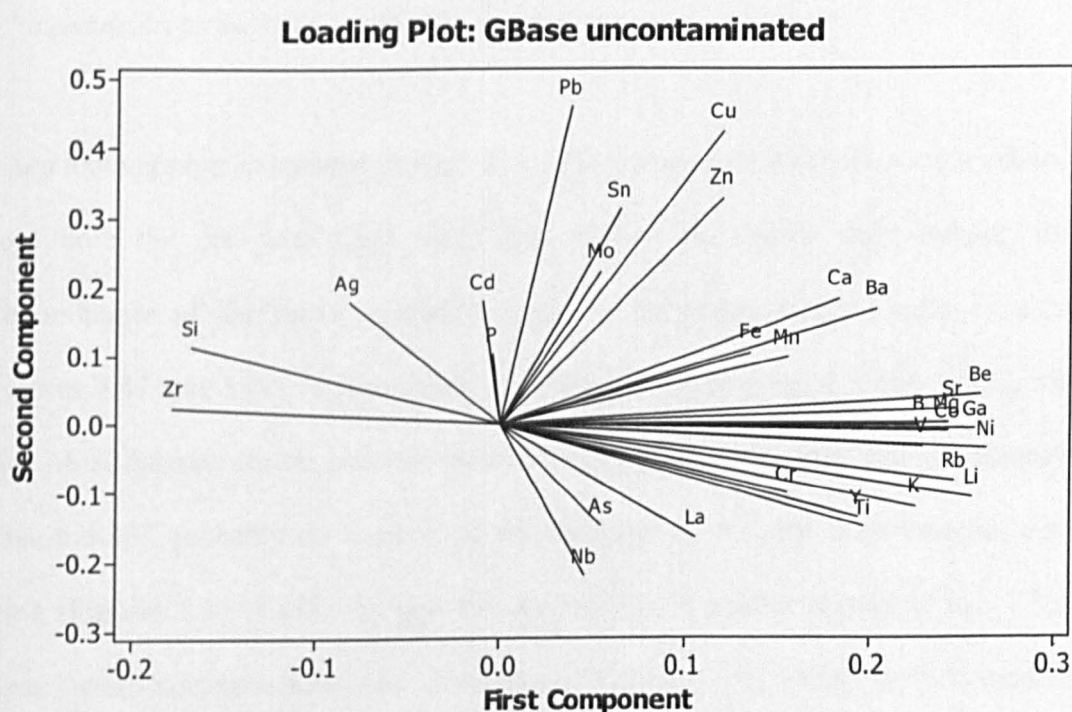


Figure 3.45: Principal Component Analysis of uncontaminated data from GBASE dataset $Pb < 300 \text{ mg kg}^{-1}$; Loading plot for the first two components, number of data points = 32.

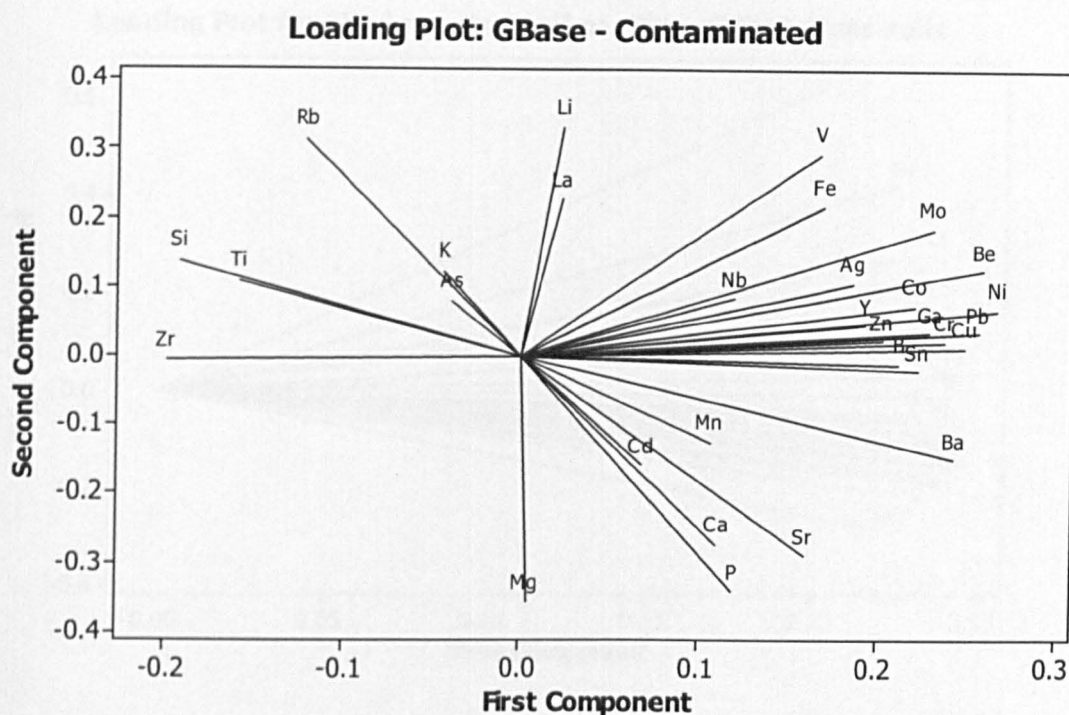


Figure 3.46: Principal Component Analysis of contaminated data from GBASE dataset $Pb > 300 \text{ mg kg}^{-1}$: Loading plot for the first two components, number of data points = 20.

When loading plots calculated through Principle Component Analysis were produced from both the complete Chat Moss dataset and the topsoil only dataset, the predominance of one factor, probably depth, on all elements could again be seen (Figures 3.47 and 3.48), in agreement with the scree plot (Figure 3.41). Using the Chat Moss dataset, cluster analysis showed strong associations between all elements (Figure 3.49), probably as a result of the decrease in element concentration with depth (Figures 3.3 – 3.22). To test this assumption, a smaller dataset of only Chat Moss topsoil concentrations was investigated (Figure 3.50), which showed weaker associations between elements, confirming that the associations between elements in the complete dataset were most likely a result of the influence of depth.

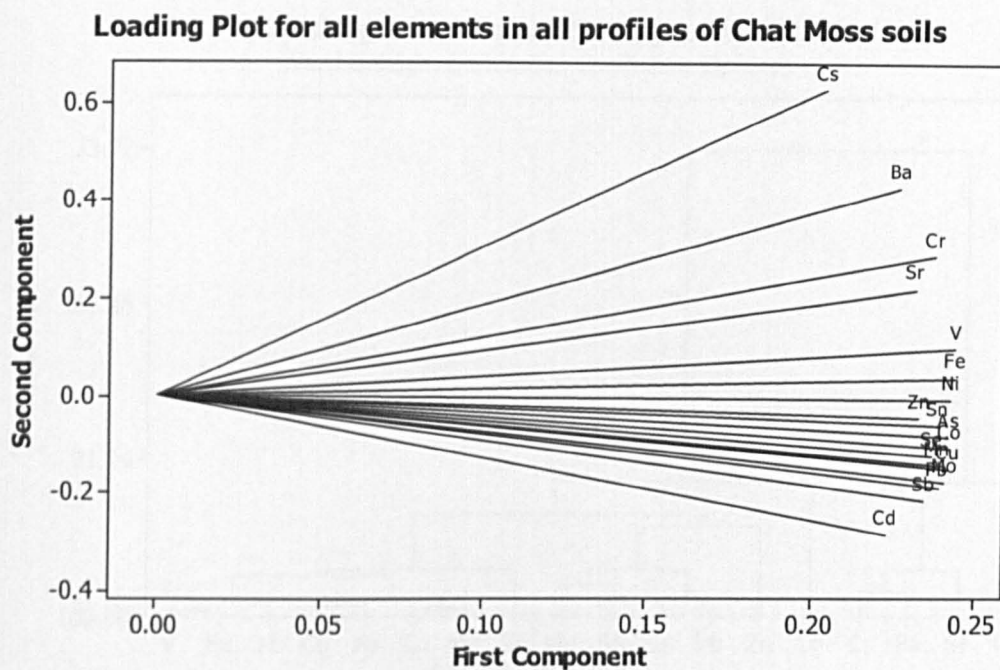


Figure 3.47: Principal Component Analysis of all elemental data at all depths in Chat Moss soils (CM-1, CM-3, CM-9 and CM-12): Loading plot for the first two components, number of data points = 45.

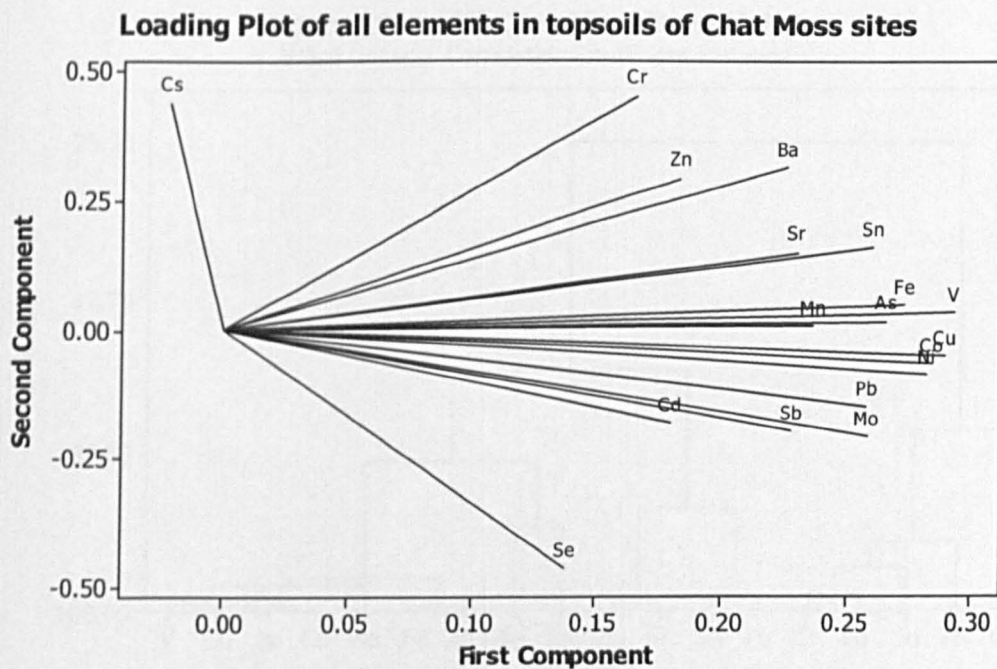


Figure 3.48: Principal Component Analysis of all elemental data in topsoils at the Chat Moss sites (CM-1, CM-3, CM-9 and CM-12): Loading plot for the first two components, number of data points = 8.

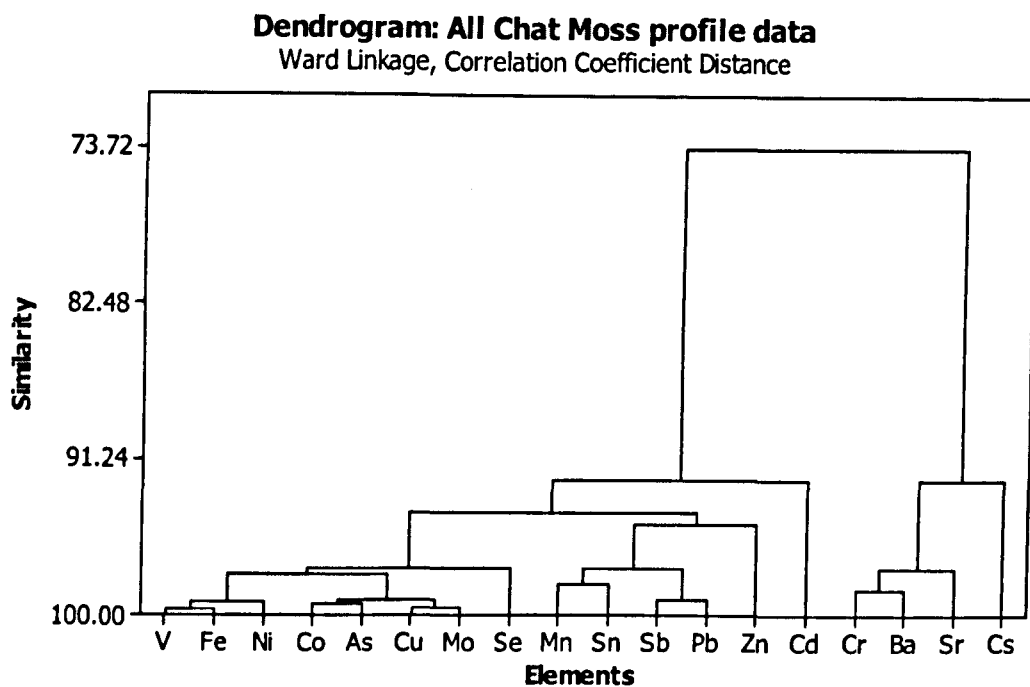


Figure 3.49: Dendrogram of the entire Chat Moss dataset showing clustering of elements, number of data points = 45.

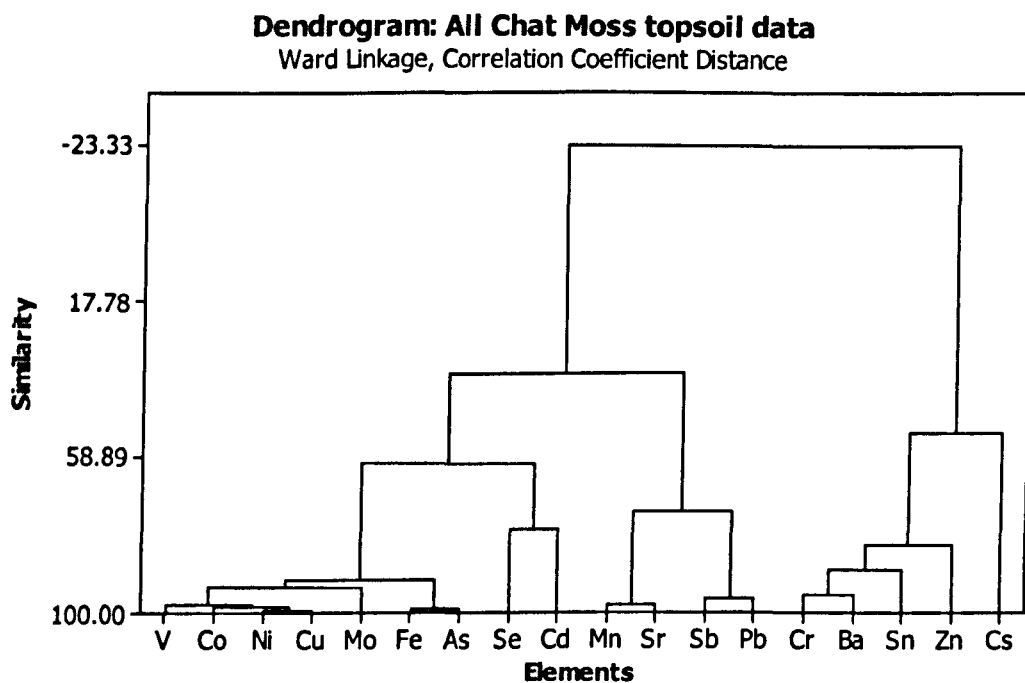


Figure 3.50: Dendrogram showing clustering of elemental analysis data for Chat Moss topsoils, number of data points = 8.

Several elemental associations were apparent in the topsoil dataset, although the small number of data points ($n = 8$) means that these results may be unreliable. Associations indicating industrial waste were identified, including the association of Pb and Sb indicating batteries and Pb alloys, Cu, Ni, V, Co, Mo, Fe and As indicating steelworks waste (Mattigod & Page, 1983) and Zn, Sn, Ba and Cr indicating paints and fillers (Reimann & de Caritat, 1998). The strong association of Fe and As may indicate the presence of sedimentary Fe ore used in steelworks (Kabata-Pendias, 2001). All of the indicated sources are consistent with historical research of the waste types disposed of on Chat Moss, which lasted from 1900 to 1964 and so a wide variety of historical and modern wastes would have been disposed on Chat Moss.

To compare the elemental associations in the small scale Chat Moss dataset with the wider region, the relevant GBASE data for the area was also examined. The GBASE dataset was divided into contaminated and uncontaminated sites based on total Pb content, with 300 mg kg^{-1} taken as the boundary, as there was a natural division in the dataset at this Pb concentration. This Pb soil concentration is also the maximum permissible lead concentration in soils amended with sewage sludge (MAFF, 1998). Cluster analysis of the uncontaminated dataset showed associations such as Si and Zr perhaps representing silicates and zircons, possibly in sand fractions (Figure 3.51). The association of Rb, Mg, Sr and B most likely reflects limestone and clay components, either native to the soil or introduced to the soil through liming procedures. However Ca is not within this cluster, which may be an artefact due to the limited size of the dataset ($n = 32$).

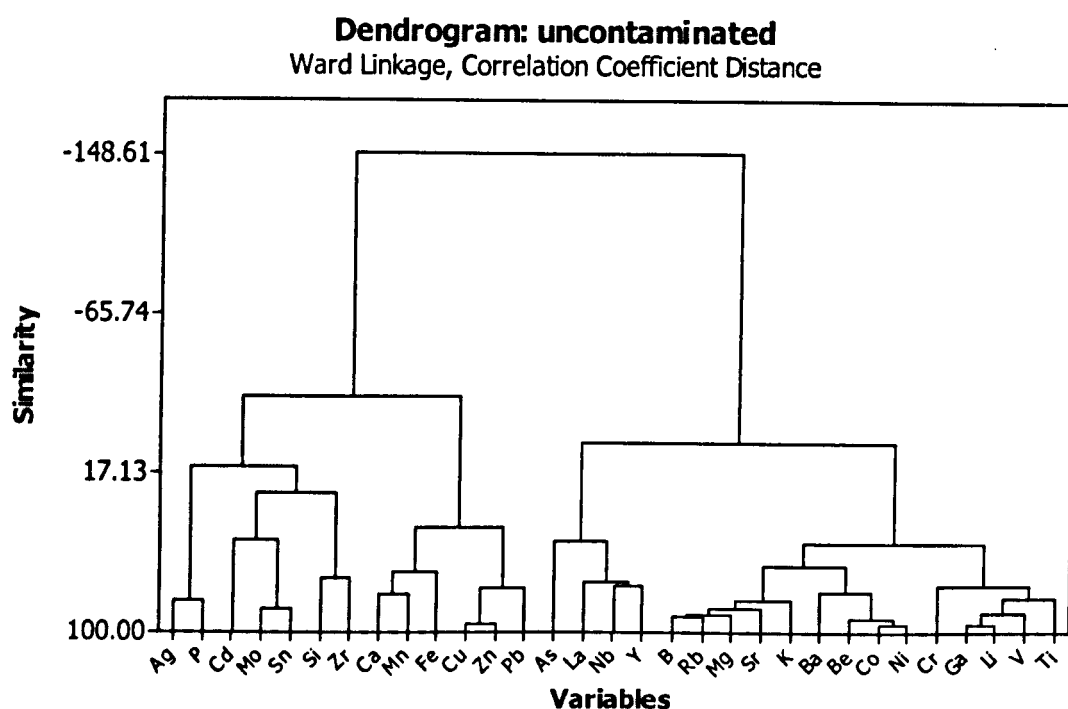


Figure 3.51: Dendrogram showing clustering of elemental analysis data for uncontaminated data of GBASE dataset, Pb content < 300 mg kg⁻¹, number of data points = 32.

The contaminated GBASE data also showed associations typical of soil components such as clay (Rb and K), silicates and sand (Ti, Si and Zr) and carbonates (Mg, Cd, Sr, Ca and P) (Figure 3.52). The association of Cd with the carbonate and phosphate elements indicates that these elements are derived from phosphatic fertilisers (Mattigod & Page, 1983) and so are anthropogenic in origin and not due to native soil components. The association of the heavy metal suite (Ni, Ba, Pb, Cr, Sn, Co, Cu, Zn and Mn) are indicative of industrial waste. Mo and V showed a strong association which is often seen with black shales, which are often used in steelworks and so may indicate furnace waste.

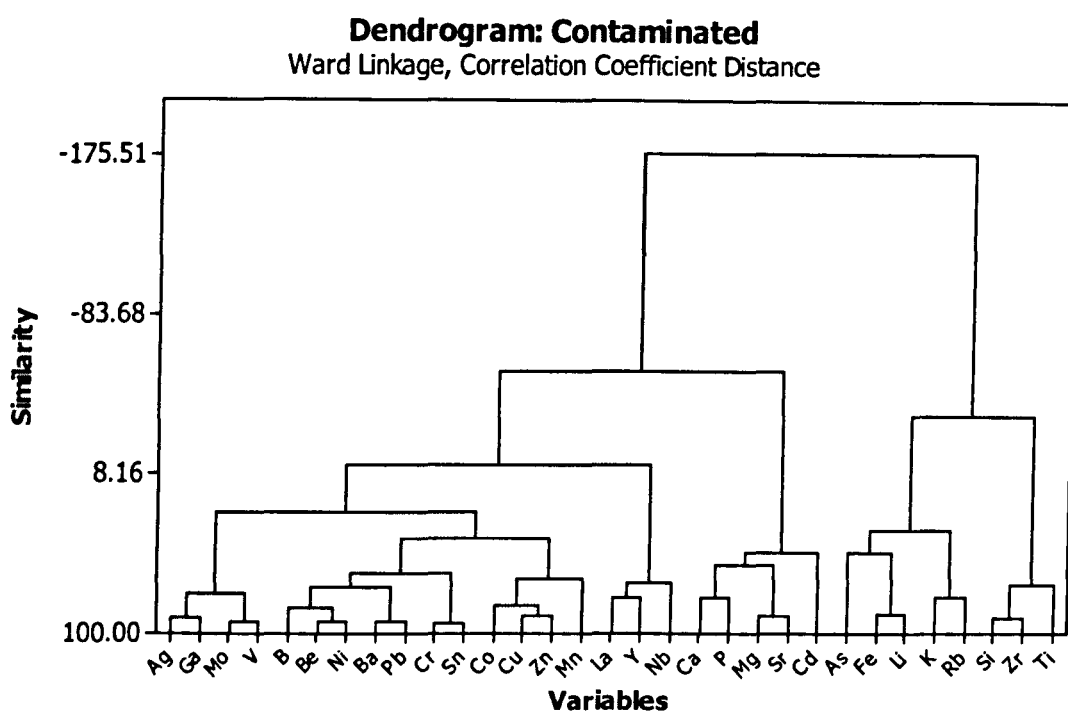


Figure 3.52: Dendrogram showing clustering of elemental analysis data for contaminated data of GBASE dataset, Pb content > 300 mg kg⁻¹, number of data points = 20.

Cluster analysis of the contaminated dataset showed many associations typical of industrial waste (Figure 3.52), similar to the dataset from CM-1, CM-3, CM-9 and CM-12, although the exact associations were not the same, reflecting the relatively small sizes of the datasets, or the different sampling methodologies of the two datasets.

3.4 Conclusions

Through pH, organic matter and trace metal analysis it was possible to characterise the soils across Chat Moss and Halsall Moss. The control site on Chat Moss (CM-1) was a reclaimed peat site characterised by the highest topsoil organic matter content and the lowest trace metal content of the four Chat Moss sites. The depth of the trace metal enrichment was shallow (30 cm) possibly indicating that this metal enrichment was due to atmospheric deposition from the industrial centre of Manchester and the Pennine ore field which had then been ploughed into the soil, resulting in shallower contamination than the soils exposed to waste disposal. The high organic matter content indicated that there had been no waste addition to the soil at this site, which was also supported by field observations, as the waste incorporated to Chat Moss soil was dominated by mineral components such as ash, slag and domestic waste.

The site at the edge of Chat Moss on the sand just off the peat layer (CM-9) was characterised by the same trace metal signal in the topsoil as CM-1, indicating that this had also been affected by atmospheric pollution. The organic matter content in the subsoil was very low, corresponding to the sandy nature of the soil. The topsoil also had the lowest organic matter content of all the Chat Moss and Halsall Moss sites. This combined with the low trace metal content suggested that there had been no waste incorporation into the soil at this site, and that the only source of the elevated trace metals was atmospheric deposition, as any waste incorporation would have the effect of increasing both the organic matter content (through the deposition of nightsoil) and the trace metal content.

The two contaminated sites on Chat Moss (CM-3 and CM-12) show similar profiles of pH, organic matter content and trace metal content with depth. These sites had the highest trace metal content, most likely as a consequence of historical waste incorporation at these sites. This was supported by field observations of pottery, slag and coal fragments in the soils, as well as the reduced organic matter content in the topsoil compared to the control site (CM-1) as more mineral material had been incorporated into the soils at these contaminated sites.

The spatial variability of CM-3 was assessed using Field Portable XRF analyser, although the results were affected by organic matter content, moisture content and counting time, resulting in a poor correlation with ICP-MS analysis on the same samples. However there was large variation seen for Pb across the field, with no obvious patterns, showing that either the cultivation of the field during and since waste incorporation has caused the waste to become distributed throughout the entire field, or that the waste was distributed unevenly.

The topsoil pH of the contaminated sites (CM-3 and CM-12) was higher than the control site (CM-1), although the subsoil pH was similar for the peat sites on Chat Moss (CM-1, CM-3 and CM-12). The change in pH occurred very sharply in the contaminated sites, and was concurrent with the boundary changes between topsoil and peat. This sharp pH change could potentially represent a zone of mobilisation of trace metals, although the increase in organic matter content with the peat subsoil would most likely mediate this and help to keep any trace metals in solution by binding with the trace metals and remaining in the soil solids. Trace metal profiles

showed little evidence for the movement of trace metals into the subsoil, so it was likely that the low pH is not causing mobilisation of the metals.

The site on Halsall Moss (HM-1) had a similar soil profile to the sandy site on Chat Moss (CM-9) although the Halsall Moss site had a much greater organic matter content in the topsoil, caused by the incorporation of waste which was dominated by organic wastes such as manures (Section 1.2.2.2). The trace metal content of this Halsall Moss site was lower than the atmospherically polluted sites on Chat Moss. This was because the waste incorporated into Halsall Moss was mainly organic manures which will have had a low trace metal content, and there are no major industrial centres within the prevailing winds on Halsall Moss so the levels of atmospheric pollution will also be low compared to Chat Moss.

Chapter 4:

Characterisation of contaminants in Chat and Halsall Moss

4.1 Source apportionment using lead isotopes

4.1.1 Introduction

To help characterise the source of Pb contamination at Chat and Halsall Mosses, stable lead isotope ratios in soils were determined. Lead was the dominant contaminant within these soils and the isotopic ratios of many common UK lead sources have been well characterised (Farmer *et al.*, 2005; Bacon *et al.*, 1996; Farmer *et al.*, 2002). Each source of lead has a unique mix of the stable isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb , determined by the age, geochemistry and geological history of the source rock. By comparing the isotopic ratios of soil samples to those of a suite of known materials it may be possible to quantify the proportions of different sources of contamination present in the sample. However, this will only be successful if the lead contamination is derived from a limited number of identifiable sources (Figure 4.1). The most commonly used, and most sensitive, ratio for source apportionment studies in environmental media is $^{206}\text{Pb}/^{207}\text{Pb}$ (Weiss *et al.*, 1999a; Weiss *et al.*, 1999b; Semlami *et al.*, 2004). In this study the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has been plotted against the $^{206}\text{Pb}/^{208}\text{Pb}$ ratio to more easily compare the suite of isotopes present in the soil samples with known sources (Figure 4.1, S. Chenery, unpublished data, R. McGill, unpublished data). Further discussion of the background to source apportionment studies is in Section 1.3.2.3.

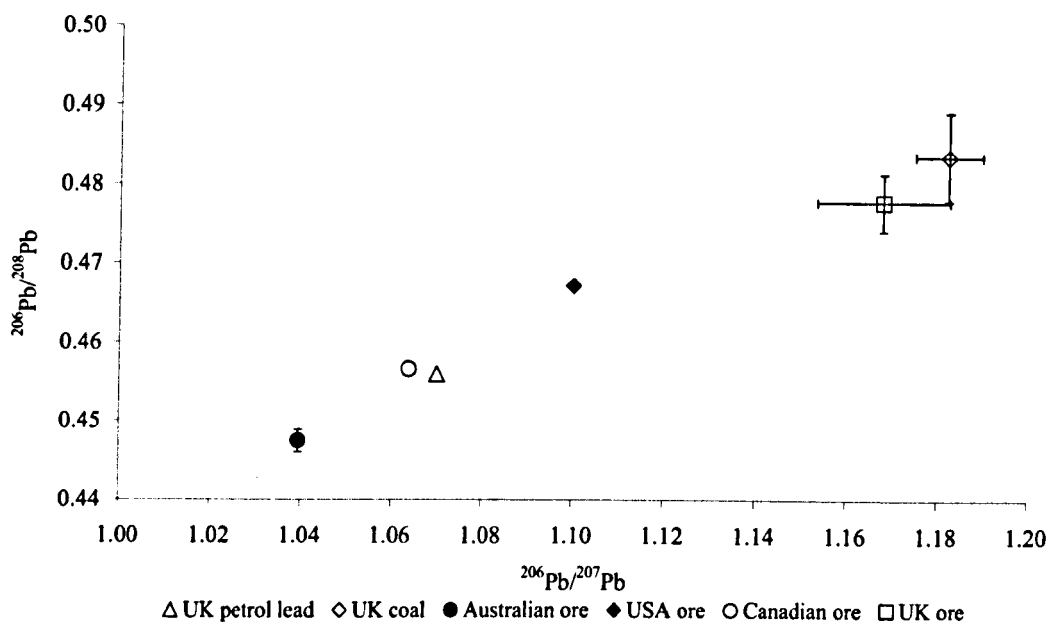


Figure 4.1: Typical ranges of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{208}\text{Pb}$ for common anthropogenic lead sources, data taken from R. McGill (unpublished) and S. Chenery (BGS, unpublished). Error bars show standard deviation of data. UK coal $n = 6$, UK ore $n = 18$, Australian ore $n = 2$.

4.1.2 Materials and Methods

Soil samples were collected from Chat Moss and Halsall Moss (see Chapter 2.1). Lead isotope ratios were measured for the sites amended with waste materials at Chat Moss (CM-3 and CM-12) and Halsall Moss (HM-1) as well as a control site located at Chat Moss (CM-1). The Pb isotope ratios were measured on soil samples at all sites (0 – 20 cm depth) using samples that had been digested for total element analysis (Section 2.5.1). Isotope ratios were measured using the experimental approach and ICP-MS operating conditions described in Section 2.7.

4.1.3 Results and Discussion

Lead isotope ratios were successfully measured on 21 samples from Chat Moss and 9 samples from Halsall Moss all collected from 0-20 cm depth. The $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{208}\text{Pb}$ ratios for soils from Chat and Halsall Mosses were plotted alongside the lead isotope ratios from known sources (Figure 4.2).

The historical record suggests that the source of lead contamination on Chat Moss should be mixed due to the variable nature of the waste incorporated into the moss, such as industrial and domestic wastes. The proximity to the UK Pb ore fields in the peak district, the known application of coal ash and increasing inputs of petrol-derived Pb from the 1950s up to 2000 must all have contributed to Pb inputs to the site. On Halsall Moss and the control site on Chat Moss a shallower depth of Pb contamination was observed (Chapter 3.1.3.3). This may indicate that the contamination was dominated by atmospheric sources of lead rather than deep incorporation of solid waste. However, as seen from Figure 4.2, the data collected for Chat Moss, Chat Moss control and Halsall Moss are all similar, and seem to correspond closely to UK ore-derived Pb as seen from literature values for $^{206}\text{Pb}/^{207}\text{Pb}$ (McGill *et al.*, 2003; Farmer *et al.*, 2005). However examining the $^{206}\text{Pb}/^{208}\text{Pb}$ ratios, all three sites, but particularly the two Chat Moss sites, appear depleted in ^{206}Pb or enriched in ^{208}Pb compared to the literature values for UK ore. The UK ore fields have a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 0.480 ± 0.003 , compared to the Chat Moss samples with a $^{206}\text{Pb}/^{208}\text{Pb}$ ratio of 0.472 ± 0.001 for the contaminated site and 0.470 ± 0.003 for the control site. It may be that these sites are being influenced, to a greater extent, by petrol-derived Pb, which has a very low $^{206}\text{Pb}/^{208}\text{Pb}$ ratio (0.456).

Unfortunately the data could suggest at least two different explanations for the range of Pb sources. Instead of showing UK Pb ore as the main source of lead contamination, the data may be showing a mix between UK coal-derived lead and petrol-derived lead if UK coal was the dominant end member of the mixed sources. This would fit with the historical evidence, and also with evidence from the field where many of the artefacts seen in the soil at site CM-3 were coal fragments (See Chapter 4.2). There would be inputs to both the CM-1 and the CM-3 sites from coal burning but the latter should include relatively large contributions from coal ash whereas only atmospheric contributions from coal burning should have affected the control site, CM-1. Furthermore, the contributions from the coal ash added to CM-3 may have been substantial, considering the difference in Pb concentrations at the two sites (section 3.1.3.3). Surprisingly, however, the isotopic signatures of sites CM-1 and CM-3 do not support this hypothesis; Figures 4.2 and 4.3 show very little difference in their position on the ratio mixing line. From the Pb isotope data gathered, it was therefore not possible to distinguish between sources of Pb contamination. In combination with the historical research, all that can be concluded is that Pb in both control and waste-amended sites is derived from a similar mixture of UK coal burning and Pb ore smelting with minor contributions from petrol-derived tetra-methyl Pb.

The results for Chat and Halsall Mosses were similar to those obtained by Le Roux *et al.*, (2003) for an ombotrophic peat bog to the south of Manchester (Lindow bog). They suggested the contamination was dominated by UK ore and coal-derived Pb rather than petrol-derived lead. The authors also found that the signatures of ore and coal-derived Pb were difficult to separate, as seen in this project.

A further complication lies in evidence that, during the 19th Century, Australian ore became more widely used within the UK than UK ores and that, in the south of England, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in herbage samples fell from 1.170 in the last 20 years of the 19th Century to 1.145 by 1930 (Shotyk *et al.*, 1998). Thus it is possible that the ratios seen for the lead contamination on the mosses may be dominated by coal rather than Pb ore smelting, as (latterly) the ores used would have been dominated by Australian rather than UK ore, and so would have a more radiogenic signature than those observed in the data.

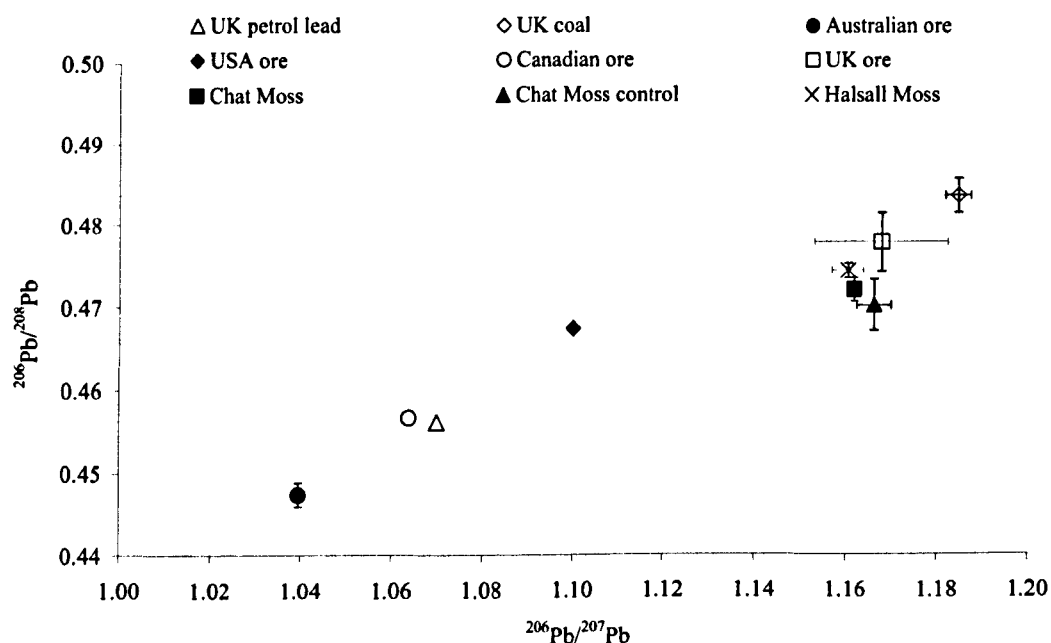


Figure 4.2: Lead isotope ratios $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{208}\text{Pb}$ for a range of known lead sources and soils samples from Chat and Halsall Mosses (full range). Error bars show standard deviation.

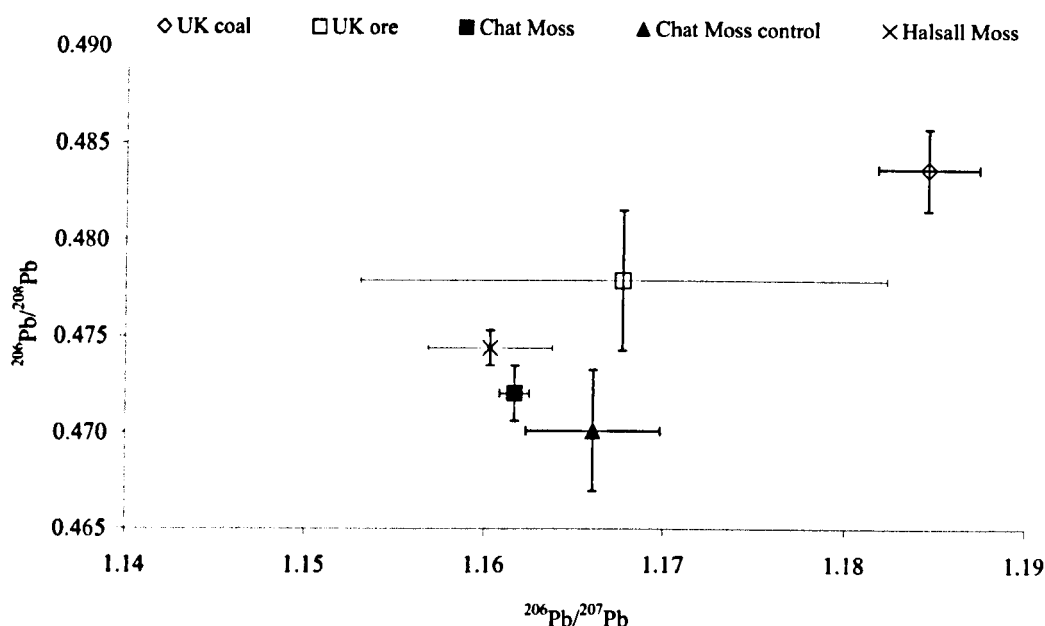


Figure 4.3: Lead isotope ratios $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{208}\text{Pb}$ for a range of known lead sources and soil samples from Chat and Halsall Mosses (restricted range). Error bars show standard deviation.

4.1.4 Conclusions

Lead isotope ratios were successfully measured on topsoil samples from Chat and Halsall Mosses. Surprisingly, despite substantial differences in total soil Pb concentrations, and the expectation that the contaminated sites would be dominated by the influence of coal ash, it was found that the two contaminated sites on Chat Moss and Halsall Moss and the control site on Chat Moss had very similar $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios. Thus, no distinct single source of lead contamination at Chat and Halsall Mosses could be identified due to the varied nature of the contamination and minor differences between the sites were difficult to interpret convincingly. There were broadly two explanations for the range of isotope ratios seen: either the contamination was almost entirely Pb ore based, with a slight influence of petrol-derived lead, or the contamination was the result of a mixture of

coal-derived Pb and petrol-derived Pb. Evidence from historical archives and field observations make the second explanation more likely, as it could be seen in the field that coal made up a large amount of waste incorporated into the mosses. Coal-derived and petrol-derived Pb would be atmospheric contaminants, and so could be introduced to the control soils in this way. The contamination sources at Chat and Halsall Mosses are most likely a result of mixing between UK coal, UK ore (as well as Australian ore, which became widely used in 19th Century) and a minor contribution from petrol-derived lead (derived from Australian and Canadian ores).

4.2 Examination of foreign objects present in the soil by Scanning Electron Microscopy

4.2.1 Introduction

Numerous foreign objects, including fragments of pottery, were observed in soils known to have had waste added at both Chat and Halsall mosses. It is likely that these objects were present in the waste material when it was incorporated. To assess whether these items contributed to the levels of trace elements in the soils a range were selected for examination using Scanning Electron Microscopy (SEM) and qualitatively analysed by examination of the key peaks present in the Energy Dispersive X-ray (EDX) spectrum.

4.2.2 Materials and Methods

Objects for examination were selected by hand picking from air-dried <2mm sieved soils collected at sites CM-3, CM-12 and HM-1. They were chosen to reflect the diverse range of foreign items present in the soils at the sites and at different depths.

Prior to examination by SEM they were fixed on a stub using carbon dag and sputter-coated with gold. Images and associated EDX spectra were collected for each object.

4.2.3 Results and Discussion

Most fragments were readily identified by their morphological features and X-ray spectrum as coal, bone, glass and slag material (Figure 4.4). One grey-white object was identified as quartz and a reddish-coloured fragment as a sample of rusting iron (Figure 4.5). Most are likely to be anthropogenic additions to the soils.

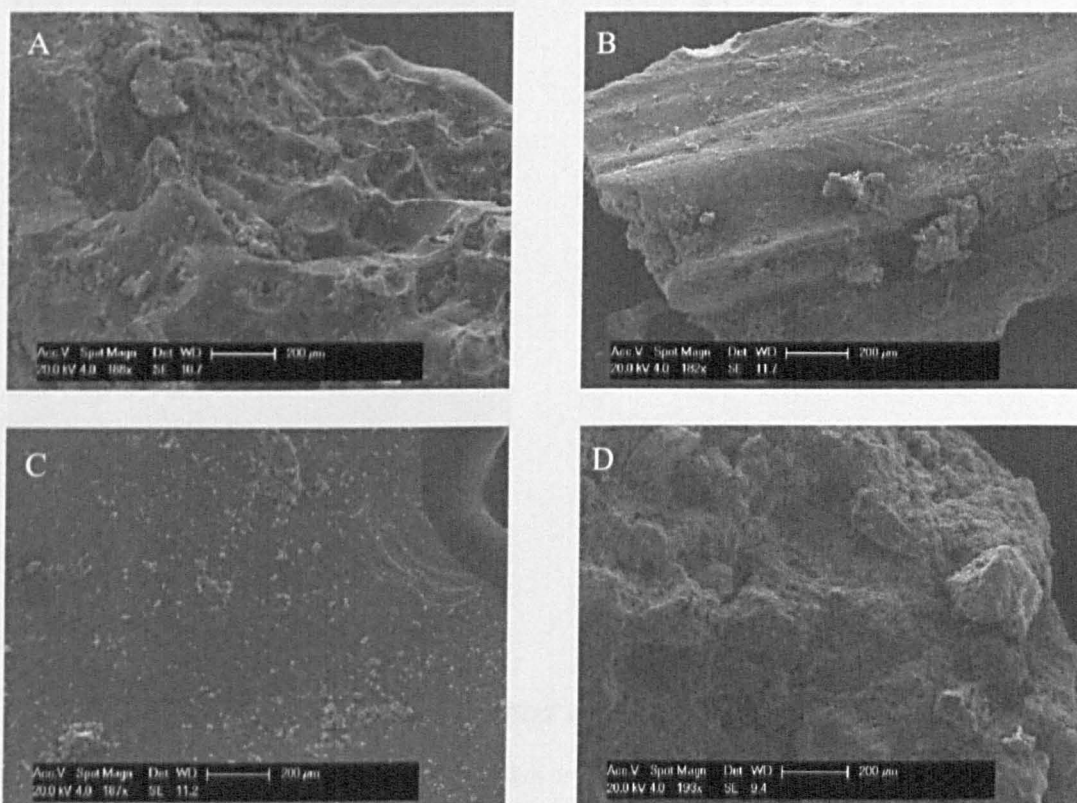


Figure 4.4: SEM images of fragments recovered from waste-amended soils on Chat Moss. Fragments include Coal (A) identified by its vesicular texture formed as a consequence of exposure to high temperature (soil CM-12, 30 cm depth), Bone (B) (CM-12, 20 cm depth), Glass (C) showing typical conchoidal fracture with high Si and trace Na present (CM-12, 20 cm depth) and slag material (D) containing Si, Al, K, O and Fe.

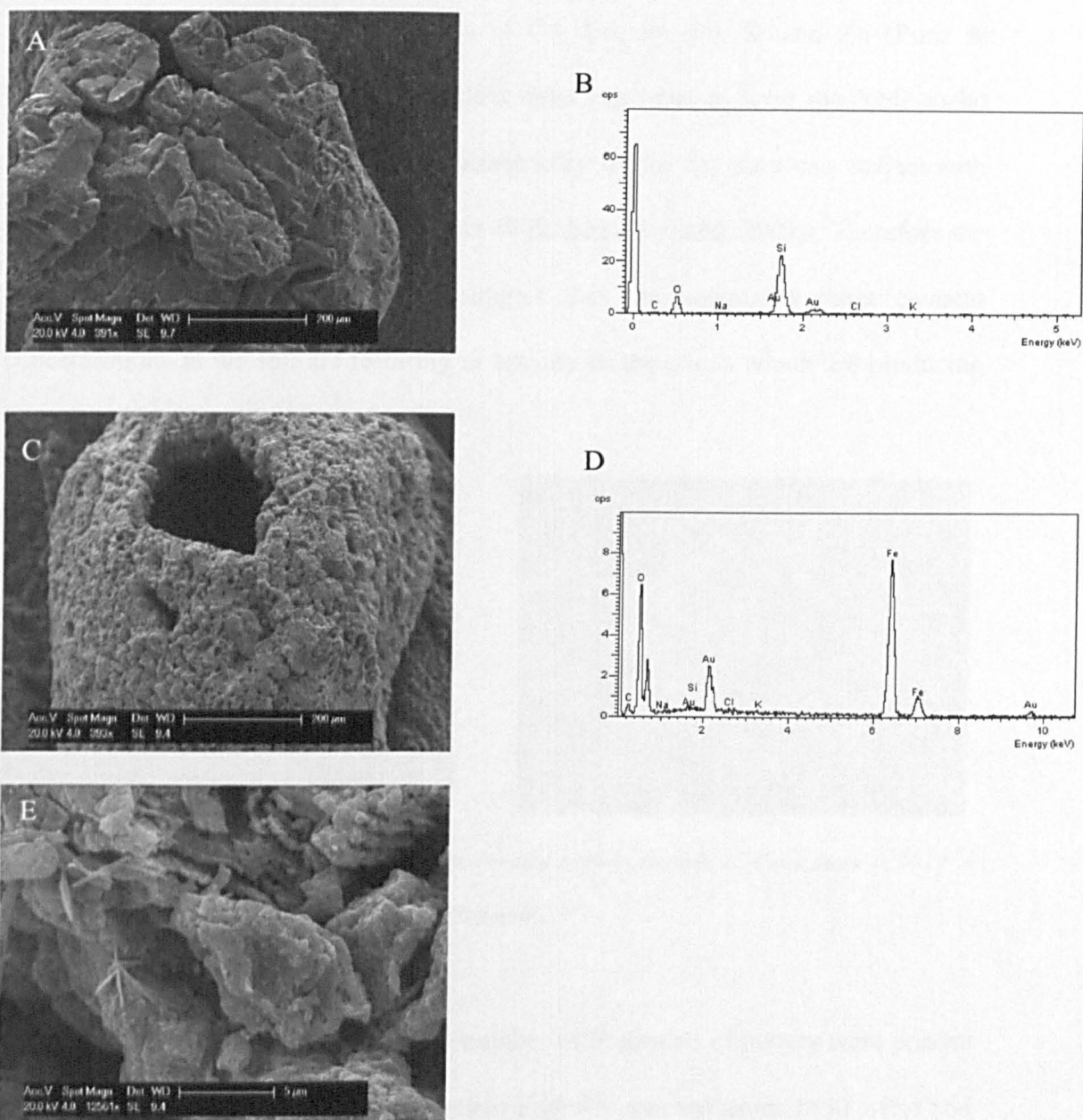


Figure 4.5: SEM images and accompanying EDX spectra of quartz particle (A and B) and rusting iron (C, D and E) (both CM-3 topsoil). Resolution at 200 μm (C) and 5 μm (E).

Also observed within the soils were white particles, initially thought to be fly-ash or pottery fragments (Fig. 4.6). SEM-EDX analysis showed that the particles were crystalline and composed of calcium, carbon and oxygen. This indicates the presence of calcium oxalate, which is produced by plants as a response to heavy

metal toxicity, particularly high levels of Cd, Co, Fe, Pb, Sr and Zn (Punz & Sieghart, 1993). Oxalate exuded by plant roots can react to form insoluble metal oxalates, alternatively oxalate produced internally within the plant can chelate with metals to render them unavailable (Jarosz-Wilkolazka & Gadd, 2003). Therefore the presence of calcium oxalate might suggest that the potentially toxic element concentrations in the soil are resulting in toxicity to the plants which are producing oxalate as a response.

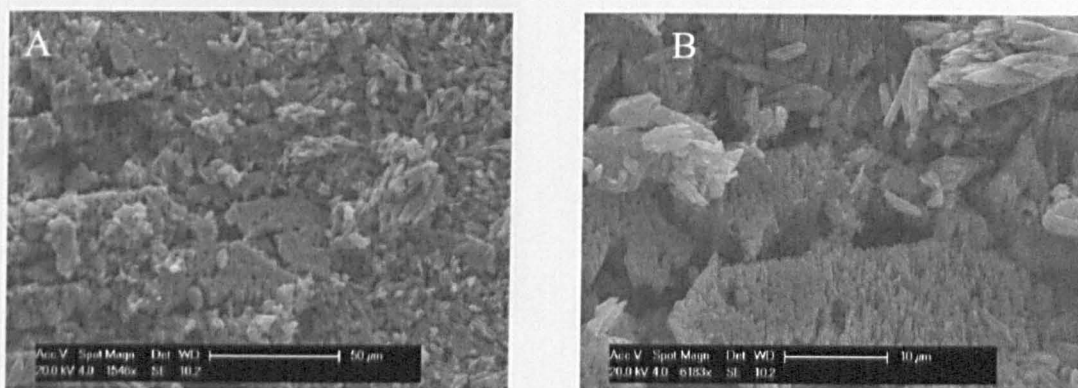


Figure 4.6: SEM images of calcium oxalate crystals present in soils at Chat Moss (CM-12 at multiple depths). Resolution at 50 μm (A) and 10 μm (B).

At both Chat and Halsall mosses a large number of fragments of pottery were present in the soil. Pottery glazes typically contain high Pb concentrations (>50 wt%) and may contribute to the elevated Pb concentrations measured in these soils. Lead was used in the manufacture of pottery until 1947 when its use was banned (Buckley, 1990). In some regions lead glazing is still commonly used in pottery and ceramic manufacturing, and it has been shown that in Mexico the lead glazing in pottery is a major source of lead exposure through leaching from the glazes (Tunstall & Amarasiriwardena, 2002). The presence of pottery in the soils of Chat and Halsall Mosses could represent a source of lead contamination to the soil if leaching under acidic conditions were to take place.

High concentrations of Pb were observed within the glazes in the pottery samples analysed (Fig. 4.7). However, only limited evidence of etching or erosive dissolution of the glaze was observed and some areas where glaze was absent may be a result of abrasion (see e.g. Figure 4.7 C).

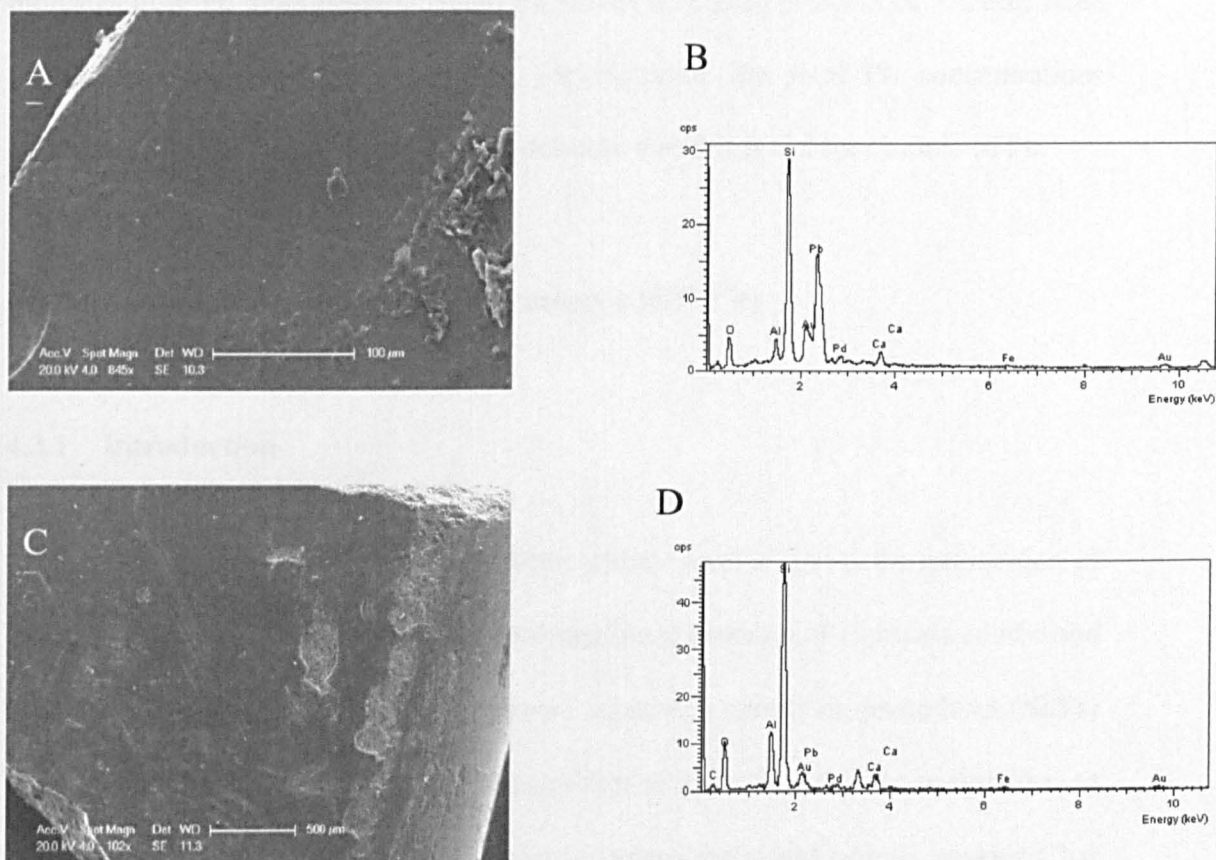


Figure 4.7: SEM images (A & C) and associated EDX spectra (B & D)) of the surface of glaze on pottery (recovered from HM-1 topsoil).

4.2.4 Conclusions

Objects selected and identified within the soils reflect the anticipated range of inorganic additions that were likely to comprise the wastes. With the exception of pottery glazes all the fragments were low in potentially toxic elements. Pottery glazes contained significant Pb concentrations but the absence of dissolution features indicates little Pb mobilisation. Small fragments of glazed pottery (i.e. < 2mm sized pieces) may however be responsible for elevating the total Pb concentrations determined for these soils although it is unlikely that this is the sole source of Pb.

4.3 Sequential extraction procedures (SEP's)

4.3.1 Introduction

Sequential extraction procedures have been widely used to assess the association of trace metals with soil fractions by determining the proportion of elements solubilised by selective reagents. A review of common sequential extraction procedures (SEPs) is presented in Section 1.3.2.1. The primary aim of using SEPs in this project was to compare the fractionation of metals in the uncontaminated and waste-amended Chat Moss soils (CM-1 and CM-3; Chapter 2.1). It was decided to use the well known Tessier scheme and an additional procedure that has been designed for highly organic soils (Breward *et al.*, 1996). It was hoped that using two different SEPs would provide more information on the nature of metal binding in these organic soils and the robustness of the results could be more fully assessed. An additional aim of this chapter was to compare the Chat Moss results with a suite of soils with known contamination history (Pb/Zn minespoil, sewage sludge and roadside deposition).

The range of soils was intended to reflect a range of contamination sources of lead, and therefore it was hoped to use the SEP to distinguish between these contamination sources based on the fractionation of lead.

4.3.2 Experimental design for Tessier and Breward methods

The Tessier method used in this study is a modified scheme taken from Li & Thornton (2001) and the Breward method is described by Breward *et al.*, (1996). The fractions isolated by the two schemes are summarised in Table 4.1. Both SEPs use an initial soil weight of 1.00 g of air-dried soil sieved to < 2 mm.

Table 4.1: Sequential extractions procedures for Tessier and Breward methods

Fraction	Tessier	Breward
F1	Exchangeable: 0.5 M MgCl ₂	Exchangeable: 1 M NH ₄ OAc
F2	Carbonate bound: 1 M NaOAc (adjusted to pH 5 with HOAc)	Carbonate bound: 1 M NaOAc (at pH 5)
F3	Fe/Mn oxide bound: 0.04 M NH ₂ OH.HCl	Organically bound; humic and fulvic acids: 1 M ammonia
F4	Organic and sulphide bound: 0.02 M HNO ₃ and H ₂ O ₂ , 3.2 M NH ₄ OAc.	Mn oxide bound: 0.1 M NH ₂ OH.HCl
F5	Residual: HNO ₃ , HF, HClO ₄ .	Fe oxide bound: Tamm's reagent
F6		Residual: HNO ₃ , HF, HClO ₄ .

The Tessier scheme and its variants are perhaps the most widely used schemes for soil metal fractionation. It is broadly similar to the BCR scheme sanctioned by the EC (Quevauviller *et al.*, 1997) (Chapter 1.3.2.1 and Table 1.3). The Tessier scheme was employed here to try and relate contamination source to current soil

fractionation. The Breward scheme was selected for use on the Chat Moss soils as it has been specifically developed for organic soils. It differs markedly from the Tessier scheme in that trace elements bound to the molecular and colloidal fractions of humus (fulvic and humic acids) are extracted before the reduction step used to dissolve Fe/Mn hydrous oxides. In addition, the humic and fulvic acids (and associated metals) are mobilised into solution by raising the soil suspension pH rather than an oxidation step to destroy the humus fraction, as in the Tessier method (Table 4.1). In addition, the Breward scheme distinguishes between humic and fulvic acid fractions and also between Mn and Fe hydrous oxide fractions; again this contrasts with the Tessier scheme which identifies a single fraction for metals bound to hydrous oxides and to humus. Considering the imperfect nature of SEPs it therefore seems likely that (for example) the Tessier scheme will over-estimate the oxide-bound fraction by mobilizing organically-bound trace metals through exchange with dissolved Fe^{2+} and Mn^{2+} during extraction of F3 (Fe/Mn oxide fraction). By contrast, the Breward scheme is likely to under-estimate the organically-bound fraction by re-adsorption of metals at high pH on to Fe/Mn hydrous oxides and by failure to mobilize surface-adsorbed metals in the remaining solid-phase organic sites during extraction of F3 (organic fraction). Both these potential deficiencies will act in the same direction: to increase the size of the apparent oxide-bound fraction and reduce the size of the apparent organic fraction.

The topsoils analysed for this experiment were from Chat Moss (19th century urban contamination), Clough Wood (Pb/Zn minespoil contamination), a Sewage disposal farm (sewage sludge contamination) and a roadside soil. Chat Moss, Lancashire (grid reference SJ 724 973) is the moorland site which is the main subject of this project. It was reclaimed for arable agriculture in the 19th Century, during which

large quantities of waste from Manchester was incorporated into the soil (Phillips, 1980). Clough Wood, Derbyshire (grid reference SK 257 617) was directly contaminated by Pb/Zn minespoil, mined in the region since the 17th century, particularly between 1859 and 1939 (Young *et al.*, 2000). Stoke Bardolph, Nottinghamshire (grid reference SK 641 409) has been used as a sewage processing farm for over 100 years, and is currently run by a major UK water company, under licence from DEFRA, as a dedicated site for production of animal fodder. The roadside location, off the A6 near Kegworth, Leicestershire (grid reference SK 489 260) has a high traffic density but was expected to have a low natural soil Pb content so that the majority of the soil Pb would be derived from petrol additives. The Chat Moss soils were collected from sites CM-1 (Chat Moss control) and CM-3 (Chat Moss contaminated), representing control and waste-amended sites for comparison (Chapter 2.1). Using Ward-linkage dendrogram analysis, it was shown that there was a strong degree of similarity between all four soils when comparing total metal contents, with Chat Moss and Minespoil being the most similar (Figure 4.8). This apparently supports the use of the Sewage farm, Minespoil and Roadside soils as compositional proxies for the waste incorporated into Chat Moss. However it is also likely that the similarities observed between the soils are coincidental, or represent deeper geochemical linkages unrelated to the soils.

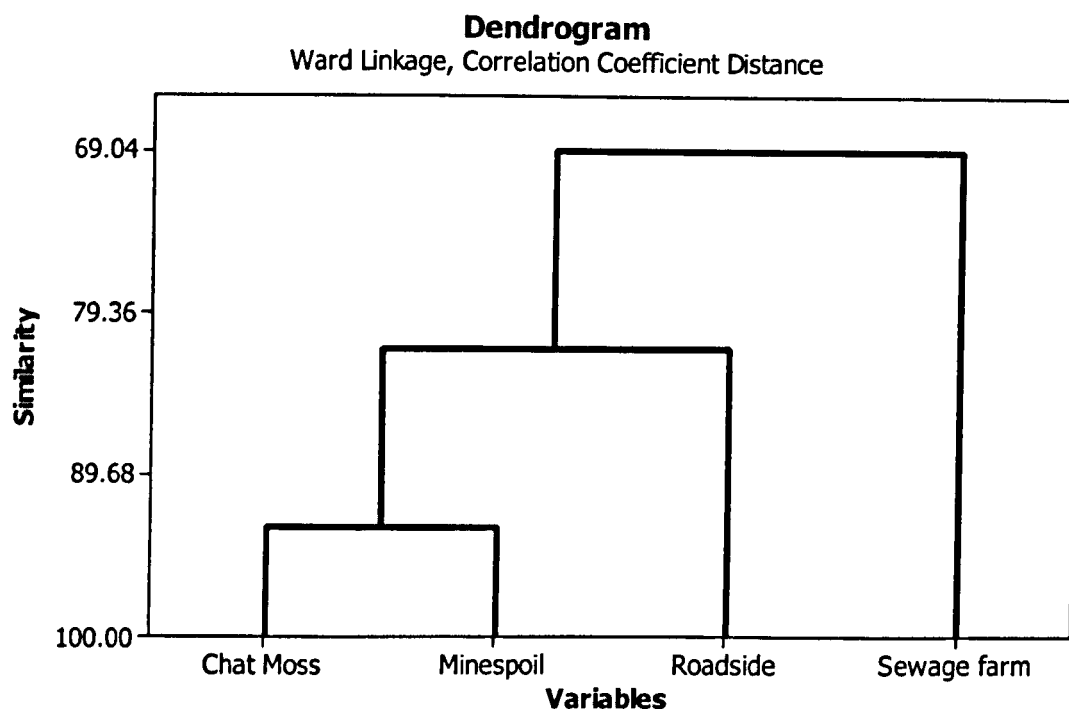


Figure 4.8: Dendrogram showing clustering of soils using total elemental data. Number of data points = 72.

Apparent recoveries deviating from 100% during SEP's indicate an error within the scheme due to experimental or analysis error. There is considerable scope for such errors during sequential extraction procedures partly due to the large number of steps involved, each of which can result in contamination or carry-over into the next step (Young *et al.*, 2006). To account for these errors a blank was taken for analysis at each step, and the residual weight of the centrifuged soil sample was recorded to measure carry-over of the extracting solution into the next step to account for the amount of trace metals entrained in the pore solution. The sequence of operations used in the modified Tessier and Breward schemes are described in Table 4.2. The extracts from each step of the SEPs were analysed by ICP-MS following the method described in Section 2.6.

Table 4.2: Sequential extraction methods for modified Tessier and Breward schemes

Tessier method (Li & Thornton, 2001)	Breward method
Weigh 1.0 g soil into centrifuge tube	Weigh 1.0 g soil into centrifuge tube
Add 8.0 mL 0.5 M MgCl ₂ ; shake for 20 min.	Add 20 mL 1 M NH ₄ OAc (pH 7); shake for 1 hour.
Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.	Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.
Analyse supernatant for Exchangeable elements (ICPMS)	Analyse supernatant for Exchangeable elements (ICPMS)
Add 8.0 mL 1 M NaOAc at pH 5.0 to residue; shake for 5 hours.	Add 20 mL 1 M NaOAc to residue; shake for 2 hours.
Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.	Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.
Analyse supernatant for Carbonate-bound and Specifically adsorbed elements (ICPMS)	Analyse supernatant for Carbonate-bound elements (ICPMS)
Add 20 mL 0.04 M NH ₂ OH.HCl in 25% (v/v) HOAc to residue; extract at 96°C for 6 hours with occasional agitation; dilute samples to 20 mL with deionised water; shake for 10 minutes.	Add 20 mL 1M NH ₃ to residue; shake for 1 hour.
Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.	Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.
Analyse supernatant for elements bound to Fe/Mn oxides (ICPMS).	Acidify supernatant to pH 1.0 with conc. HCl Remove supernatant containing Fulvic acid Oxidise remaining solid with acidified H ₂ O ₂ at 80°C Recover digestate of Humic acid.
Add 3.0 mL 0.02 M HNO ₃ and 5.0 mL H ₂ O ₂ at pH 2.0 to residue. Heat at 85°C for 2 hours with occasional agitation. Cool, add 3 mL H ₂ O ₂ and heat again at 85°C for 3 hours with occasional agitation. Cool, add 5 mL 3.2 M NH ₄ OAc in 20% (v/v) HOAc and dilute with DI water to 20 mL. Agitate for 30 min.	Analyse both Fulvic and Humic acid fractions for bound metals (ICPMS).
Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.	Add 20 mL 0.1 M NH ₂ OH.HCl to soil residue; shake for 1 hour.
Analyse supernatant for elements bound to organic matter and sulphides	Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue.
Digest residue with HNO ₃ , HF and HClO ₄ (Section 2.5.1)	Analyse supernatant for elements bound to secondary Mn oxides (ICPMS)
Analyse digestate for Residual elements.	Add 20 mL Tamm's reagent (oxalic acid and NH ₄ OAc) and mix; stand in dark for 2 hours Centrifuge for 15 min at 2500 rpm, filter supernatant (< 0.2 µm), weigh residue. Analyse supernatant for elements bound to secondary Fe oxides Digest residue with HNO ₃ , HF and HClO ₄ (Section 2.5.1) Analyse digestate for Residual elements.

4.3.3 Results and Discussion

4.3.3.1 Comparison between Breward and Tessier methods using control and contaminated Chat Moss soils.

Due to the unknown mineralogy of the Chat Moss soil, it was not possible to categorically assess which extraction method generated the most meaningful results, however some assumptions can be made by comparing the two methods. It must be noted that any conclusions drawn here about the effectiveness of the two methods for defining the fractionation of the Chat Moss soil are only assumptions and should be considered as such.

4.3.3.1.1 Group 2 metals – Sr, Ba

Strontium

The recoveries for Sr were close to the digestion total for both the Tessier and Breward methods, and for both soils (Chat Moss contaminated and Chat Moss control). Both methods showed the same proportion of Sr in the exchangeable fraction for both soils (32% - 33%) (Figure 4.8). However, the Tessier method showed a greater concentration of Sr in the Fe/Mn oxide and the organic fractions for both soils whereas the Breward method suggested greater concentrations in the residual and carbonate fractions (Figure 4.9). Strontium is often found as a structural component in clay minerals, which would be expected to remain in the residual fraction, but in acidic soils Sr can be easily mobilised (Kabata-Pendias, 2001), explaining the relatively large proportion of Sr in the exchangeable fraction, as the Chat Moss soils had pH values around 5.5. Strontium would also be expected to be present within the carbonate fraction of soils, as it often substitutes for Ca, however both Chat Moss soils had a very low carbonate content.

The increased extraction of Sr in the organic phase with the Tessier method suggested that the Breward extractant for this step (ammonia) was relatively inefficient for Sr, or that the Tessier extractant was over-extracting Sr (Figure 4.8). The Tessier extraction for this step relies on the destruction of organic matter with hydrogen peroxide and retention of liberated ions in solution with nitric acid and ammonium acetate. This seemed to be more effective at mobilising organically bound Sr for this highly organic soil. Strontium is relatively weakly bound to organic matter and it is possible that, following dissolution of humic and fulvic acids in the Breward method, there was re-adsorption of Sr on to the (still intact) clay and hydrous oxides at the high pH produced. There was also a higher proportion (+ 3.4%) of Sr in the carbonate step of the Breward method. This could explain the reduced organic Sr (- 3.3%) seen in the Breward method as some may have been mobilised in the carbonate step (Figure 4.9). However it cannot be stated which method was the more accurate in measuring fractionation due to the unknown mineralogy of the Chat Moss soil. To resolve this issue, a soil with known mineralogy and response to sequential extraction procedures could be used.

The difference seen in the Fe/Mn oxide fraction for Sr was unexpected as the extractants for this step are similar in both schemes, with the Tessier scheme using hydroxylamine hydrochloride, and the Breward scheme using hydroxylamine hydrochloride and Tamm's Reagent. However in the Breward scheme the length of the extraction step was only 1 hour at room temperature with hydroxylamine hydrochloride whereas the Tessier scheme has a 6 hour step at 96°C. This operational difference may explain why the Breward scheme extracts less Sr. This,

in turn, would result in more Sr being extracted in the final residual step with the Breward method, which was seen for both soils.

Barium

The recovery for Ba was greater with the Breward method (101%) than with the Tessier method (86%), although both were within acceptable experimental limits (Figure 4.10). The fractionation of Ba was broadly similar as measured by both methods and for both soils, with most of the Ba (43 – 56%) being extracted in the residual fraction. Barium is commonly associated with clay minerals which would be expected to be unaffected by the extractants and so found in the residual fraction (Kabata-Pendias, 2001). As seen for Sr, for both the contaminated and control soils, the Breward scheme measured lower recoveries of Ba in the Fe/Mn oxide and organic fractions, although it cannot be determined whether the Breward or Tessier methods were more accurate.

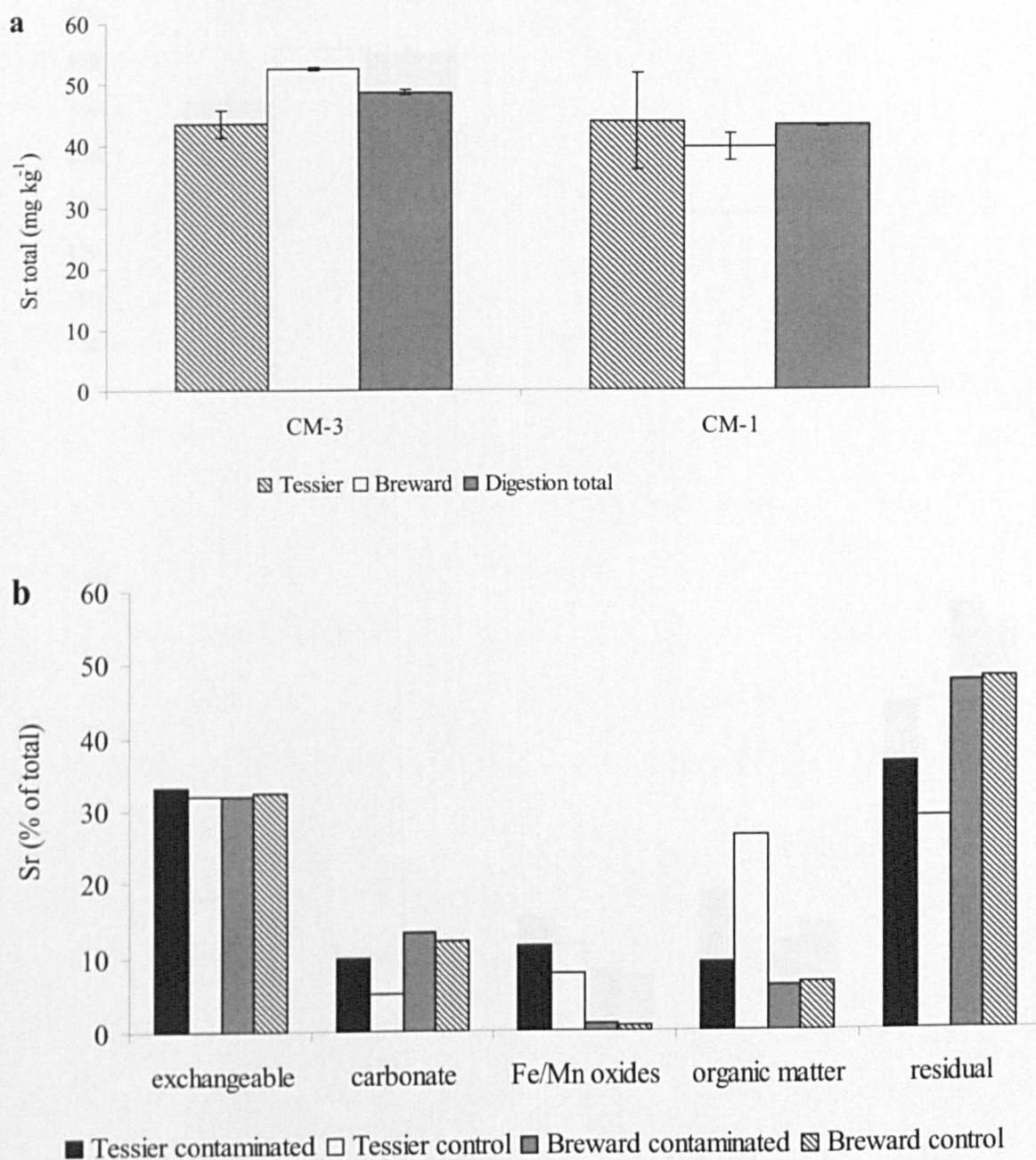


Figure 4.9: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Sr for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Sr fractionation pattern for the Tessier and Breward SEPs.

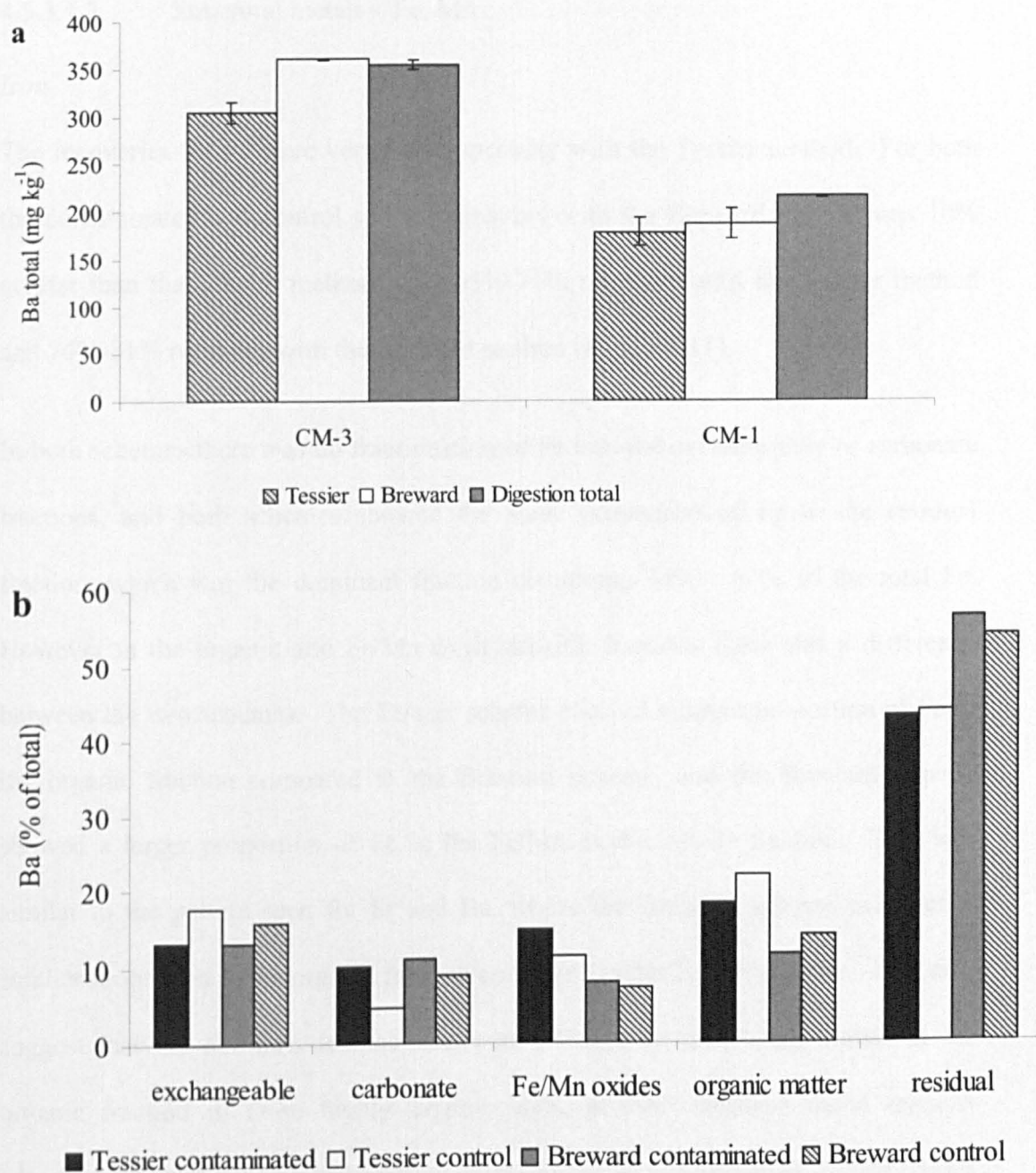


Figure 4.10: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Ba for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Ba fractionation pattern for the Tessier and Breward SEPs.

4.3.3.1.2 Structural metals – Fe, Mn

Iron

The recoveries for Fe were very low, especially with the Tessier method. For both the contaminated and control soil the recovery with the Breward method was 10% greater than the Tessier method, with 65%-71% recovery with the Tessier method and 74%-81% recovery with the Breward method (Figure 4.11).

In both schemes there was no fractionation of Fe into the exchangeable or carbonate fractions, and both schemes showed the same proportion of Fe in the residual fraction, which was the dominant fraction containing 54% - 64% of the total Fe. However in the organic and Fe/Mn oxyhydroxide fractions there was a difference between the two schemes. The Tessier scheme showed a larger proportion of Fe in the organic fraction compared to the Breward scheme, and the Breward scheme showed a larger proportion of Fe in the Fe/Mn oxyhydroxide fraction. This was similar to the pattern seen for Sr and Ba, where the Breward scheme extracted a smaller proportion in the organic fraction compared to the Tessier scheme. This may suggest that the Breward scheme is not as effective at mobilising metals in the organic fraction in these highly organic soils, possibly because metal remains adsorbed on solid phase humus during extraction or re-adsorption on Fe/Mn oxides occurs.

For both soils most of the Fe was in the residual phase either as resistant Fe oxides that are not affected by the Fe/Mn oxide step, or as clay minerals that would remain in the residual phase (Li & Thornton, 2001; Deer *et al.*, 1992). The fractionation of Fe in both SEPs was the same for both the control and the contaminated soil,

indicating that the addition of waste to the soil had not affected the form of Fe in the soil.

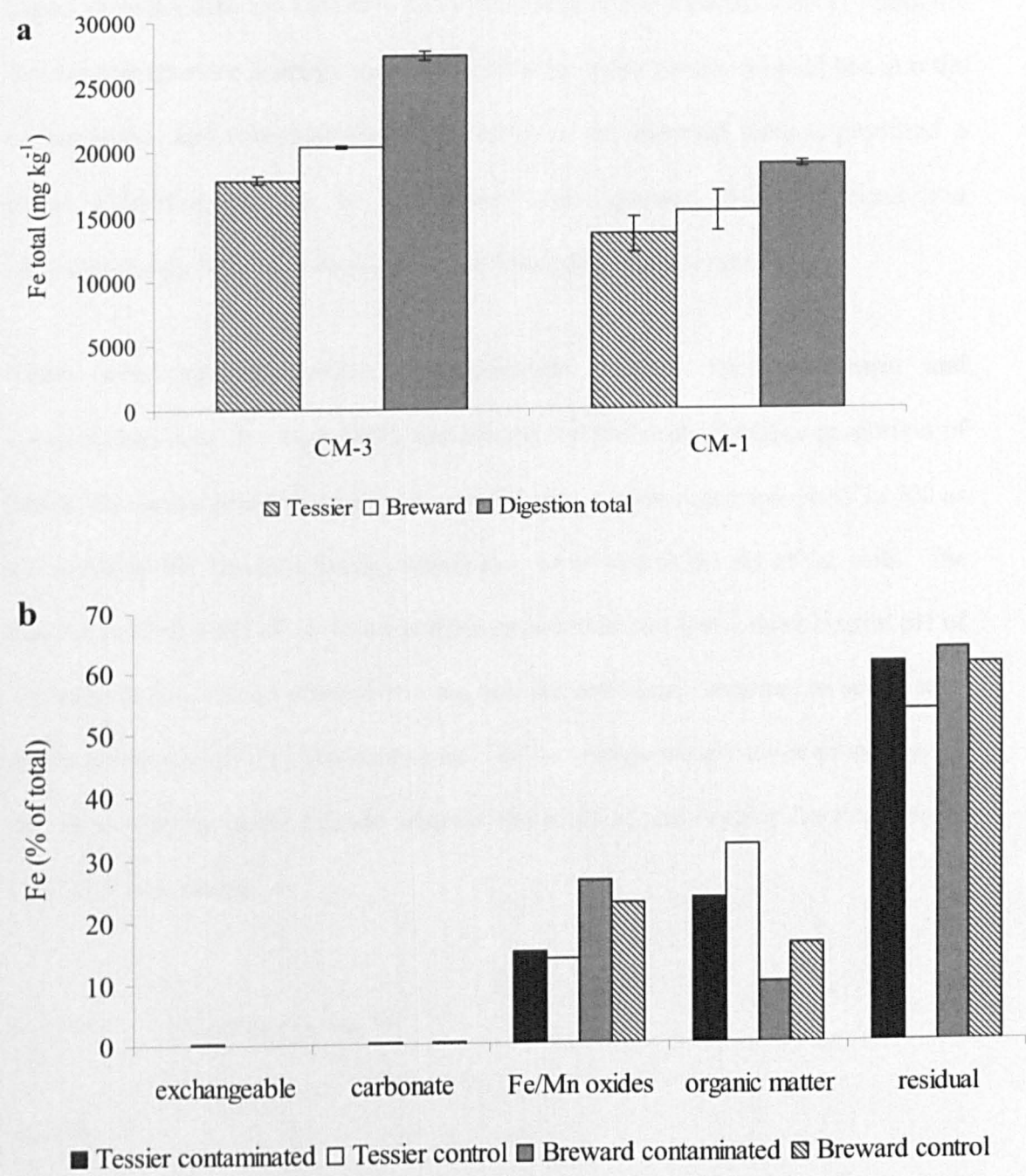


Figure 4.11: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Fe for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Fe fractionation pattern for the Tessier and Breward SEPs.

Manganese

The recovery of Mn was good for both methods, although the Breward method had a higher recovery than the Tessier method (96% recovery compared to 85%). Both the Tessier and Breward schemes showed broadly the same fractionation of Mn into the exchangeable and carbonate fractions. However the Breward method produced a lower proportion of Mn in the organic and hydrous oxides fractions and correspondingly higher levels of Mn in the residual fraction (Figure 4.12).

There were markedly different fractionation patterns for the control and contaminated soil. For both SEPs, the control soil had a much higher proportion of Mn in the exchangeable fraction compared to the contaminated soil (40% to 3% as measured by the Tessier scheme), which may be related to the pH of the soils. The control soil had a pH of ~5 whereas the contaminated soil had a more neutral pH of ~6, and Mn has a lower solubility in the near-neutral range compared to acidic soils (Kabata-Pendias, 2001). The control soil had a correspondingly lower proportion of Mn in the Fe/Mn oxide fraction whereas the residual and organic fractionation in both soils was similar.

4.3.3.1.3 Metalloids – As, Se

Arsenic

The recovery for As was high with both the Tessier and Breward methods, with average recoveries of 100% and 118% respectively. Selenium showed similar recoveries for both methods, with 103% and 112% for the Tessier and Breward methods respectively (Figure 4.13a).

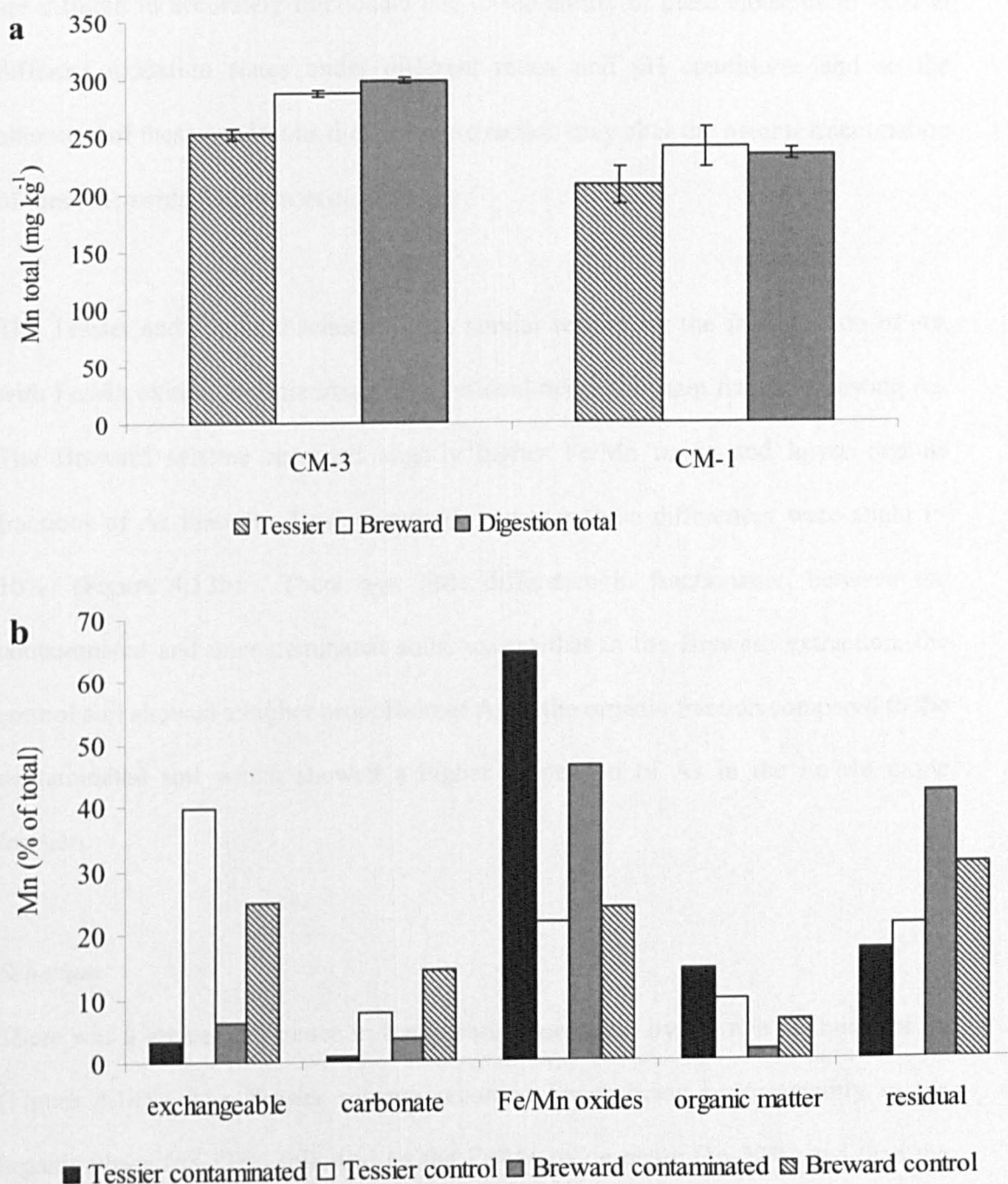


Figure 4.12: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Mn for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Mn fractionation pattern for the Tessier and Breward SEPs.

When considering the fractionation for As and Se, it must be noted that As and Se are difficult to accurately fractionate due to the ability of these elements to exist at different oxidation states under different redox and pH conditions, and so the alteration of these conditions during the extraction may alter the natural fractionation of these elements (Gleyzes *et al.*, 2002).

The Tessier and Breward schemes gave similar results for the fractionation of As, with Fe/Mn oxides, organic matter and residual being the main fractions hosting As. The Breward scheme recorded slightly higher Fe/Mn oxide and lower organic fractions of As than the Tessier method, however these differences were slight (< 10%) (Figure 4.13b). There was little difference in fractionation between the contaminated and uncontaminated soils, except that in the Breward extraction, the control soil showed a higher proportion of As in the organic fraction compared to the contaminated soil which showed a higher proportion of As in the Fe/Mn oxide fraction.

Selenium

There was a greater difference in fractionation measured by the two methods for Se (Figure 4.14). The Tessier scheme recorded Se as being predominantly in the organic phase (68-71%) followed by the Fe/Mn oxide phase (16-22%) and then the residual phase (8-14%), whereas the Breward scheme extracted Se mainly in the residual phase (47-51%), followed by the organic phase (33-34%) and then the Fe/Mn oxide phase (15%). The proportion of Se in the Fe/Mn oxide phase was reasonably consistent for both methods, suggesting that this may be a reliable result. However the results for the other fractions were very different, with up to 38%

difference in the proportion of Se extracted in the organic phase between the two methods. The different approaches to mobilizing the organic Se pool taken by the two SEPs may explain the disparity in results. The Tessier method employs complete oxidation of all organic matter which will convert all remaining (and accessible) Se to soluble selenate. By contrast, the Breward method is non-destructive in its approach and relies simply on mobilization of humic and fulvic acids. This means that any Se bound into skeletal organic forms (e.g. humin, plant fragments etc) will not be accessed and any selenite still adsorbed to Fe oxides will not be transformed to selenate and solubilised.

There was little difference seen between the two soils for each method, indicating that waste amendment has not altered the form of Se in these soils. The total Se concentrations were also similar (CM-3 < CM-1) suggesting that, in contrast to As, the waste had not enriched the soil with Se.

4.3.3.1.4 Trace metals

For all trace metals with the exception of Ti, Zn and Cd, the Breward method gave significantly better recoveries than the Tessier scheme. In the case of Ti, the Tessier method gave the best recovery, although this was still less than 100% (76%). For Zn and Cd, both methods gave approximately 100% recovery.

The fractionation varied for the trace metals, although all except Cd, Zn and Co were concentrated in the residual, organic and Fe/Mn oxide fractions. As expected, Ti was

almost completely hosted by the residual fraction (85-98%) in both SEPs, with only 2% being extracted in the organic fraction (Figure 4.15).

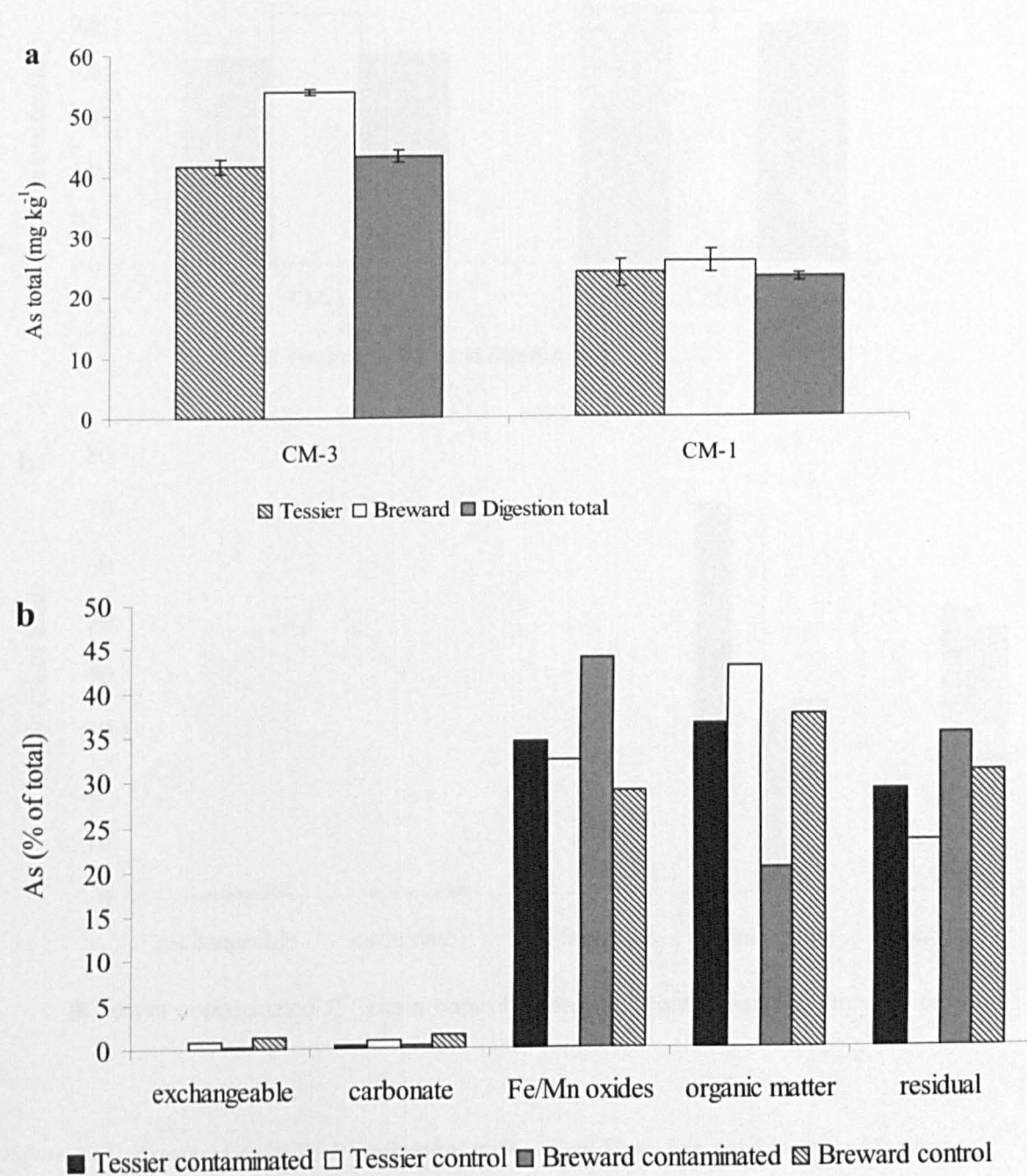


Figure 4.13: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of As for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) As fractionation pattern for the Tessier and Breward SEPs.

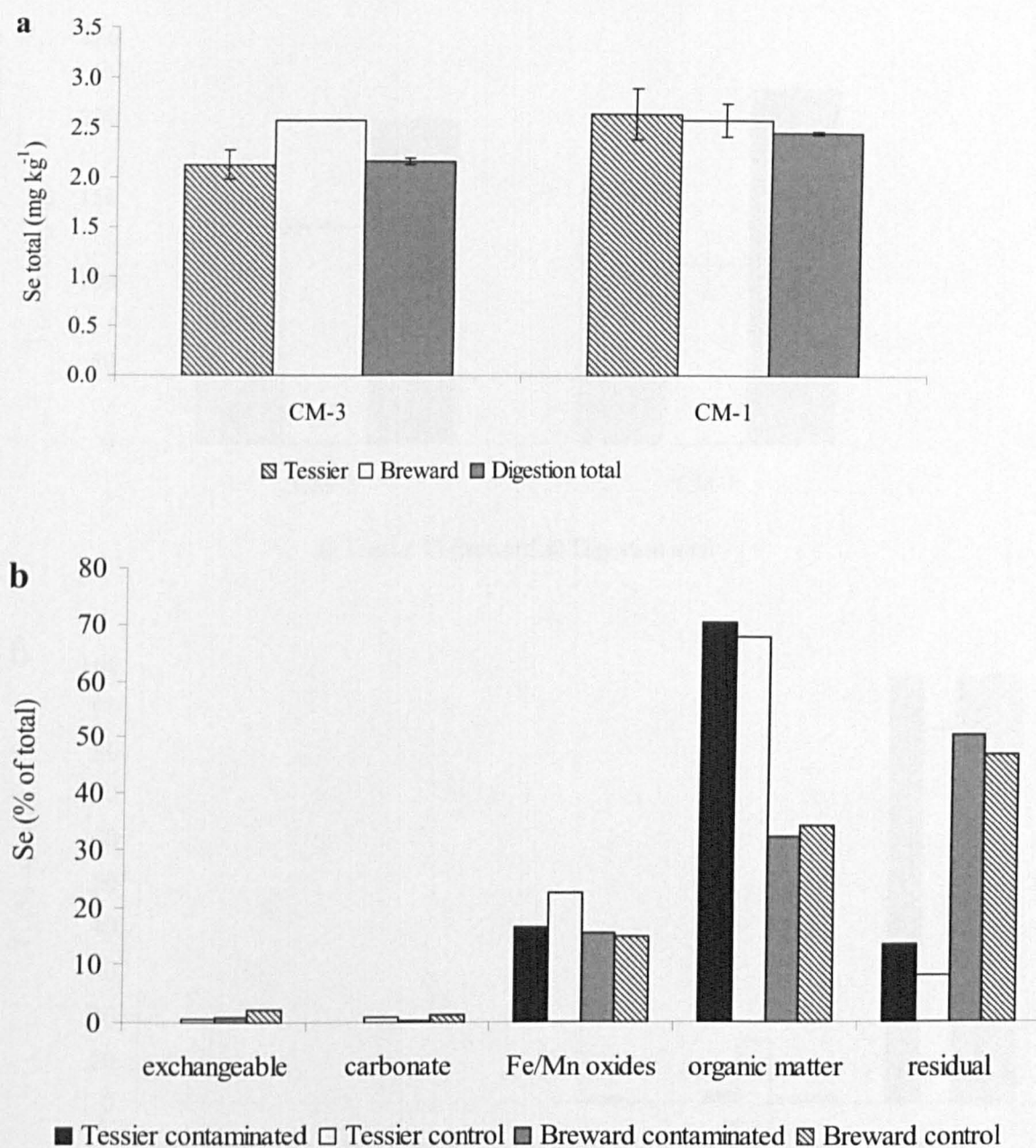


Figure 4.14: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Se for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Se fractionation pattern for the Tessier and Breward SEPs.

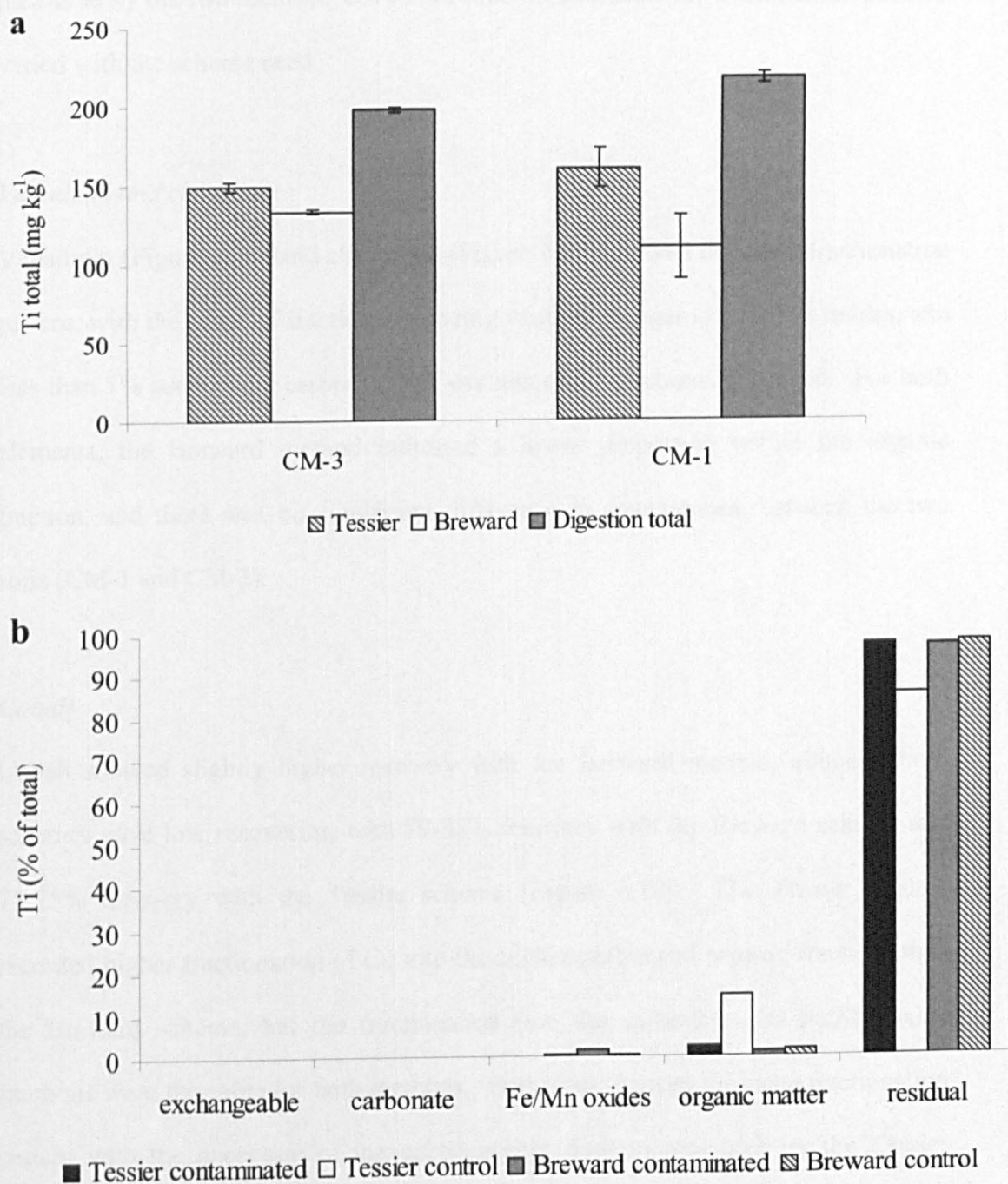


Figure 4.15: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Ti for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Ti fractionation pattern for the Tessier and Breward SEPs.

There was no significant difference in fractionation pattern for V, Cr and Zn as measured by the two methods, but for all other trace metals the fractionation patterns varied with the scheme used.

Vanadium and chromium

Vanadium (Figure 4.16) and chromium (Figure 4.17) showed the same fractionation pattern, with the order of fractionation being residual > organic > Fe/Mn oxides, and less than 1% seen in the carbonate and exchangeable fractions combined. For both elements, the Breward method indicated a lower proportion within the organic fraction, and there was no significant difference in fractionation between the two soils (CM-1 and CM-3).

Cobalt

Cobalt showed slightly higher recovery with the Breward method, although both schemes gave low recoveries, with 79-88% recovery with the Breward scheme and 73-75% recovery with the Tessier scheme (Figure 4.18). The Tessier scheme recorded higher fractionation of Co into the exchangeable and organic fractions than the Breward scheme, but the fractionation into the carbonate and Fe/Mn oxide fractions were the same for both methods. Both soils showed the same fractionation pattern with the exception of the exchangeable fraction measured by the Tessier scheme, which showed higher fractionation of Co in the control soil, probably related to the lower pH in this soil. The fractionation of Co followed the pattern: residual > Fe/Mn oxides = organic > exchangeable > carbonate for both soils. The Breward scheme produced a lower organic fraction and a correspondingly higher residual Co fraction compared to the Tessier scheme.

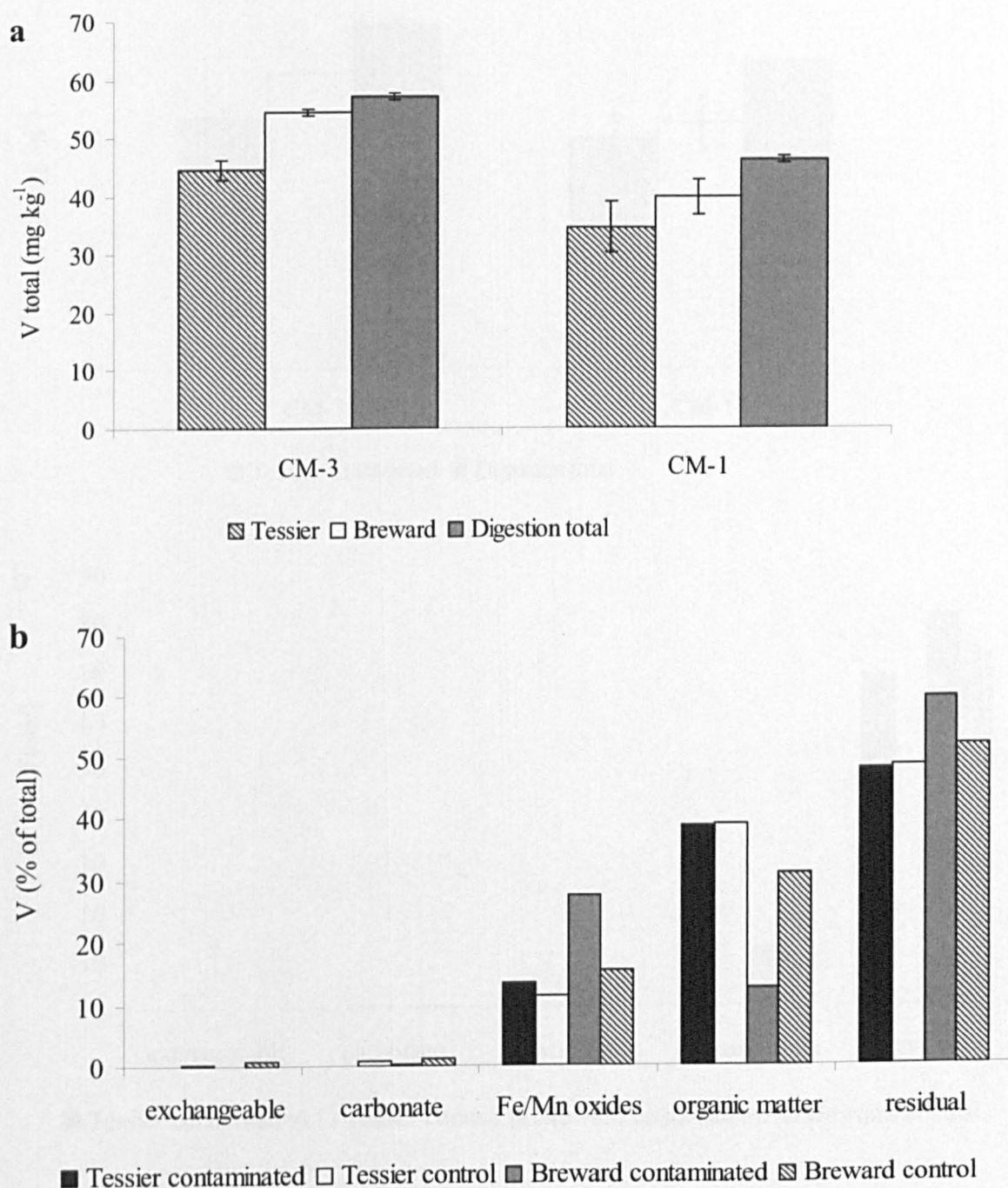


Figure 4.16: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of V for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) V fractionation pattern for the Tessier and Breward SEPs.

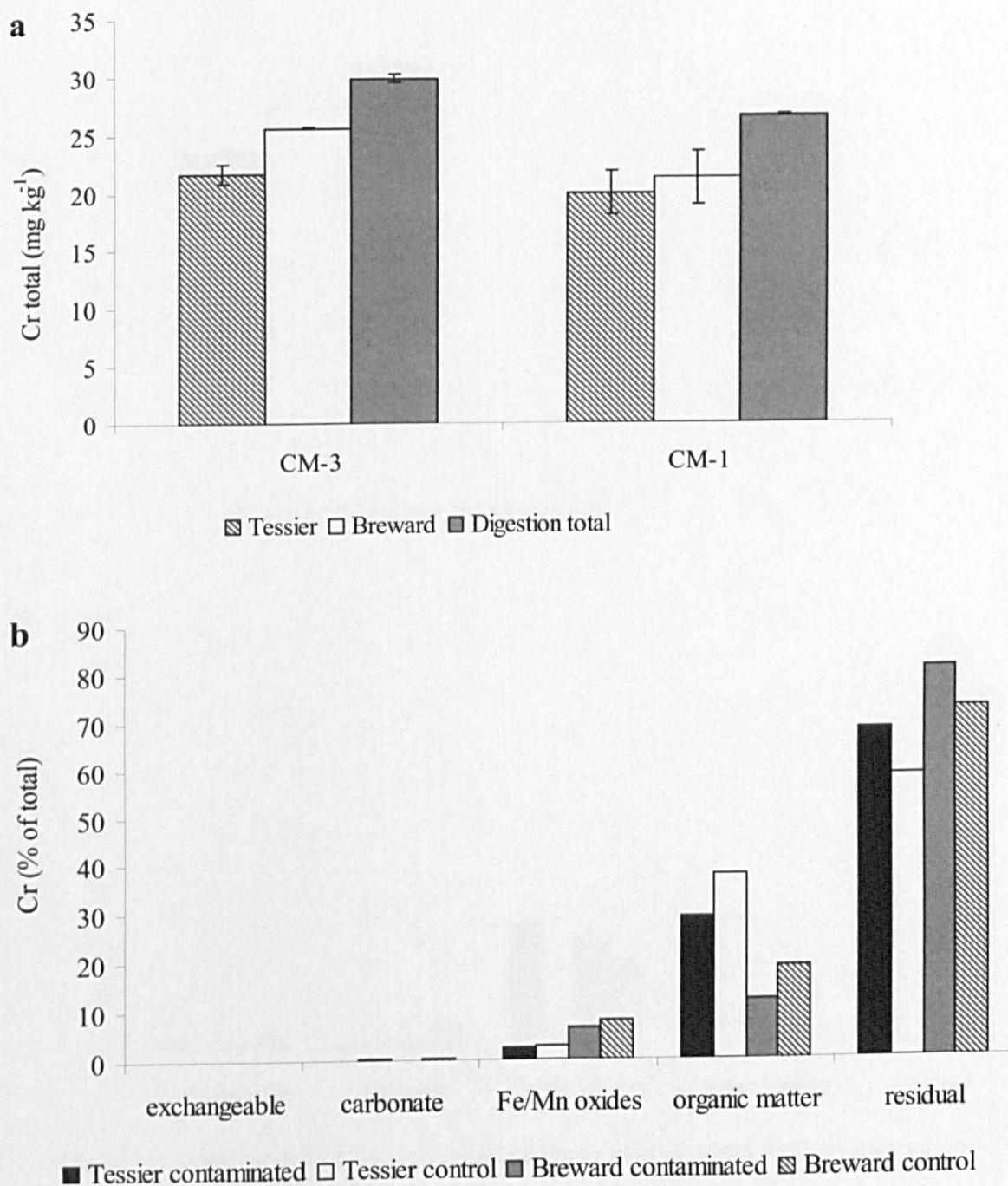


Figure 4.17: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Cr for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Cr fractionation pattern for the Tessier and Breward SEPs.

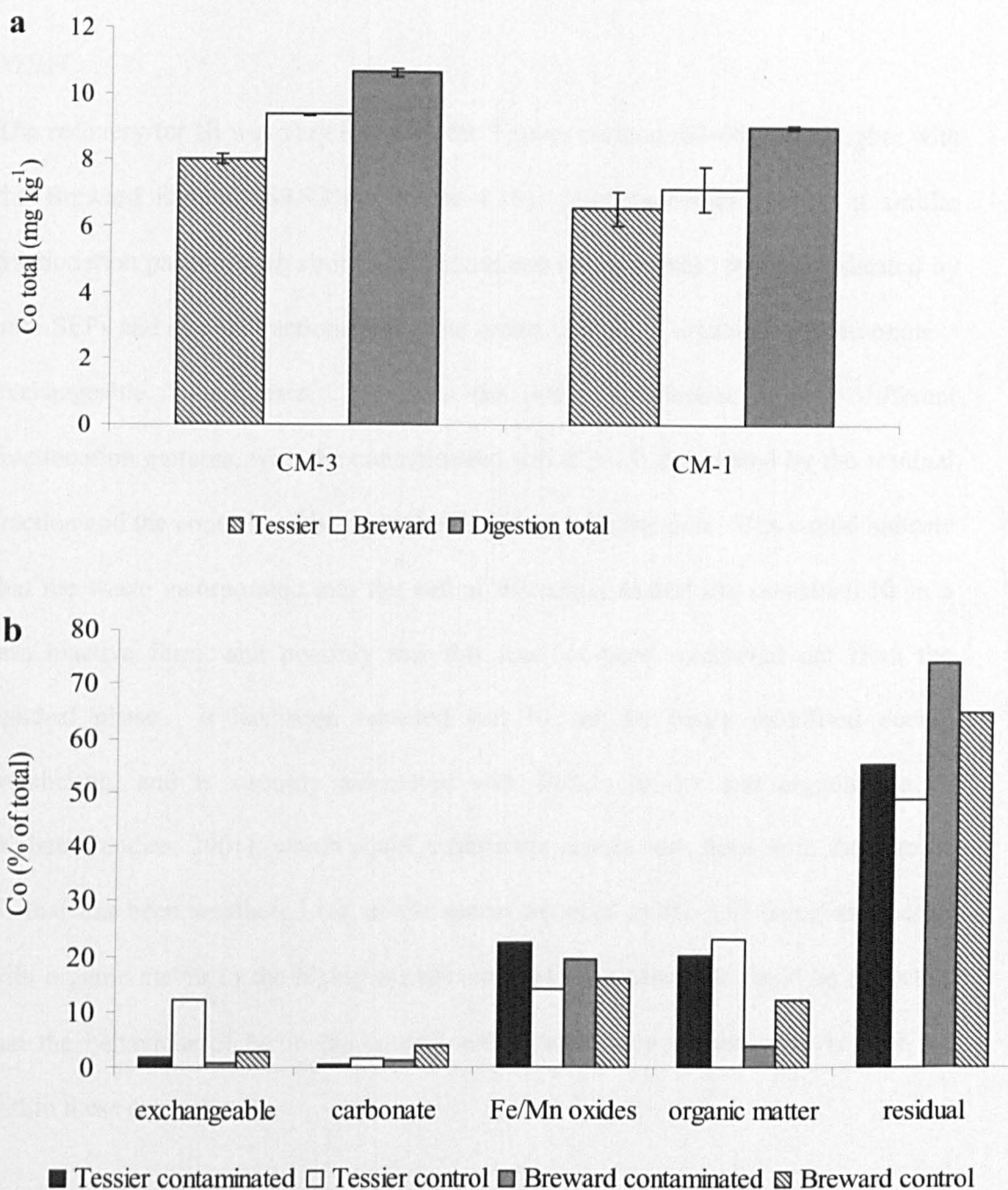


Figure 4.18: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Co for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Co fractionation pattern for the Tessier and Breward SEPs.

Nickel

The recovery for Ni was very low with the Tessier method (63-68%) but higher with the Breward method (89-93%) (Figure 4.19). Both schemes showed a similar fractionation pattern, with similar concentrations in the organic fraction indicated by both SEPs and overall fractionation in the order: residual > organic > Fe/Mn oxide > exchangeable > carbonate. However the two soils showed slightly different fractionation patterns, with the contaminated soil (CM-3) dominated by the residual fraction and the control soil being higher in the organic fraction. This would indicate that the waste incorporated into the soil at the contaminated site contained Ni in a less reactive form, and possibly that this has not been weathered out from the residual phase. It has been reported that Ni can be easily mobilised during weathering, and is strongly associated with Fe/Mn oxides and organic matter (Kabata-Pendias, 2001), which could explain the results seen here, with the natural Ni that has been weathered out of the parent material of the soil being associated with organic matter in the highly organic soils of Chat Moss. It could be expected that the behaviour of Ni in the control soil indicates the natural behaviour of Ni within these organic soils.

Copper

Both schemes showed good recoveries for Cu (Figure 4.20), with the Breward scheme again producing a recovery closer to 100% of the acid digestion value. Again, the Breward scheme yielded a smaller organic fraction in these soils, and a greater Fe/Mn oxide and residual fractions. In a study of three soils from Scotland, it was found that Cu was predominantly associated with the organic fraction in soils

with high organic matter contents (51 – 83%) (Bacon & Hewitt, 2005), which agrees with the results of the Tessier extraction of the Chat Moss soils, with 83% of Cu associated with the organic fraction. The fractionation pattern for the control and contaminated soils were remarkably similar as measured by both SEPs. The order of fractionation for the Tessier scheme was organic > residual > Fe/Mn oxides with virtually no Cu seen in the exchangeable or carbonate fractions, and for the Breward scheme the order of fractionation was residual = organic = Fe/Mn oxide with, again, no Cu seen in the exchangeable or carbonate fractions.

Zinc

Both methods gave acceptable recoveries for zinc, although the Breward scheme again achieved the highest recoveries. The fractionation measured by each scheme was different, with the Breward scheme again producing a lower organic and exchangeable fraction and a correspondingly greater residual fraction compared to the Tessier scheme (Figure 4.21). Both schemes showed very similar proportions of Zn in the carbonate and Fe/Mn fractions. Again, both soils were quite similar, although in the Tessier scheme the control soil showed greater fractionation into the exchangeable fraction and lower in the carbonate and residual fractions, again this was most likely due to the lower pH in the control soil promoting greater solubility of Zn. The general order of fractionation was residual > organic = Fe/Mn oxide = exchangeable > carbonate. Overall, substantial proportions of Zn were seen in all fractions, which was also seen in a study by Bacon & Hewitt (2005), in a study of three different soils using the BCR sequential extraction scheme, with 44 – 90% of Zn in the residual phase and the remainder distributed between the other phases.

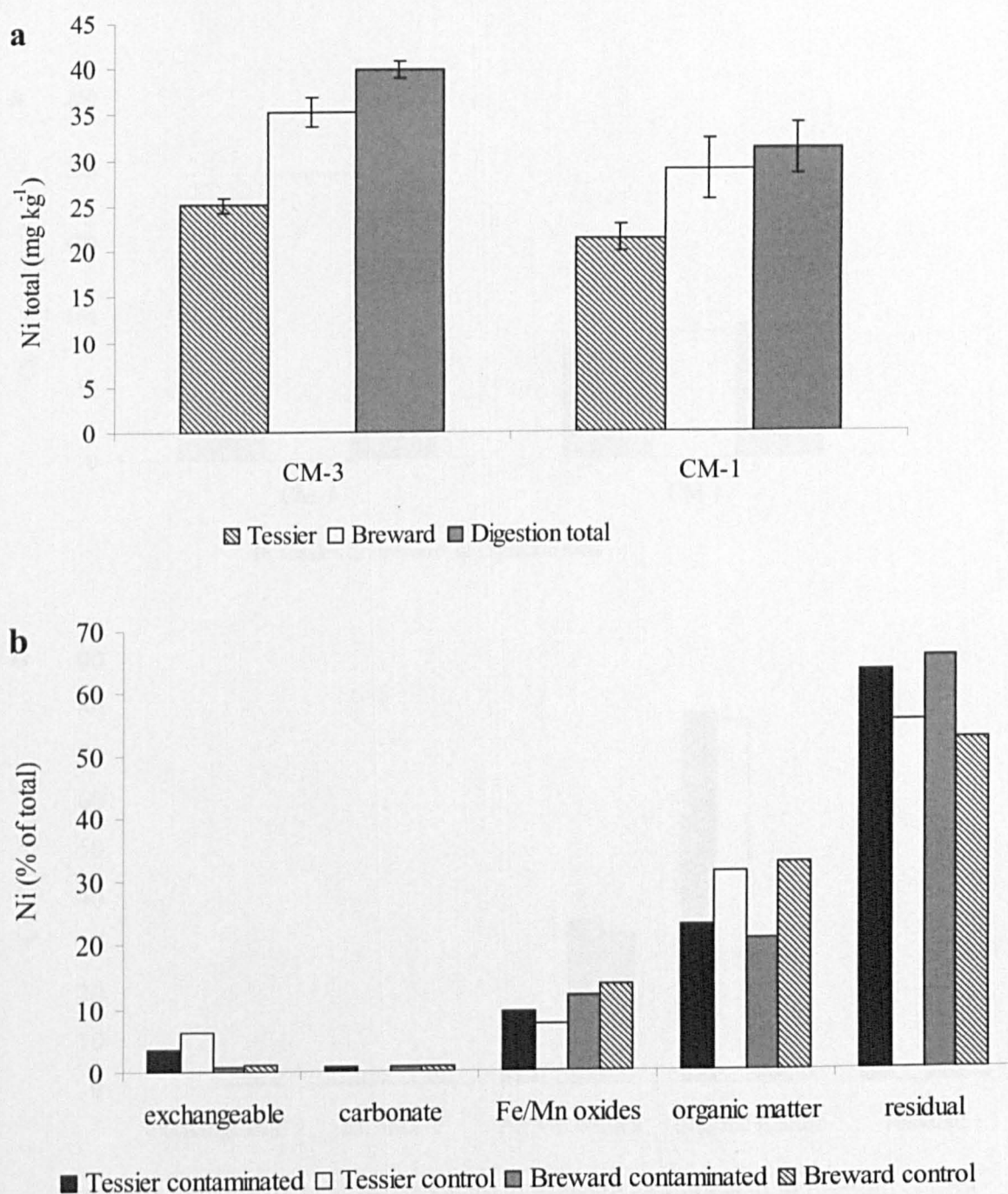


Figure 4.19: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Ni for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Ni fractionation pattern for the Tessier and Breward SEPs.

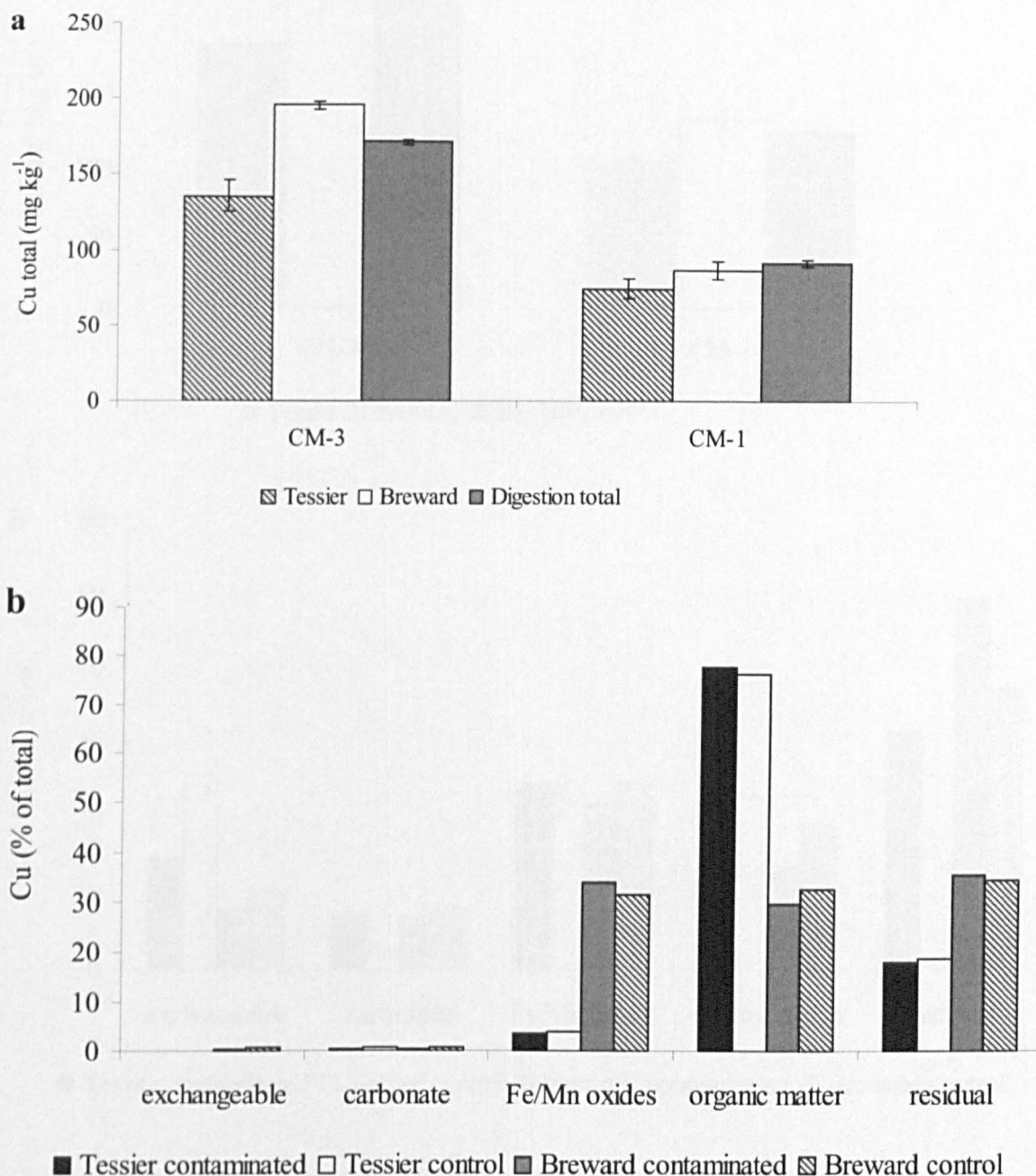


Figure 4.20: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Cu for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Cu fractionation pattern for the Tessier and Breward SEPs.

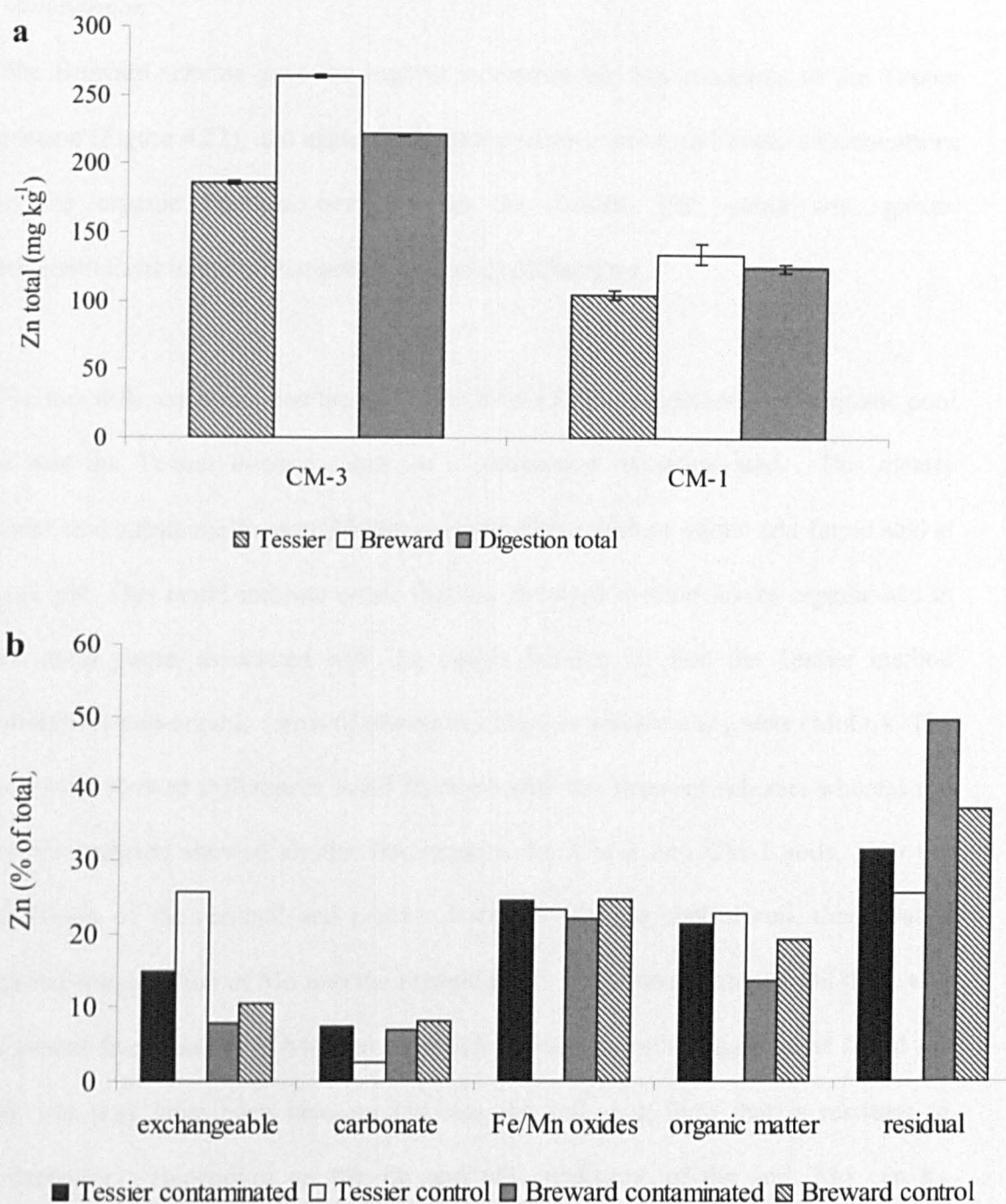


Figure 4.21: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Zn for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Zn fractionation pattern for the Tessier and Breward SEPs.

Molybdenum

The Breward scheme gave the highest recoveries for Mo compared to the Tessier scheme (Figure 4.22), and again the Breward scheme produced lower concentrations in the organic fraction, compared to the Tessier SEP, along with greater concentrations in the exchangeable and residual fractions.

The key difference between the approach of two SEPs to mobilizing the organic pool is that the Tessier method relies on a destructive oxidation step. This clearly mobilized substantially more Mo than simple dissolution of humic and fulvic acid at high pH. This could indicate either that the Breward method leaves organic-Mo in the solid phase, associated with the humin fraction, or that the Tessier method solubilises non-organic forms of Mo by oxidation to soluble molybdate (MoO_4). The two soils showed differences in all fractions with the Breward scheme, whereas the Tessier scheme showed similar fractionation for CM-3 and CM-1 soils, with the exception of the residual and organic fractions. In the control soil, there was a greater fractionation of Mo into the organic pool. In the contaminated soil there was a greater fractionation of Mo into the residual fraction, indicating that, as found for Ni, Mo may have been incorporated into the soil in a form that is resistant to weathering. Depending on the Eh and pH conditions of the soil, Mo can be associated with either organic matter or hydrous oxides (Kabata-Pendias, 2001), which would support the results seen here with naturally-derived Mo being associated with organic matter and anthropogenic Mo being unweathered and found in the residual phase. The Tessier scheme gave an order of fractionation of organic > residual > Fe/Mn oxide > carbonate with no Mo seen in the exchangeable fraction,

and the Breward scheme gave an order of fractionation of residual > organic = Fe/Mn oxide > exchangeable > carbonate.

Figure 4.22: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Mo for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Mo fractionation pattern for the Tessier and Breward SEPs.

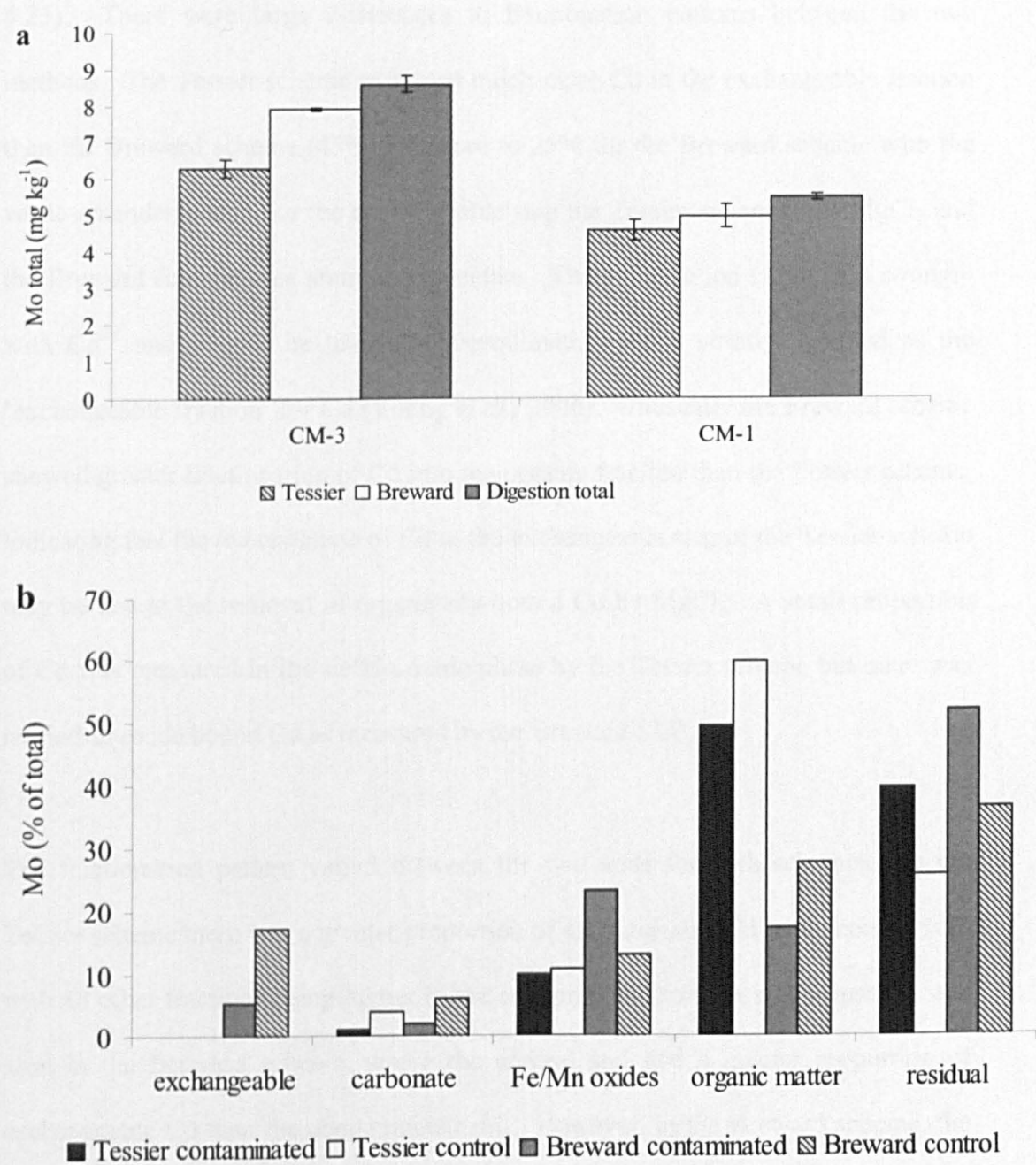


Figure 4.22: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Mo for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Mo fractionation pattern for the Tessier and Breward SEPs.

Cadmium

Both schemes showed excellent recoveries for Cd, with the Tessier scheme giving 95-101% recovery and the Breward scheme producing 89-110% recovery (Figure 4.23). There were large differences in fractionation patterns between the two methods. The Tessier scheme extracted much more Cd in the exchangeable fraction than the Breward scheme (45% compared to 25% for the Breward scheme with the waste-amended soil). For the exchangeable step the Tessier scheme uses MgCl_2 and the Breward scheme uses ammonium acetate. The chloride ion complexes strongly with Cd^{2+} and so will be likely to overestimate what is strictly regarded as the 'exchangeable fraction' for Cd (Young *et al.*, 2006). Unusually the Breward scheme showed greater fractionation of Cd into the organic fraction than the Tessier scheme, indicating that the overestimate of Cd in the exchangeable step of the Tessier scheme may be due to the removal of organically-bound Cd by MgCl_2 . A small proportion of Cd was measured in the Fe/Mn oxide phase by the Tessier scheme but there was no Fe/Mn oxide bound Cd as measured by the Breward SEP.

The fractionation pattern varied between the two soils for both schemes. In the Tessier scheme there was a greater proportion of exchangeable Cd in the control soil, with all other fractions being higher in the contaminated soil. A similar pattern was seen in the Breward scheme, where the control soil had a greater proportion of exchangeable Cd than the contaminated soil. However, in the Breward scheme, the control soil also had a greater proportion of Cd in the organic phase compared to the contaminated soil. These observations might suggest that the Cd incorporated into the soil within the waste was in a form resistant to weathering, whereas the natural Cd within the soil was held weakly on humus. However, the difference in pH

between the two soils is also likely to have contributed to this difference. The pattern of fractionation seen with the Breward scheme was residual > exchangeable = organic > carbonate with no Cd extracted in the Fe/Mn oxide step. The order of fractionation for the Tessier scheme was exchangeable > Fe/Mn oxide = organic > carbonate > residual.

Lead

For Pb, the Breward scheme had excellent recoveries (91-98%); recovery by the Tessier scheme was lower (80-84%) (Figure 4.24). Lower representation in the organic fraction was seen again with the Breward method, as well as the Fe/Mn fractionation, and there was a corresponding increase in the residual fractionation compared to the Tessier method. There was no difference between the two soils for the exchangeable, carbonate and Fe/Mn bound Pb but for the organic and residual Pb there was a difference between the two soils. For both schemes, the more acidic control soil had higher organic Pb pools and lower residual fractionation, as seen for Cd and Ni. It is likely that a similar process controls this pattern, with Pb introduced to the contaminated soil being within a resistant phase, and that once the Pb is sufficiently weathered, it will become organically bound as in the control soil which demonstrates the natural behaviour of metals within these soils. The fractionation order for the Tessier method was organic > residual = Fe/Mn oxide > carbonate > exchangeable and the fractionation order for the Breward method was residual > organic > Fe/Mn oxide > carbonate = exchangeable.

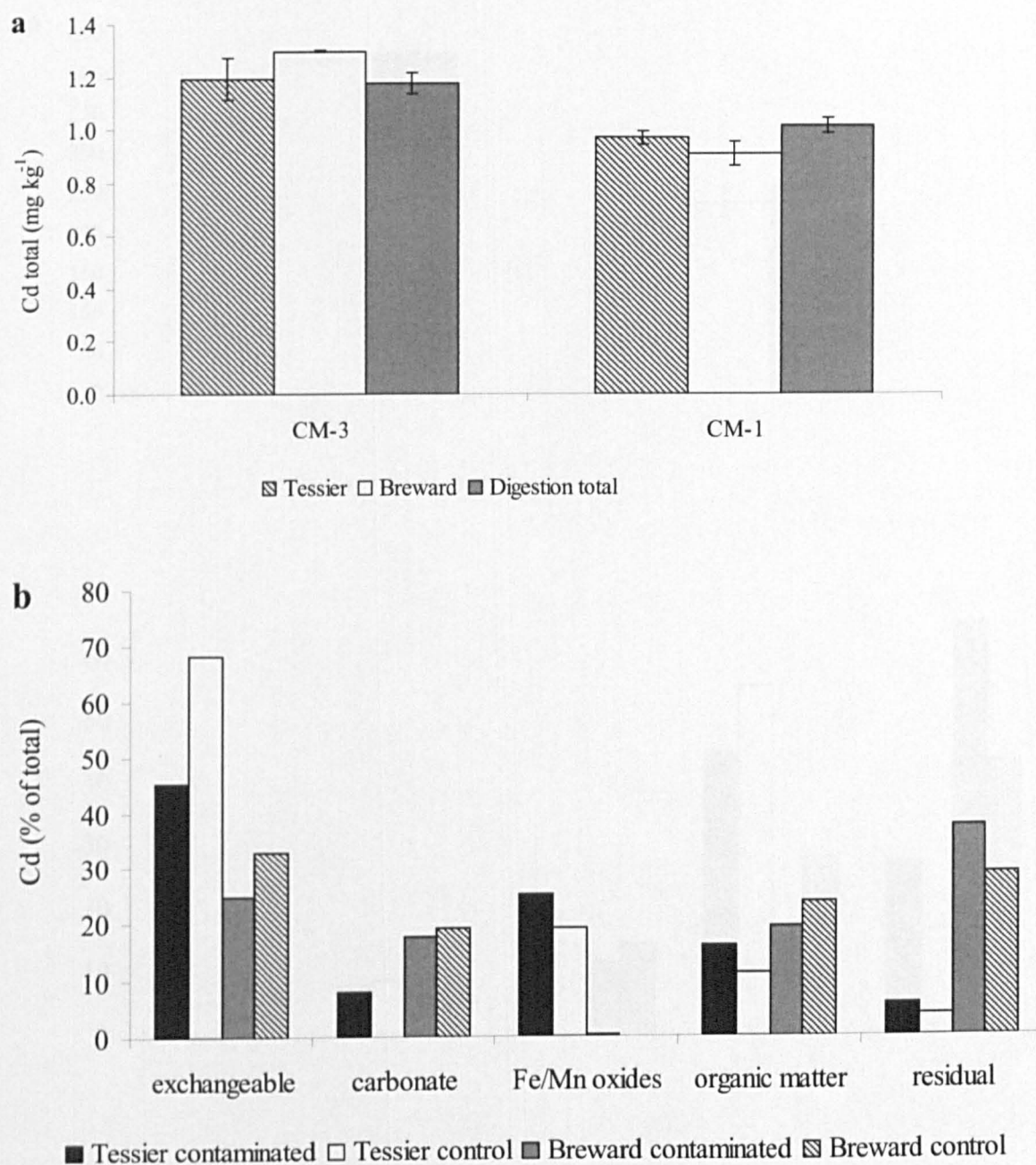


Figure 4.23: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Cd for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Cd fractionation pattern for the Tessier and Breward SEPs.

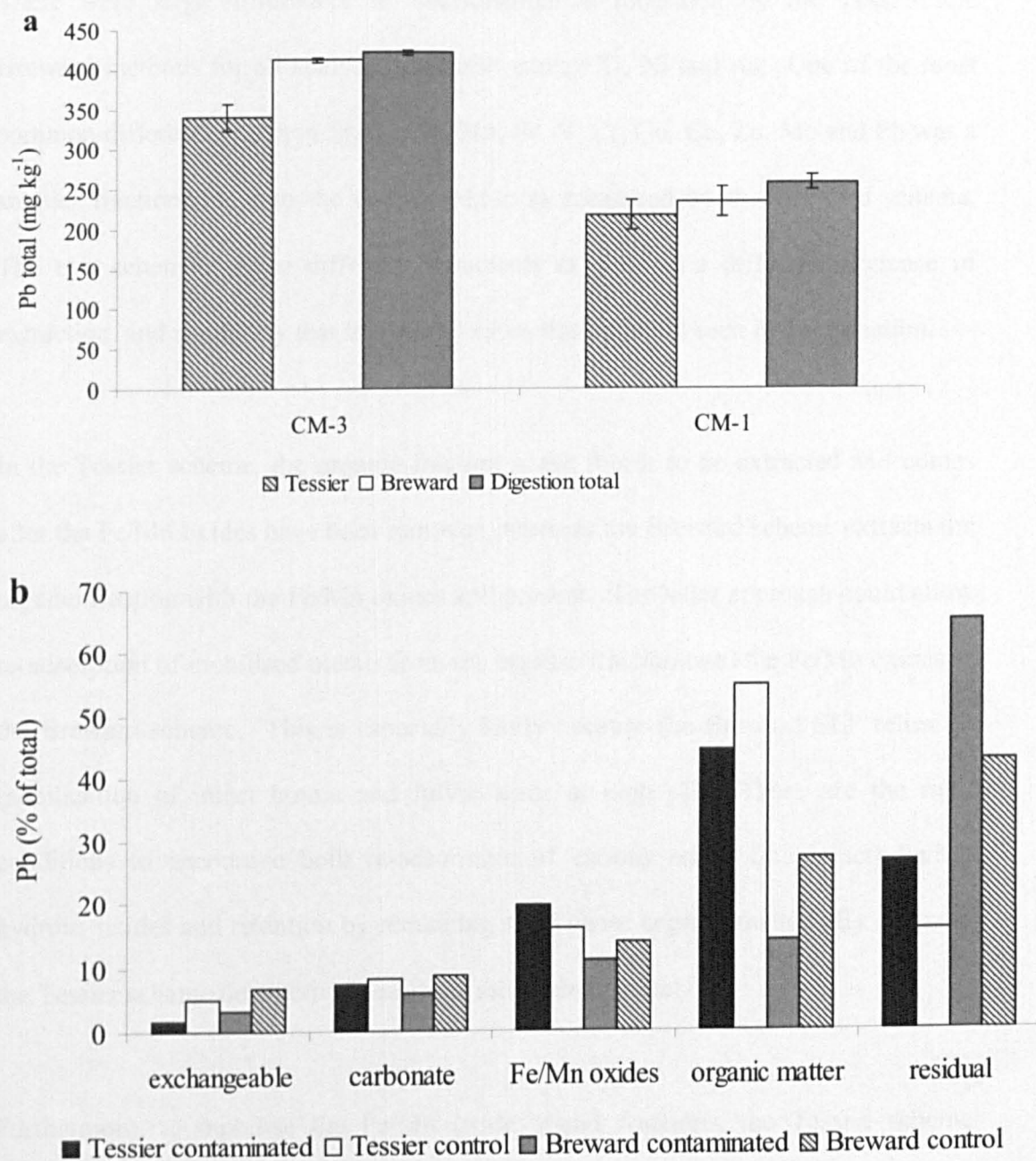


Figure 4.24: Contaminated (CM-3) and control (CM-1) Chat Moss soils: (a) Recovery of Pb for the Tessier and Breward SEPs; error bars show standard error of three replicates (b) Pb fractionation pattern for the Tessier and Breward SEPs.

There were large differences in fractionation as measured by the Tessier and Breward methods for all analysed elements except Ti, Ni and As. One of the most common differences seen in Sr, Ba, Fe, Mn, Se, V, Cr, Co, Cu, Zn, Mo and Pb was a smaller fractionation into the organic phase as measured by the Breward scheme. The two schemes utilise different extractants as well as a different sequence of extraction, and it is likely that this would cause the variation seen in fractionation.

In the Tessier scheme, the organic fraction is the fourth to be extracted and comes after the Fe/Mn oxides have been removed, whereas the Breward scheme extracts the organic fraction with the Fe/Mn oxides still present. The latter approach could allow re-adsorption of mobilised metals from the organic fraction onto the Fe/Mn oxides in the Breward scheme. This is especially likely because the Breward SEP relies on mobilization of intact humic and fulvic acids at high pH. These are the right conditions to encourage both re-adsorption of cations on to (the intact) Fe/Mn hydrous oxides and retention by remaining solid phase organic matter. By contrast, the Tessier scheme destructively oxidises the organic matter.

Furthermore, to mobilise the Fe/Mn oxide bound fractions, the Tessier scheme reduces Fe/Mn oxides using hydroxylamine hydrochloride. This step takes place before the organic step, and so any $\text{Fe}^{2+}/\text{Mn}^{2+}$ ions that are liberated during reduction may compete for exchange sites on the organic matter, which could have the effect of liberating organically bound metals early and so giving a falsely large estimate of the Fe/Mn oxide bound fraction of metals. There was a higher proportion of Mn in the Fe/Mn oxide fraction as measured by the Tessier scheme as opposed to the Breward scheme for the contaminated soil, indicating that competition, from Fe^{2+} , for organic

binding sites may have liberated organically bound Mn. The liberation of the organic phase through oxidation rather than solubilisation may also affect metal sulphides. If any metal sulphides were present within the soil, under the Tessier scheme these would be brought into solution during extraction of the organic phase; there is no equivalent reaction in the Breward scheme. This may also have produced larger apparent metal fractionation into the organic phase under the Tessier scheme rather than the Breward scheme although the presence of metal sulphides is difficult to confirm.

For many elements there were no differences observed between the control and contaminated soils, however Sr, Mn, Co, Ni, Zn, Mo, Cd and Pb all showed different fractionation patterns. The most common difference seen was a greater fractionation into the residual phase in the waste-amended soil compared to the control soil; this was observed for Sr, Ni, Mo, and Pb. This may indicate a residual characteristic of the waste. The waste is believed to have contained slag material, and certainly contained coal ash, which would have contained minerals likely to fractionate into the residual phase under sequential extraction procedures. However, another explanation may lie in the lower pH of the control soil (c. pH 5.0) which is likely to produce greater fractionation in more easily mobilised pools. In the control soils, the elements tended to fractionate into the organic phase more than the residual phase, indicating that this was the phase that the elements would naturally fractionate into after weathering. Another difference observed between the control and waste-amended soils was the greater fractionation of elements into the exchangeable fraction in the former. This was seen for Mn, Co, Zn and Cd and again may be a function of pH or of the original characteristic of waste constituents.

4.3.3.2 Effect of contamination source on metal fractionation

In order to further investigate the effect of contamination source on the fractionation of trace metals within soils, four soils of different contamination histories were studied using the modified Tessier scheme (Li & Thornton 2001). This was to investigate the effect of contamination source and soil properties on the fractionation of metals. The four soils chosen were contaminated with urban waste (Chat Moss), Pb/Zn minespoil, petrol-derived lead from a roadside site and sewage sludge. The main sources of contamination on Chat Moss were organic wastes, industrial steelworks waste and petrol-derived lead, all of which are represented by the Sewage farm, Minespoil and Roadside soils. These soils cannot be considered representative of all soils contaminated by petrol-derived, sewage-derived or ore-derived lead due to the relatively small sample area and sample size. However for the Minespoil soil, a comparison can be gained using Li & Thornton (2001) who also studied minespoil soils from the Peak District using sequential extractions. By studying the effect of contamination source on metal fractionation, a better understanding of the behaviour of metals within Chat Moss soils can be gained, and potentially aid in assessing risk of the metal contamination on Chat Moss. The four soils chosen gave a range of contamination sources and soil conditions including organic matter content, phosphate content and pH. Soil properties are summarised in Table 4.3. The Chat Moss soil had a high organic matter content (61.5%) and low pH (5.28), whereas the other soils had circum-neutral to alkaline pH values (6.24 – 7.90). The Sewage farm soil was characterised by very high phosphate content, and the Roadside and Minespoil soils were similar in terms of pH, organic matter and phosphate content but showed the greatest contrast in terms of concentration of metallic contaminants. The Tessier scheme used is detailed in section 4.3.2.

Table 4.3: Selected soil properties of Chat Moss, sewage farm, minespoil and roadside soils

	pH	Organic matter (LOI %)	Available phosphate (mg kg ⁻¹)	Total phosphate (mg kg ⁻¹)	Total Pb (mg kg ⁻¹)
Chat Moss	5.28	61.5	44.3	1920	364
Sewage farm	6.24	26.3	453	9540	525
Minespoil	7.65	13.6	9.70	832	13600
Roadside	7.90	8.59	2.37	213	217

4.3.3.2.1 Group 2 metals – Sr, Ba

Strontium

For the Chat Moss and Roadside soils, the recoveries were excellent compared to digestion totals, with 98.6% and 99.5% recoveries respectively. For the sewage farm soil, the recovery was 116% of the digestion total, however the recovery for the Pb/Zn minespoil soil was much lower at 72% of the digestion total (Figure 4.25).

The distribution of Sr varied between soils, in all four soils the dominant fraction of Sr was the residual fraction, although in the Chat Moss soil the exchangeable fraction contained the same proportion of Sr as the residual fraction (31%). This was very similar to the results seen in the previous experiment with both the Breward and Tessier methods. The minespoil soil was found to have 92% of Sr in the residual fraction, with the exchangeable fraction having the next greatest concentration of Sr (4%). The Roadside and Sewage farm soils show the same pattern of fractionation, with the residual fraction being dominant followed by the Fe/Mn oxides, organic,

exchangeable and carbonate fractions. The Roadside soil had a higher proportion of Sr in the residual fraction than the Sewage farm soil, which had a higher proportion of Sr in the Fe/Mn oxide, organic and carbonate fractions.

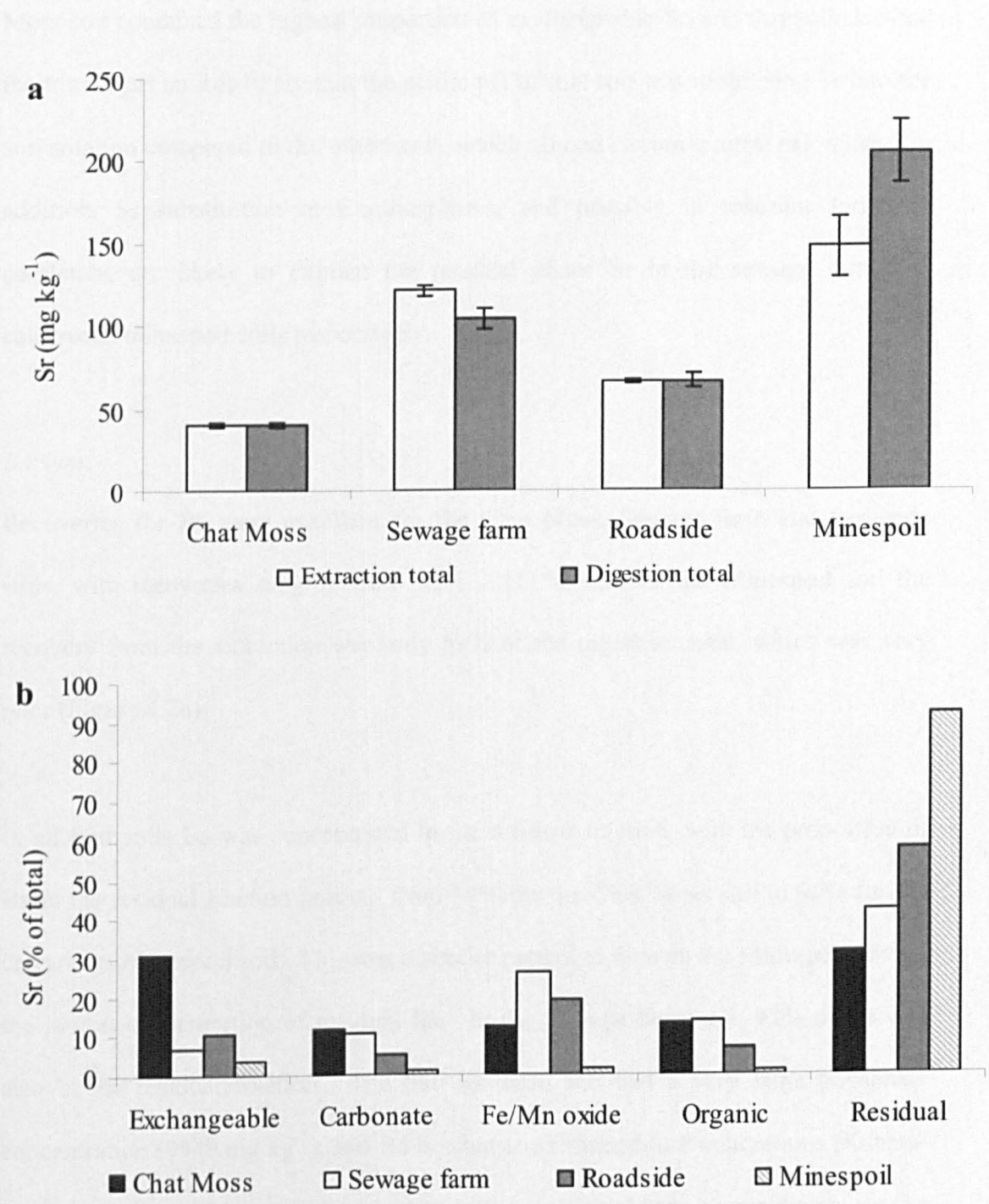


Figure 4.25: (a) Recovery of Sr for different soils using Tessier SEP; error bars show standard error of three replicates (b) Sr fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

The high proportion of Sr in the residual fraction of all four soils is most likely related to clay materials which often contain Sr in the chemical lattice. The Chat Moss soil contained the highest proportion of exchangeable Sr, and this soil also had the lowest pH so it is likely that the acidic pH of this soil was mobilising Sr into the soil solution compared to the other soils, which all had circum-neutral pH values. In addition, Sr substitution in Ca-phosphates, and possibly in resistant forms of carbonate, are likely to explain the residual phase Sr in the sewage farm and calcareous minespoil soils respectively.

Barium

Recoveries for Ba were excellent for the Chat Moss, Sewage farm and Roadside soils, with recoveries ranging from 98% - 111%, but for the Minespoil soil the recovery from the extraction was only 59% of the digestion total, which was very poor (Figure 4.26).

In all four soils Ba was concentrated in the residual fraction, with the proportion of Ba in the residual fraction ranging from 39% for the Chat Moss soil to 96% for the calcareous Minespoil soil. This was a similar pattern to Sr with the Minespoil having the largest concentration of residual Ba. In the Sewage farm soil, 92% of Ba was also in the residual fraction. The Sewage farm soil had a very large phosphate concentration (9540 mg kg^{-1}), and Ba is often concentrated in P concretions (Kabata-Pendias, 2001) which would be resistant to the sequential extraction scheme. In the Chat Moss soil, the remainder of the Ba not in the residual fraction was distributed between the exchangeable, carbonate, Fe/Mn oxide and organic fractions. The

organic fraction contained the highest proportion of Ba after the residual fraction (22%) and the Fe/Mn oxide, carbonate and exchangeable fractions contained roughly the same proportion of Ba (11-16%). It is not surprising to find Ba in the carbonate and Fe/Mn oxide phases as Ba is adsorbed to oxides and is often precipitated as carbonates (Kabata-Pendias, 2001). A similar pattern of fractionation was also seen for the Sewage farm soil, with the Ba not in the residual fraction distributed between the remaining fractions in roughly equal proportions (7-11%). The dominant soil component affecting Sr and Ba distribution was most likely clay content, as both Sr and Ba are commonly found in clay minerals.

4.3.3.2.2 Structural metals – Fe, Mn

Iron

No data was available on the recoveries of the sequential extraction compared to digestion totals for Fe. All four soils showed the same pattern of fractionation, with the residual fraction containing the highest proportion of Fe, ranging from 54% in the Chat Moss soil to 91% in the Sewage farm soil (Figure 4.27).

There was no Fe seen in the exchangeable or carbonate fractions for all four soils, and the remaining Fe was distributed between the Fe/Mn oxide and organic fractions, with the Fe/Mn oxide fraction having the next greatest proportion of Fe after the residual phase for all the soils except Chat Moss. This was a similar result to that of Li & Thornton (2001) who carried out sequential extractions on Pb/Zn minespoil soils. They found that approximately 20% of total Fe was found in the Fe/Mn oxide fraction and the remainder was found in the residual fraction. The authors attributed

the Fe in the residual fraction to crystalline Fe oxides and Fe in primary silicate minerals, while the Fe in the Fe/Mn oxide fraction was attributed to amorphous Fe oxides or hydroxides.

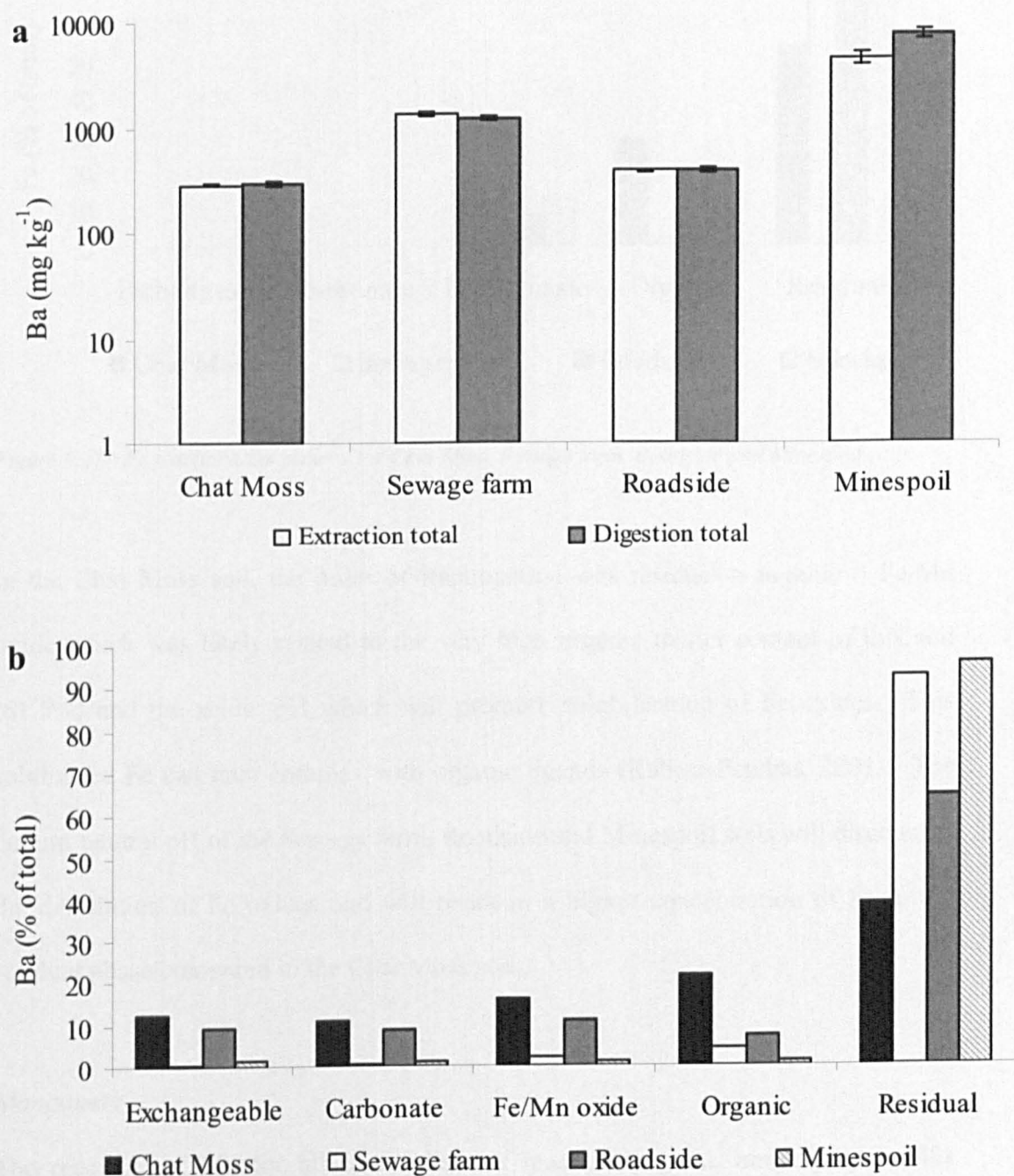


Figure 4.26: (a) Recovery of Ba for different soils using the Tessier SEP; error bars show standard error of three replicates (b) Ba fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

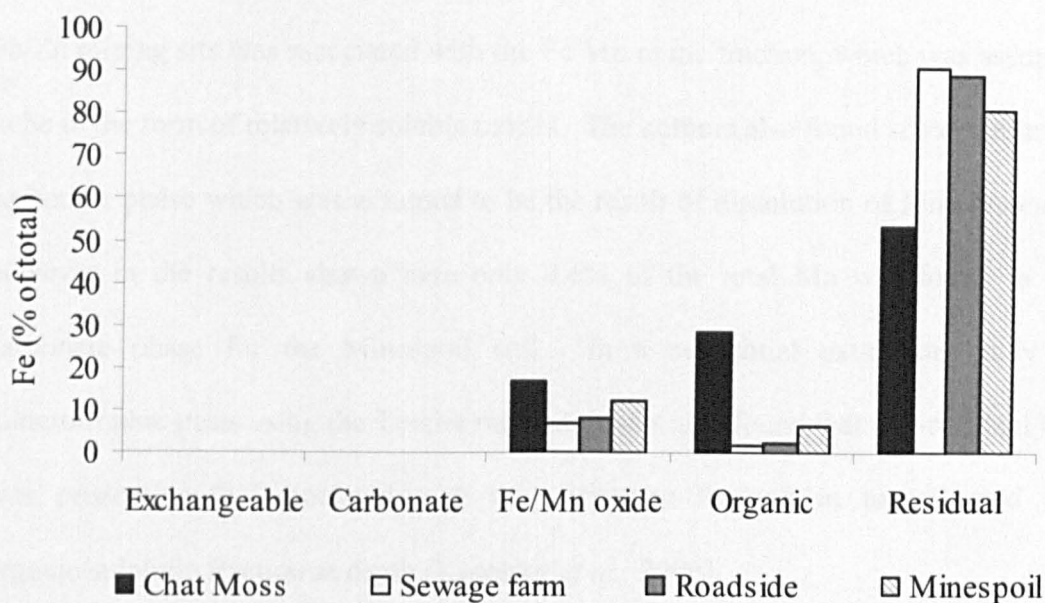


Figure 4.27: Fe fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

In the Chat Moss soil, the order of fractionation was residual > organic > Fe/Mn oxide which was likely related to the very high organic matter content of this soil (61.5%) and the acidic pH which will promote solubilisation of Fe oxides. This solubilised Fe can then complex with organic ligands (Kabata-Pendias, 2001). The circum-neutral pH of the Sewage farm, Roadside and Minespoil soils will discourage the dissolution of Fe oxides and will result in a higher concentration of Fe in the residual phase compared to the Chat Moss soil.

Manganese

The recovery of Mn for all four soils was reasonably good, ranging from 94% (Minespoil soil) to 121% (Roadside soil). For all four soils, the main fraction containing Mn was the Fe/Mn oxide phase, with the order of fractionation for all four soils being Fe/Mn oxide > residual > organic > exchangeable = carbonate (Figure

4.28). The predominance of Mn in the Fe/Mn oxide fraction was in agreement with the findings of Li & Thornton (2001) who found that up to 80% of the Mn from a Pb/Zn mining site was associated with the Fe/Mn oxide fraction, which was assumed to be in the form of relatively soluble oxides. The authors also found some Mn in the carbonate phase which was assumed to be the result of dissolution of Mn carbonate, however in the results shown here only 0.6% of the total Mn was found in the carbonate phase for the Minespoil soil. In a sequential extraction study of minerotrophic peats using the Tessier method, it was also found that non-residual Mn was predominantly associated with the carbonate fraction in topsoil, and the organic/sulphide fraction at depth (Koretsky *et al.*, 2006).

4.3.3.2.3 Metalloids – As, Se

The results of sequential extractions for As and Se must be considered with restraint, as the changing pH and redox conditions throughout the extraction steps can cause changes in the oxidation states of these elements and may alter the fractionation during the extraction (Gleyzes *et al.*, 2002).

Arsenic

The recovery of As varied between the four soils, with recoveries for the Sewage farm and Chat Moss soils measuring as 140% and 122% of the digestion total respectively. However for the Roadside and Minespoil soils the recovery was 71-72% of total, which was poor (Figure 4.29).

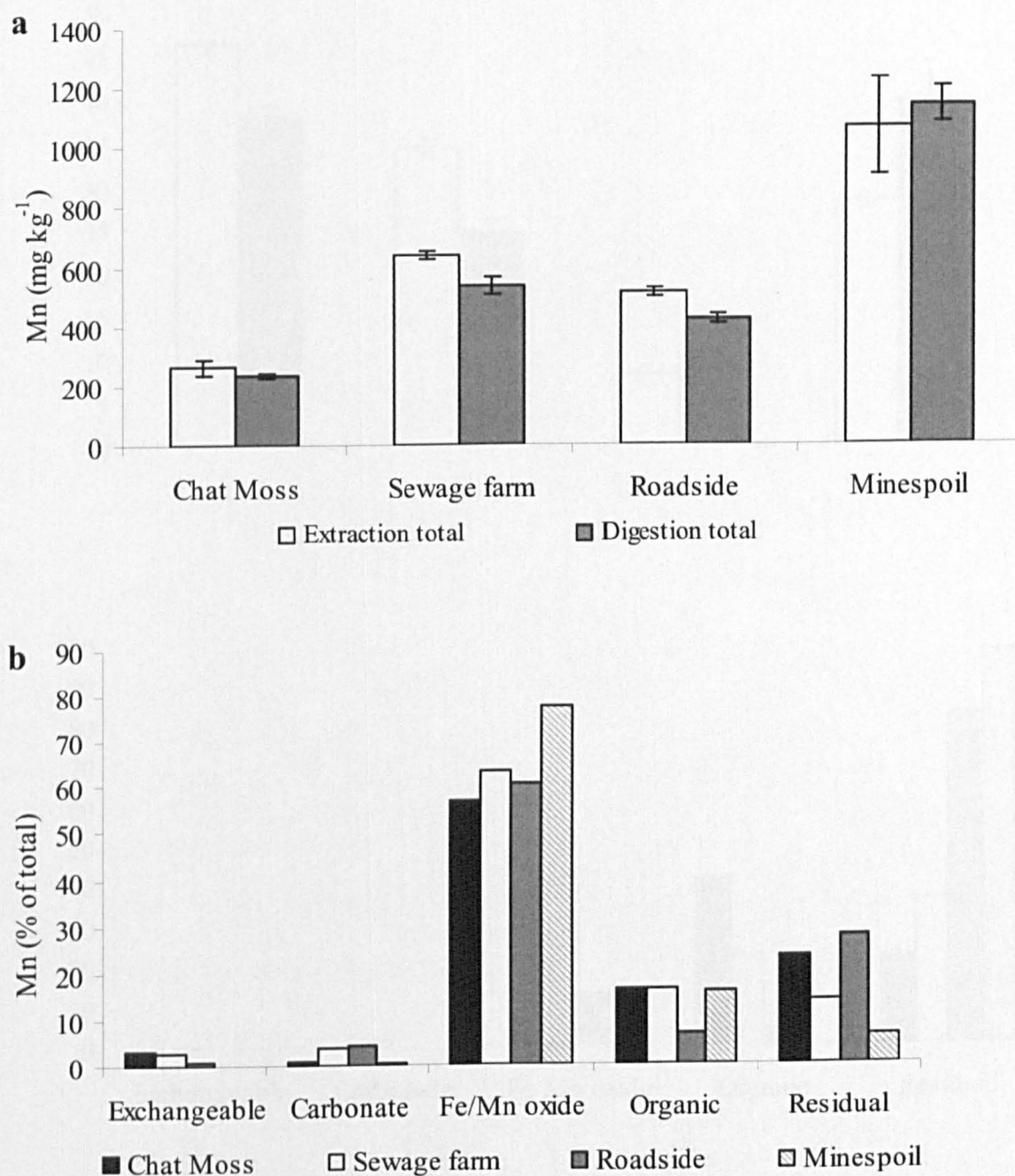


Figure 4.28: (a) Recovery of Mn for different soils using Tessier SEP; error bars show standard error of three replicates (b) Mn fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

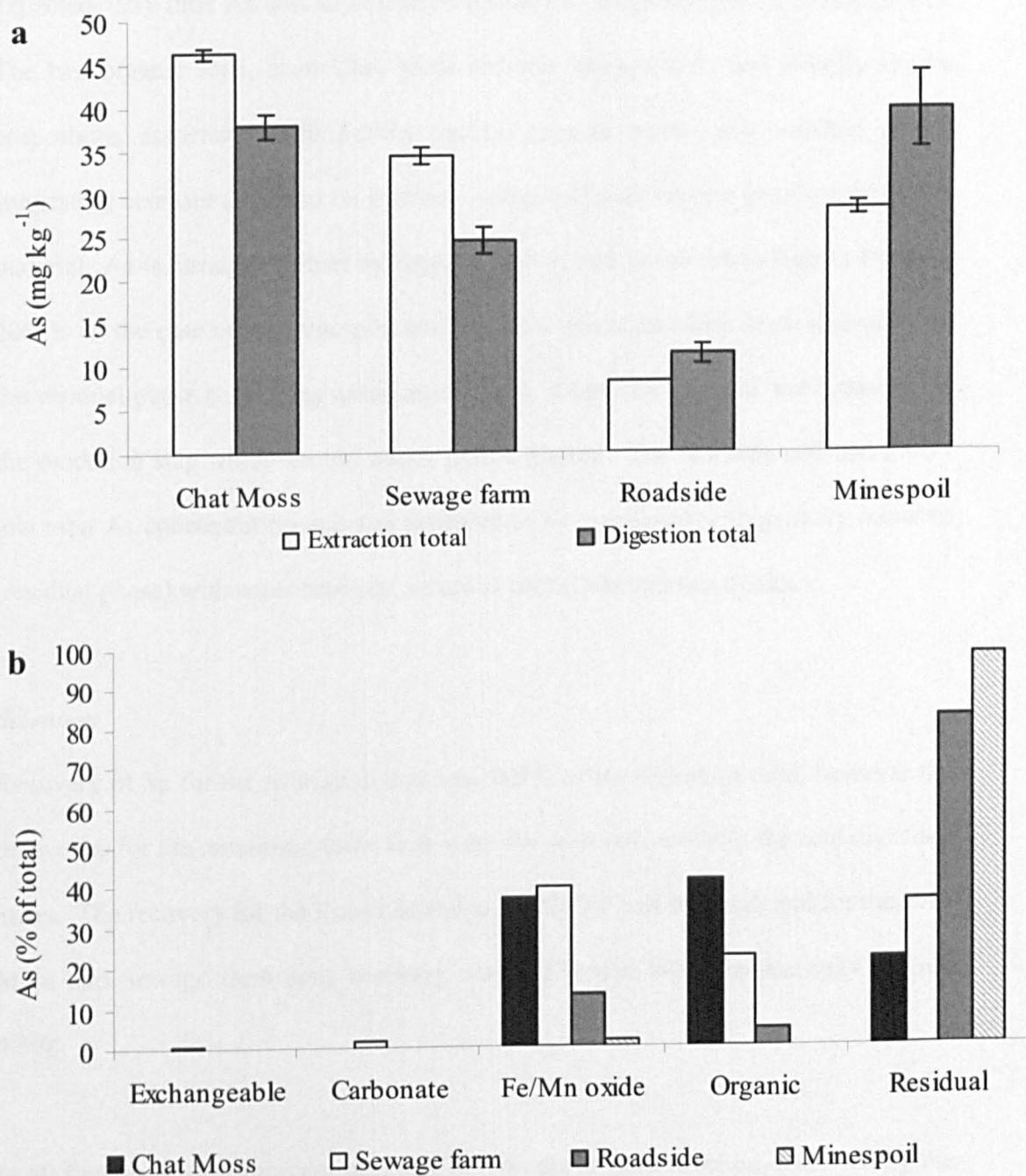


Figure 4.29: (a) Recovery of As for different soils using Tessier SEP; error bars show standard error of three replicates (b) As fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

There was a large variation between the soils in terms of fractionation patterns. As expected, very little As was solubilised with the exchangeable and carbonate phases. The two organic soils, from Chat Moss and the Sewage farm had broadly similar proportions associated with Fe/Mn oxides, organic matter and residual phases suggesting arsenate adsorbed on hydrous oxides and possibly the presence of pyritic material; As is strongly sorbed by organic matter, and hydroxides (Kabata-Pendias, 2001). In the case of the minespoil soil the As is associated almost exclusively with the residual phase suggesting association with primary ore material, notwithstanding the oxidation step which should attack pyritic phases. The roadside soil had a very low total As concentration and this appeared to be associated with primary minerals (residual phase) with some arsenate adsorbed on Fe/Mn hydrous oxides.

Selenium

Recovery of Se for the Minespoil soil was 109% of the digestion total, however the recoveries for the remaining three soils were not as consistent with the acid digestion assay. The recovery for the Roadside soil was only 74% of the total, and for the Chat Moss and Sewage farm soils recovery was 115% and 143% respectively (Figure 4.30).

In all four soils, the dominant phase of Se was the organic fraction, followed by the residual and Fe/Mn oxide fractions. There was less than 1% Se in the exchangeable fractions of all four soils, and only the Sewage farm and Roadside soils had greater than 1% Se in the carbonate fraction (1.4% and 1.3% respectively). Kabata-Pendias (2001) report that organic Se ranges from 4-22% of total Se soil contents in a range of soils, which is much lower than the Se content seen here in the organic fraction of

the four soils. The complex behaviour of Se in soils makes it difficult to predict the fractionation of Se in a given soil, and the dominance of Se in the organic fraction as seen here is not supported in the literature, which may indicate that the sequential extraction scheme is artificially removing Se in the organic step. This was supported by the similar levels of Se seen in the organic phase for all four soils even though the organic matter contents vary greatly. It is likely that the alteration of redox potential and pH during the sequential extraction is artificially altering the fractionation of Se (Gleyzes *et al.*, 2002).

4.3.3.2.4 Trace metals

Titanium

The recoveries for Ti were excellent, with the exception of the Minespoil soil, which extracted more than the digestion total (Figure 4.31). The recoveries for the other three soils were all within error of the digestion totals, and ranged from 102% - 113%. The fractionation for all four soils was the same, with almost 100% of the extracted Ti (98-100%) in the residual phase. This agrees with Kabata-Pendias (2001), who report that Ti minerals remain practically unweathered in soils.

Vanadium

The recoveries seen for V were excellent for all four soils, with 95-105% of V extracted across all soils (Figure 4.32). The fractionation of V varied for the four soils, with the order of fractionation for the Minespoil, Roadside and Sewage farm soils being residual > organic > Fe/Mn oxides, although for the Minespoil and Roadside soils the levels of V in the organic and Fe/Mn fractions were almost equal.

The order of fractionation for the Chat Moss soil was very different, with the organic fraction being dominant followed by the residual and Fe/Mn oxide fractions. The high organic matter content of the Chat Moss soil was most likely causing the concentration of V within this fraction. Vanadium in soils is often associated with Fe oxides (Terzano *et al.*, 2007) and clay minerals which would be extracted in the residual fraction, or organic matter (Kabata-Pendias, 2001), which was seen for these four soils.

Chromium

Recoveries of Cr ranged from 84% for the Chat Moss soil to 132% for the Sewage farm soil. The Sewage farm soil was the only one to overestimate the recovery relative to the digestion total, with the Roadside soil extracting 100% of the digestion total and the Minespoil soil extracting 98% (Figure 4.33). For the two mineral soils (Roadside and Minespoil), Cr was concentrated in the residual fraction. This agrees with the results of Burt *et al.*, (2003), who found in a study of Cu smelter contaminated soils that Cr was predominantly (>80%) within the residual fraction. However, for the Sewage farm and Chat Moss soils, Cr was almost equally present in the organic fraction. Chromium is considered to be stable in soils when in the Cr^{3+} form and so it is likely that in all four soils the Cr was concentrated in Cr and Fe oxides in the residual phase (Kabata-Pendias, 2001). However, Cr can also form organic complexes in soils which explains its presence in the organic phase in the Sewage farm soil (60%) and the Chat Moss soil (39%). There was a very small amount of Cr in the Fe/Mn fraction of all the soils, which corresponds with Cr commonly being associated with Fe oxides (Kabata-Pendias, 2001), which if in a

crystalline form will remain in the residual fraction rather than the Fe/Mn oxide fraction (Li & Thornton, 2001).

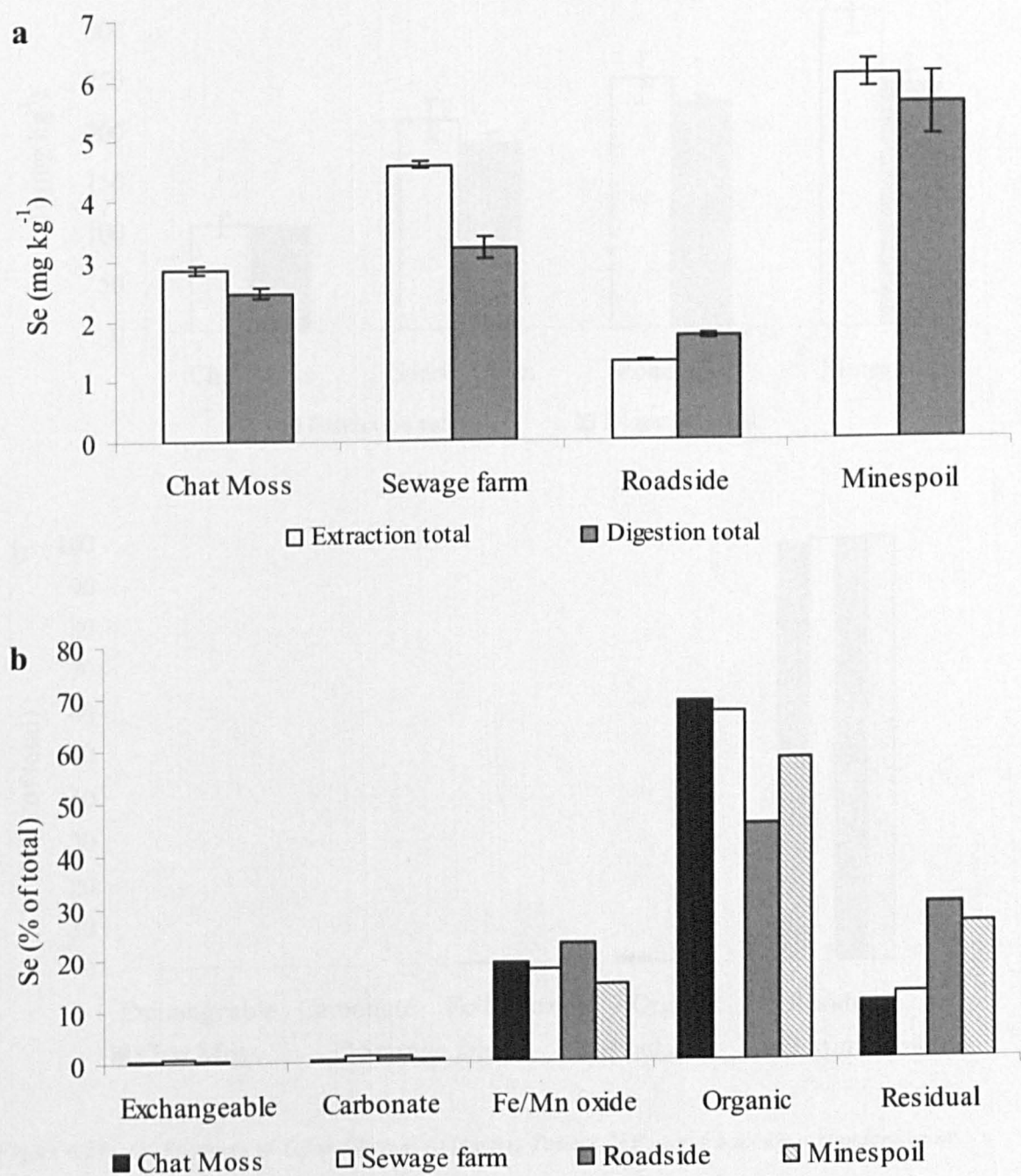


Figure 4.30: (a) Recovery of Se for different soils using Tessier SEP; error bars show standard error of three replicates (b) Se fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

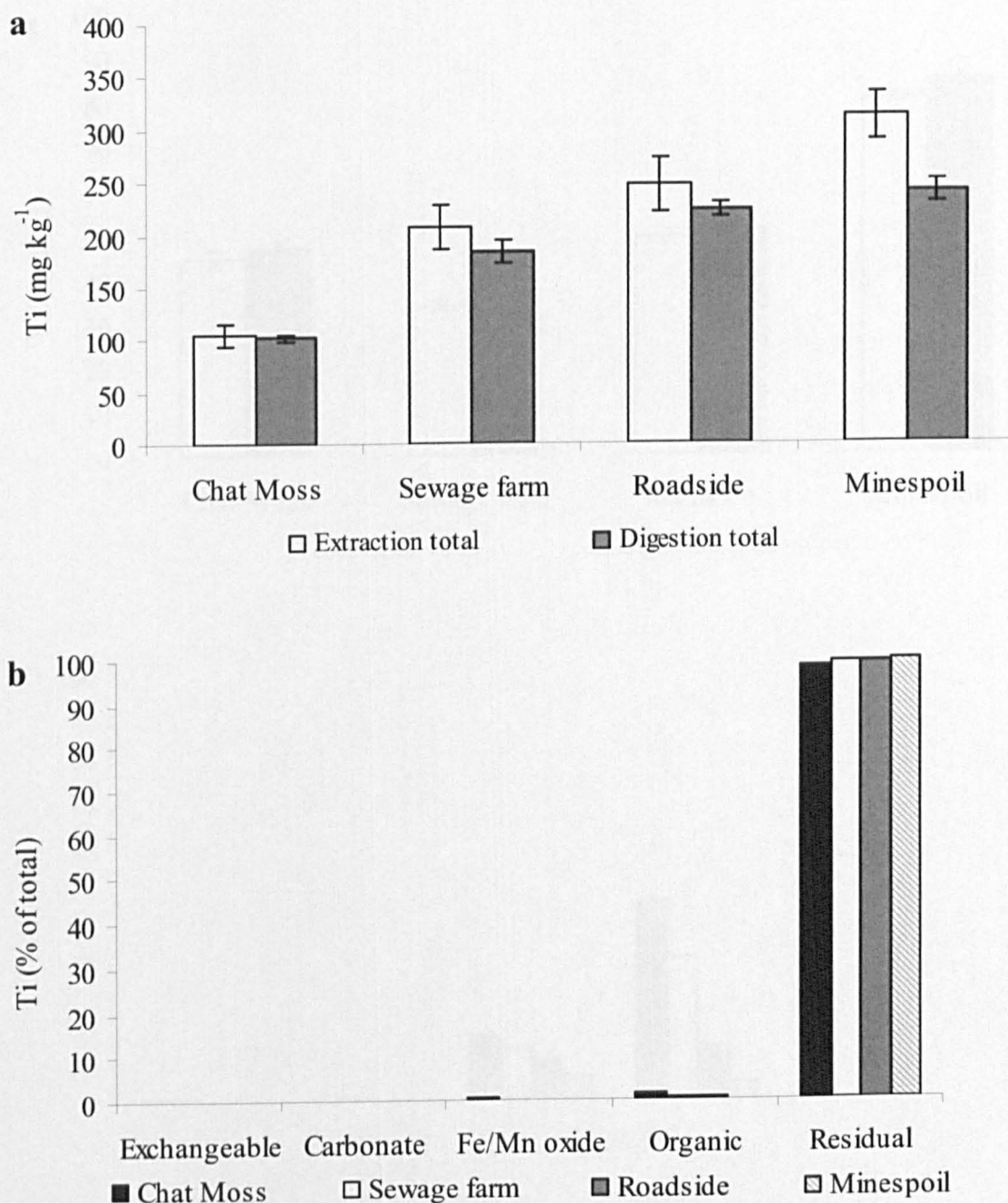


Figure 4.31: (a) Recovery of Ti for different soils using Tessier SEP; error bars show standard error of three replicates (b) Ti fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

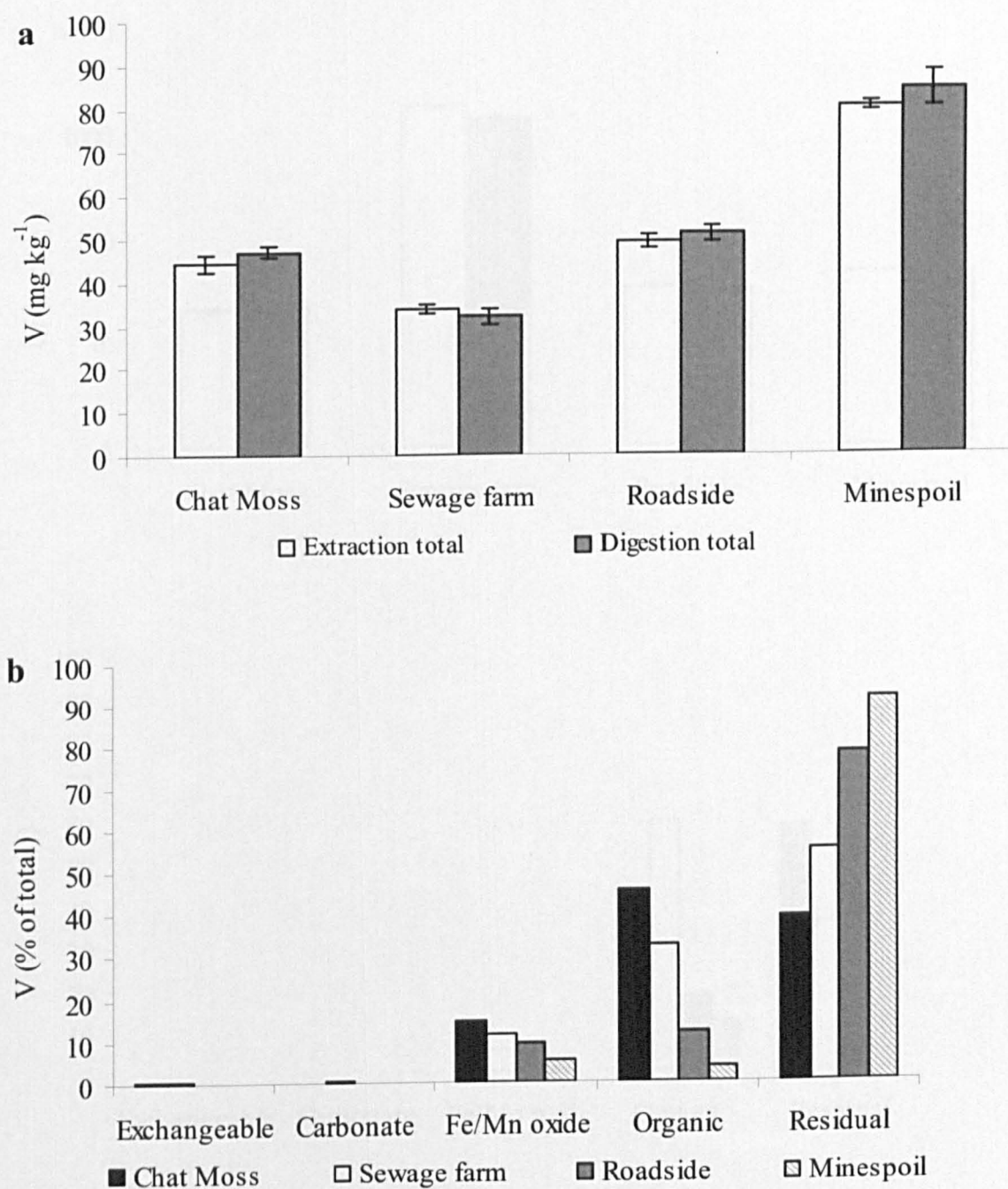


Figure 4.32: (a) Recovery of V for different soils using Tessier SEP; error bars show standard error of three replicates (b) V fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

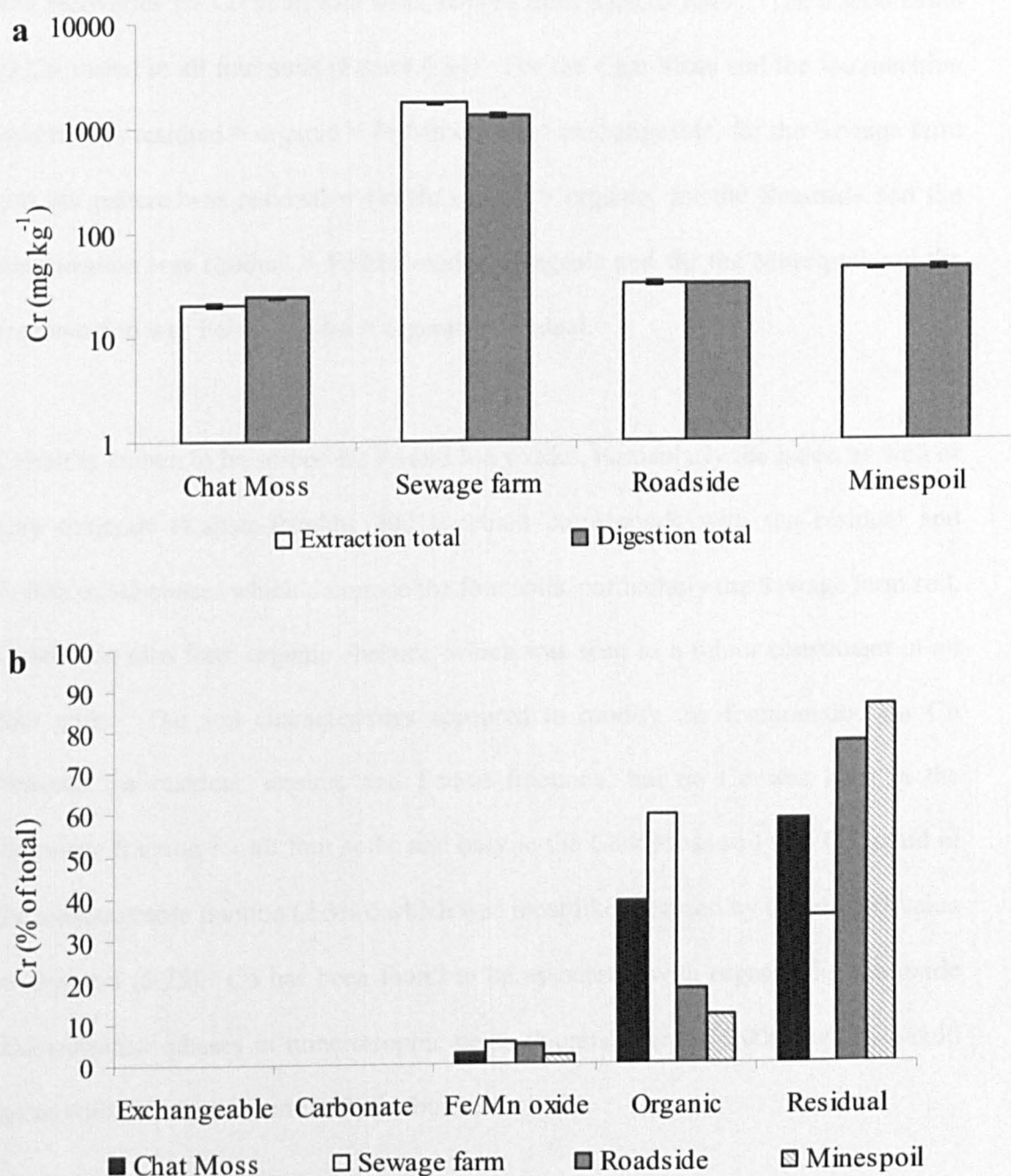


Figure 4.33: (a) Recovery of Cr for different soils using Tessier SEP; error bars show standard error of three replicates (b) Cr fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

Cobalt

The recoveries for Co in all four soils, ranged from 83% to 104%. The fractionation of Co varied in all four soils (Figure 4.34). For the Chat Moss soil the fractionation pattern was residual > organic = Fe/Mn oxides > exchangeable, for the Sewage farm soil the pattern was residual = Fe/Mn oxides > organic, for the Roadside soil the fractionation was residual > Fe/Mn oxides > organic and for the Minespoil soil the fractionation was Fe/Mn oxides > organic = residual.

Cobalt is known to be sorbed by Fe and Mn oxides, particularly the latter, as well as clay minerals (Kabata-Pendias 2001), which corresponds with the residual and Fe/Mn oxide phases which dominate the four soils, particularly the Sewage farm soil. Cobalt can also form organic chelates, which was seen as a minor constituent in all four soils. The soil characteristics appeared to modify the fractionation for Co between the residual, organic and Fe/Mn fractions, but no Co was seen in the carbonate fraction for all four soils, and only in the Chat Moss soil was Co found in the exchangeable fraction (2.3%), which was most likely caused by the low pH value of this soil (5.25). Co has been found to be associated with organic, Fe/Mn oxide and carbonate phases in minerotrophic peats (Koretsky *et al.*, 2006), which would agree with the results seen for these four soils.

Nickel

The recoveries for Ni across all four soils ranged from 82% for the Chat Moss soil to 114% for the Sewage farm soil, and the fractionation of Ni was different for all four soils (Figure 4.35). In the Minespoil soil, the Ni was evenly distributed between the residual, organic and Fe/Mn fractions with ~2.5% in both the exchangeable and

carbonate fractions. In the Chat Moss soil the order of fractionation was residual > organic > Fe/Mn oxides > exchangeable. In the Sewage farm soil, most of the Ni was found in the Fe/Mn oxide fraction, followed by the organic fraction and then the residual, exchangeable and carbonate each with 6 – 8.5% Ni. The Roadside soil consisted mainly of residual Ni (70%) followed by organically bound Ni (18%) and Fe/Mn oxide bound Ni (11%).

Nickel has a strong affinity for organic matter and Fe and Mn oxides, which would result in the Ni being distributed between the organic, Fe/Mn oxide and residual phases depending on organic matter content and the form of the Fe/Mn oxides (Burt *et al.*, 2003; Bacon & Hewitt, 2005; Terzano *et al.*, 2007). The difference in fractionation between the soils was most likely due to the different characteristics of the soil including clay and Fe oxide content, organic matter content as well as pH.

Copper

In all cases for Cu, the extraction total exceeded the digestion total, with recoveries ranging from 114% to 136% (Figure 4.36). All four soils displayed similar fractionation of Cu. The organic fraction was the dominant phase with 53% (Roadside soil) to 83% (Chat Moss) of Cu found in this fraction. This is in agreement with the known behaviour of Cu, which is known to strongly bind to organic material within soils (Kabata-Pendias, 2001; Bacon & Hewitt, 2005). The soils with the lowest organic matter content as measured by Loss on Ignition (Minespoil and Roadside) also showed the lowest fractionation of Cu into the organic phase, with the residual phase being more important in these soils than in the Chat Moss or Sewage Farm soils. There was also slight fractionation of Cu into the

Fe/Mn oxide phase which corresponds with the known behaviour of Cu, which also adsorbs to hydrous oxides (Kabata-Pendias, 2001).

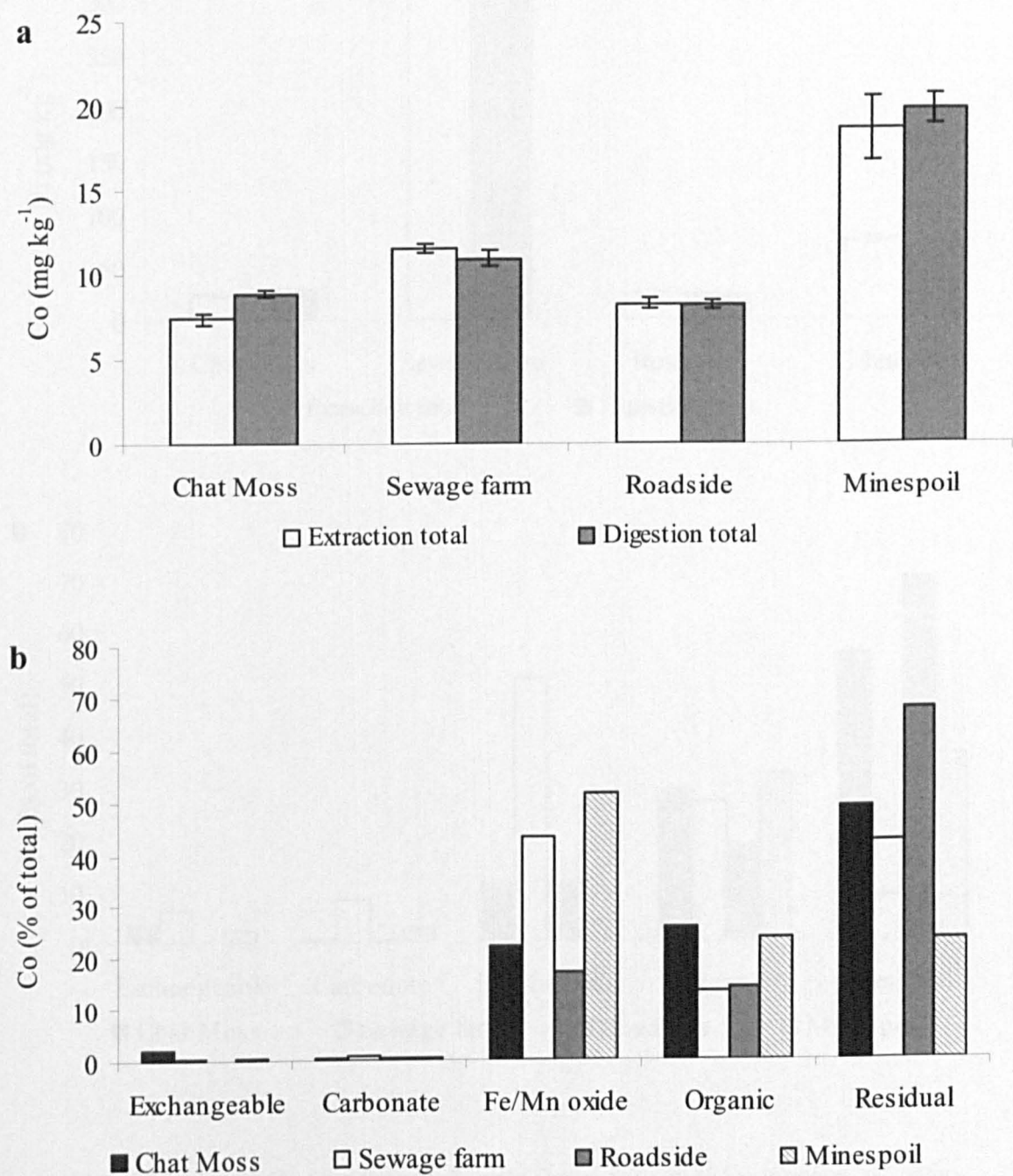


Figure 4.34: (a) Recovery of Co for different soils using Tessier SEP; error bars show standard error of three replicates (b) Co fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

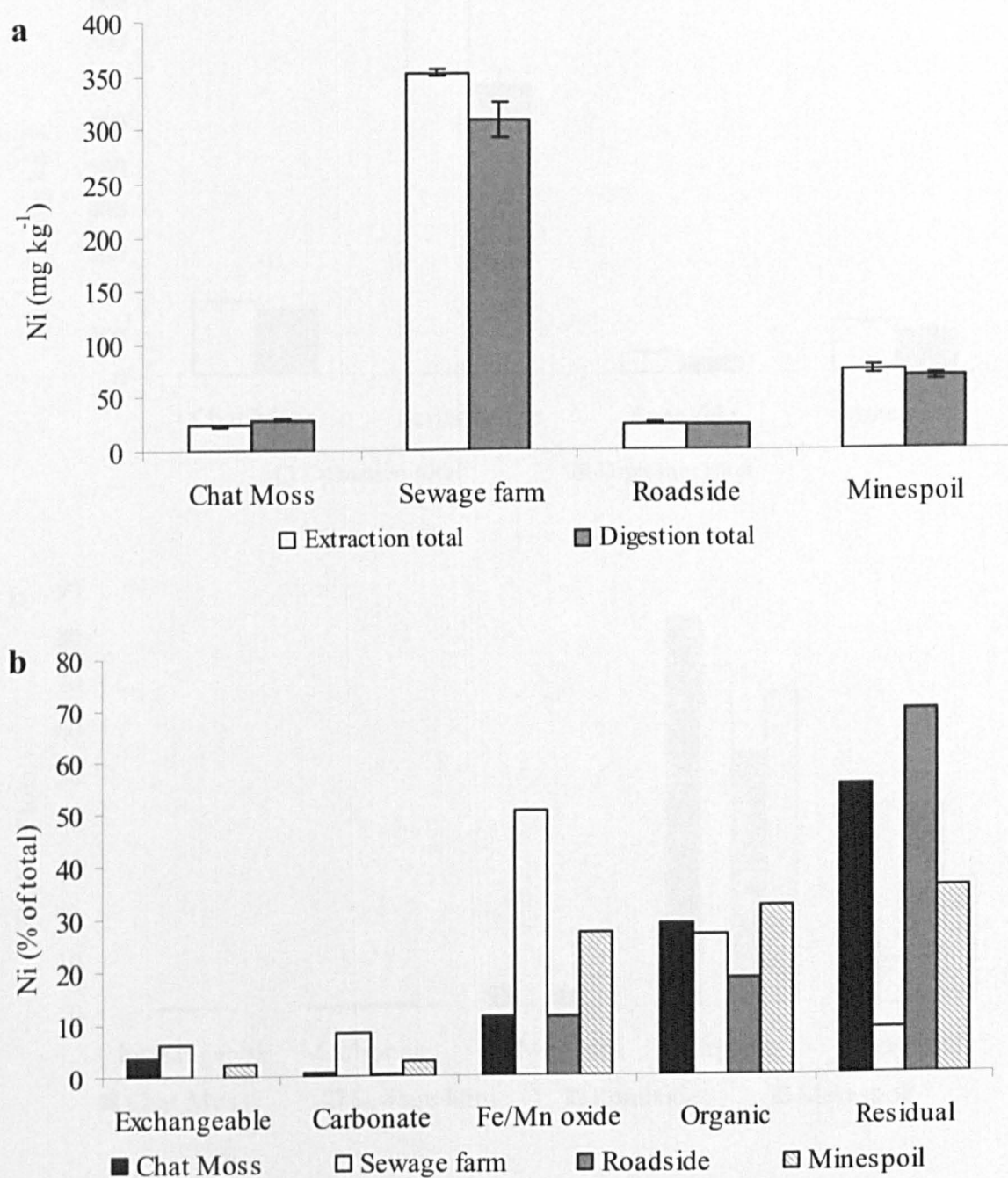


Figure 4.35: (a) Recovery of Ni for different soils using Tessier SEP; (b) Ni fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

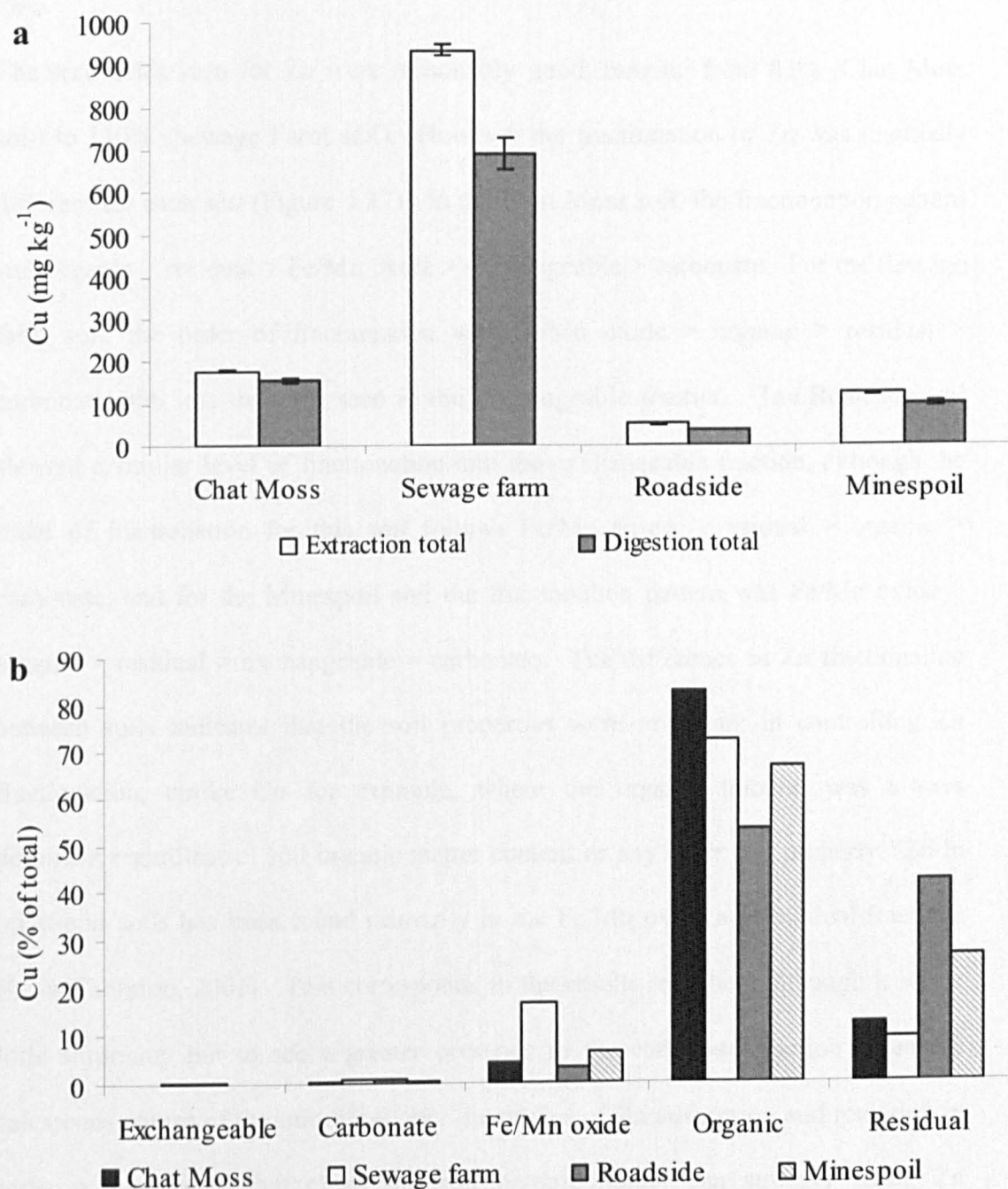


Figure 4.36: (a) Recovery of Cu for different soils using Tessier SEP; error bars show standard error of three replicates (b) Cu fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

Zinc

The recoveries seen for Zn were reasonably good, ranging from 83% (Chat Moss soil) to 110% (Sewage Farm soil). However the fractionation of Zn was markedly different for each soil (Figure 4.37). In the Chat Moss soil, the fractionation pattern was organic > residual > Fe/Mn oxide > exchangeable > carbonate. For the Sewage farm soil, the order of fractionation was Fe/Mn oxide > organic > residual > carbonate with less than 1% seen in the exchangeable fraction. The Roadside soil showed a similar level of fractionation into the exchangeable fraction, although the order of fractionation for this soil follows Fe/Mn oxide > residual > organic > carbonate, and for the Minespoil soil the fractionation pattern was Fe/Mn oxide > organic > residual > exchangeable = carbonate. The difference in Zn fractionation between soils indicates that the soil properties were important in controlling Zn fractionation, unlike Cu for example, where the organic fraction was always dominant regardless of soil organic matter content or any other soil property. Zn in minespoil soils has been found primarily in the Fe/Mn oxide and residual fractions (Li & Thornton, 2001). This corresponds to the results seen here although it was a little surprising not to see a greater presence in the carbonate fraction given the calcareous nature of the minespoil site. In studies of Zn adsorption and retention in soils, it was found that clays and soil organic matter can strongly retain Zn (Horckmans *et al.*, 2007; Sarret *et al.*, 2004), which is also in agreement with the results here, with the Chat Moss soil (high organic matter) having a high proportion of Zn in the organic fraction, and the soils with higher clay content as seen by Ba and Sr fractionation (Roadside, Sewage farm, Minespoil) showing higher fractionation into the residual fraction. However the Fe/Mn oxide fraction was also a dominant fraction in the Sewage farm and Minespoil soils, which was in agreement with

results reported in Kabata-Pendias (2001), where Zn in soils was mainly associated with hydrous Fe and Al oxides, followed by clay minerals.

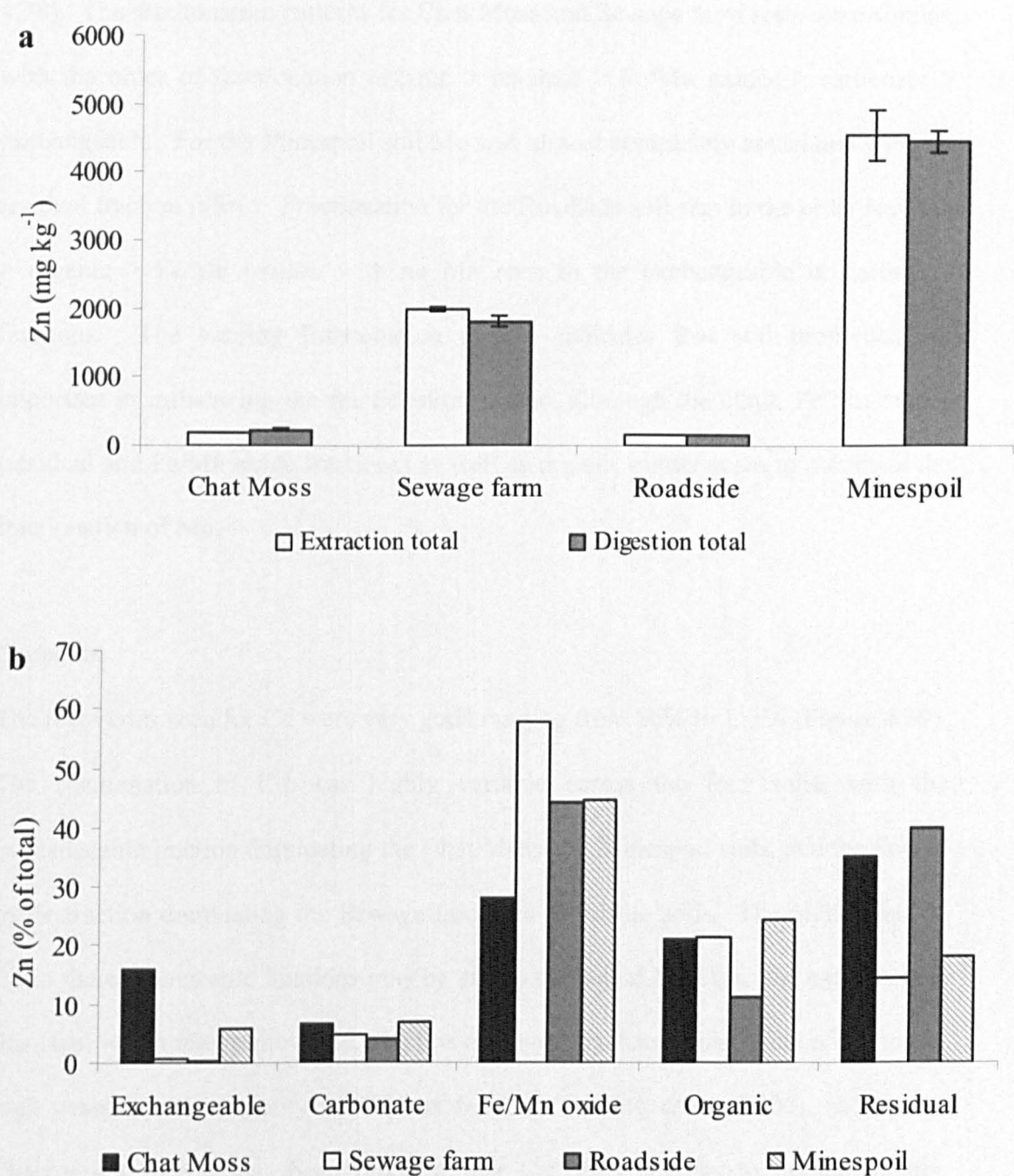


Figure 4.37: (a) Recovery of Zn for different soils using Tessier SEP; error bars show standard error of three replicates (b) Zn fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

Molybdenum

Recoveries seen for Mo for all soils ranged from 518% (Chat Moss soil) to 694% (Sewage Farm soil). These unusual recoveries are currently unexplained (Figure 4.38). The fractionation patterns for Chat Moss and Sewage farm soils were similar, with the order of fractionation organic > residual > Fe/Mn oxides > carbonate > exchangeable. For the Minespoil soil Mo was almost completely associated with the residual fraction (95%). Fractionation for the Roadside soil was in the order residual > organic > Fe/Mn oxides, with no Mo seen in the exchangeable or carbonate fractions. The varying fractionation of Mo indicates that soil properties are important in influencing the fractionation of Mo, although the clays, Fe/Mn oxides (residual and Fe/Mn oxide fractions) as well as organic matter seem to dominate the fractionation of Mo.

Cadmium

The recoveries seen for Cd were very good ranging from 86% to 111% (Figure 4.39). The fractionation of Cd was highly variable across the four soils, with the exchangeable fraction dominating the Chat Moss and Minespoil soils, and the Fe/Mn oxide fraction dominating the Sewage farm and Roadside soils. The high levels of Cd in the exchangeable fractions may be due to the use of MgCl_2 as the extractant in this step, which may remove Cd which is not in the exchangeable fraction due to the high complexation capacity of Cl ions for Cd^{2+} (Young *et al.*, 2006), as seen in Chapter 4.3.3.1. It has been reported that Cd often adsorbs to organic matter (Horckmans *et al.*, 2007). However, in these results for the Chat Moss soil, the dominant fraction after the exchangeable was the residual rather than the organic fraction. This almost certainly indicates that, in the Chat Moss soil, the Cd weakly

bound to organic matter was largely extracted by MgCl_2 through chloro-complexation which reduced the apparent level of fractionation into the organic phase.

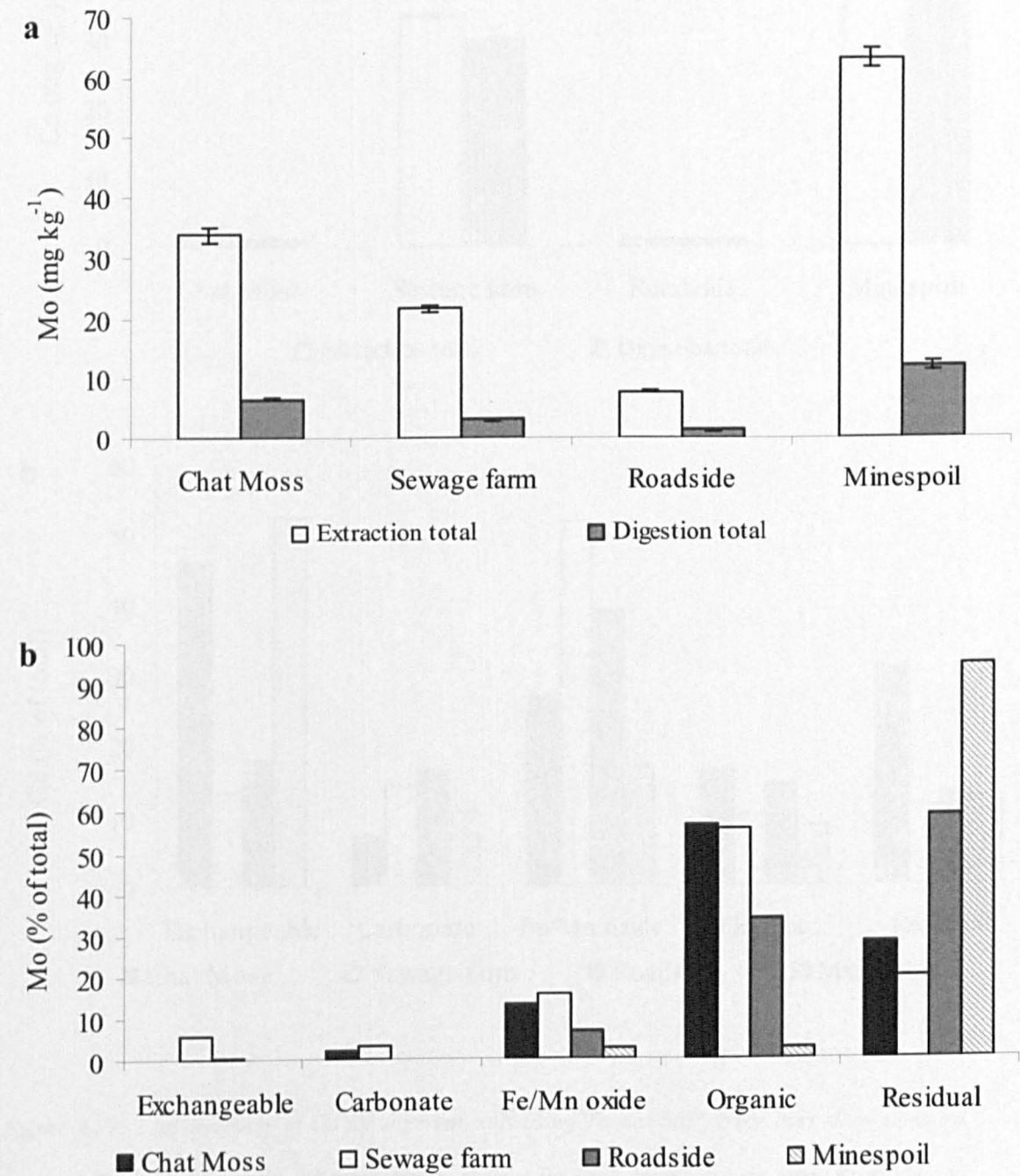


Figure 4.38: (a) Recovery of Mo for different soils using Tessier SEP; error bars show standard error of three replicates (b) Mo fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

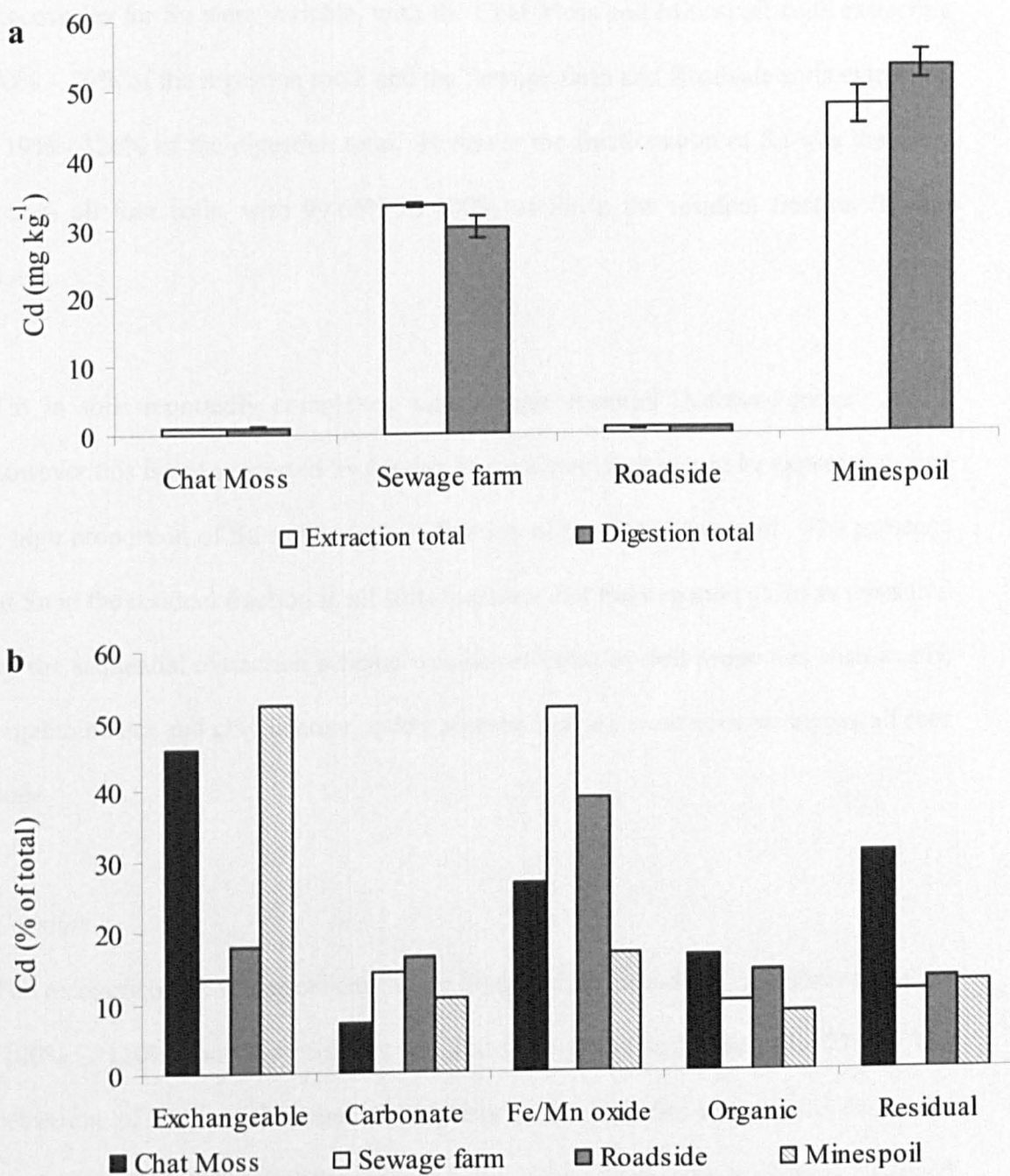


Figure 4.39: (a) Recovery of Cd for different soils using Tessier SEP, error bars show standard error of three replicates; (b) Cd fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

Tin

Recoveries for Sn were variable, with the Chat Moss and Minespoil soils extracting 70% – 79% of the digestion total, and the Sewage farm and Roadside soils extracting 119% - 126% of the digestion total. However the fractionation of Sn was the same across all four soils, with 99.65% to 100% of Sn in the residual fraction (Figure 4.40).

Tin in soils reportedly complexes with organic material (Kabata-Pendias, 2001), however this is not supported by the results seen here, as it would be expected to find a high proportion of Sn in the organic fraction of the Chat Moss soil. The presence of Sn in the residual fraction in all soils indicates that fractionation of Sn as measured by the sequential extraction scheme was not affected by soil properties such as pH, organic matter and clay content, redox potential, which were variable across all four soils.

Caesium

The recovery of Cs was excellent for the Sewage farm, Roadside and Minespoil soils (100% - 110%) but the recovery for the Chat Moss soil was only 77%. The behaviour of Cs was the same for all four soils, with the majority of Cs in the residual fraction (93% - 100%) (Figure 4.41). Caesium in soils is strongly adsorbed and largely present within primary minerals which suggests that Cs would be poorly liberated through sequential extractions, (Kabata-Pendias, 2001); this corresponds with the results seen here where Cs was largely in the residual phase. There was slight fractionation of Cs into the organic and Fe/Mn fractions (Chat Moss and Sewage farm soils), but the residual fraction was dominant across all four soils. The

major source of Cs in all the soils was probably substituted for K in 2:1 aluminosilicate clays and feldspar minerals.

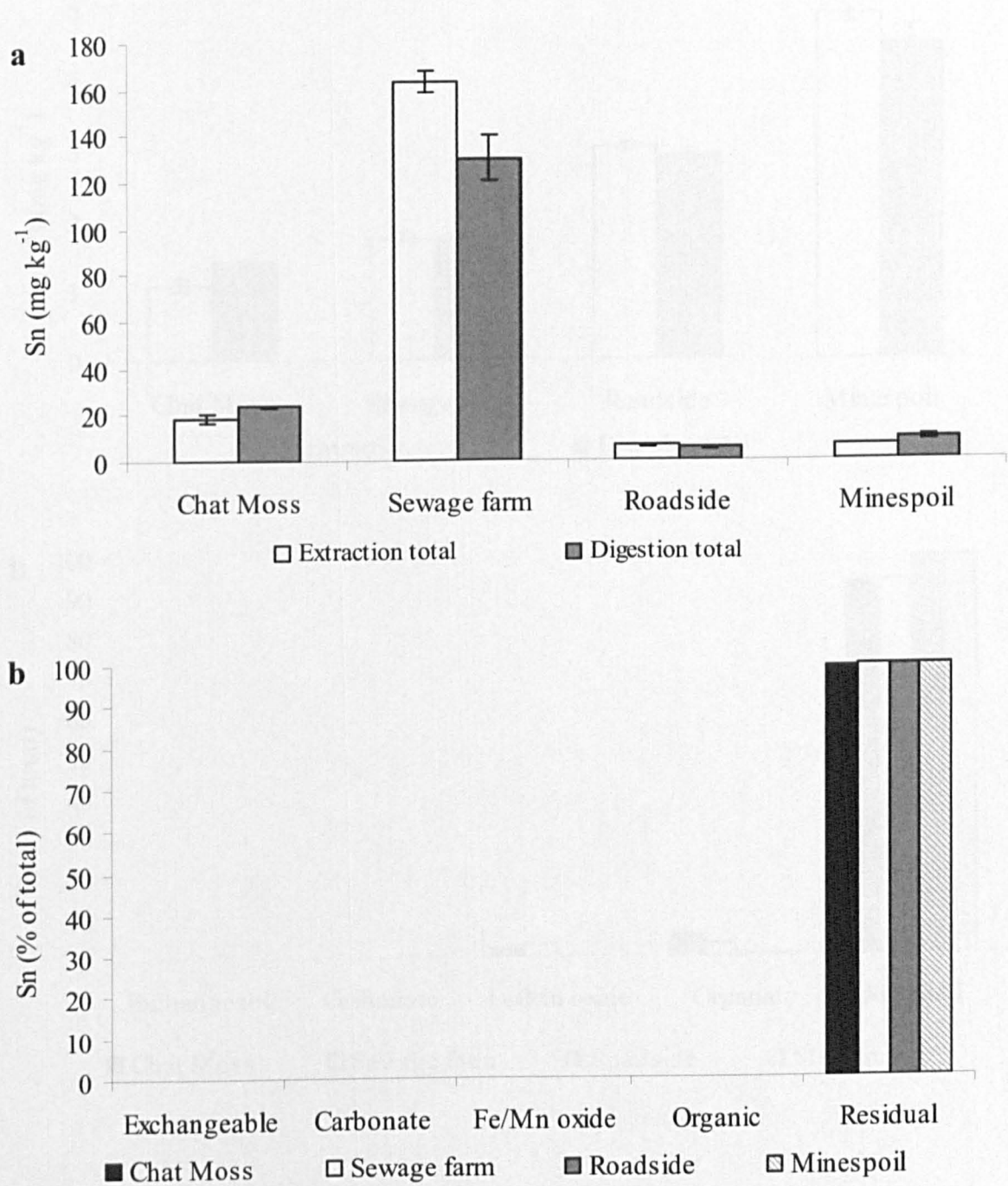


Figure 4.40: (a) Recovery of Sn for different soils using Tessier SEP; error bars show standard error of three replicates (b) Sn fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

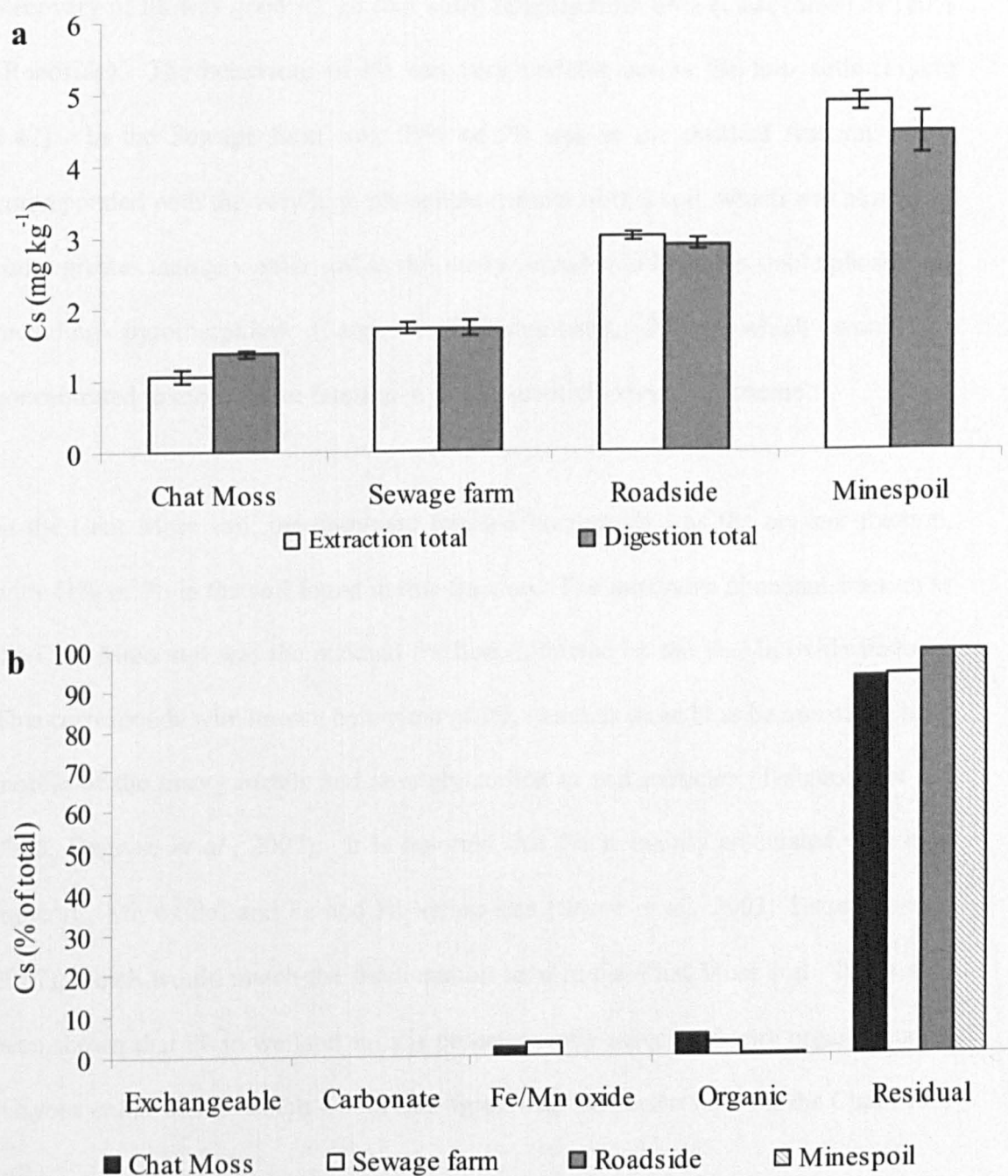


Figure 4.41: (a) Recovery of Cs for different soils using Tessier SEP; error bars show standard error of three replicates (b) Cs fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

Lead

Recovery of Pb was good for all four soils, ranging from 88% (Chat Moss) to 110% (Roadside). The behaviour of Pb was very variable across the four soils (Figure 4.42). In the Sewage farm soil, 99% of Pb was in the residual fraction. This corresponded with the very high phosphate content of this soil, which was almost 10 times greater than any other soil in this study. Lead readily forms stable phosphates including pyromorphites (Lang & Kaupenjohann, 2003), which would be concentrated in the residual fraction in this sequential extraction scheme.

In the Chat Moss soil, the dominant fraction hosting Pb was the organic fraction, with 41% of Pb in the soil found in this fraction. The next most abundant fraction in the Chat Moss soil was the residual fraction, followed by the Fe/Mn oxide fraction. This corresponds with known behaviour of Pb, which is thought to be one of the least mobile of the heavy metals and strongly sorbed to soil particles (Tongtavee *et al.*, 2005; Degryse *et al.*, 2007). It is reported that Pb is mainly associated with clay minerals, Mn oxides and Fe and Al hydroxides (Sauve *et al.*, 2003; Terzano *et al.*, 2007), which would match the fractionation seen in the Chat Moss soil. It has also been shown that Pb in wetland soils is predominantly associated with organic matter (Grybos *et al.*, 2007), which would also agree with the results here for the Chat Moss soil.

In the Roadside soil, the fractionation was dominated by the Fe/Mn oxide fraction. Fe/Mn oxides can be significant scavengers of heavy metals, particularly at high pH levels (Li & Thornton, 2001), and pH levels in the Roadside soil were 7.90 which would encourage adsorption of Pb by oxides. The residual and organic fractions are

the next most dominant in this soil, with 15% - 21% of Pb found in these fractions. There was a small proportion of Pb in the carbonate fraction (6.28%) and there was a similar proportion of Pb in the carbonate fraction in the Chat Moss soil, which may have originated from liming practices. The Minespoil soil had similar fractionation to the Roadside soil, although the Pb was more evenly fractionated between the Fe/Mn oxide, organic and residual fractions. This soil had the highest fractionation of Pb into the carbonate phase, which would be expected in a soil such as this which is derived from Pb/Zn minespoil hosted in limestone, so carbonates would be very high in this soil. In all four soils, there was a very low proportion of Pb in the exchangeable fraction with no soil having greater than 1.75% Pb in the exchangeable fraction. The fractionation of Pb in these soils seems to be dominated by a combination of the original form of the Pb contamination and the characteristics of the soils, as opposed to elements such as Ti and Cs, which show the same fractionation for all four soils.

From the results of this experiment, it seems that soil characteristics in a range of soils with different contamination sources were important in controlling the fractionation of elements, such as Fe/Mn oxide and organic matter content, however the source of the elements may also be an influencing factor as this could determine the original form of the elements when they were introduced to the soil. The soils used for this experiment were chosen to represent a range of sources of lead contamination, and the variation in Pb fractionation may be a result of this. However, for Pb it seems that soil characteristics were important in determining fractionation, with the high phosphate content of the Sewage farm soil resulting in large residual fractionation and the high organic matter content of the Chat Moss soil resulting in a dominance of the organically-bound fraction.

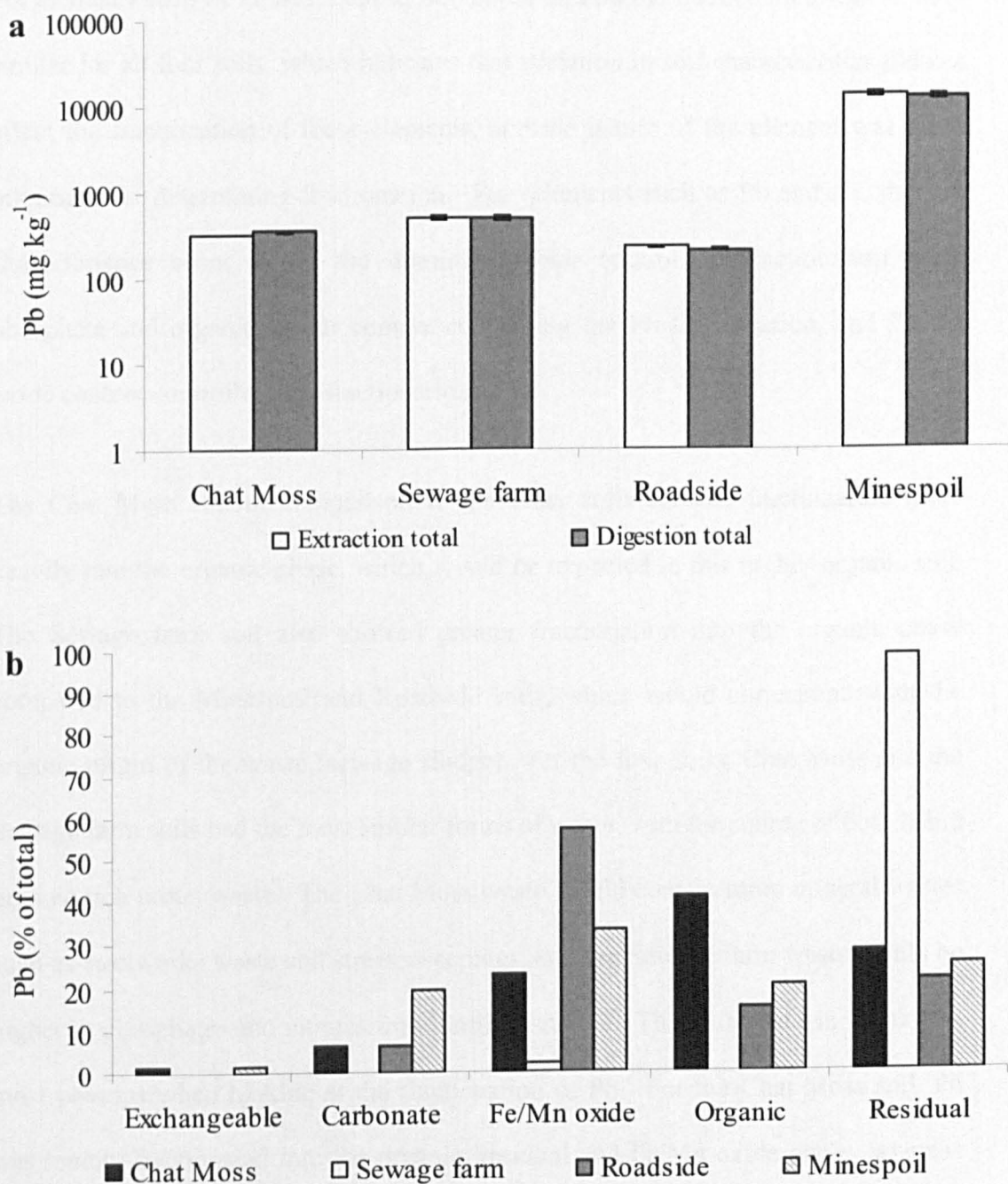


Figure 4.42: (a) Recovery of Pb for different soils using Tessier SEP; error bars show standard error of three replicates (b) Pb fractionation pattern for Chat Moss, Sewage farm, Roadside and Minespoil soils.

For elements such as Ti, Mn, Fe, Cu, Se, Sn, Cs and Ba the fractionation was broadly similar for all four soils, which indicates that variation in soil characteristics did not affect the fractionation of these elements, and the nature of the element was more important for determining fractionation. For elements such as Pb and As, the soil characteristics seem to be the dominant factor controlling fractionation, with phosphate and organic matter content controlling the Pb fractionation, and Fe/Mn oxide content controlling the fractionation of As.

The Chat Moss soil in comparison to the other soils showed fractionation more heavily into the organic phase, which would be expected in this highly organic soil. The Sewage farm soil also showed greater fractionation into the organic phase compared to the Minespoil and Roadside soils, which would correspond with the organic origin of the waste (sewage sludge). Of the four soils, Chat Moss and the Sewage farm soils had the most similar forms of waste, with the source of both being organic rich urban waste. The Chat Moss waste would contain more mineral wastes such as steelworks waste and street sweepings, and the Sewage farm waste would be higher in phosphates and nitrates from fertiliser runoff. This difference in waste was most obvious when looking at the fractionation of Pb. For the Chat Moss soil, Pb was mainly fractionated into the organic, residual and Fe/Mn oxide phase, whereas for the Sewage farm soil Pb was almost exclusively fractionated into the residual phase (99%). This was most likely due to formation of Pb phosphates which are shown to be very stable (Lang & Kaupenjohann, 2003). Pb was the dominant contaminant of interest in the Chat Moss soil, and the difference in fractionation between the four soils would be expected to result in different reactivity of Pb, for

example the Sewage farm soil would be expected to show very low Pb reactivity. This will be further studied using ^{204}Pb stable isotope dilution (Chapter 4.4).

4.4 Isotopically exchangeable Pb

4.4.1 Introduction

Human activities have resulted in the accumulation of lead in the biosphere, through processes including smelting of lead ore, atmospheric deposition from leaded petrol, coal and oil combustion, and the production of steel and non-ferrous metals (e.g. Semlami *et al.*, 2004; Weiss *et al.*, 1999a). Lead in soil is considered to be relatively unreactive and strongly sorbed to soil components such as humus and hydrous oxides of Fe (Morin *et al.*, 1999). Sequential extraction of soils have shown that Pb is often associated with Fe and Mn oxide fractions and organic / sulphide fractions (Wilson *et al.*, 2006; Burt *et al.*, 2003). Strawn *et al.*, (2007) showed Pb was associated with Mn oxides and poorly crystallised Fe oxides, using electron microprobe and X-ray diffraction analyses of contaminated wetland soils. However, Lang and Kaupenjohann, (2003) suggested that Pb phosphates, especially pyromorphites, are the most stable Pb-containing minerals under a wide range of conditions, and so would be expected to be present in all Pb contaminated soils.

Due to the assumption of low Pb reactivity in soil, most regulations for soil Pb contamination are based on total lead content, as it is considered that little Pb will move into soil solution and be available for plant uptake, limiting the pathway of human risk to direct ingestion of soil. UK 'soil guideline values' (SGVs) have been developed by the Department for Environment, Food and Rural Affairs (DEFRA)

and the Environment Agency based on total Pb concentration in soil, with the underlying assumption that only a small proportion of Pb in soil is available for uptake by plants (Environment Agency, 2002b). These SGVs are used as a screening tool by DEFRA and the Environment Agency in England and Wales, and place different limits on soil Pb concentration based on land use; the strictest limits are reserved for land classified as residential land with/without plant uptake, and allotments. However a single value for soil Pb limits based on total soil Pb may not be realistic, and ideally the reactivity or 'lability' of Pb should be considered as a criterion when assessing risk. The SGV for Pb is based on the uptake of lead and the response of blood lead concentration. This in turn is based on the total lead levels in soil, with the assumed uptake pathway being ingestion of soil and soil dust. Instead of total soil lead, only that part which is labile will be bioaccessible, and so this may represent a more accurate assessment of risk from soil lead contamination. Lability represents the ability of soil-borne metals to transfer between the soil solid and solution phases, which may have implications both for plant uptake and the bioaccessibility of ingested soil Pb. Lability, or the 'E-value', of trace metals can be easily measured as the degree of 'isotopic exchangeability' in a soil suspension (Young *et al.*, 2000). Early studies used radio-isotopes with the advantage that a small spike is easily measurable without altering the pre-existing solid-solution equilibrium (Hammer *et al.*, 2006; Nolan *et al.*, 2005; Sinaj *et al.*, 1999; Young *et al.*, 2000). Unfortunately, the lack of suitable radio-isotopes for Pb and Cu means that there is little data on the lability of these important metals (Degryse *et al.*, 2007). However, in recent years with wider access to inductively coupled plasma- mass spectrometry (ICP-MS) technology, the use of stable isotopes has become more common. The stable isotope ^{65}Cu was used by Nolan *et al.*, (2004) to measure the

lability of Cu in soil and isotopically exchangeable Pb has now also been determined (Degryse *et al.*, 2007; Tongtavee *et al.*, 2005; Gabler *et al.*, 1999). Measurements of the E value for Pb in soil have shown surprisingly high proportions of labile Pb: Tongtavee *et al.*, (2005) reported an average of 58% (40.36% - 64.9%) of total soil Pb as labile using a ^{207}Pb spike (22.1% natural abundance). Degryse *et al.*, (2007), using a ^{208}Pb spike (52.4% natural abundance), also reported an average of 58% (45% - 78%) Pb lability found in historically contaminated soils. These studies suggest that the lability of Pb in soil may be greater than was previously predicted (Welp & Brummer, 1999) or assumed from the relative strength of Pb sorption and the suggestion that Pb forms discrete solid phases in soil, such as chloropyromorphite (Cotter-Howells and Thornton, 1991).

The aim of this part of the study was to further develop a Pb stable isotope dilution method using ^{204}Pb (1.4% natural abundance). The low natural abundance of ^{204}Pb allows a small amount of Pb to be used as a spike, which minimises any impact of the spike on the soil Pb equilibrium. The methodology was developed using the same four soils used in section 4.3.3.2 with markedly different Pb concentrations and sources of contamination; these were intended to provide a range of Pb solubility and isotopic exchangeability. The effect of suspending electrolyte and spike equilibration time were investigated.

4.4.2 Materials and Methods

4.4.2.1 Soil sampling

Soil samples from the four sites described in section 4.3.3.2 were collected to represent a range of Pb contamination histories and metal concentrations in order to

test various forms of the isotope dilution method using ^{204}Pb . Further details about sample sites can be found in section 4.3.3.2.

4.4.2.2 Soil characterisation

Topsoil samples (0 – 20 cm) were collected at all sites, these were then air-dried and sieved to < 2 mm. Organic matter content was estimated by loss on ignition of a 5 g oven-dried (105°C) subsample at 550°C for 7 hours (Chapter 2.4). Soil pH value was measured in deionised water suspension (1:2.5 soil: solution ratio) after shaking for 30 minutes (Chapter 2.2). Subsamples of the < 2 mm sieved soil were milled using a Retsch PM400 ball mill prior to acid digestion for trace element analysis, using the method described in Chapter 2.5.1 and 2.6. Available phosphate analysis was carried out using Olsen's method (Rowell, 1994) and measurement carried out by spectrophotometer (CECIL CE1011). Total soil phosphate was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) on the digested soils.

4.4.2.3 Measurement of Pb isotope ratios

Pb isotope ratios were measured by ICP-MS (standard mode) on total acid digests, using the protocol detailed in Section 2.7.

4.4.2.4 Lability measurement

The labile Pb pool was measured on < 2 mm sieved air-dry soil. The method was developed in two stages: (i) determination of a suitable electrolyte and (ii) determination of appropriate post-spike equilibration time. At both stages, 30 ml of

electrolyte was pre-equilibrated with 2 g soil on a rotary shaker for 3 days. Six replicates for each sample were used, three of which were used to measure natural Pb isotope ratios, and three of which were spiked after this equilibration period with 400 μL of ^{204}Pb solution (99.7% ^{204}Pb , Oak Ridge National Laboratories). The spike concentration was chosen to double the natural ^{204}Pb content of the most contaminated soil, and equated to 0.023 mg ^{204}Pb added to the samples. All six suspensions were then equilibrated further before sampling of the soil solution. After this equilibration period, samples were centrifuged (2200 g for 15 minutes) and the supernatant filtered through 0.2 μm cellulose acetate filters. The resulting solutions were then analysed by ICP-MS for $^{204}\text{Pb}/^{208}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$.

In Stage 1, four electrolytes were tested: 0.01 M $\text{Ca}(\text{NO}_3)_2$, 0.0005 M EDTA, 0.005 M EDTA and 0.05 M EDTA. EDTA used was in the form of $\text{Na}_2\text{-EDTA}$ throughout the study. These electrolytes were chosen to investigate the effect of increasing extraction strength of the electrolyte on the measured labile pool. In Stage 2, post-spike equilibration times of 2, 3, 4 and 7 days were used. The labile pool of Pb (E value) was calculated from Equation (4.1).

$$\text{E value} = \left(\frac{M_{\text{Pb soil}}}{W} \right) \left(\frac{C_{\text{spike}} V_{\text{spike}}}{M_{\text{Pb spike}}} \right) \frac{(^{204}\text{IA}_{\text{spike}} - ^{208}\text{IA}_{\text{spike}} R_{\text{SS}})}{(^{208}\text{IA}_{\text{soil}} R_{\text{SS}} - ^{204}\text{IA}_{\text{soil}})} \quad (4.1)$$

Where M_{Pb} is the average atomic mass, C is gravimetric Pb concentration, V is the volume of added spike, W is the weight of soil, IA denotes isotopic abundance of a particular isotope and R_{SS} denotes the ratio of isotopic abundances for ^{204}Pb to ^{208}Pb calculated for the spike + soil supernatant.

4.4.3 Results and Discussion

4.4.3.1 Soil characteristics

Soil characteristics for the four soils are summarised in Chapter 4.3.3.2. The total Pb concentration for the four soils ranged from 217 mg kg⁻¹ to 13600 mg kg⁻¹. pH ranged from 5.28 to 7.90, and organic matter content varied from 61.5 % (Chat Moss soil) to 8.59% (Roadside soil).

Figure 4.43 shows Pb isotopic ratios measured in the HF acid digests of the four soils under study are shown in Figure 4.43. The data are presented as $^{206}\text{Pb}/^{207}\text{Pb}$ plotted against $^{206}\text{Pb}/^{208}\text{Pb}$, which is a format commonly used to aid the identification of the source of the Pb in soil (Bacon *et al.*, 1996, Weiss *et al.*, 1999a). Thus Figure 4.43 includes significant reference materials, including Pb from 'petrol-derived', UK coal and UK Pb ore sources.

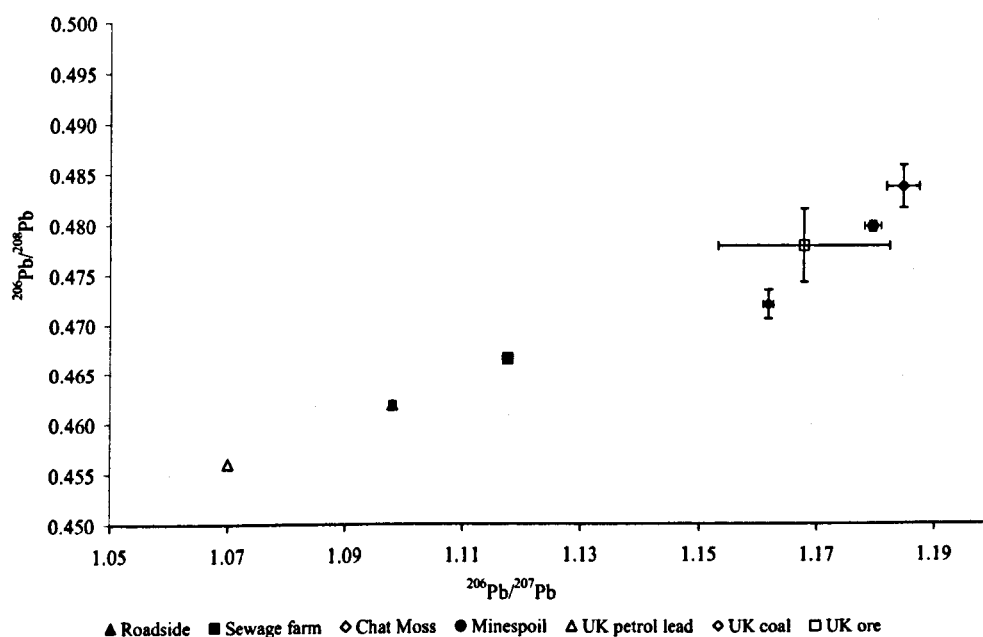


Figure 4.43: $^{206}\text{Pb}/^{207}\text{Pb}$ ratios plotted against $^{206}\text{Pb}/^{208}\text{Pb}$ to show source of contamination for Chat Moss, Sewage farm, Roadside and Minespoil soils. Reference data of UK ore, coal and petrol-derived lead also included. Error bars show standard deviation.

The soils showed a range of Pb sources from highly radiogenic (Minespoil; Pb/Zn ore) to low radiogenic (Roadside; petrol-derived). Measurements of these ratios showed the four soil types used here to be distinct from each other and to represent a range of isotope ratios, which highlights that each soil has a unique source of Pb contamination, and that the original form of the contamination was likely to be different for each site. The Chat Moss soil showed a mixed source of Pb contamination, with contributions from UK coal, UK ore and petrol-derived Pb. More details can be found in Section 4.1. The Sewage farm soil was characterised by a highly mixed Pb isotope signal, with no single source identifiable but a probable combination of petrol-derived Pb and UK ore and coal contributing to the contamination. The Minespoil soil falls within the range of UK Pb ore, which confirms that the source of Pb to this soil was UK Pb ore. The Roadside soil again showed a mixed source of contamination, suggesting that petrol-derived Pb, UK ore and coal may have contributed to the soil Pb loading. However the proximity of the Roadside data to the petrol-derived Pb field indicates that this was a dominant source of contamination to this soil. The varied combination of Pb sources to these soils combined with the variation in soil characteristics such as organic matter and phosphate content suggested that there would be a range of Pb availability across the suite of soils, for example the high organic matter content of the Chat Moss soil could affect the lability of Pb through the strong affinity of Pb for organic matter.

4.4.3.2 Optimising the suspending electrolyte

The results from Stage 1 of the method development are presented in Figure 4.44. Increasing EDTA concentration caused a general increase in the measured E value of all four soils, suggesting that non-labile Pb was progressively mobilised with increasing concentration of the chelating agent. However, 0.01 M $\text{Ca}(\text{NO}_3)_2$ and 0.0005 M EDTA showed very similar results for all soils, suggesting that this concentration of EDTA, while significantly increasing solubility, did not cause significant mobilisation of 'non-labile' Pb.

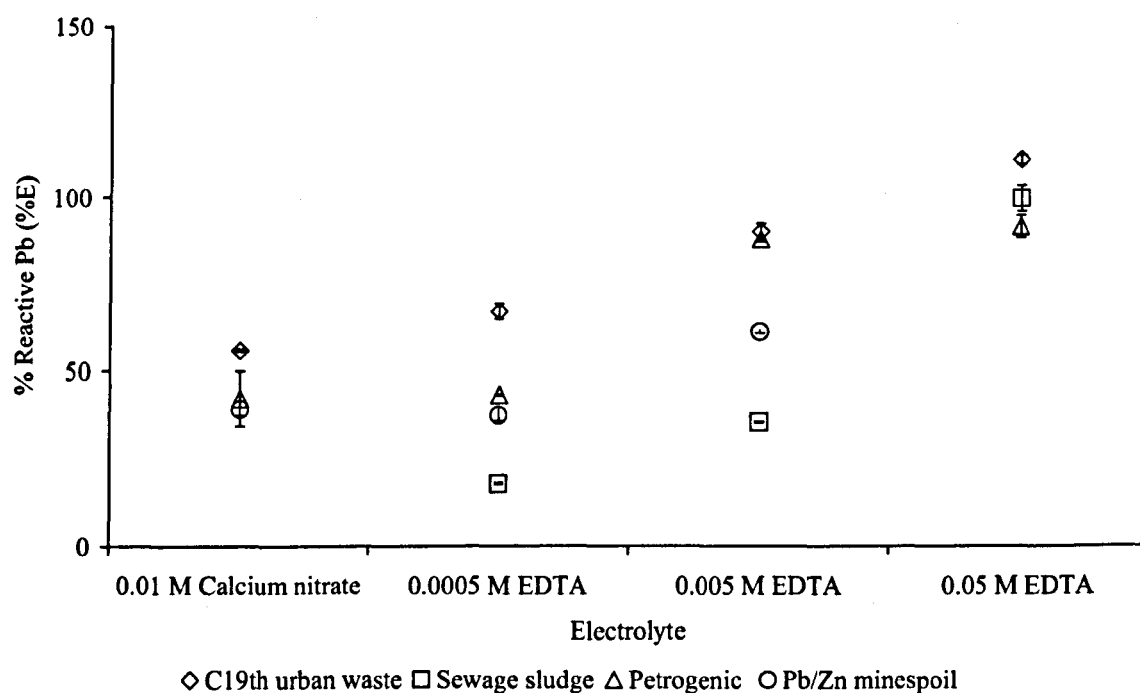


Figure 4.44: Labile Pb (%E) as % of total Pb plotted against electrolyte. Error bars show standard error of three replicates.

An average of 101 % Pb was mobilised (92% – 111%) for Chat Moss, Roadside and Sewage farm soils using 0.05 M EDTA. Data for Minespoil soil suspended in 0.05

0.05 M EDTA is not presented, as the mobilisation of large amounts of Pb (total Pb 13600 mg kg⁻¹) rendered the spike indistinguishable from background and so the change in isotope ratio required for calculation of E-value was not measurable with sufficient accuracy. This is an important issue in measuring isotopic exchangeability with stable, rather than radioactive, isotopes. The presence of the spiking isotope in the natural system means that the spike must be sufficient to alter the natural isotope ratios. However, a large addition may chemically alter the system under study or may even cause precipitation at the point of addition. By contrast, the radio-isotopes typically used in isotopic exchange studies are generally not present in nature and, additionally, can be added in chemically insignificant quantities. The isotope ²⁰⁴Pb was chosen as the spike because of its low natural abundance (1.4 %), so that a small spike will cause a relatively large change in the natural ratio with limited potential to chemically alter the soil system. However, there is clearly a greater need to try and tailor the level of spike to the labile lead content when using stable isotopes and so for soils with very large labile lead contents, such as the example of Minespoil soil in 0.05 M EDTA, the spike concentration would need to be increased.

The purpose of this experiment was to determine the effect of electrolyte on Pb solubilisation and lability measurements. The optimum electrolyte would be one that solubilised sufficient Pb to be analytically robust without bringing non-labile Pb into solution. By comparing the results for varying EDTA concentrations with 0.01 M Ca(NO₃)₂, which would not solubilise non-labile Pb it was possible to identify the optimum electrolyte. It was determined that 0.0005 M EDTA measured similar lability to 0.01 M Ca(NO₃)₂, whereas increasing concentrations of EDTA caused an increase in the measured lability (Figure 4.44).

The advantage in using 0.0005 M EDTA over 0.01 M $\text{Ca}(\text{NO}_3)_2$ lies in the amount of Pb solubilised. Using $\text{Ca}(\text{NO}_3)_2$ as the electrolyte, 0.06 % of total lead was solubilised, whereas 8.38 % of total lead was solubilised by 0.0005 M EDTA. For the Minespoil, Roadside and Chat Moss soils, there was good agreement between lability measured using 0.01 M $\text{Ca}(\text{NO}_3)_2$ and 0.0005 M EDTA (Figure 4.44). For the Sewage farm soil, the lability measured using $\text{Ca}(\text{NO}_3)_2$ as the suspending electrolyte was 83% which was not in agreement with the 0.0005 M EDTA or the 0.005 M EDTA results, which indicated that the very low level of solubilisation (0.004% of total) was analytically unreliable.

An additional experiment was set up with 7 different EDTA concentrations, ranging from 0.0000337 M to 0.05 M on a roughly logarithmic scale, to further study the effects of low EDTA concentrations on the measured lability of Pb. It was found that even at low concentrations of EDTA (0.000114 M EDTA) an increase in the measured lability occurred, indicating that accurate lability measurement required low concentrations of EDTA to maximise the solubility of Pb without altering the lability. The impact of errors within the analysis was assessed through arbitrarily imposing a 10% and 1% error on the isotopic abundance calculation of ^{204}Pb . As seen in Figure 4.45, at the lowest EDTA concentrations these errors are much smaller than at the higher EDTA concentration, further supporting the use of 0.0005 M EDTA as the suspending electrolyte.

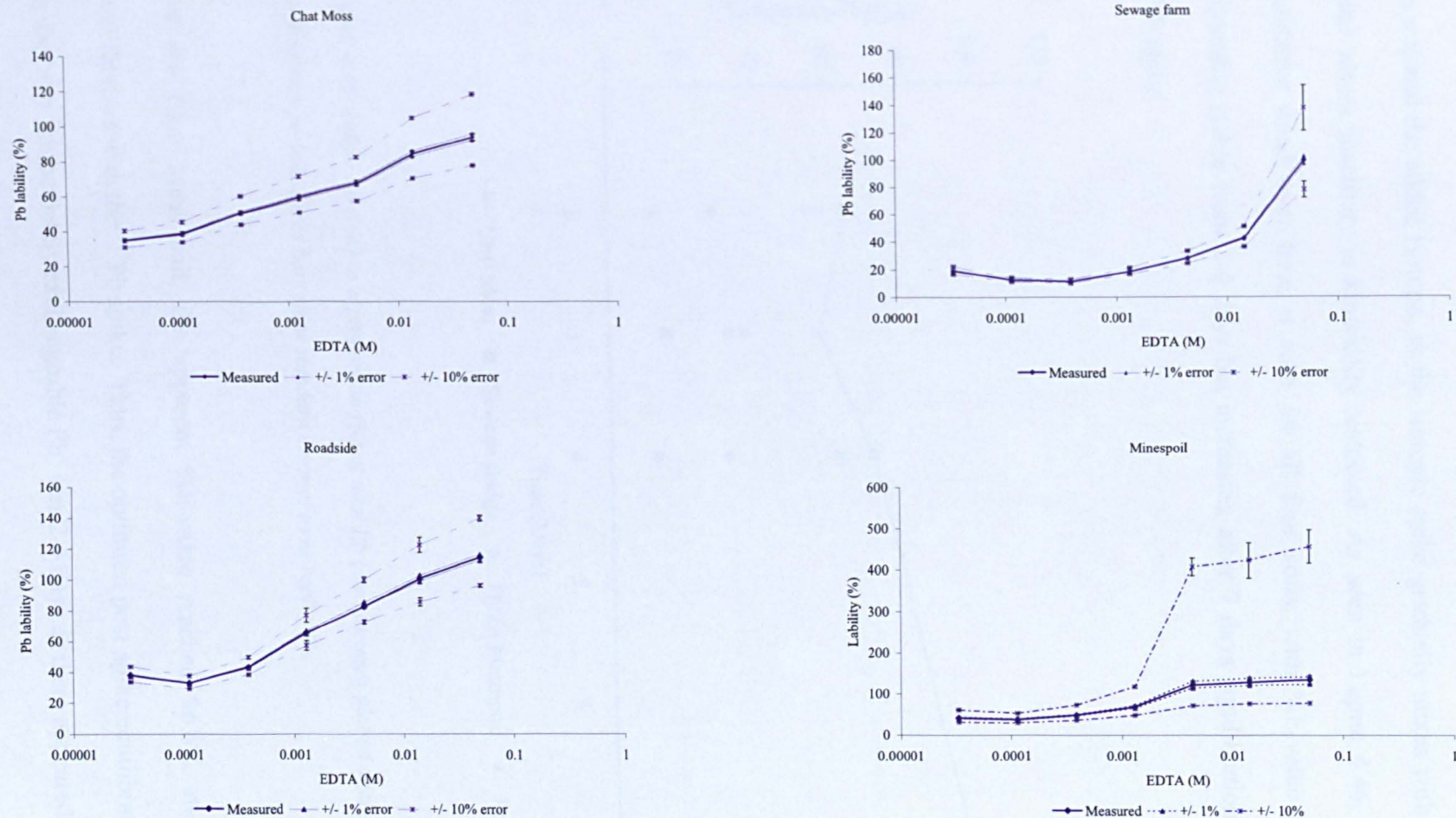


Figure 4.45: Labile Pb (%E-value; equation 4.1) as a proportion (%) of total Pb plotted against EDTA concentration, with +/- 1% and +/- 10% errors applied to the estimation of the isotopic abundance of the isotope (^{204}Pb) used to spike the soil suspensions. Error bars show standard error of three replicates.

4.4.3.3 **Determination of optimum post spike equilibration time**

The measured E-value was expected to slowly increase with contact time between the soil and the added isotope, as the isotopic spike gradually mixes with forms of metal whose reactivity is kinetically restricted. As seen in Figure 4.46, a similar qualitative trend over time is seen for all four soils, with %E-value appearing reasonably stable from 2-4 days but increasing after 7 days equilibration with the ^{204}Pb spike.

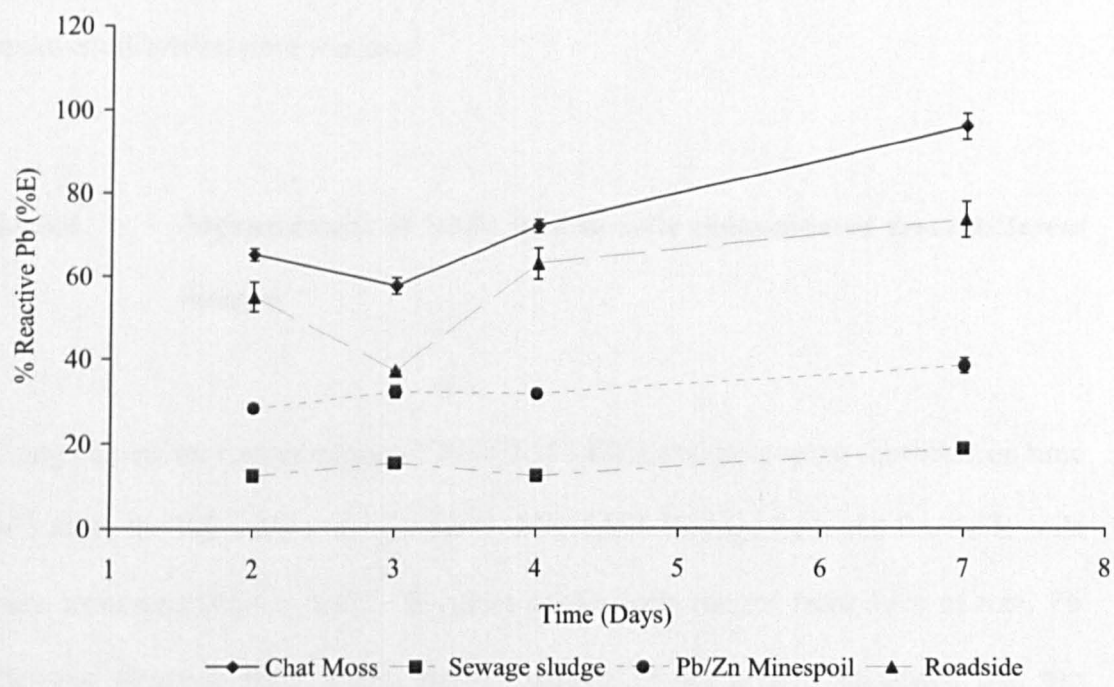


Figure 4.46: Labile Pb (%E) as a proportion (%) of total Pb concentration plotted against post-spike equilibration period. Error bars show standard error of three replicates.

For the Chat Moss soil, the apparent %E-value reached 96.6% after 7 days equilibration with the ^{204}Pb spike. Thus, the optimum post-spike equilibration period to measure ‘immediately exchangeable Pb’ was 2-4 days as there appeared to be little

change in the measured Pb lability of the soils over this period. This was similar to findings using ^{109}Cd , where there was very little change in measured Cd lability with equilibration periods of 1-6 days (Young *et al.*, 2000). The measured lability increased after 7 days equilibration period, but the pattern of increase in lability was not as would be expected from diffusion of the ^{204}Pb spike into less accessible sites. Fe and Mn solution concentrations were not measured in this experiment but it may be that reduction of the soils over the experimental period caused dissolution of Fe/Mn oxides which could release previously bound Pb, thereby increasing the lability of Pb. For the final measurement of %E-value for the four soils, 3 days post-spike equilibration time was used.

4.4.3.4 Measurement of labile lead in soils contaminated from different sources

Using electrolyte concentration of 0.0005 M EDTA and post-spike equilibration time of 3 days, the %E-values of Chat Moss, Minespoil, Sewage farm and Roadside soils were measured (Figure 4.47). E-values of the soils ranged from 13% of total Pb (Sewage farm) to 65% (Chat Moss). Jensen *et al.*, (2006) suggested that the chemistry of Pb in soils is affected by specific adsorption to mineral colloids, precipitation of sparingly soluble compounds and the formation of complexes with organic matter. The authors also report that the first factors affecting the bonding of Pb in industrially contaminated soils is the contamination level and the stability of the original forms of the contaminant metal during incorporation into the soil. The soils used here represent a wide range of all of these conditions, and so should provide an adequate test of the method.

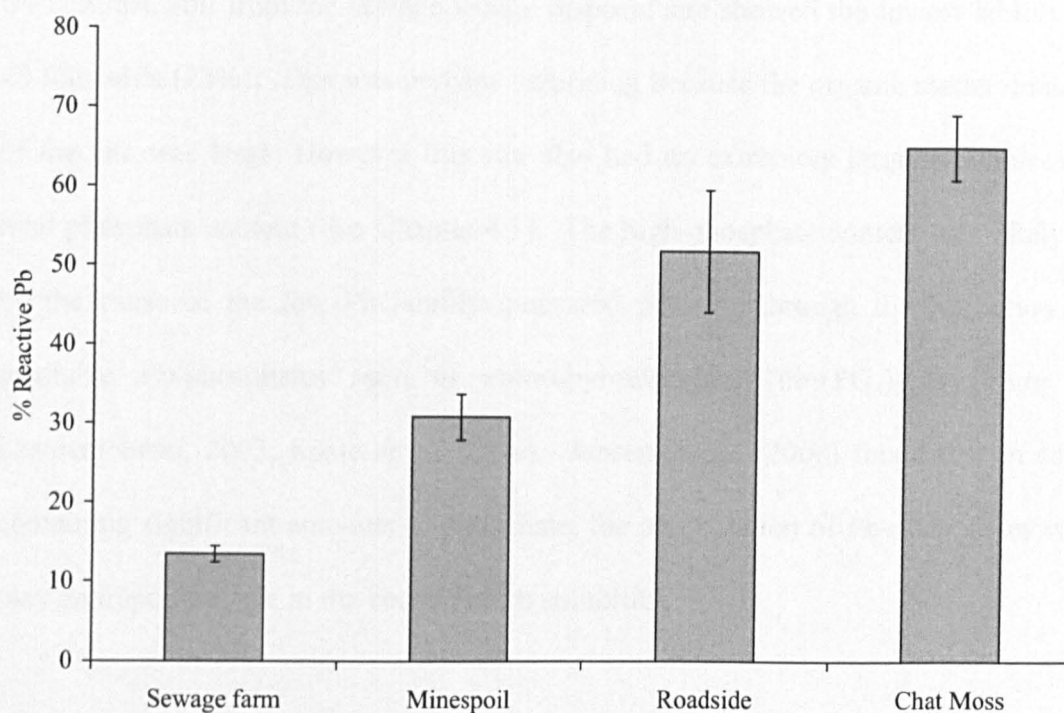


Figure 4.47: Labile Pb (%E) as % of total Pb concentration measured for all four soils after 3 days post-spike equilibration period and 0.0005 M EDTA suspending electrolyte. Error bars show standard error of three replicates.

The Chat Moss soil had a varied contamination source of municipal waste, and was characterised by an exceptionally high organic matter content (61.5%) originating partly from waste disposal (e.g. 19th Century night soil) and also from the underlying peat into which the waste materials were incorporated. It is likely that the high organic matter content was the principle cause of the high lability of Pb in this soil (65%) with dissolved organic matter able to bring Pb into solution. It is well known that Pb strongly binds to organic matter (Jensen *et al.*, 2006; Kaste *et al.*, 2006; McBride *et al.*, 1997), but sorption on humus is unlikely to lead to physical occlusion as would be expected in Pb compounds such as chloropyromorphite, or within the matrix of Fe hydrous oxides.

By contrast, soil from the sewage sludge disposal site showed the lowest lability of all four soils (13%). This was perhaps surprising because the organic matter content of the site was large. However this site also had an extremely large available and total phosphate content (See Chapter 4.3). The high phosphate content was likely to be the cause of the low Pb lability measured possibly through the formation of insoluble Pb-phosphates such as chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) (Lang & Kaupenjohann, 2003; Kaste *et al.*, 2006). Jensen *et al.*, (2006) found that in soils containing significant amounts of phosphate, the precipitation of Pb-phosphates will play an important role in the control of Pb solubility.

The Pb lability measured in Minespoil soil was most likely to be affected by the original form of the contamination. Pb mineralisation in the Derbyshire region is in the form of galena (PbS), cerrusite (PbCO_3) and pyromorphites, which can all be stable forms of Pb depending on soil conditions (Jensen *et al.*, 2006). Through sequential extractions, Li & Thornton (2001) showed that Pb in soils from old Derbyshire mining sites is predominantly associated with the carbonate phase, and that thermodynamic predictions identify cerrusite as the dominant Pb mineral. Nevertheless, despite an extremely large Pb content, calcareous nature and high pH the lability of Pb in the Minespoil soil was surprisingly high, at 30%, suggesting that substantial re-adsorption on humus and other colloidal phases had occurred.

The isotopic exchangeability of Pb in the Roadside soil was 52% of the total Pb content. For this soil, the original form of the Pb contamination was probably not important in determining lability. PbO particles emitted from car exhausts would be expected to dissolve on contact with soil and immediately sorb on Fe hydrous oxides

and humus, as other studies have shown that petrol-derived Pb has a strong affinity for Fe oxides in roadside soils (Teutsch *et al.*, 2001). Once adsorbed the Pb could be slowly fixed through processes such as redox cycling (Contin *et al.*, 2007) and occlusion or solid phase diffusion. The level of lability determined (52%) was therefore mainly a product of prevailing soil characteristics and conditions.

The ^{204}Pb isotope dilution method developed here was reliable for all four soils, which represent a range of conditions including Pb concentration, form of contamination, organic matter and phosphate content. The spike concentration needs to be considered based on total Pb content, although for these four soils a spike concentration of 57 mg L^{-1} total Pb was sufficient. This represented a ^{204}Pb enrichment of 1200% for Chat Moss, 837% for Sewage farm, 1760% for the Roadside soil and 30% for Minespoil. The results obtained here were comparable to those obtained by Degryse *et al.*, (2007), who recorded a range of Pb lability from 45 to 78% in field contaminated soils using a ^{208}Pb spike. Tongtavee *et al.*, (2005) also recorded lability of 57% in smelter contaminated soils using a ^{207}Pb spike. These results show that Pb is labile to a greater extent than previously thought, which may have implications for environmental risk assessments where Pb is considered to be immobile in soil horizons. The results shown here may also suggest that phosphate is the best way to immobilise Pb in soils, as shown by the Sewage farm soil (lability of 13%, total phosphate 9540 mg kg^{-1}).

4.4.4 Conclusions

A lead stable isotope dilution method using ^{204}Pb was developed and tested on four soils, with different Pb contamination levels and histories, as well as varying soil

characteristics such as organic matter content and phosphate levels. The method development involved testing the electrolyte concentration and the post-spike equilibration time. The most effective electrolyte concentration was found to be 0.0005 M EDTA, and a post-spike equilibration time of 3 days was determined to be suitable. 0.05 M EDTA was found to mobilise 100% of the total soil Pb. Lability for the four soils was measured using the developed method, and ranged from 13% of total soil Pb (Sewage farm) to 65% (Chat Moss). Lability in these soils was controlled by organic matter and phosphate content, as well as the original form of the contamination.

The high lability in the Chat Moss soil was surprising as the dominant Pb-bearing waste constituent of the soil was assumed to be mineral wastes such as steelworks waste and organic waste such as coal. These forms of waste would most likely be resistant to weathering, and so the lead would be expected to be fixed and not labile. The acidity of the soils and high organic matter content may have caused the Pb to be weathered out and bound with the organic matter. This would correspond with the sequential extractions, which showed that the organic phase was the dominant Pb-bearing phase in the Chat Moss soils. The results of the sequential extraction and stable isotope dilution of the four soils are summarised in Table 4.4, and by comparing the percentage of labile Pb to the percentage of Pb in each fraction, the phases contributing to the labile Pb can be predicted. For example, the sum of the first four fractions (exchangeable, carbonate, Fe/Mn oxide and organic bound) for the Chat Moss soil was 71.9%, which was only slightly outside the estimate of labile Pb using stable isotope dilution, indicating that all four of these fractions contributed labile Pb. However for the Sewage farm soil, 99% of Pb was measured in the

residual fraction, and while the Pb lability was low (13.5%) this would assume that some of the Pb was liberated from the residual phase.

Table 4.4: Summary of labile Pb and Pb fractionation for the four study soils, expressed as % of total Pb.

	Lability (% of total)	Exchangeable (% of total)	Carbonate- bound (% of total)	Fe/Mn oxide bound (% of total)	Organic- bound (% of total)	Residual (% of total)
Chat Moss	65.3 ± 4	1.42	6.35	23.0	41.0	28.1
Sewage farm	13.5 ± 1	0.00	0.19	1.86	0.00	99.0
Minespoil	30.8 ± 3	1.75	19.4	33.4	20.3	25.2
Roadside	52 ± 8	0.07	6.28	57.2	15.1	21.4

4.5 Conclusions

It was assumed from historical research that the contamination on Chat Moss would be derived from urban and industrial waste. Using lead isotope source apportionment it was determined that the most likely source of lead contamination was a mixture of UK lead ore, UK coal and petrol-derived lead. The identification of UK ore and coal as dominant sources was in agreement with the historical research, and indicative of industrial and urban waste disposal. Scanning Electron Microscopy also confirmed urban and industrial waste as dominant sources of the contamination, with coal, slag and Fe oxide particles all identified within the soil. Pottery fragments were also identified and the glazes analysed for Pb content, which showed that the

glazes were composed of up to 50% lead, but that minimal degradation of the glazes had occurred.

Following the identification of the source of contamination on Chat Moss, the properties of the contaminant metals were studied using sequential extractions, to investigate the association of the metals with soil components and provide an assessment of the potential mobility of the metals. Two methods were compared for the sequential extractions, a modified Tessier scheme (Li & Thornton, 2001) and a scheme developed for organic soils (Breward *et al.*, 1996). Initially these sequential extractions were carried out on contaminated and control soils from Chat Moss, sites CM-3 and CM-1 respectively. This was to investigate whether there was a difference in metal behaviour induced by the waste disposal. It was found that many elements showed the same fractionation for contaminated and control soils, suggesting that either the metals were derived from a common source (e.g. atmospheric contamination) or that the common soil properties dictated the fractionation more than the original form of the metal. This was further investigated through applying sequential extractions to four soils of different contamination histories and soil properties. There were some metals that showed differences in fractionation between the contaminated (CM-3) and control (CM-1) soils, and there were two key differences identified. The first was an increased partitioning into the exchangeable fraction in the control soil, which was seen for Mn, Co, Zn, and Cd. This was attributed to the lower pH of the control soil (5 as opposed to 6.03) causing increased solubilisation of the metals, and so increasing the fractionation into the exchangeable phase. The second difference identified was increased partitioning into the residual phase in the contaminated soil, and this was seen with Sr, Ni, Mo and

Pb. This was attributed to the incorporation of waste into the contaminated soil, which would most likely have contained elements in a phase resistant to weathering, such as furnace slag, which would result in an increased fractionation into the residual phase.

Through studying four soils of varying contamination histories and soil properties to assess the extent to which soil properties dictated fractionation, it was found that organic matter and Fe/Mn oxides were the main factors controlling metal fractionation in all four soils. It was found for some metals (Ti, Mn, Fe, Cu, Se, Sn, Cs and Ba) that the fractionation was the same irrespective of soil type or contamination source, which indicated that for these metals the nature of the metal was more important in controlling fractionation than soil characteristics or contamination source.

Sequential extractions showed that no metals with the exception of Cd, Mo, Sr and Zn were present in the exchangeable fraction to any great amount, which suggested that the mobility of the metals would be limited. To further study the mobility, or lability, of lead, an isotope dilution experiment was developed. This involved the development of a method using ^{204}Pb to investigate the lability of Pb. The method development involved the testing of the suspending electrolyte and post-spike equilibration times to determine the optimum conditions for the analysis. The method was then used to study the lability of Pb in the four soils used for the sequential extractions. During the method development phase, it was determined that 0.0005 M EDTA was the optimum electrolyte as it caused the greatest solubilisation of Pb without affecting non-labile Pb. The optimum post-spike

equilibration period was found to be 2-4 days, and for the analysis, a 3 day post-spike equilibration period was chosen. Lability measurement showed that Pb lability was strongly dependent on soil conditions. In the Sewage farm soil where there was a high phosphate content the lability was very low (~13%) due to the high Pb-phosphate bonding capacity (Jensen *et al.*, 2006) whereas in the Chat Moss soil with a large organic matter content lability was measured as 65.3%, possibly due to large amounts of dissolved organic matter. These results showed that lead, which was commonly thought to be highly immobile in soils, can show significant lability, with measured lability for the soils ranging from 13.5% to 65.3%. This was in agreement with Tongtavee *et al.*, (2005) and Degryse *et al.*, (2007) who also measured lead lability as 57% and 45-78%, showing that lead is more mobile than previously considered.

Having shown that lead is potentially mobile in the Chat Moss soils, it was important to understand how changing soil conditions could affect this and other metals, through flooding and anaerobic soil conditions. As Chat Moss was developed from wetland soils, there would be a strong possibility for flooding events causing soil reduction. As sequential extractions showed that most metals were bound to Fe/Mn oxides or organic matter, which can be affected by changes in redox potential and pH, there is a strong possibility that flooding events could affect the mobility of metals in these Chat Moss soils. This was studied through the use of incubation experiments to simulate flooding events and impose redox and pH changes on the soil system (Chapter 5).

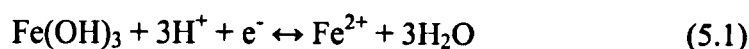
Chapter 5:

Mobilisation of metals in Chat Moss soil under anaerobic conditions

5.1 Introduction

The soils on Chat Moss were developed from drained wetland soils (Chapter 1.2.1.2), and as such have the potential to undergo periodic waterlogging due to events such as increased rainfall or impaired drainage. Site CM-3 on Chat Moss is located at 53°28'06 N and 2°24'48 W at an elevation of 26 m. There is currently no flood risk on Chat Moss as assessed by the Environment Agency, and water table levels observed during sampling fluctuated between 90 cm to greater than 1 m deep, also indicating a low risk of flooding. Current annual rainfall is 807 mm, however climate change predictions indicate that by 2050, while the annual rainfall for the NW England will decrease by 11 mm, the average winter rainfall will increase by 43 mm (Met. Office, 2009), suggesting more intense periods of rainfall, which could be expected to lead to saturation of the soils on Chat Moss. As wetland soils become saturated, the redox potential decreases and pH often increases, whereas under drought conditions the soils become more oxidised and the pH becomes more acidic. It has been shown that under drought conditions, wetland soils can become acidified due to the oxidation of sulphur contained within the peat to sulphuric acid (Tipping *et al.*, 2003). This can lead to the release of trace metals contained within the peat as the binding strength of metals adsorbed to organic matter decreases as pH decreases. In this way fluctuating pH, partly caused by changes in aeration, can be an important control on the mobility of metals within wetland soils. Under anaerobic conditions,

there are several processes which can affect pH change, for example the reduction of Fe oxides will consume H^+ ions and increase the pH, as in the reduction half-reaction shown in Equation (5.1).



However, in wet soils there will also be a build up of CO_2 through microbial respiration, and this can have the contradictory effect of reducing pH through the generation of H^+ through hydrolysis of CO_2 to HCO_3^- (Equation 5.2).



Soil pH can affect metal solubility through changes induced by reductive dissolution, organic acid formation, CO_2 formation and carbonate precipitation (Charlatchka & Cambier, 2000). Soil pH is an important control on metal solubility, with cationic metals being more soluble at lower pH (Qureshi *et al.*, 2004) while oxy-acids such as molybdate, arsenate and selenite will be adsorbed more strongly at low pH. However in a study of metal solubility in contaminated soils, Chuan *et al.*, (1996) found that whilst pH was the main factor controlling metal solubility, redox potential may also independently affect metal solubility. For example, under oxidising conditions, Fe and Mn oxyhydroxides within the peat act as sinks for trace metals. But as the soil becomes reduced under flooding conditions, these oxyhydroxides can undergo reductive dissolution, liberating any bound trace metals and metalloids (Grybos *et al.*, 2007). In fact the reduction in soil redox potential can affect the release of metals to soil solution in at least three ways which are independent of

accompanying changes in soil pH: (i) by alteration of the redox state of the metal causing a change in adsorption affinity, as in As, Se, Cu, Cr and Fe and Mn (Chuan *et al.*, 1996; Ma & Dong, 2004; Grybos *et al.*, 2007); (ii) through the dissolution of Fe/Mn oxides hosting trace metals (Chuan *et al.*, 1996) and (iii) through increased competition for binding sites on organic matter and other soil components (Ma & Dong, 2004), principally from dissolved Fe^{2+} and Mn^{2+} .

Dissolved organic matter (DOC) content can also affect the solubility of metals, through the formation of stable soluble complexes of trace metals and DOC. It has been shown by sequential extraction procedures that organic matter can be a sink for trace metals (Chapter 4.3), and the dissolution of organic matter under increasing pH conditions can release these metals to solution, as well as through complexation of previously adsorbed metals. At lower pH values, the dependence of trace metal solubilisation on DOC is lessened due to the high degree of protonation of the DOC which will result in reduced binding strength with trace metals (Kalbitz & Wennrich, 1998). However, as pH increases under anaerobic conditions, organic matter becomes increasingly soluble and binds metal more strongly and thereby can bring more trace elements into solution. The increase in DOC accompanying pH increase is due to the deprotonation of hydroxyl groups at mineral surfaces which decreases the positive net surface charge and the increase in electronegativity of organic molecules. This causes humic acids to become more hydrophilic, and mineral surfaces and organic matter to repel each other, which releases DOC (Grybos *et al.*, 2007). A larger concentration of DOC also increases competition, for remaining adsorption sites on hydrous oxides, with anions such as arsenate/arsenite,

selenate/selenite, iodide and molybdate which again may help explain increased dissolution of these inorganic species.

In order to assess the potential risk of soil contamination to plants and the wider environment, the solubility and mobility of the contamination must be studied to understand the potential for metals to move into the soil solution and become bioavailable. If the metals move into solution then there is a possibility that they will be introduced to the groundwater and leached out of the soil, thereby contaminating the groundwater posing possible ecological risks. However if dissolved metals move down the soil profile into the peat layer, the high capacity of organic matter to bind metals (Alloway & Jackson, 1991) may immobilise the metals through complexation with insoluble organic matter in the peat. To understand the potential risk of mobilization of metals as a result of soil flooding, an incubation experiment was set up. This approach was primarily to investigate changes in solubility as a consequence of changes in redox potential, pH and DOC concentration. The objective was to simulate potential flooding of the soil through a rise in the water table, increased rainfall or inadequate soil drainage.

5.2 Materials and Methods

Four hundred grams of <2 mm sieved air dried topsoil collected from CM-3 in August 2006 was incubated with 1.2 L deionised water in 2 L PTFE bottles. Six soil suspensions were established, three of which had powdered straw added initially to simulate the enhancing effect of crop residues on the development of anaerobic conditions in wet autumns. The bottles were closed with screw-cap lids and sealed with 'Parafilm' to exclude oxygen. The bottles were kept sealed unless being

sampled. The experiment lasted for 21 weeks, with sampling at weekly intervals, with the soil suspensions stored in a controlled temperature room (21°C) and shaken at the beginning of the experiment and prior to each sampling.

Sampling was carried out by removing 20 ml of homogenised soil suspension followed by centrifuging at 2500 rpm and filtration to <0.2 µm. A 5 ml aliquot of solution was acidified with 0.2 ml 50% HNO₃ and 1 ml 0.001 M EDTA to stabilise any dissolved metals, especially ferrous and manganous ions. The filtered and stabilised solution was analysed for total metal content by ICPMS on the same day as sampling. The remaining 15 ml was kept unacidified and frozen until the end of the experiment when it was analysed for dissolved organic carbon content. At each sampling interval, pH and redox potential were measured following the method described in Chapter 2.

5.3 Results and Discussion

5.3.1 Changes in pH, redox potential (Eh) and dissolved organic carbon (DOC) concentration

Over the course of the experiment, there was a decrease in redox potential and an increase in pH for both the organically-amended and the control sets of samples (Figure 5.1 a and b). pH increased from 5.12 to 6.00 for the control samples and 6.17 for the organically amended samples. This was accompanied by an Eh decrease from 487 mV to 196 mV (control) and 164 mV (organically amended).

There was a strong relationship between the pH increase and Eh decrease ($R^2 = 0.925$ and 0.932) for both the control and organically-amended samples, suggesting a

common underlying cause. This trend is often seen as soils become progressively more anaerobic, as H^+ ions are consumed by reduction processes (Bartlett, 1999).

The control and organically amended samples showed no differences in pH or Eh until day 42 of the experiment, when the organically amended samples became more reduced than the control samples, and continue to undergo reduction at a greater rate. This may have been related to an increase in the release of dissolved organic carbon at this point, allowing an increase in microbial activity and so a greater reduction in the amount of oxygen in the soil.

Dissolved organic carbon (DOC) in the soil solution peaked in both the control and organically amended samples between days 42 and 84, and then gradually decreased (Figure 5.1 c). The peak DOC concentration for the control samples was 174 mg L^{-1} and for the organically amended samples the peak DOC concentration was 207 mg L^{-1} . The initial increase in DOC was much greater in the organically amended samples, with the peak DOC concentration reached after 42 days, whereas the control samples reach a peak DOC concentration after 84 days. The organically amended samples had a greater DOC concentration from the 14th day of the experiment, but DOC concentrations were initially the same for both the organically amended and control samples.

5.3.2 Changes in Fe/Mn oxide solubility with progressive reduction

Over the course of the experiment there was a steady increase in Fe solubility, with a larger increase in the soil subject to organic amendment. Iron concentration in solution increased from 0.281 mg L^{-1} to 22.3 mg L^{-1} for the control samples and 46.1

mg L⁻¹ for the organically amended samples (Figure 5.2 a). For both treatments Fe concentration increased steadily after 21 days until the end of the experiment after 147 days. Concentration of Fe showed a strong relationship with redox potential, with R² values of 0.790 (control) and 0.894 (organic amendment) (Figure 5.2 b). This is most likely due to the reductive dissolution of Fe oxides releasing Fe to soil solution, which has been seen in many studies (Chuan *et al.*, 1996; Ma & Dong, 2004; Grybos *et al.*, 2007; Pareuil *et al.*, 2008).

Manganese concentration in solution increased from 0.346 mg L⁻¹ to 1.08 mg L⁻¹ (control) and 1.88 mg L⁻¹ (organically amended) following a similar trend to that shown by Fe solubility (Figure 5.3 a). Correlations between Mn and Fe concentrations produced R² = 0.939 and 0.988 for control and organically amended samples respectively (Figure 5.3 b).

The offset shown in Figure 5.3 b is consistent with the earlier reductive dissolution of Mn oxides following the onset of anaerobic conditions. The magnitude of hydrous oxide dissolution under relatively mild reducing conditions (Eh = 150 – 200 mV) indicated that this could be an important mechanism for the release of trace metals to soil solution.

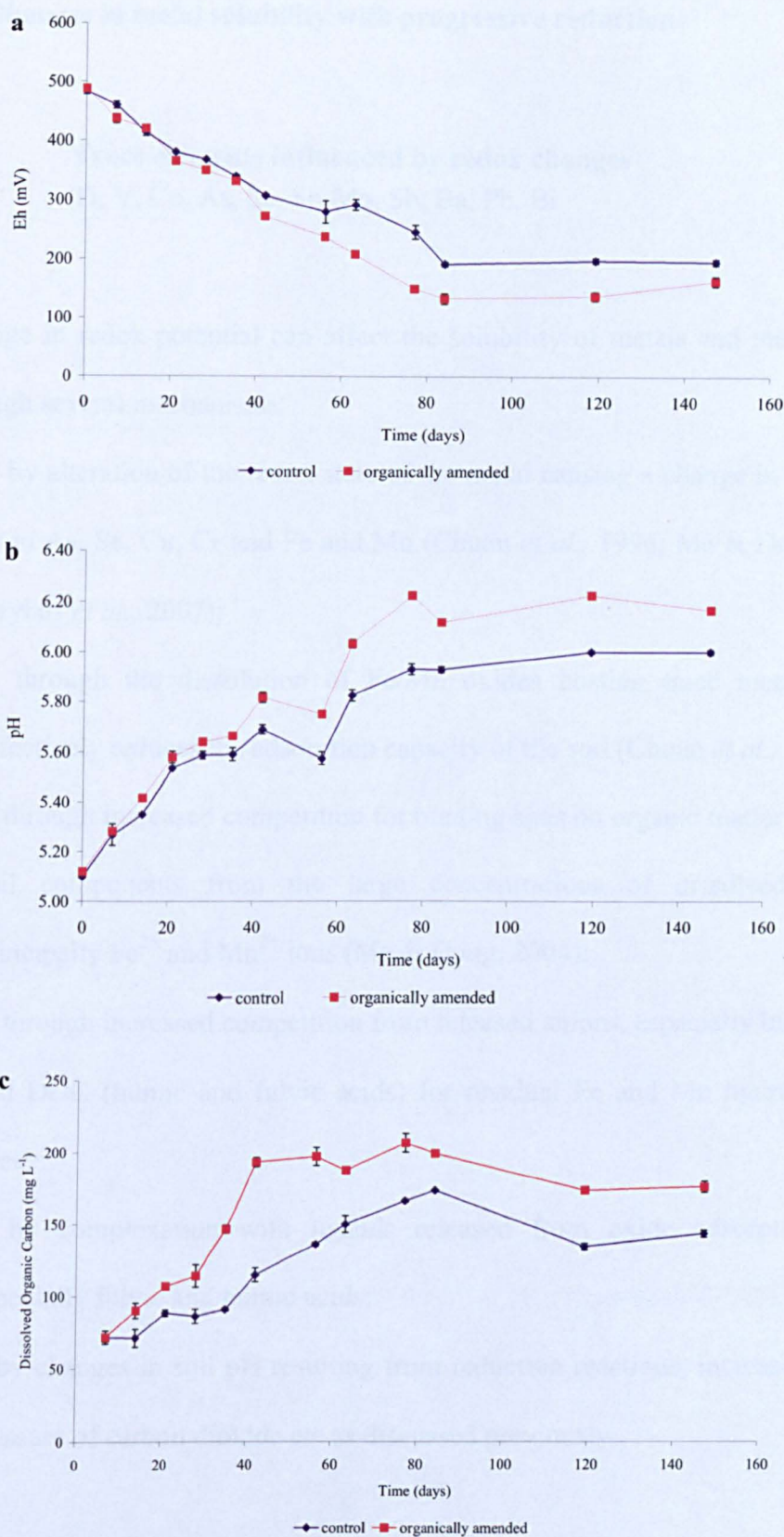


Figure 5.1: Changes in (a) redox potential, (b) pH value and (c) DOC with time 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without amendment with powdered straw. Error bars show standard error of three replicates.

5.3.3 Changes in metal solubility with progressive reduction

5.3.3.1 Trace elements influenced by redox changes

Ti, V, Co, As, Se, Sr, Mo, Sb, Ba, Pb, Bi

The change in redox potential can affect the solubility of metals and metalloids in soil through several mechanisms:

- a. by alteration of the redox state of the metal causing a change in solubility, as in As, Se, Cu, Cr and Fe and Mn (Chuan *et al.*, 1996; Ma & Dong, 2004; Grybos *et al.*, 2007);
- b. through the dissolution of Fe/Mn oxides hosting trace metals which effectively reduces the adsorption capacity of the soil (Chuan *et al.*, 1996);
- c. through increased competition for binding sites on organic matter and other soil components from the large concentrations of dissolved cations, principally Fe^{2+} and Mn^{2+} ions (Ma & Dong, 2004);
- d. through increased competition from released anions, especially bicarbonate and DOC (humic and fulvic acids) for residual Fe and Mn hydrous oxide sites;
- e. by complexation with ligands released from oxide adsorption sites, especially fulvic and humic acids;
- f. by changes in soil pH resulting from reduction reactions, increased partial pressure of carbon dioxide etc as discussed previously

For both experimental conditions (control and amended with organic matter), the release of Co, As, Sb and Mo to soil solution was found to have a strong relationship with redox potential. Regressions of metal concentration in solution against redox

potential, dissolved organic carbon content and Fe content in soil solution, for the elements above, were found to have the strongest relationships with either redox potential or Fe concentration. It could be suggested that those elements that had the strongest relationship with Fe concentration in soil solution were bound to Fe oxides and released by Fe oxide reductive dissolution, whereas those elements that showed the strongest relationship with redox potential were redox sensitive elements. However, simple regression cannot decouple the covariance of Eh value and Fe or Mn concentration in solution in the current experiment.

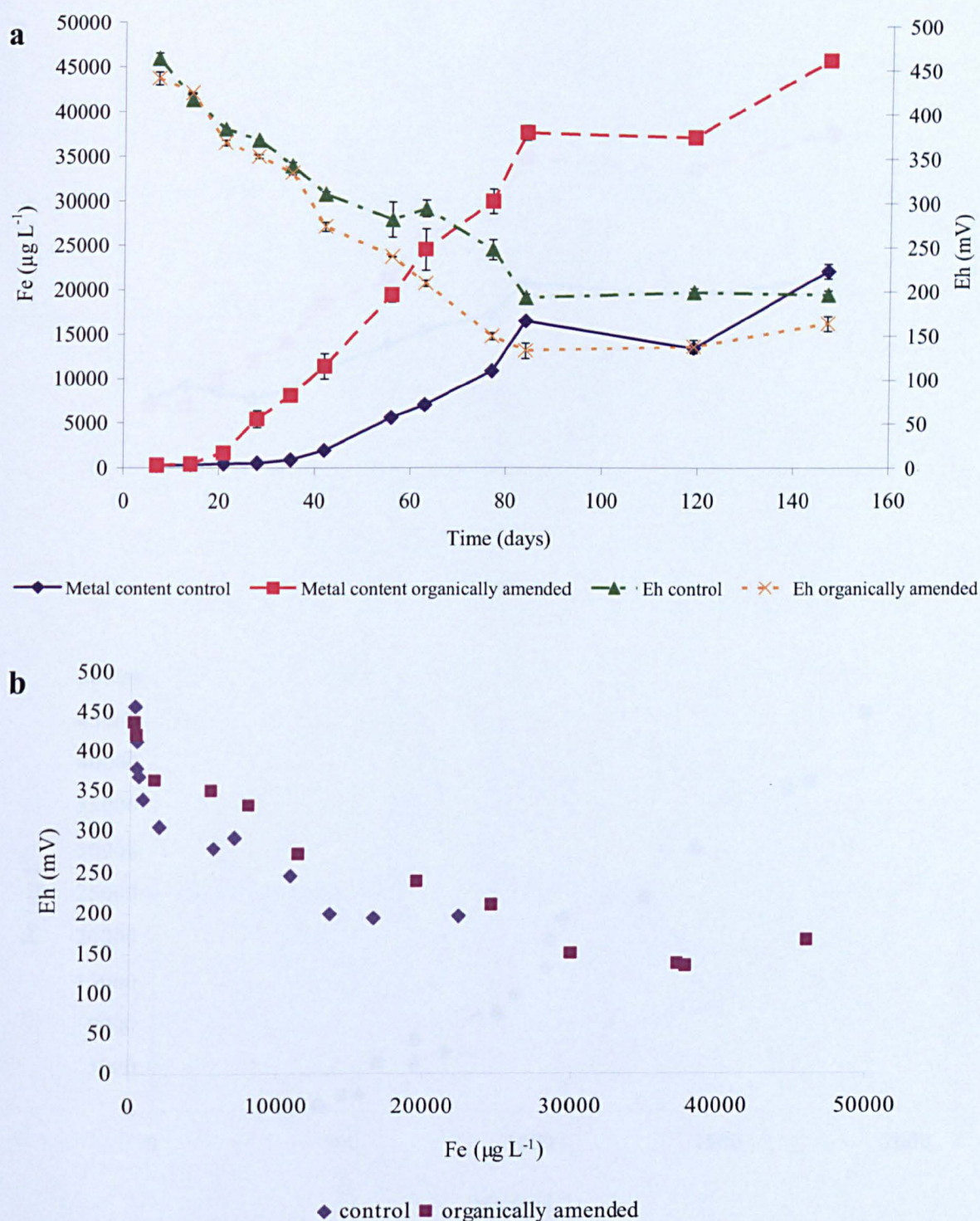


Figure 5.2: Changes in Fe concentration (a) with time and (b) as a function of Eh ($R^2 = 0.79$ control, 0.894 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates

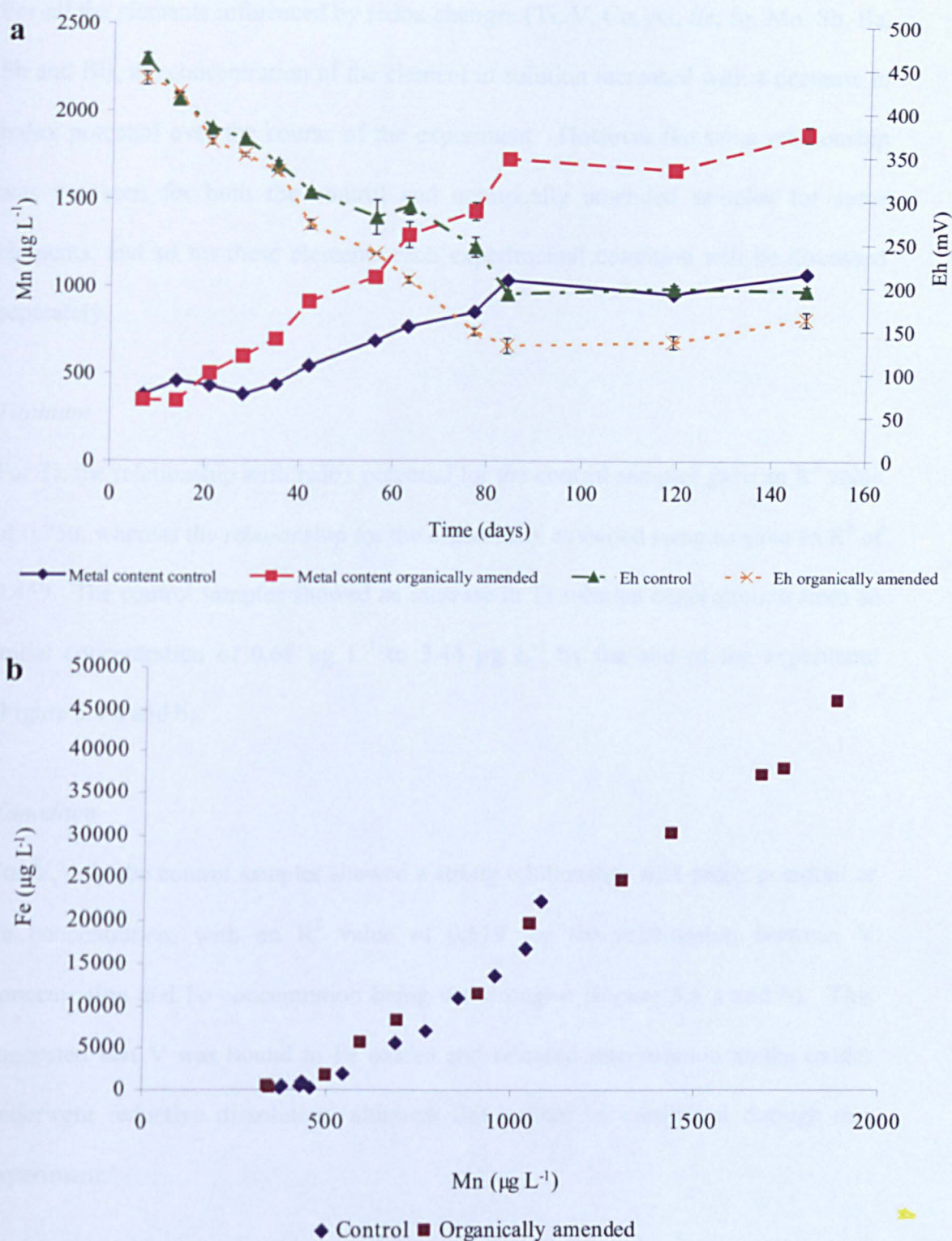


Figure 5.3: Changes in Mn concentration (a) with time and (b) as a function of Fe concentration ($R^2 = 0.939$ control and 0.988 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

For all the elements influenced by redox changes (Ti, V, Co, As, Se, Sr, Mo, Sb, Ba, Pb and Bi), the concentration of the element in solution increased with a decrease in redox potential over the course of the experiment. However the same relationship was not seen for both the control and organically amended samples for some elements, and so for these elements each experimental condition will be discussed separately.

Titanium

For Ti, the relationship with redox potential for the control samples gave an R^2 value of 0.750, whereas the relationship for the organically amended samples gave an R^2 of 0.459. The control samples showed an increase in Ti solution concentration from an initial concentration of $0.68 \mu\text{g L}^{-1}$ to $3.44 \mu\text{g L}^{-1}$ by the end of the experiment (Figure 5.4 a and b).

Vanadium

For V, only the control samples showed a strong relationship with redox potential or Fe concentration, with an R^2 value of 0.619 for the relationship between V concentration and Fe concentration being the strongest (Figure 5.5 a and b). This suggested that V was bound to Fe oxides and released into solution as the oxides underwent reductive dissolution, although this cannot be confirmed through this experiment.

Cobalt

For Co, both experimental conditions showed strong relationships with redox potential, with R^2 values of 0.949 for the control samples and 0.891 for the organically amended samples, and an increase in Co concentration from $2.89 \mu\text{g L}^{-1}$

to $10.43 \mu\text{g L}^{-1}$ (control) and $15.80 \mu\text{g L}^{-1}$ (organically amended) (Figure 5.6 a and b). This strong relationship of Co to redox potential indicated that Co was strongly influenced by Fe oxide chemistry, either through competition with Fe ions or through dissolution of oxides hosting Co. This is in agreement with the results of Grybos *et al.*, (2007), who found that Co was strongly controlled by Fe oxyhydroxides, as well as the results of sequential extractions of this soil (Chapter 4.3), where it was found that up to 71% of Co was in the Fe/Mn oxide and residual fractions combined, with the remaining Co mainly in the organic fraction. This is also in agreement with Grybos *et al.*, (2007) who found that 72% of the Co mobilised under reducing conditions was due to Fe oxyhydroxide reduction and 28% was due to organic matter mobilisation.

Arsenic

Arsenic showed strong relationships with redox potential (organically amended samples) and Fe solution concentration (control samples), with R^2 values of 0.868 and 0.821 respectively. The concentration of As increased from $7.49 \mu\text{g L}^{-1}$ at the start of the experiment to $143.8 \mu\text{g L}^{-1}$ (control) and $251.5 \mu\text{g L}^{-1}$ (organically amended), with a peak concentration of $308 \mu\text{g L}^{-1}$ in the organically amended samples (Figure 5.7 a, b and c).

The relationship with redox potential and Fe concentration indicated that As solubility is controlled by redox potential, although the exact mechanisms for this cannot be determined. It is known that As is strongly adsorbed to iron oxides (Hartley *et al.*, 2004), and that As can be reduced from As (V) to soluble As (III) (Ma & Dong, 2004). It has also been found that As solubilisation increases as pH increases (Hartley *et al.*, 2004), however this may be due to reduction accompanying

the pH increase so it is difficult to separate these effects. Using Geochemists Workbench (Table 5.1), the speciation of As under different Eh and pH conditions was simulated (Figure 5.8), and it was observed that there was a potential change in As speciation from arsenate to more soluble arsenite. However As solution concentration began to increase when the redox potential was ~370 mV, and as seen from Figure 5.8, the pH values in this experiment were not low enough to allow reduction of arsenate at this Eh value. This would indicate that the mechanism of initial As solubilisation was release from Fe/Mn oxyhydroxides, with reduction to arsenite becoming a factor towards the end of the experiment, when the decreased Eh and increased pH would allow this reduction. The shallower trend at the start of the experiment shown in Figure 5.7 b suggests the opposite as As solubility is increasing with minimal release of Fe but this may be due to the rapid increase in pH and (anionic) DOC at the start of the anaerobic incubation (Fig. 5.1 b and c). Using Geochemist Workbench it was also predicted that solid phases such as orpiment could be produced under reducing conditions. However the redox and pH conditions of the experiment were insufficiently reducing to precipitate the solid phase as predicted by Geochemist Workbench.

Selenium.

Selenium showed a strong relationship with redox potential for the control sample ($R^2 = 0.899$) but not the organically amended samples. The strong relationship with redox potential is as expected as Se has complex redox chemistry in soils (Chuan *et al.*, 1996). The Se concentration in the control samples increased from $0.48 \mu\text{g L}^{-1}$ to $2.22 \mu\text{g L}^{-1}$ over the course of the experiment (Figure 5.9 a and b). Using Geochemists Workbench, the speciation of Se was predicted, and it was found that

for all Eh and pH values found in this experiment, there should have been no change in Se speciation, with selenite (HSeO_3^-) being the only stable species. This would indicate that Se solubility was dominated by reductive dissolution of Fe/Mn oxyhydroxides and/or competition for binding sites with other anions (HCO_3^- and DOC).

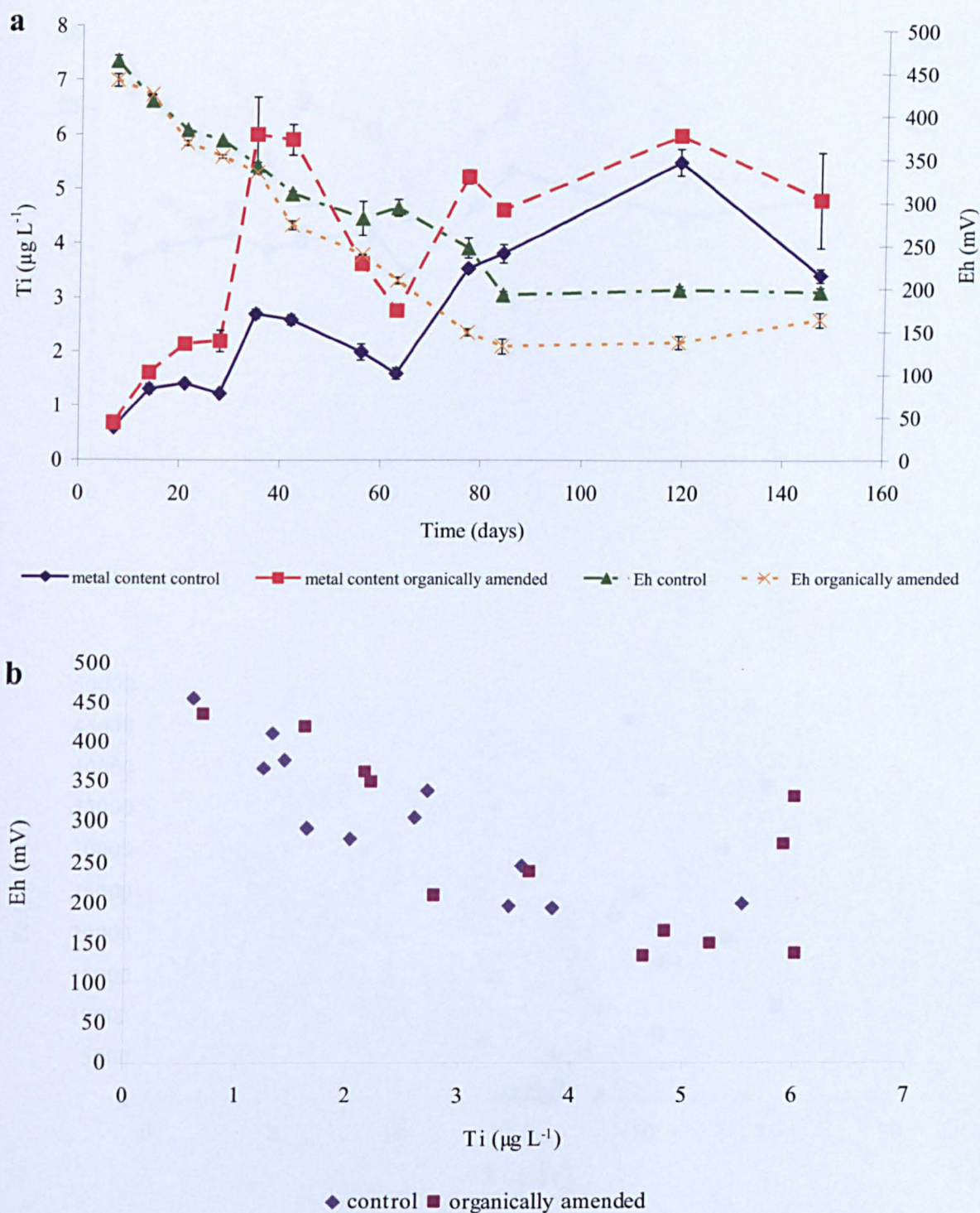


Figure 5.4: Changes in Ti concentration (a) with time and (b) as a function of redox potential ($R^2 = 0.750$ control and 0.459 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

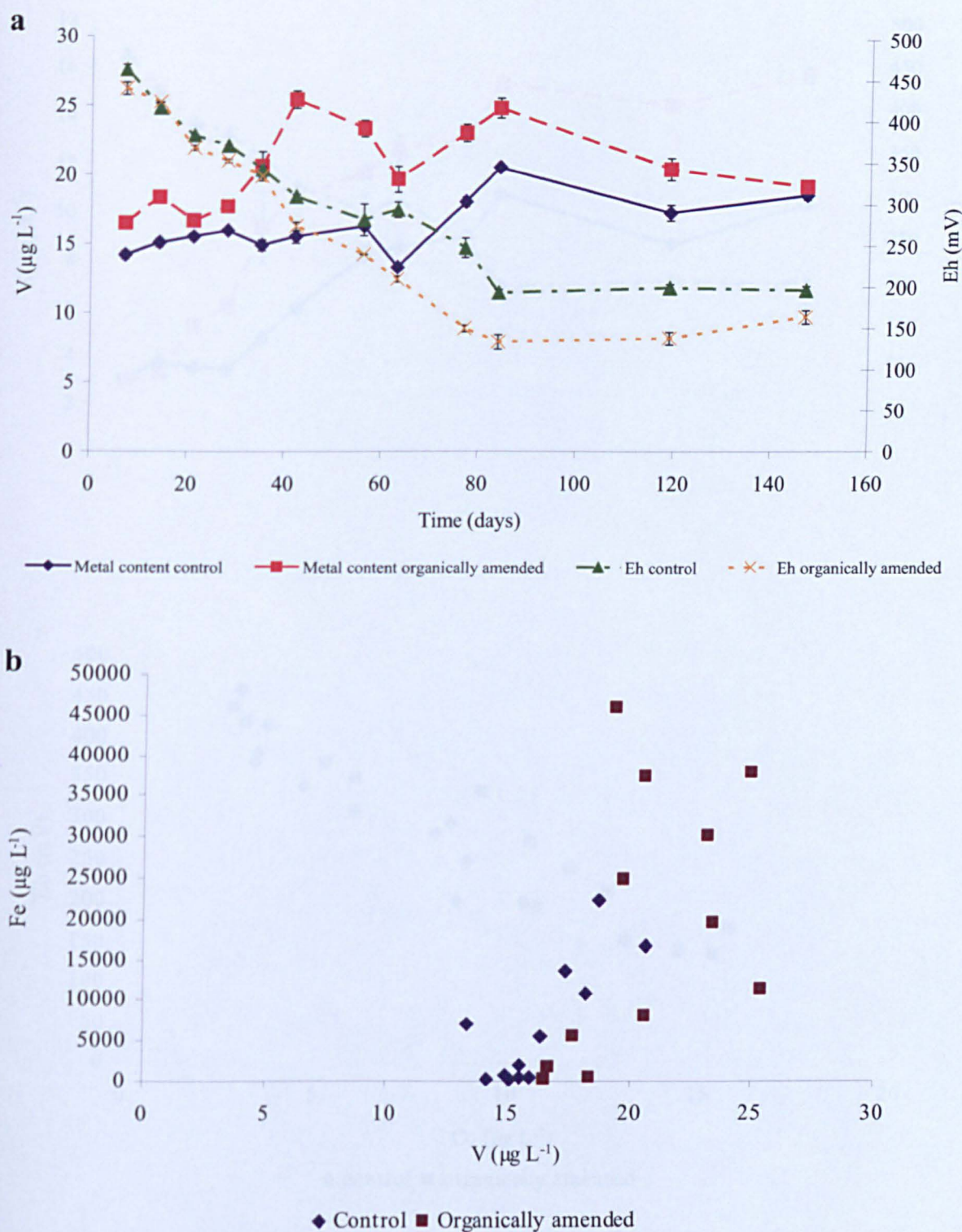


Figure 5.5: Changes in V concentration (a) with time and (b) as a function of Fe concentration ($R^2 = 0.619$ control) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

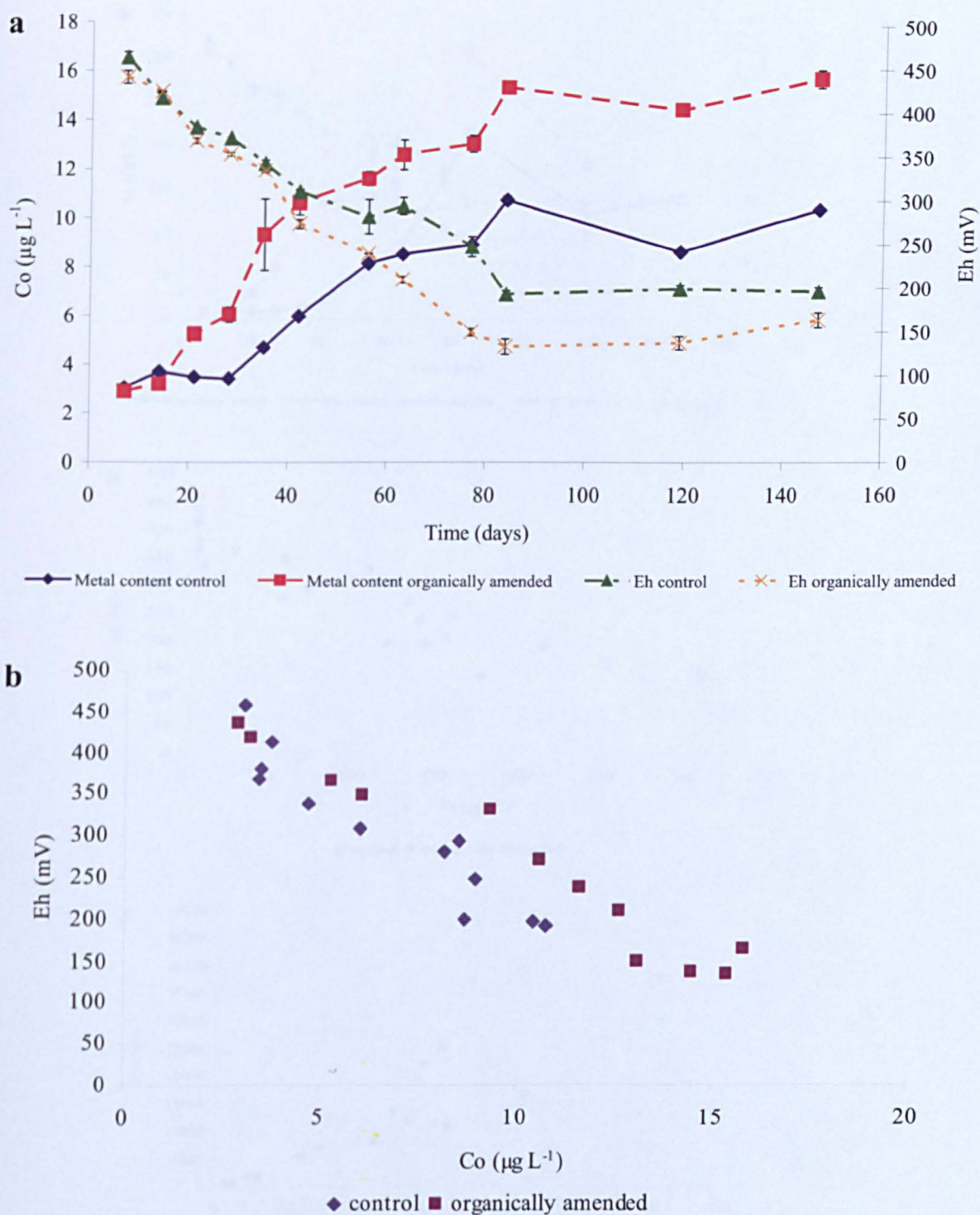


Figure 5.6: Changes in Co concentration (a) with time and (b) as a function of redox potential (0.949 control and 0.891 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

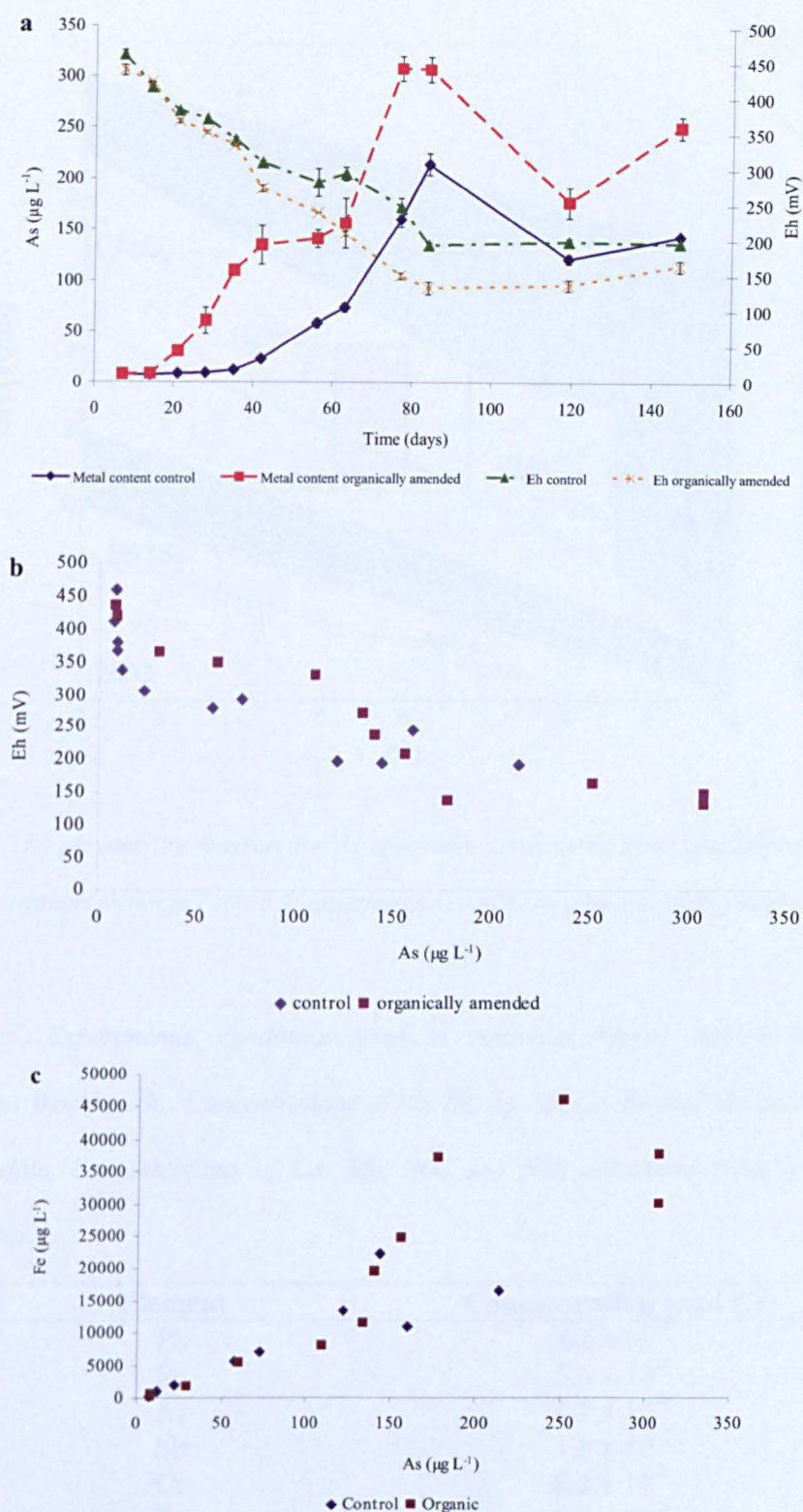


Figure 5.7: Changes in As concentration (a) with time, (b) as a function of redox potential ($R^2 = 0.868$ organically amended) and (c) as a function of Fe concentration ($R^2 = 0.821$ control) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

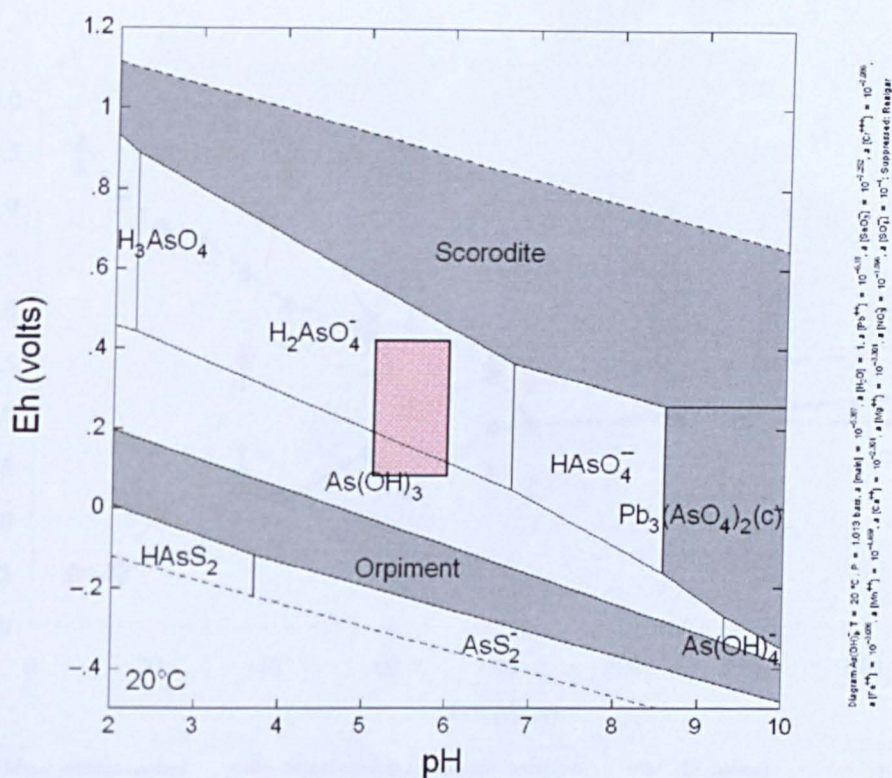


Figure 5.8: Eh-pH stability diagram for As speciation constructed from Geochemists Workbench assuming conditions shown in Table 5.1; experimental conditions shown in highlighted area.

Table 5.1: Experimental conditions used to construct Eh-pH stability diagram in Geochemists Workbench. Concentrations of Pb, Se, As, Sb, Cr, Fe and Mn calculated from measured data, concentrations of Ca, Mg, SO_4 and NO_3 calculated from assumed soil concentrations.

Element	Concentration (mol/L)
Pb	6.6×10^{-7}
Se	5.6×10^{-8}
As	4.1×10^{-6}
Sb	1.6×10^{-7}
Cr	8.2×10^{-8}
Fe	8.2×10^{-4}
Mn	3.4×10^{-5}
Ca	5×10^{-3}
Mg	5×10^{-4}
NO_3	1.27×10^{-2}
SO_4	1×10^{-4}

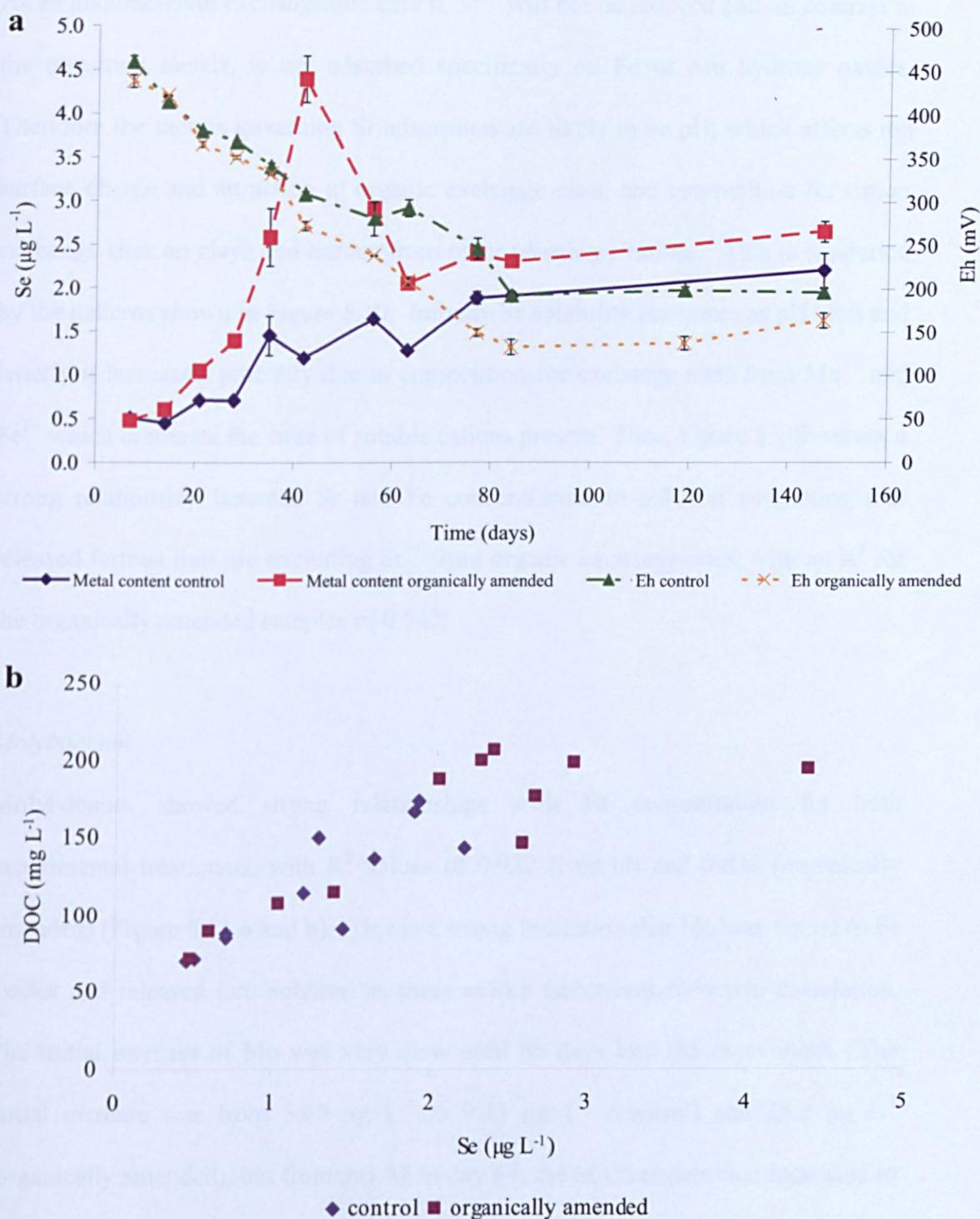


Figure 5.9: Changes in Se concentration (a) with time and (b) as a function of redox potential ($R^2 = 0.899$ control) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

Strontium

As an alkaline-earth exchangeable cation, Sr^{2+} will not be reduced and, in contrast to the transition metals, is not adsorbed specifically on Fe or Mn hydrous oxides. Therefore the factors governing Sr adsorption are likely to be pH, which affects the surface charge and attraction to organic exchange sites, and competition for cation exchange sites on clays and humus from other (divalent) cations. This is supported by the patterns shown in Figure 5.10. Initially Sr solubility decreases as pH rises and latterly it increases, probably due to competition for exchange sites from Mn^{2+} and Fe^{2+} which dominate the suite of soluble cations present. Thus, Figure 5.10b shows a strong relationship between Sr and Fe concentration in solution suggesting that released ferrous ions are excluding Sr^{2+} from organic exchange sites, with an R^2 for the organically amended samples of 0.742.

Molybdenum

Molybdenum showed strong relationships with Fe concentration for both experimental treatments, with R^2 values of 0.922 (control) and 0.832 (organically amended) (Figure 5.11 a and b). This is a strong indication that Mo was bound to Fe oxides and released into solution as these oxides underwent reductive dissolution. The initial increase of Mo was very slow until 56 days into the experiment. The initial increase was from $3.63 \mu\text{g L}^{-1}$ to $9.73 \mu\text{g L}^{-1}$ (control) and $28.2 \mu\text{g L}^{-1}$ (organically amended), but from day 56 to day 84, the Mo concentration increased to $82.4 \mu\text{g L}^{-1}$ (control) and $170 \mu\text{g L}^{-1}$ (organically amended). After this peak the Mo concentration levelled off for the control samples, with a final concentration of $90.3 \mu\text{g L}^{-1}$, but for the organically amended samples there was a decrease in Mo concentration, with a final concentration of $130 \mu\text{g L}^{-1}$. In contrast to elements such

as arsenic, molybdate is the only stable form present under the experimental conditions, and release to solution will be governed mainly by Fe hydrous oxide dissolution, as well as pH changes and competition with other anions.

Antimony

Antimony showed relationships with redox potential (control samples) and Fe concentration (organically amended samples), with R^2 values of 0.706 and 0.869 respectively. There was an overall increase in Sb concentration from $6.94 \mu\text{g L}^{-1}$ to $10.6 \mu\text{g L}^{-1}$ for the control samples and $18.9 \mu\text{g L}^{-1}$ for the organically amended samples; the increase in Sb concentration was continuous throughout the experimental period (Figure 5.12 a, b and c).

Barium

For Ba, there was a significant relationship between the organically amended samples and redox potential ($R^2 = 0.790$), but for the control samples, there was no relationship with any investigated factors. The pattern of Ba solubilisation was very similar to that of Sr, which suggests that these elements have a similar affinity to soil components (Figure 5.13 a and b). This had also been seen in the sequential extractions, and Sr and Ba are often found in clay minerals and are likely to be adsorbed as exchangeable cations on humus in organic soils. It is likely therefore that the main mechanism governing Sr and Ba solubilisation was competitive exchange with Fe^{2+} or Mn^{2+} on clay and humus surfaces.

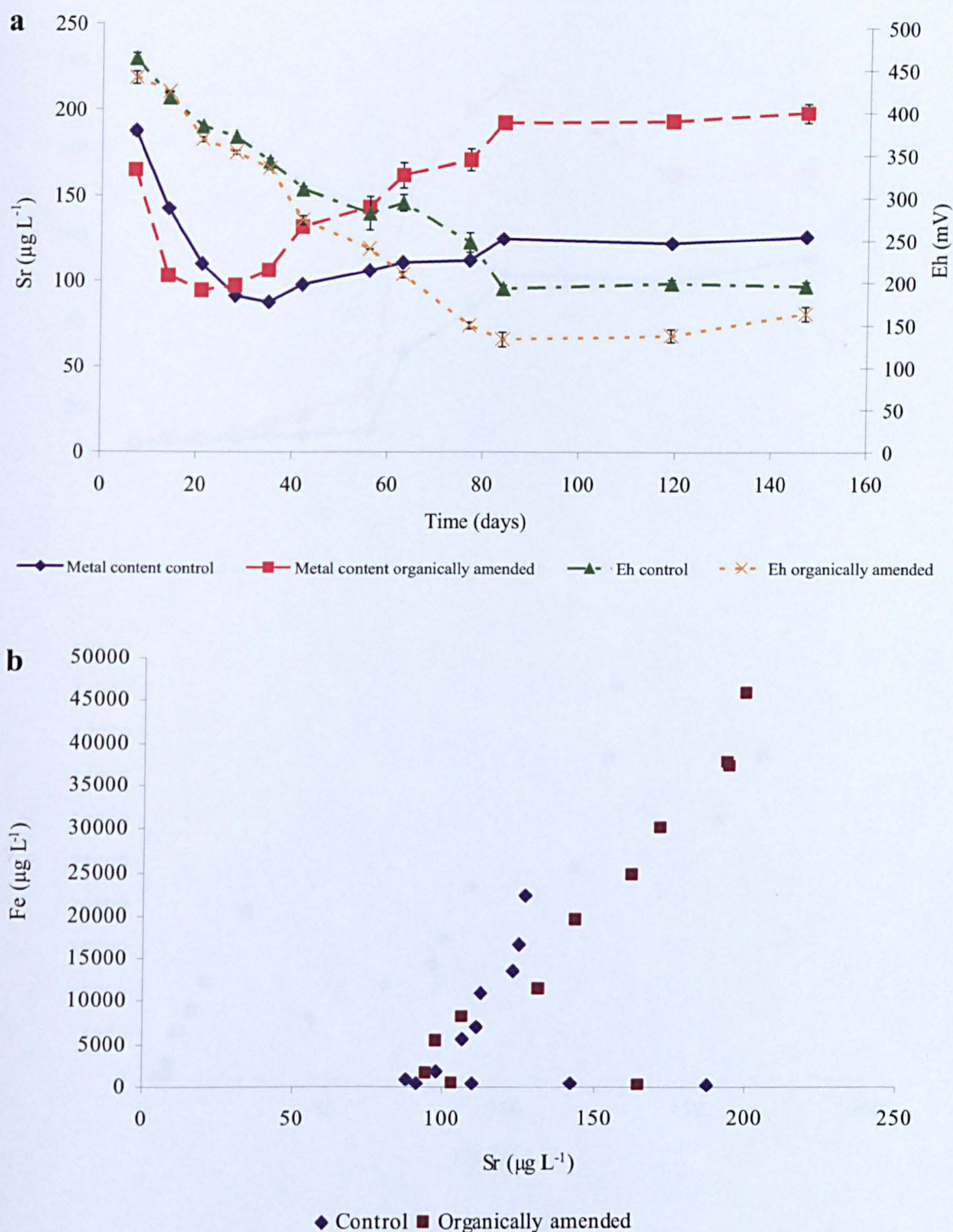


Figure 5.10: Changes in Sr concentration (a) with time and (b) as a function of Fe concentration ($R^2 = 0.742$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

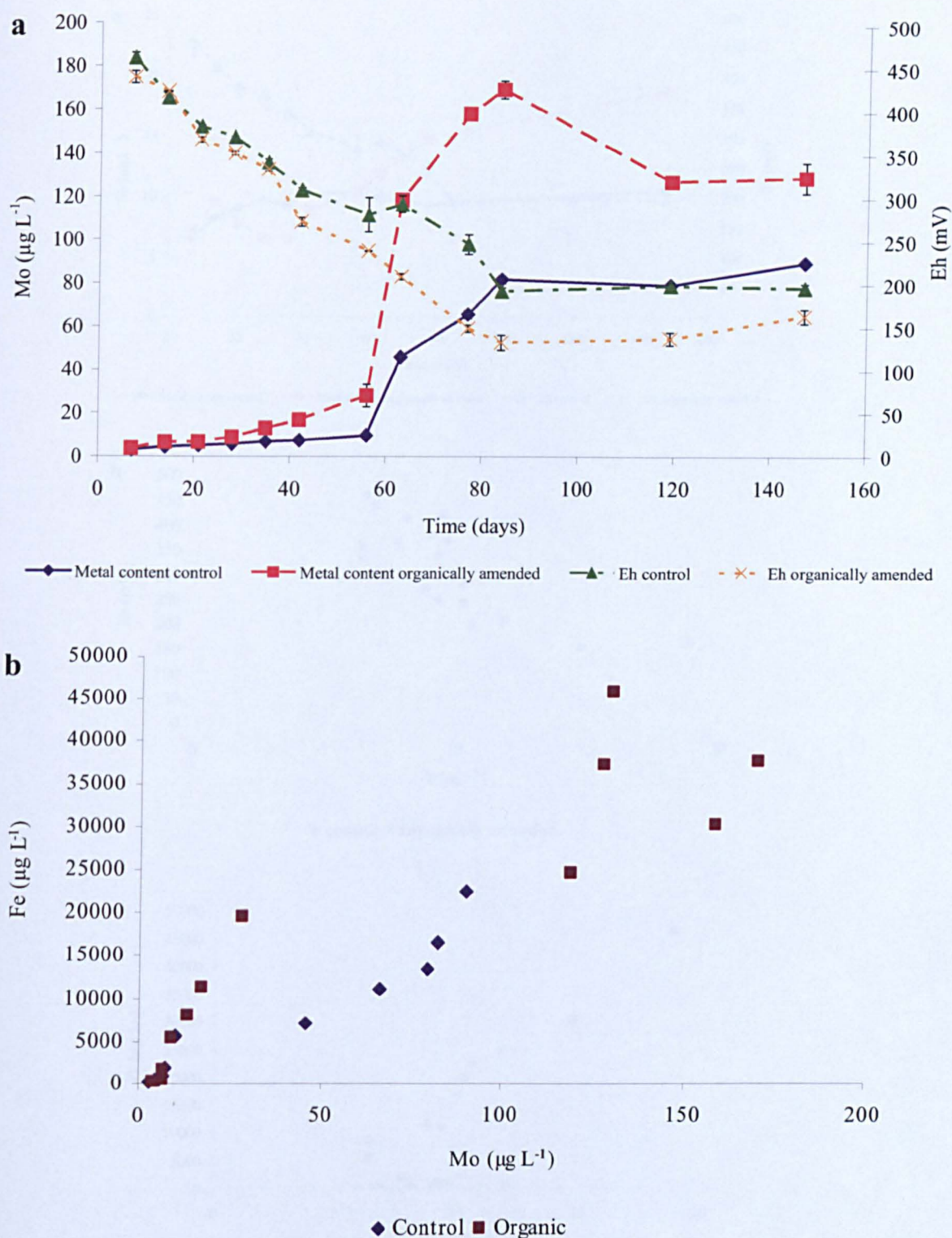


Figure 5.11: Changes in Mo concentration (a) with time and (b) as a function of Fe concentration ($R^2 = 0.922$ control and 0.832 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

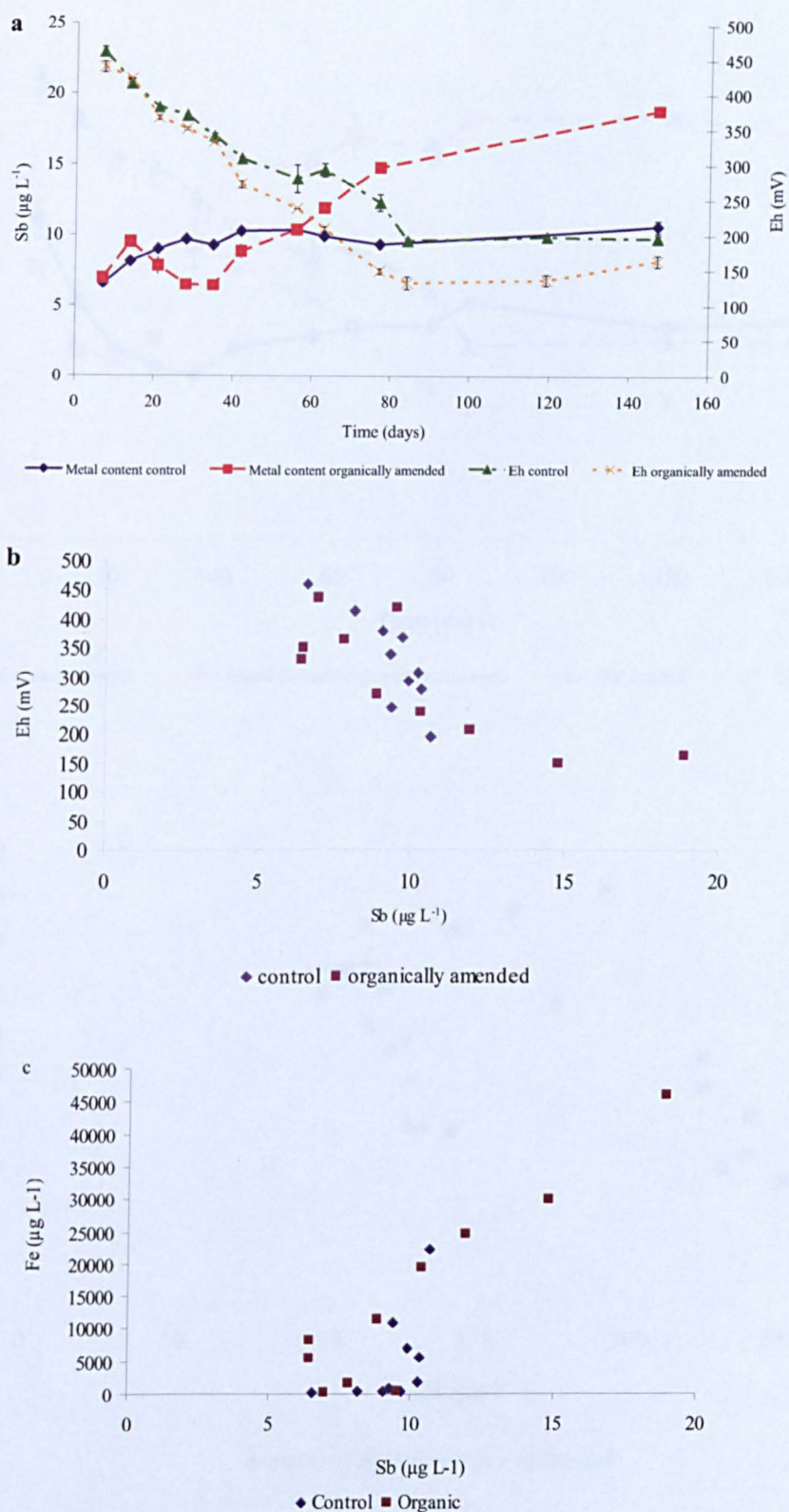


Figure 5.12: Changes in Sb concentration (a) with time, (b) as a function of redox potential ($R^2 = 0.706$ control) and (c) as a function of Fe concentration ($R^2 = 0.869$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

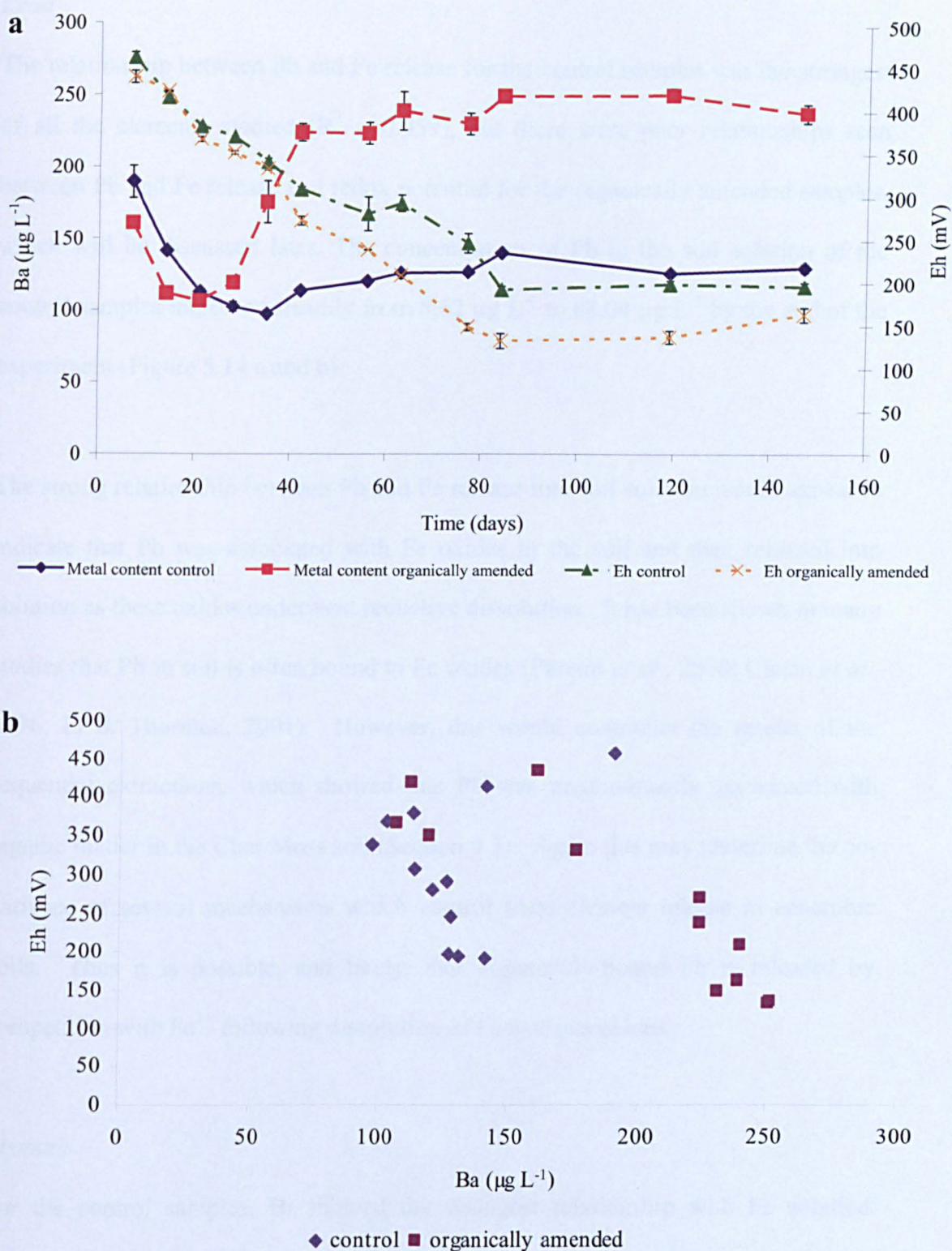


Figure 5.13: Changes in Ba concentration (a) with time and (b) as a function of redox potential ($R^2 = 0.790$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

Lead

The relationship between Pb and Fe release for the control samples was the strongest of all the elements studied ($R^2 = 0.959$), but there were poor relationships seen between Pb and Fe release and redox potential for the organically amended samples, which will be discussed later. The concentration of Pb in the soil solution of the control samples increased steadily from $8.62 \mu\text{g L}^{-1}$ to $88.04 \mu\text{g L}^{-1}$ by the end of the experiment (Figure 5.14 a and b).

The strong relationship between Pb and Fe release into soil solution would appear to indicate that Pb was associated with Fe oxides in the soil and then released into solution as these oxides underwent reductive dissolution. It has been shown in many studies that Pb in soil is often bound to Fe oxides (Pareuil *et al.*, 2008; Chuan *et al.*, 1996; Li & Thornton, 2001). However, this would contradict the results of the sequential extractions, which showed that Pb was predominantly associated with organic matter in the Chat Moss soil (Section 4.3). Again this may underline the covariance of several mechanisms which control trace element release in anaerobic soils. Thus it is possible, and likely, that organically-bound Pb is released by competition with Fe^{2+} following dissolution of Fe hydrous oxides.

Bismuth

For the control samples, Bi showed the strongest relationship with Fe solution concentration, with an R^2 value of 0.766, although a similar relationship was not seen for the organically amended samples. The concentration of Bi in solution increased from $0.11 \mu\text{g L}^{-1}$ to $0.56 \mu\text{g L}^{-1}$ with the greatest increase seen between 56 days into the experiment and at the end (Figure 5.15 a and b). This relationship indicated that

Bi was associated with Fe oxides and that the mechanism of release into solution was through reductive dissolution rather than competition with Fe^{2+} and H^{+} ions, although this cannot be confirmed.

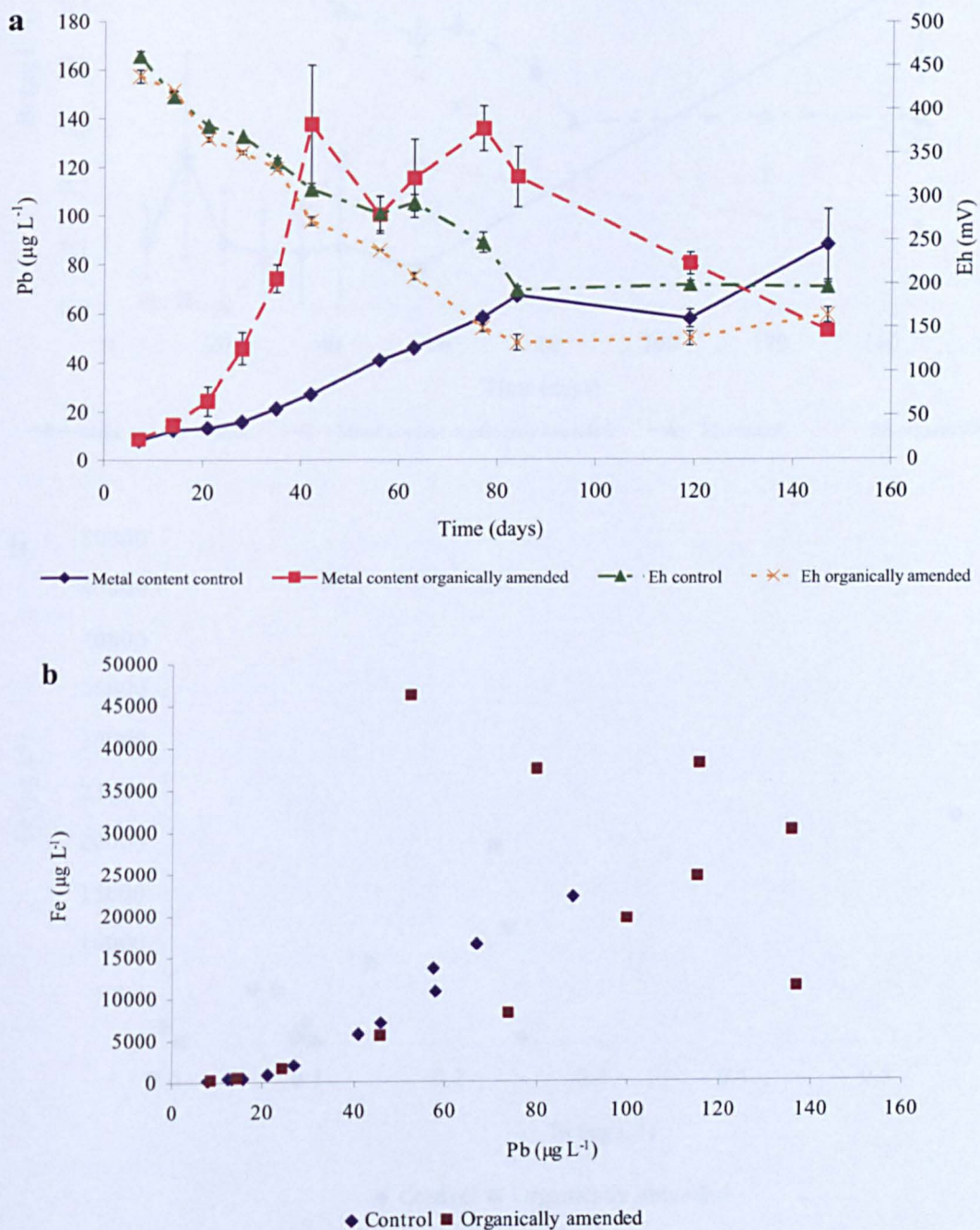


Figure 5.14: Changes in Pb concentration (a) with time and (b) as a function of Fe concentration ($R^2 = 0.959$ control) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

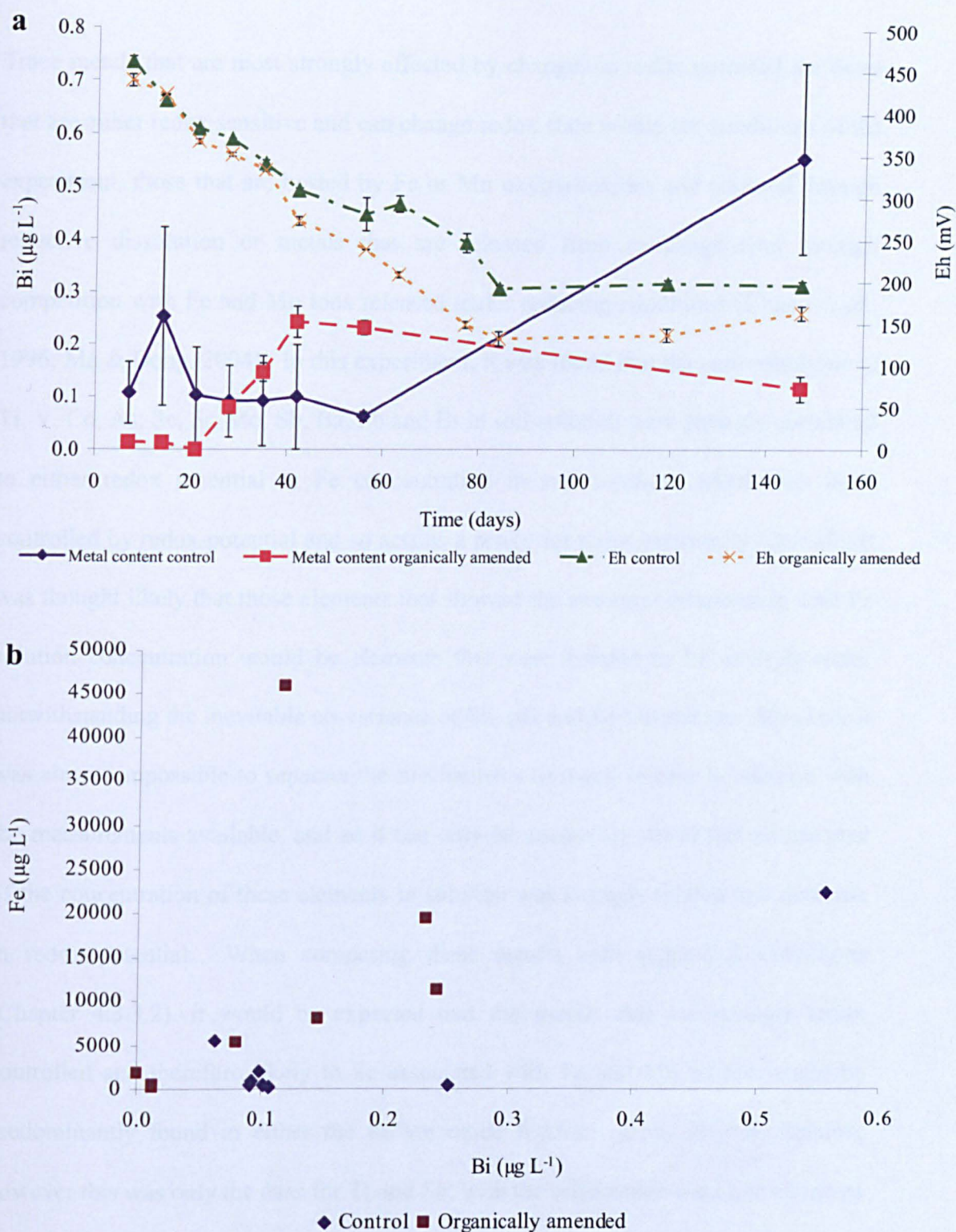


Figure 5.15: Changes in Bi concentration (a) with time and (b) as a function of Fe concentration ($R^2 = 0.766$ control) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

Trace metals that are most strongly affected by changes in redox potential are those that are either redox sensitive and can change redox state within the conditions of the experiment, those that are hosted by Fe or Mn oxyhydroxides and released through reductive dissolution or metals that are released from exchange sites through competition with Fe and Mn ions released under reducing conditions (Chuan *et al.*, 1996; Ma & Dong, 2004). In this experiment, it was found that the concentrations of Ti, V, Co, As, Se, Sr, Mo, Sb, Ba, Pb and Bi in soil solution were strongly correlated to either redox potential or Fe concentration in soil solution, which was itself controlled by redox potential and so acts as a proxy for redox sensitivity. Initially it was thought likely that those elements that showed the strongest relationship with Fe solution concentration would be elements that were bonded to Fe oxyhydroxides notwithstanding the inevitable co-variance of Eh, pH and Fe/Mn release. However it was almost impossible to separate the mechanisms of metal release to solution with the measurements available, and so it can only be accurately stated that an increase of the concentration of these elements in solution was strongly related to a decrease in redox potential. When comparing these results with sequential extractions (Chapter 4.3.3.2), it would be expected that the metals that are strongly redox controlled and therefore likely to be associated with Fe and Mn oxides would be predominantly found in either the Fe/Mn oxide fraction or the residual fraction, however this was only the case for Ti and Sb, with the other redox-sensitive elements showing fractionation not dominated by either the residual or Fe/Mn oxide phases. Lead epitomises this problem in that the strong correlation between Pb solubilisation and Fe release contradicts the SEP data in Chapter 4, unless competition for organic sites is regarded as the release mechanism.

The results seen here for redox sensitive elements are generally supported by other studies. Chuan *et al.*, (1996) found that under reducing conditions, the solubilisation of Pb, Cd and Zn was favoured, as well as the solubility of Fe. The authors were able to separate the effects of redox potential and pH by carrying out experiments where the pH was constant and only the redox potential was altered, and it was found that redox potential had a significant independent effect on metal solubility, with solubility increasing under reducing conditions. This was attributed to the release of metals hosted on Fe and Mn oxyhydroxides. Similar results were also found by Pareuil *et al.*, (2008) who observed a simultaneous release of Fe and Mn with Cu, Zn, Cr, Ni and Pb; again the authors attributed this to the reductive dissolution of trace metal-hosting Fe and Mn oxyhydroxides. These observations are in agreement with the current study, with the exception of Cu, Zn and Cr. However, considering the highly organic nature of the Chat Moss soils, competition for organic adsorption sites from Fe^{2+} and Mn^{2+} is likely to be a more important mechanism governing release of trace elements such as Cu and Pb. It was also seen in the current study that when the dissolved organic matter content was increased through the addition of powdered straw (organically amended samples), the concentration of some elements in soil solution were more strongly related to dissolved organic matter content rather than redox potential, for example Ti, Se, V and Pb. Similarly, it has been found that in wetland soils, dissolved organic matter can be important in controlling the solubility of trace metals (Grybos *et al.*, 2007); this will be discussed more in the following section.

5.3.3.2 Trace elements influenced by dissolved organic carbon concentration - Ti, V, Cr, Ni, Cu, Zn, Se, Sn, Pb, Bi

Titanium

For Ti, although the control samples showed a strong relationship with redox potential, the organically amended samples showed the strongest relationship with dissolved organic matter (DOM), with an R^2 of 0.570. The overall Ti concentration increased from $0.68 \mu\text{g L}^{-1}$ to $4.84 \mu\text{g L}^{-1}$ at a roughly constant rate of increase, however there was a peak in Ti concentration between days 35 and 42 of $5.91 - 6.00 \mu\text{g L}^{-1}$. The relationship was relatively weak, indicating that DOM was not a strong control of Ti solubility (Figure 5.16 a and b).

Vanadium

The relationship between V and DOC for the organically amended samples showed an R^2 value of 0.712, which was the strongest relationship seen for vanadium in this experiment. The V concentration increased from $16.5 \mu\text{g L}^{-1}$ to $19.3 \mu\text{g L}^{-1}$, with a peak concentration between days 42 and 84, which is the same period as the peak DOC concentration (Figure 5.17 a and b). Several interpretations of a potential causal link between concentration of V and DOC are possible. Reduction in general and competition for remaining hydrous oxide adsorption sites from DOC may cause anionic forms of V to dissolve. These would include both the orthovanadate and metavanadate forms (VO_4^{3-} and VO_3^-); orthovanadate would be present in solution predominantly as a monovalent anion H_2VO_4^- in the pH range measured (pK_1 and pK_2 values for vanadic acid are 2.6 and 7.9 respectively). Alternatively, Berrow *et al.*, (1978) have suggested that, in acidic organic soils, the monovalent vanadyl cation (VO_2^+) may be the dominant form of V and so mobilization would depend on

complex-formation with DOC compounds or competition with Fe^{2+} and Mn^{2+} for adsorption sites on solid phase humus.

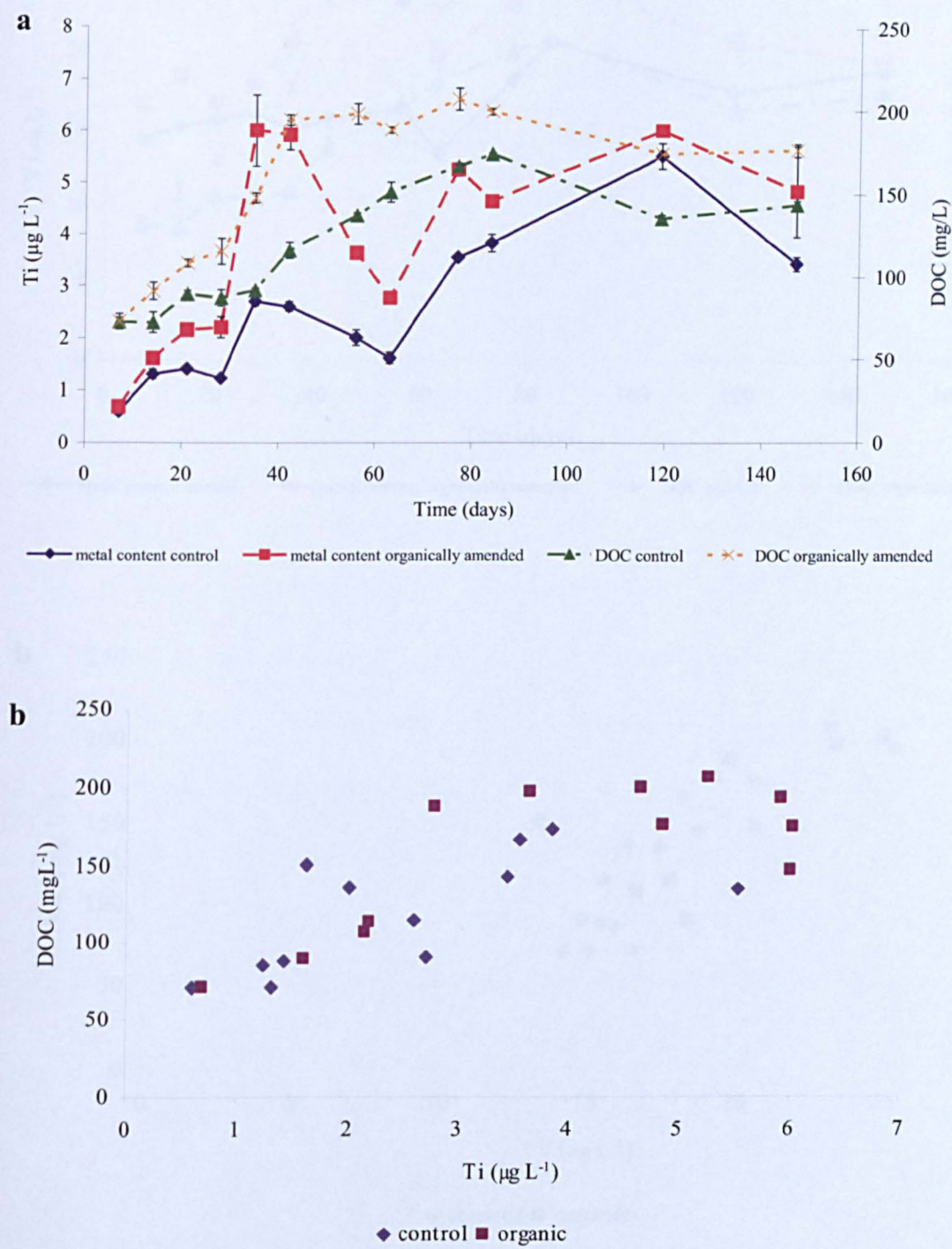


Figure 5.16: Changes in Ti concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.570$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

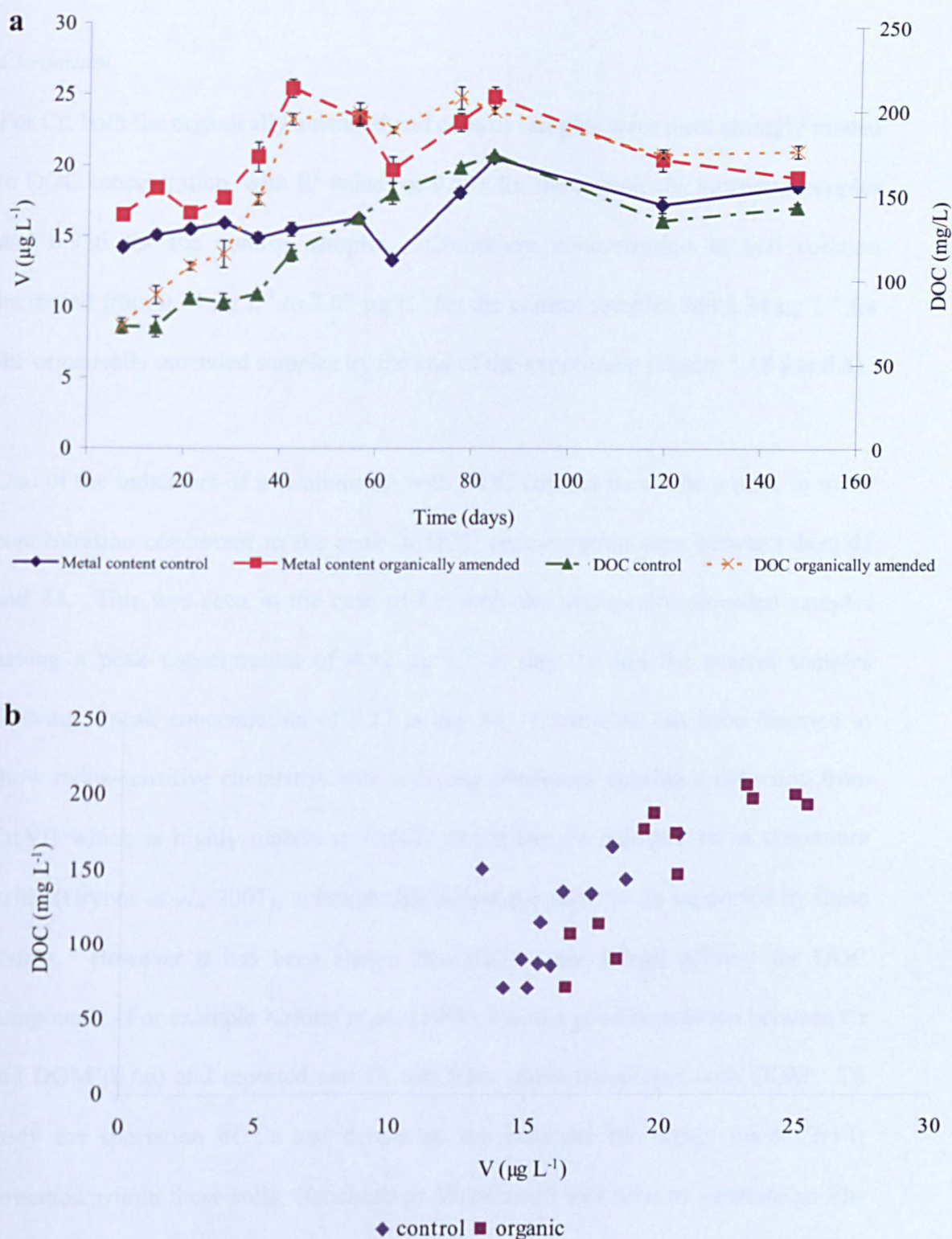


Figure 5.17: Changes in V concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.712$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

Chromium

For Cr, both the organically amended and control samples were most strongly related to DOC concentration, with R^2 values of 0.591 for the organically amended samples and 0.956 for the control samples. Chromium concentration in soil solution increased from $0.74 \mu\text{g L}^{-1}$ to $2.67 \mu\text{g L}^{-1}$ for the control samples and $2.34 \mu\text{g L}^{-1}$ for the organically amended samples by the end of the experiment (Figure 5.18 a and b).

One of the indicators of a relationship with DOC content would be a peak in metal concentration concurrent to the peak in DOC concentration seen between days 42 and 84. This was seen in the case of Cr, with the organically amended samples having a peak concentration of $4.82 \mu\text{g L}^{-1}$ at day 35 and the control samples showing a peak concentration of 3.17 at day 84. Chromium has been reported to show redox-sensitive chemistry, with reducing conditions causing a reduction from Cr(VI) which is highly mobile to Cr(III) which can be precipitated as chromium oxide (Grybos *et al.*, 2007), although this would not seem to be supported by these results. However it has been shown that Cr(III) has a high affinity for DOC compounds. For example Kalbitz *et al.*, (1998) found a good correlation between Cr and DOM (0.60) and reported that Cr can form stable complexes with DOM. To study the speciation of Cr and determine the potential for highly toxic Cr(VI) formation within these soils, Geochemists Workbench was used to generate an Eh-pH stability diagram (Figure 5.19). It is clear from Fig. 5.19 that, under the pH and redox conditions of the experiment, it was predicted that all Cr would be present as Cr(III).

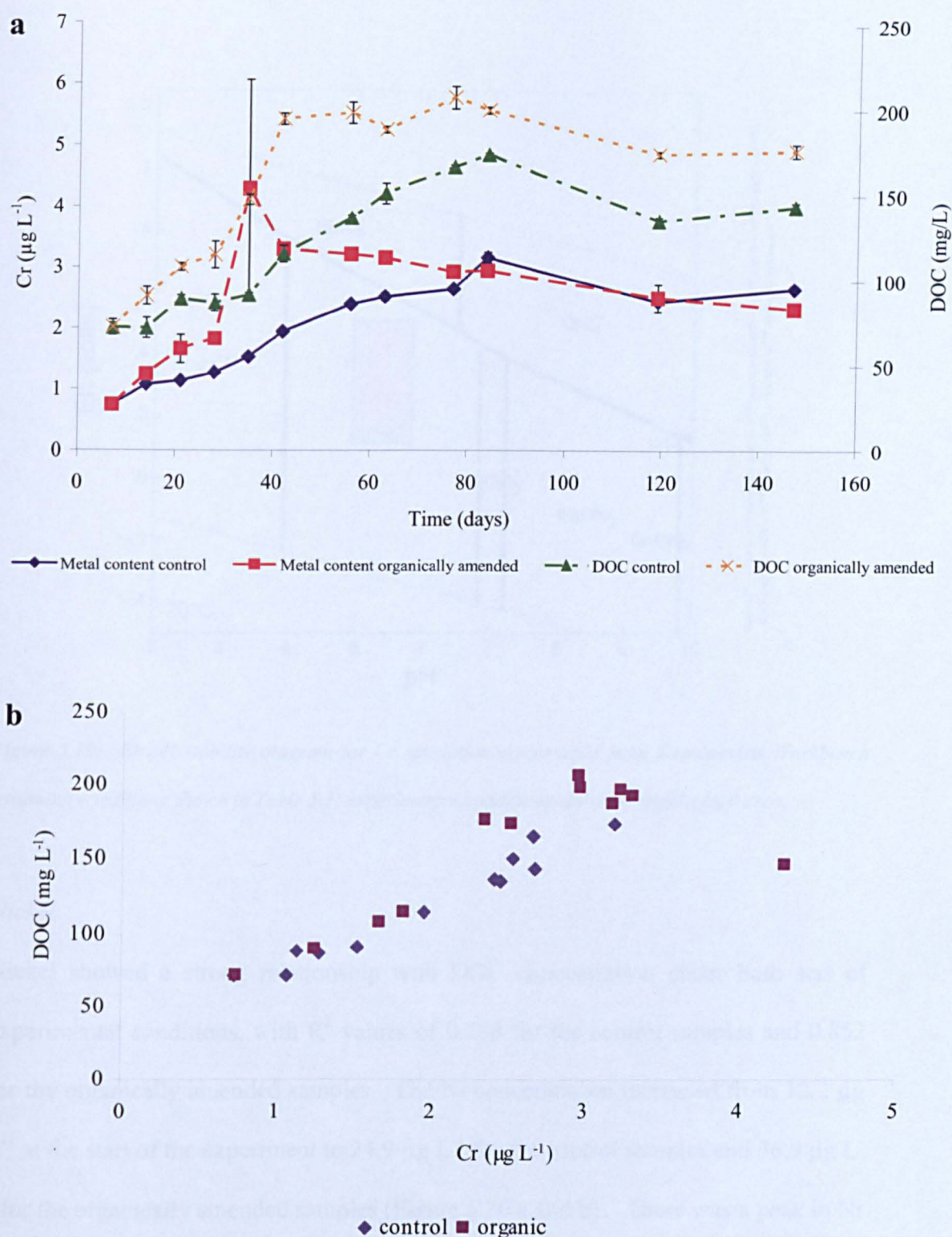
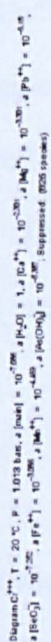


Figure 5.18: Changes in Cr concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.956$ control and 0.591 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.



Nickel

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much earlier and faster than would be seen if Ni was redox controlled but is in line with the DOC profile which peaks between days 42 and 84. It has been reported that Ni adsorbs strongly to peat, following the Irving-Williams order of $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$ (Ringqvist & Oborn, 2002), which would agree with the results seen here. Grybos *et al.*, (2007) also found a strong affinity of Ni for soil organic matter, with 85% of solubilised Ni released from humus. The authors reported that there was increased partitioning of Ni onto organic matter with increasing pH, which occurs as the redox potential decreases.

Copper

Copper release to soil solution showed a strong relationship with DOC concentration with an R^2 value of 0.894 for the control samples (Figure 5.21 a and b). However the organically amended samples showed no relationship to DOC concentration, redox potential or Fe concentration. The Cu concentration in the control samples increased from $38.5 \mu\text{g L}^{-1}$ at the start of the experiment to $77 \mu\text{g L}^{-1}$ at the end of the experiment, but the peak Cu concentration was seen between days 42 and 84, in line with the DOC concentration. This is expected behaviour of Cu which has a very strong affinity to organic matter compared to most other metals, and as seen from the sequential extractions (Chapter 4.3.3.2) 83% of Cu in Chat Moss soil was associated with the organic matter fraction. However, the organically amended samples showed no relationship with DOC which was unexpected. There was an initial peak of Cu concentration between days 35 and 42 of $203 - 214 \mu\text{g L}^{-1}$, but the Cu concentration then rapidly decreased over the course of the experiment to $25 \mu\text{g L}^{-1}$ by the end of the experiment. This may reflect the onset of Fe^{2+} competition for DOC adsorption sites causing re-adsorption of Cu by the solid phase. Alternatively, it has been shown that Cu^{2+} can be reduced to Cu(I) in reducing environments which can then

precipitate as Cu_2O , and that organic matter can enhance this reduction when humic acids act as electron mediators between micro-organisms and metals (Grybos *et al.*, 2007). This could explain the pattern of Cu solubilisation seen in the organically amended samples, with initial solubilisation followed by a decrease in Cu concentration in soil solution. In studies of metal solubilisation in wetland soils under reducing conditions, there was no relationship found between Cu and DOC concentration, and it was found that Cu solubility was mainly affected by redox state through changes in the oxidation state of Cu (Grybos *et al.*, 2007).

Zinc

There was little difference seen between the control and organically amended samples for zinc. Both showed a strong relationship with DOC concentration with R^2 values of 0.743 for the control samples and 0.759 for the organically amended samples (Figure 5.22 a and b). The solubilisation of Zn over the course of the experiment followed an unusual trend, with an initial decrease seen in Zn concentration in soil solution and then an increase followed by a constant Zn concentration in solution to the end of the experiment. The period of decrease in Zn concentration was between 14 and 35 days of the experiment and may simply reflect greater adsorption strength in the solid phase as pH rises during this period. The subsequent increase in concentration was concurrent with the start of DOC increase in solution. However continued DOC release did not seem to affect Zn concentration. It has been reported that Zn solubilisation had no relationship to DOC concentration due to low stability of Zn organic complexes (Kalbitz *et al.*, 1998) and that Zn is controlled by redox state (Chuan *et al.*, 1996; Pareuil *et al.*, 2008), which is contradictory to the results seen here.

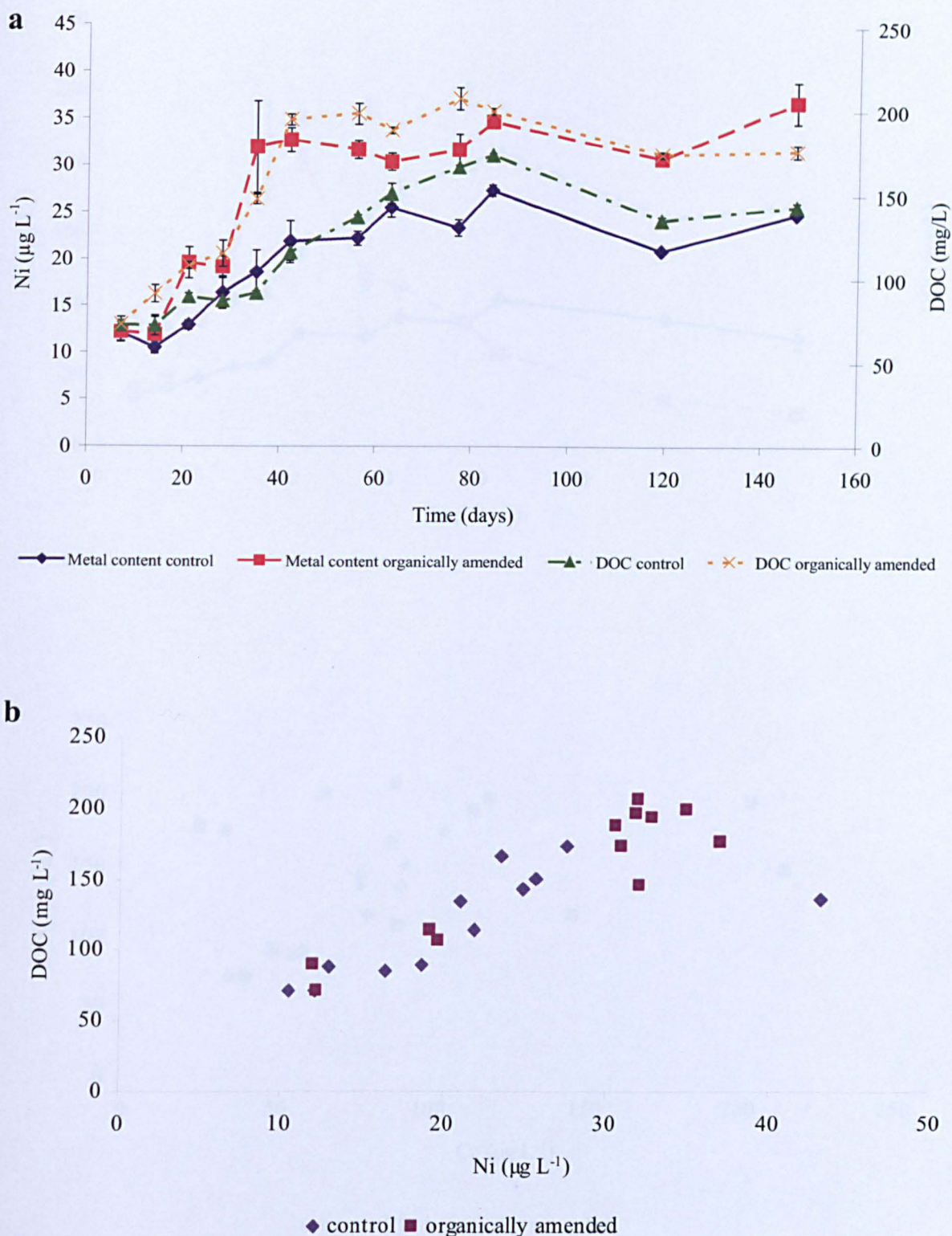


Figure 5.20: Changes in Ni concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.488$ control and 0.852 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

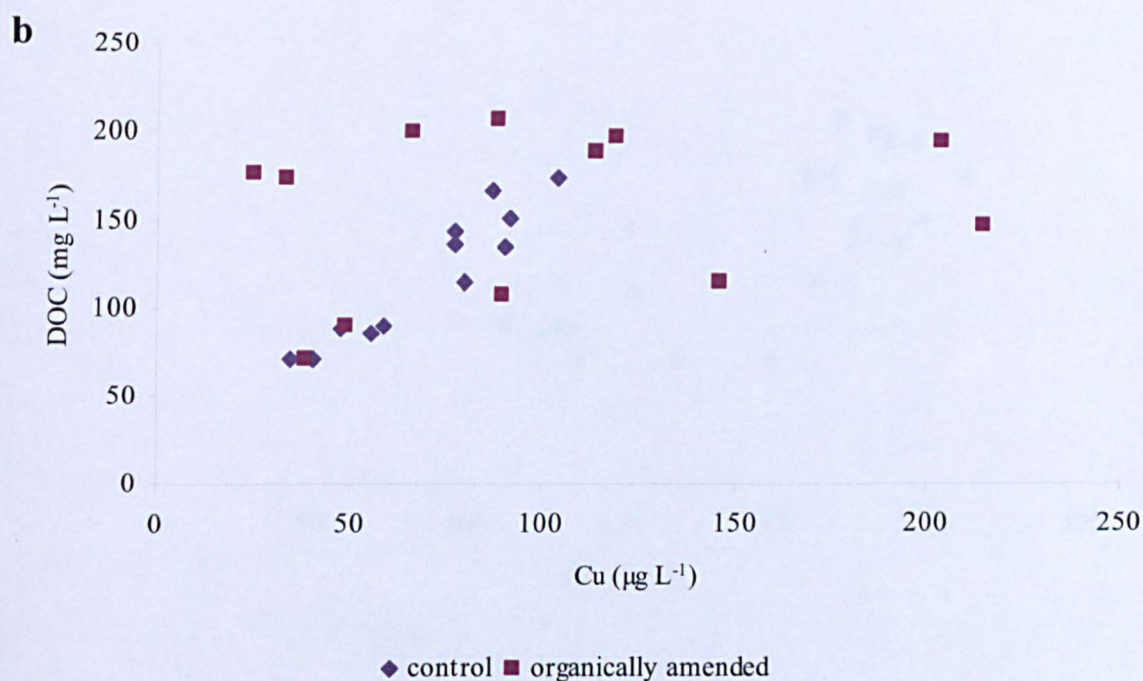
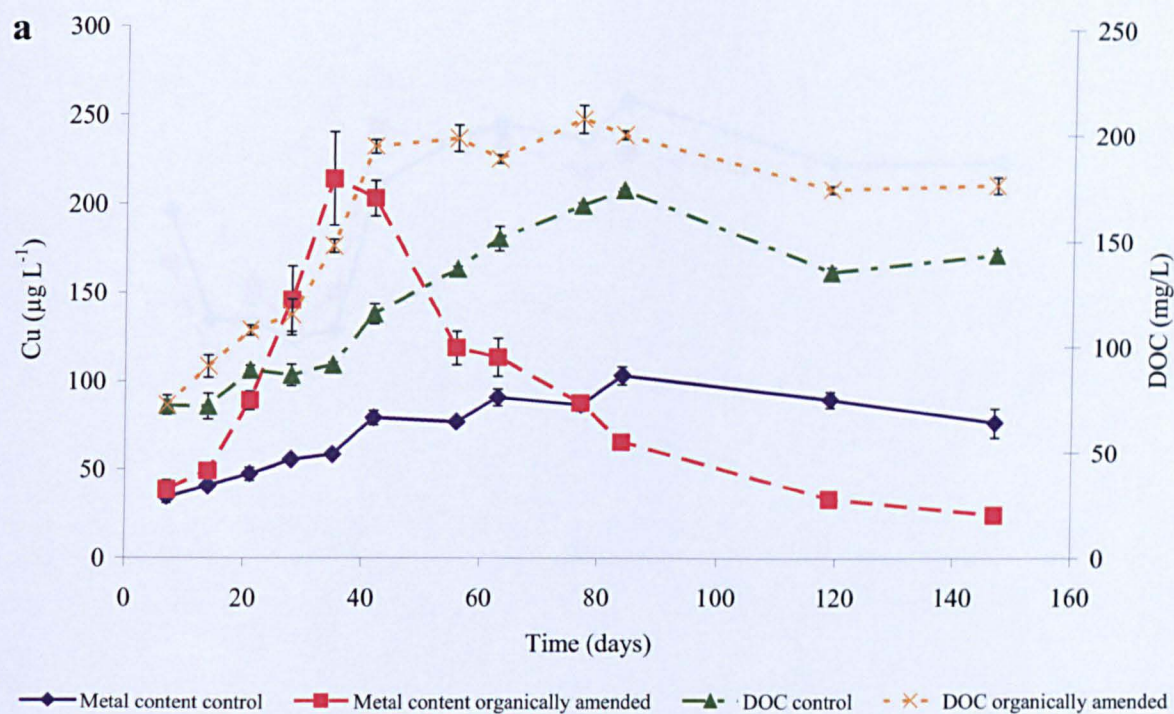


Figure 5.21: Changes in Cu concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.894$ control) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

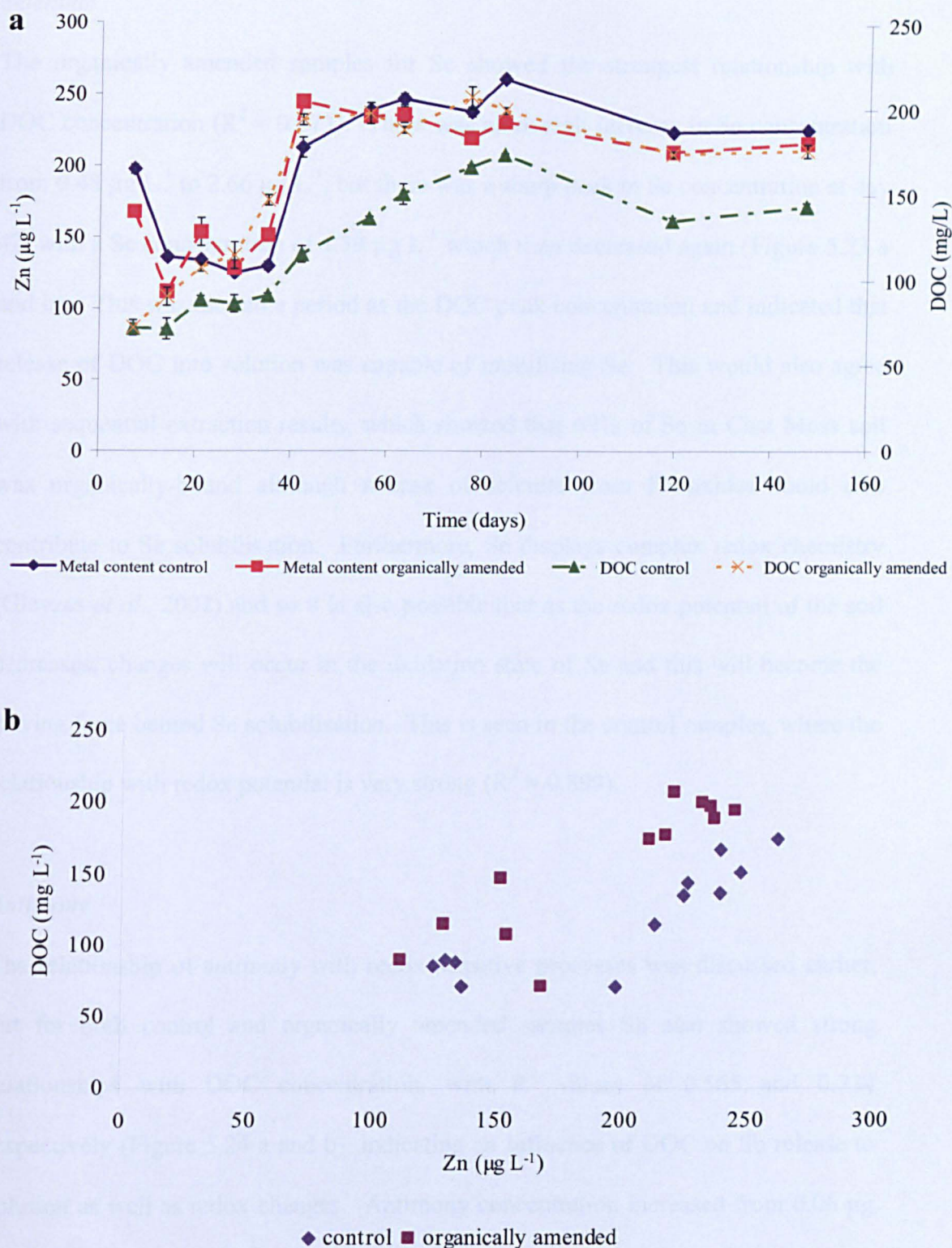


Figure 5.22: Changes in Zn concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.743$ control and 0.759 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

Selenium

The organically amended samples for Se showed the strongest relationship with DOC concentration ($R^2 = 0.673$). There was an overall increase in Se concentration from $0.48 \mu\text{g L}^{-1}$ to $2.66 \mu\text{g L}^{-1}$, but there was a sharp peak in Se concentration at day 42, with a Se concentration of $4.39 \mu\text{g L}^{-1}$ which then decreased again (Figure 5.23 a and b). This was the same period as the DOC peak concentration and indicated that release of DOC into solution was capable of mobilising Se. This would also agree with sequential extraction results, which showed that 69% of Se in Chat Moss soil was organically-bound although release of selenite from Fe oxides could also contribute to Se solubilisation. Furthermore, Se displays complex redox chemistry (Gleyzes *et al.*, 2002) and so it is also possible that as the redox potential of the soil decreases, changes will occur in the oxidation state of Se and this will become the driving force behind Se solubilisation. This is seen in the control samples, where the relationship with redox potential is very strong ($R^2 = 0.899$).

Antimony

The relationship of antimony with redox sensitive processes was discussed earlier, but for both control and organically amended samples Sb also showed strong relationships with DOC concentration, with R^2 values of 0.565 and 0.734 respectively (Figure 5.24 a and b), indicating an influence of DOC on Sb release to solution as well as redox changes. Antimony concentration increased from $0.06 \mu\text{g L}^{-1}$ at the start of the experiment to $0.26 \mu\text{g L}^{-1}$ for the control samples and $0.46 \mu\text{g L}^{-1}$ for the organically amended samples. However both sets of samples showed a peak Sb concentration between days 42 and 77 which follows the trend in DOC concentration.

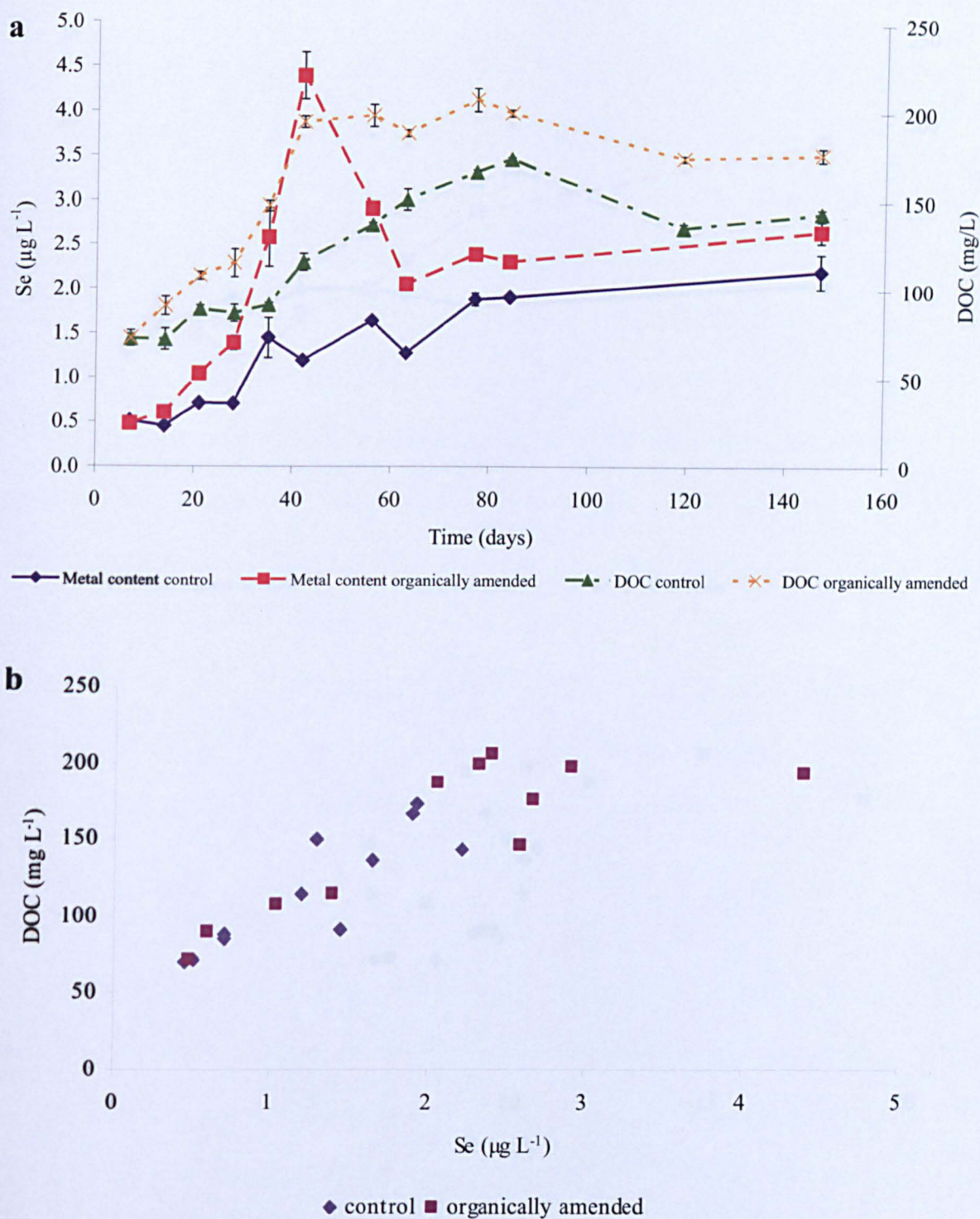


Figure 5.23: Changes in Se concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.673$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

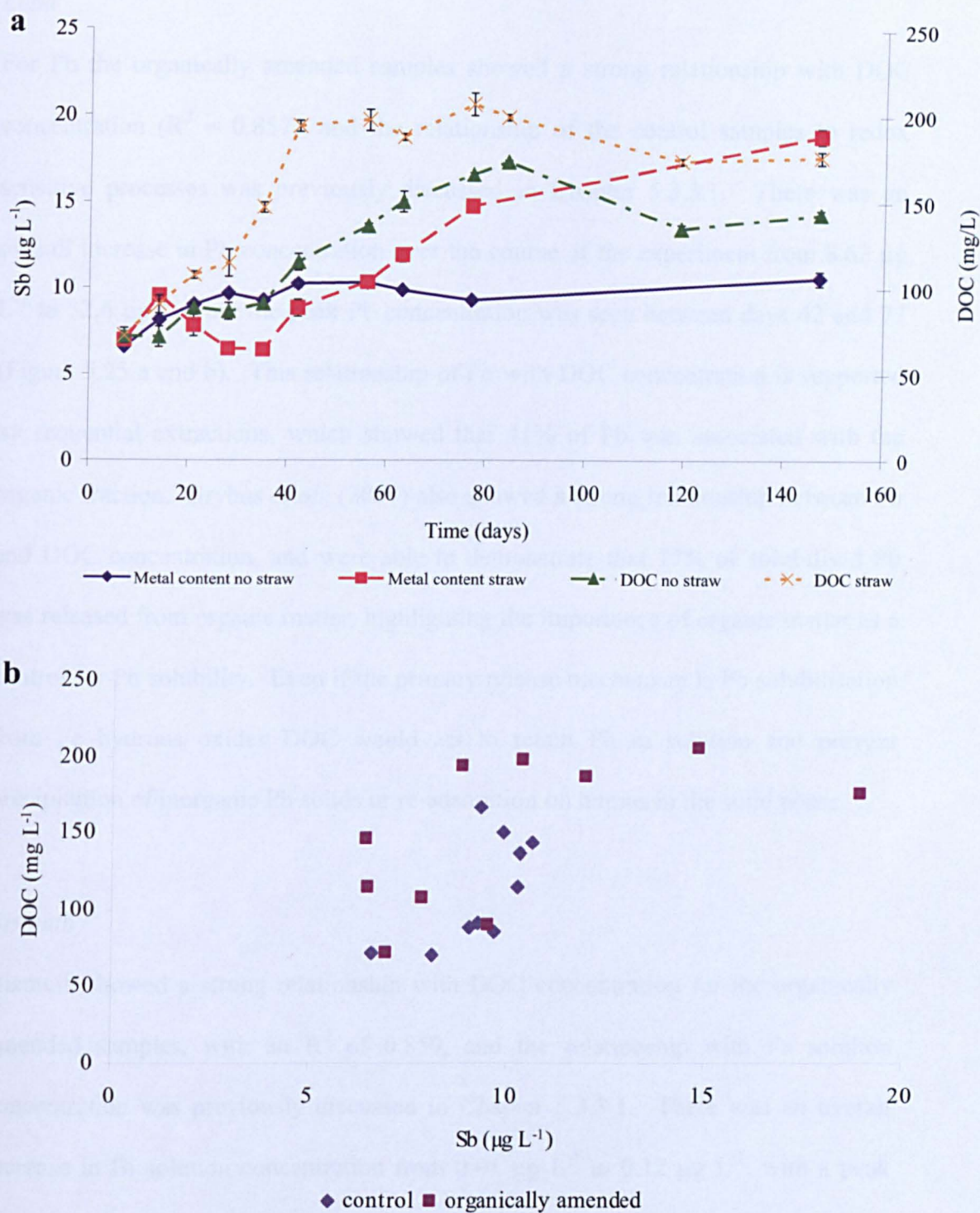


Figure 5.24: Changes in Sb concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.565$ control and 0.734 organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

Lead

For Pb the organically amended samples showed a strong relationship with DOC concentration ($R^2 = 0.857$), and the relationship of the control samples to redox sensitive processes was previously discussed in Chapter 5.3.3.1. There was an overall increase in Pb concentration over the course of the experiment from $8.62 \mu\text{g L}^{-1}$ to $52.6 \mu\text{g L}^{-1}$, but the peak Pb concentration was seen between days 42 and 77 (Figure 5.25 a and b). This relationship of Pb with DOC concentration is supported by sequential extractions, which showed that 41% of Pb was associated with the organic fraction. Grybos *et al.*, (2007) also showed a strong relationship between Pb and DOC concentration, and were able to demonstrate that 77% of solubilised Pb was released from organic matter, highlighting the importance of organic matter as a control for Pb solubility. Even if the primary release mechanism is Pb solubilisation from Fe hydrous oxides DOC would act to retain Pb in solution and prevent precipitation of inorganic Pb solids or re-adsorption on humus in the solid phase.

Bismuth

Bismuth showed a strong relationship with DOC concentration for the organically amended samples, with an R^2 of 0.859, and the relationship with Fe solution concentration was previously discussed in Chapter 5.3.3.1. There was an overall increase in Bi solution concentration from $0.01 \mu\text{g L}^{-1}$ to $0.12 \mu\text{g L}^{-1}$, with a peak concentration of $0.24 \mu\text{g L}^{-1}$ seen at day 42, corresponding with the increase in DOC concentration (Figure 5.26 a and b). Bismuth also showed a relationship with Fe concentration for the control samples.

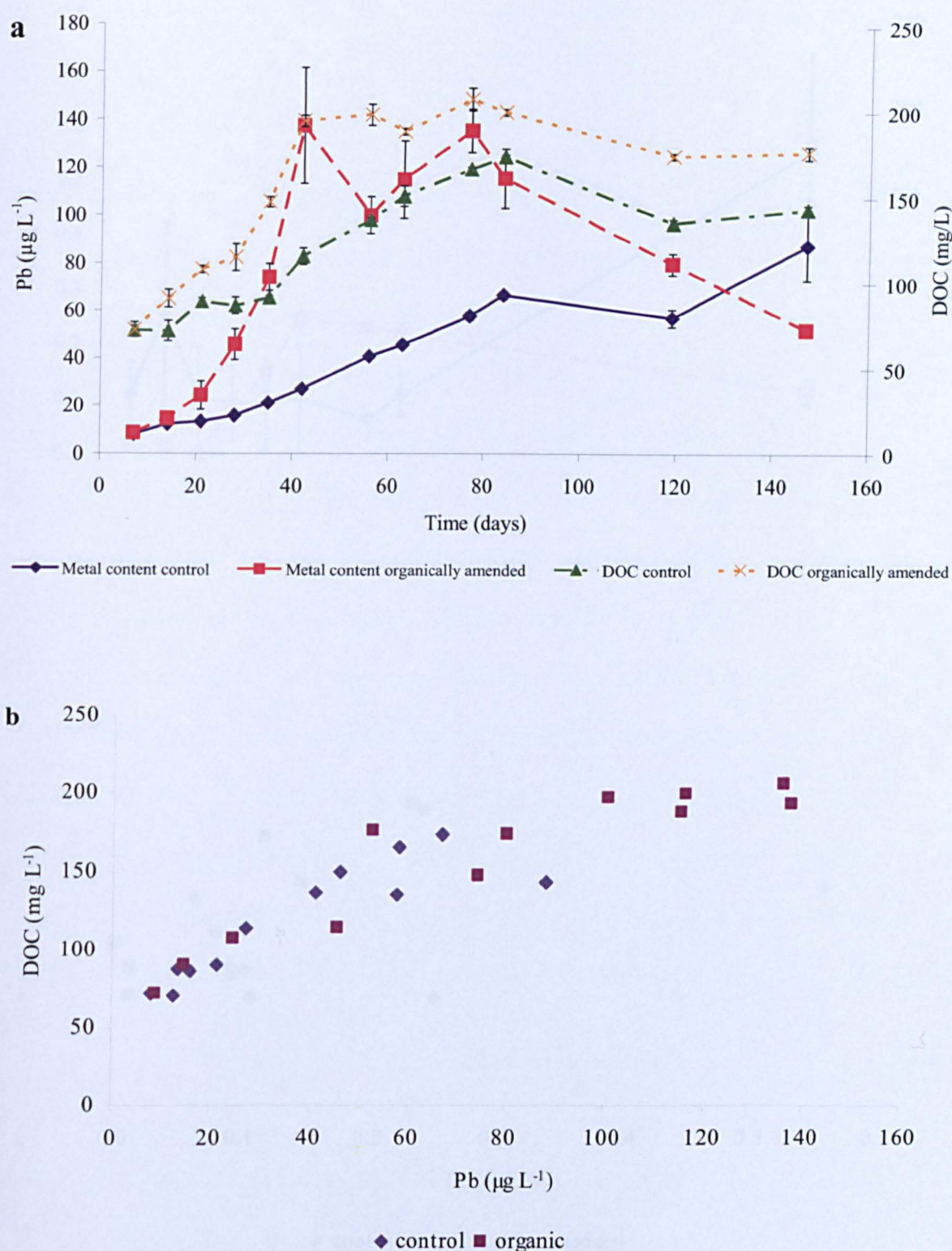


Figure 5.25: Changes in Pb concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.857$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

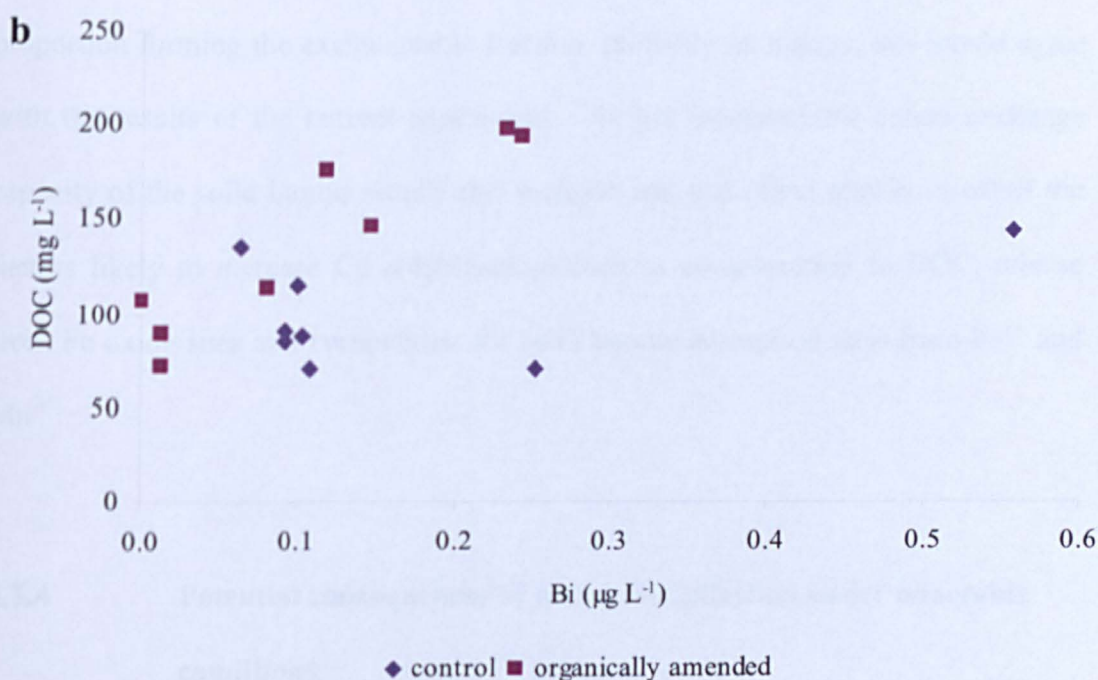
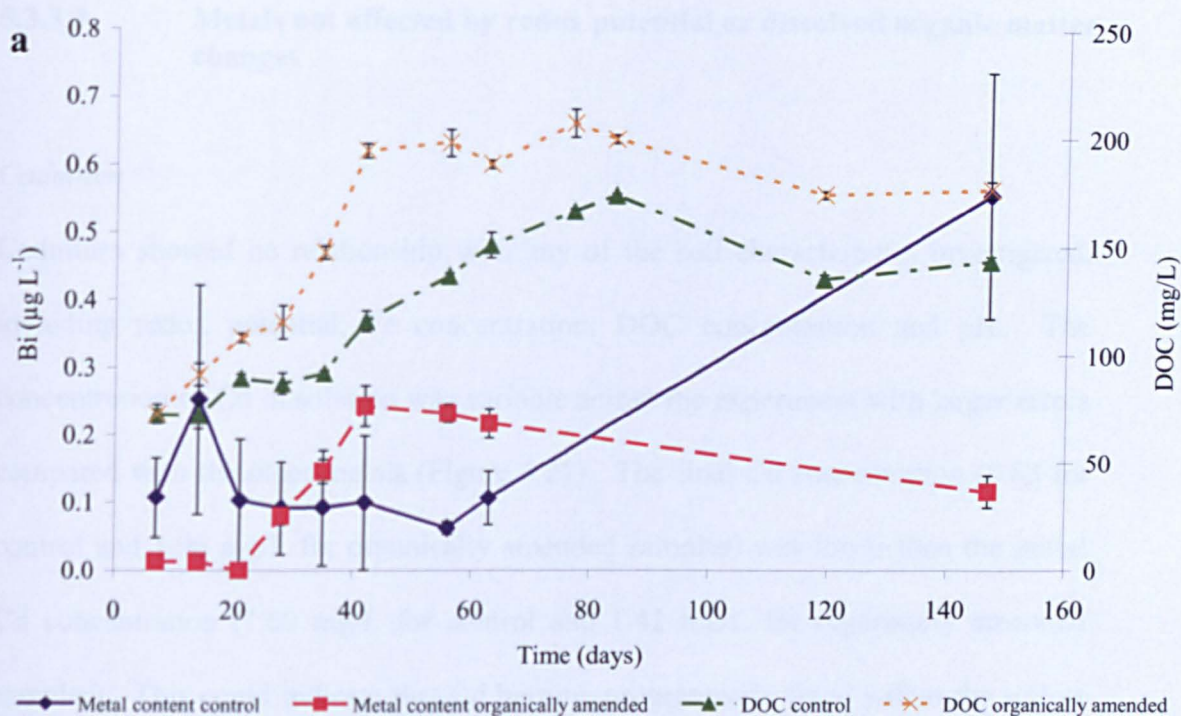


Figure 5.26: Changes in Bi concentration (a) with time and (b) as a function of DOC concentration ($R^2 = 0.859$ organically amended) in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

5.3.3.3 Metals not affected by redox potential or dissolved organic matter changes

Cadmium

Cadmium showed no relationship with any of the soil characteristics investigated, including redox potential, Fe concentration, DOC concentration and pH. The concentration of Cd in solution was variable across the experiment with larger errors compared with the other metals (Figure 5.27). The final Cd concentration (0.83 for control and 1.06 mg/L for organically amended samples) was lower than the initial Cd concentration (1.69 mg/L for control and 1.42 mg/L for organically amended samples). This could indicate that Cd became progressively fixed within the soil as the pH value increased. It can be seen from the sequential extractions (Chapter 4.3) that Cd in acidic organic soils is present in a relatively mobile form with a large proportion forming the exchangeable fraction, probably on humus; this would agree with the results of the current experiment. As pH increased the cation exchange capacity of the solid humus would also increase and this effect may have offset the factors likely to increase Cd solubilisation such as complexation to DOC, release from Fe oxide sites and competition for solid humus adsorption sites from Fe^{2+} and Mn^{2+} .

5.3.4 Potential consequences of metal solubilisation under anaerobic conditions

The results of this incubation experiment suggest that mobilization of trace contaminants can be substantial in the waste-amended acidic organic soils of Chat Moss. Thus, concentrations of the elements measured can be considered in the

context of environmental or human health standards relating to fresh water. For example, the World Health Organisation safe drinking water limits (WHO, 2008) may give an indication of the potential risk posed by flooding of these soils in the context of drainage into fresh water systems. Table 5.2 shows that for the metals listed in the safe drinking water limits (As, Ba, Mn, Mo, Se, Cd, Sb, Pb, Cu and Ni) only As, Mn, Mo, Cd and Pb exceeded WHO limits.

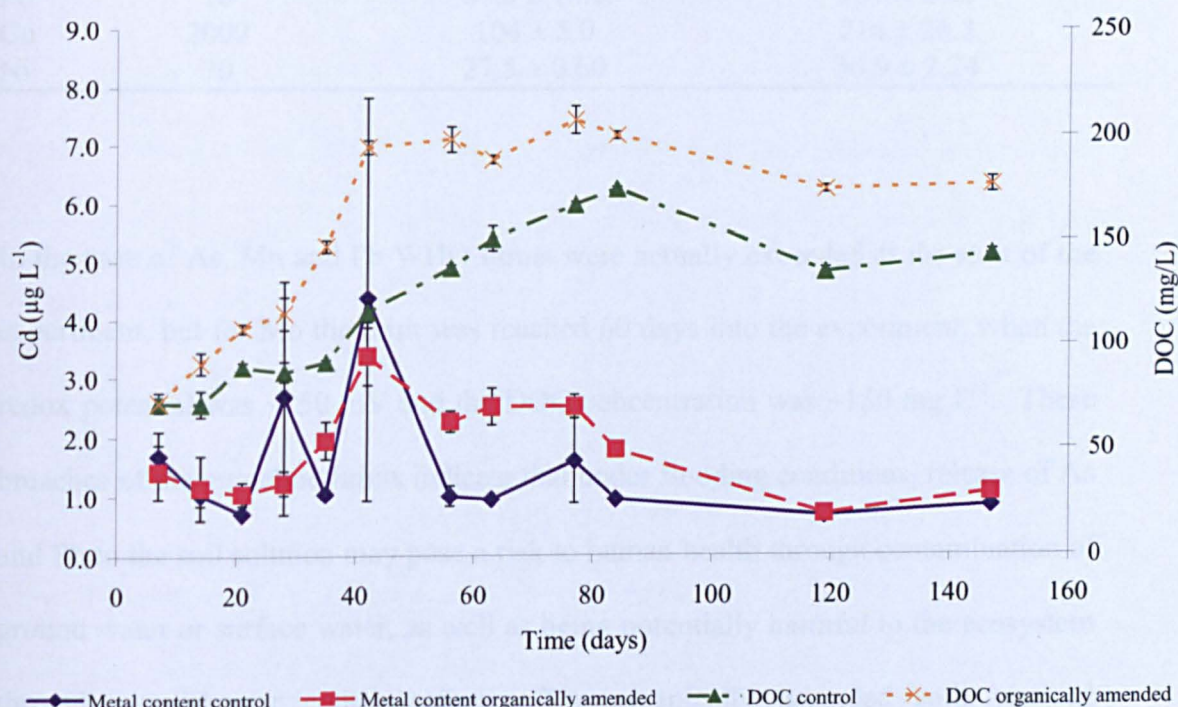


Figure 5.27: Changes in Cd concentration with time in 1:3 w/v soil suspensions from site CM-3 incubated under anaerobic conditions at 21°C with, or without organic amendment with powdered straw. Error bars show standard error of three replicates.

Table 5.2: World Health Organisation safe drinking water limits compared with Chat Moss maximum soil solution concentrations

	Drinking water limits ($\mu\text{g L}^{-1}$)	Max. Experimental Concentration ($\mu\text{g L}^{-1}$)	
		Control soil	Organically amended soil
As	10	214 ± 10.6	308 ± 12.4
Ba	700	190 ± 11.1	251 ± 4.8
Mn	400	1080 ± 13.1	1880 ± 42.5
Mo	70	90.3 ± 1.49	170 ± 4.17
Se	10	2.22 ± 0.197	4.39 ± 0.263
Cd	3	1.69 ± 0.408	3.38 ± 0.502
Sb	20	10.6 ± 0.43	18.9 ± 0.44
Pb	10	88.0 ± 14.6	137 ± 24.2
Cu	2000	104 ± 5.0	214 ± 26.3
Ni	70	27.5 ± 0.60	36.9 ± 2.24

In the case of As, Mn and Pb WHO limits were actually exceeded at the start of the experiment, but for Mo the limit was reached 60 days into the experiment, when the redox potential was ~ 250 mV and the DOC concentration was ~ 150 mg L^{-1} . These breaches of the guideline limits indicate that under flooding conditions, release of As and Pb to the soil solution may pose a risk to human health through contamination of ground water or surface water, as well as being potentially harmful to the ecosystem through groundwater contamination. The organically amended soils showed consistently higher metal concentration in solution, which would indicate that the incorporation of crop residue into the soil would result in increased mobilisation of metals under flooding conditions. To minimise the metal solubilisation, removal of the crop residue could be practised, although this does not take into account the benefits to crops of inclusion of residue.

5.4 Conclusions

Through soil incubation experiments it was found that saturation of soil for a period of 21 weeks resulted in a decrease in redox potential and an increase in pH and dissolved organic carbon concentration. Redox potential decreases under anoxic conditions through soil saturation with or without nitrogen atmospheres were similarly found by Grybos *et al.*, (2007) and Chuan *et al.*, (1996).

All measured metals with the exception of Cd showed increased concentrations in solution during the experiment. The increase in metal concentrations were analysed using regression to identify the strongest relationship with either redox potential, Fe solution concentration, DOC concentration, pH and time, however the scope of this experiment did not make it possible to determine the mechanisms of increased solubilisation. pH and time showed no relationships with any metals but redox potential, Fe concentration and DOC concentration showed strong relationships with all metals except Cd. The metals were divided into two groups, those that were affected by redox changes (strong relationships with redox potential and Fe concentration) and those affected by DOC concentration. For many elements it was found that the control samples and the organically amended samples showed different relationships, with the organically amended samples often showing a relationship with DOC. This was the case for Ti, Se, Pb and Bi.

The reduction in redox potential caused an increased solubility for Ti, V, Co, As, Se, Sr, Mo, Sb, Ba, Pb and Bi, due to either changes in the oxidation state of the metal (e.g. As), release of Fe/Mn oxyhydroxide hosted metals, or competition with Fe^{2+} for exchange sites, however it was not possible to identify the mechanism of the metal solubilisation through this experiment.

Increased DOC concentration caused an increase in solubility of Ti, V, Cr, Ni, Cu, Zn, Se, Sn, Pb, Bi through the formation of soluble stable organic complexes or the release of organically bound metals. Cadmium showed no increase in concentration throughout the experiment, and the final Cd concentration was lower than the initial concentration. This may be due to the fixation of Cd within Fe oxides throughout the experiment, as found by Contin *et al.*, (2007) but this cannot be confirmed through the current experiment.

The addition of powdered straw caused an increase in solubility for most metals; Cr, Cu and Pb all showed an early peak in concentration in the organically amended samples, with final solution concentration being the same or lower than the control samples, and for Zn there were no differences between the control and organically amended samples throughout the experiment. The addition of straw may have increased the solubility of metals in two ways. The increased organic matter from the straw would enable bacterially mediated reductive processes to occur faster, with the increased organic matter acting as 'fuel' for these processes. This would have the effect of increased the rate at which oxygen was consumed by the bacteria and so accelerating the reduction of the soil solution, as seen in Figure 5.1a. The addition of the powdered straw will also have had the effect of increasing the organic matter content of the soil system, which may have increased the DOC concentration, as seen in Figure 5.1c. This will have increased the solubility of those metals which were brought into solution through complexation with DOC. Through these two mechanisms of increased reduction and increased DOC concentration, the mobilisation of metals was increased.

For elements such as As and Pb, redox potential and dissolved organic carbon content were controlling factors on solubilisation. This was in agreement with data obtained through sequential extractions (Chapter 4.3) which showed that both As and Pb were bound to organic, residual and Fe/Mn oxide phases, which would all be affected by redox potential decrease or DOC increase. The sequential extraction data and data from this incubation experiment show the same picture of As and Pb hosted on organic matter and Fe/Mn oxides, but it is not possible using these two pieces of data to separate the mechanisms of mobilisation. This could be achieved through experiments which only vary either redox potential, Fe solution concentration or DOC concentration.

Drinking water guidelines (WHO, 2008) showed that As, Mn, Mo and Pb were all present in potentially hazardous concentrations in the soil solution under redox conditions that would typically be found in field situations. In the case of As, soil solution concentration reached a maximum of $308 \mu\text{g L}^{-1}$ in the organically amended samples, which was comparable to the high levels of As seen in Bangladesh groundwater ($461 \mu\text{g L}^{-1}$, Halim *et al.*, 2009). Arsenic, lead and manganese all exceeded the drinking water guidelines before any reduction had taken place, which suggests that under field conditions these guidelines would also be exceeded under average redox conditions. However under natural conditions, redox changes would also follow a cycle of reduction and oxidation as the soil undergoes flooding and drying events. This could result in the immobilisation of metals through fixation in Fe oxides (Contin *et al.*, 2007) and so these high metal concentrations in soil solution may not be seen.

Chapter 6:

Vegetable uptake from waste-amended Chat Moss soil

6.1 Introduction

Most of Chat Moss is currently under arable cultivation, with cereal crops being the main product. However there have been suggestions that some farms on Chat Moss may return to market gardening, producing vegetables for nearby Manchester, stimulated by the consumer trend for organic and locally grown crops (Stringer, Pers. Comm.¹). Unfortunately, elevated concentrations of metals in Chat Moss soils (Chapter 3) raise the possibility that vegetable crops may present a potential risk to human health.

It has been shown by many authors that vegetables grown in contaminated soils can take up metals, the mechanisms and factors affecting this are discussed in Chapter 1.4. The uptake of metals from soils is complex; partly controlled by soil conditions and partly by the different affinities that vegetables express for individual trace elements. In a study of vegetables grown on a soil spiked with cadmium nitrate, copper sulphate, lead nitrate and zinc sulphate, it was found that the order of accumulation varied for each metal (Alexander *et al.*, 2006). Alexander *et al.*, (2006) found that for Cd, the preference expressed was lettuce > spinach > onion > carrot > pea > French bean, for Cu, spinach > lettuce > pea > French bean > carrot > onion, for Pb, lettuce > onion > carrot > spinach > pea > French bean and for Zn, the order of accumulation was spinach > lettuce > onion > pea > carrot > French bean.

¹ Conversation with farmer of CM-3 during sampling visit in August 2007.

It has been reported that As, Cd and Pb are the metals most likely to be found as contaminants in vegetables (Kachenko & Singh, 2006), and it is well known that these metals can pose a significant risk to human health. Cadmium concentrations in plants have been positively correlated with soil Cd concentration, soil Zn concentration and plant Zn concentration (Kachenko & Singh, 2006), which indicates that there may be an interaction between Cd and Zn for plant uptake.

Vegetables show highly variable levels of metal concentration, with many factors affecting uptake rates (Chapter 1.4.1). For many metals, soil concentration is a key factor controlling plant uptake, particularly Zn, Mo, Cr and Se (Kabata-Pendias, 2001), with Zn uptake strongly related to soil Zn concentration (Kachenko & Singh, 2006). It has been reported that leafy vegetables and root vegetables often show different levels of metal contamination; in particular Cd, which accumulates markedly more in leafy than root vegetables (Podar & Ramsey, 2005). In a study of vegetables and herbs sampled from urban allotments, it was found again that Cd accumulated in the leaves of all plants, and also that young plants were more likely to take up Cd. It was also found that soil factors affected the uptake of metals, with Cu and Pb affected by organic matter content and Zn and Ni affected by clay content (Mocko & Waclawek, 2004).

Limits have been placed on metal concentrations in saleable foods by the EU (European Union, 2006) for Pb, Cd and Hg, but variation in uptake between species suggests that limits based on generic classes such as 'leaf' or 'root' vegetables may not be effective. The standard index used to express 'non-cancer' risk from consumption of food, such as vegetables grown in metal contaminated soils, is the 'Hazard Quotient' (Chapter 1.4.2). These are simply the ratio of actual 'average

daily dose' to a safe 'reference dose' based on toxicological information. The average daily dose is calculated from plant metal content, average body weight and daily vegetable ingestion.

To assess the risk of consuming plants grown on Chat Moss, greenhouse trials were carried out using nine vegetables and herbs grown on topsoil collected from Chat Moss. Using the data from these trials, Hazard Quotients were calculated based on UK dietary considerations (Section 6.2).

6.2 Materials and methods and trial design

A combination of nine vegetable and herb crops were grown in glasshouse experiments using topsoil from the waste-amended Chat Moss site CM-3 in two growth seasons, 2006 (October to December) and 2007 (July to October) (see Chapter 3 for soil characteristics). The plants used were carrot (*Daucus carota* var. Early Scarlet Horn), lettuce (*Lactuca sativa* var. Little Gem), spinach (*Spinacia oleracea* var. Perpetual), mint (*Mentha viridis*), parsley (*Petroselinum crispum* var. Plain), cabbage (*Brassica oleracea* var. Golden Acre), leek (*Allium ampeloprasum* var. Atal), onion (*Allium cepa* var. White Lisbon) and radish (*Raphanum sativus* var. Scarlet Globe). These were chosen to represent common market garden crops that could be grown on Chat Moss for local consumption. Field-moist soil from site CM-3 was collected on 10th August 2006, air-dried and sieved to 6 mm before being potted in 800 g aliquots in 1 L plastic plant pots. Pots were sown with five seeds of each vegetable, although for parsley and mint this was increased to 10 and 25 seeds respectively due to the smaller seed size of these plants. Once the seedlings had germinated, they were thinned out to two seedlings per pot, with the exception of parsley and mint. A randomised block design was used to lay out the nine vegetables

with five replicates of each. The pots were blocked to minimise variation in the greenhouse environmental factors, temperature and light. The plants were then grown to a stage less than full maturity, which was taken to be the point at which they were potentially edible (Plate 6.1) but had not outgrown the pots. The growth period of each plant is summarised in Table 6.1. Once harvested, the edible parts of each plant were processed as detailed in Section 2.5.2 and analysed for total metal content as described in Section 2.6. Dry weight (DW) concentration data was converted to fresh weight (FW) data using a vegetable-specific conversion factor calculated using the measured fresh and dry weights. It should be noted that metals such as Al, Ti, Cr, and to some extent Mn and Fe, are commonly present as soil dust contamination rather than as a consequence of systemic uptake into plant tissues. Therefore washing of the plant tissues was conducted to minimise these effects. Extremely poor growth of spinach in 2006 resulted in unrealistic data and this has been excluded.



Plate 6.1: Images of vegetables grown in waste-amended Chat Moss soil (CM-3) collected immediately prior to harvest from the 2006 season.

Table 6.1: Growth periods of vegetables grown in waste-amended Chat Moss soil (CM-3) for 2006 and 2007 seasons.

	2006 growth period (days)	2007 growth period (days)
Carrot	83	89
Radish	35	35
Leek	107	105
Onion	107	105
Spinach	65	63
Lettuce	65	89
Cabbage	65	89
Parsley	75	89
Mint	83	89

6.3 Results and Discussion

6.3.1 Essential plant elements: Al, Mn, Fe, Cu, Zn, Mo

Aluminium

Aluminium is a common constituent of most plants with concentrations ranging from $10^1 - 10^2$ mg kg⁻¹ (DW), although the physiological function of Al is unclear (Kabata-Pendias 2001). Concentrations in the vegetables grown in Chat Moss soils ranged from 0.4 mg kg⁻¹ (FW) (radish, 2007) to 3.7 mg kg⁻¹ (FW) (carrot, 2007) (Figure 6.1), which was within the range reported by Kabata-Pendias, 2001. Results differed between 2006 and 2007, although there was no consistent variation seen, with mint, parsley and spinach accumulating more Al in the 2007 season, and the remaining vegetables accumulating more Al in the 2006 season.

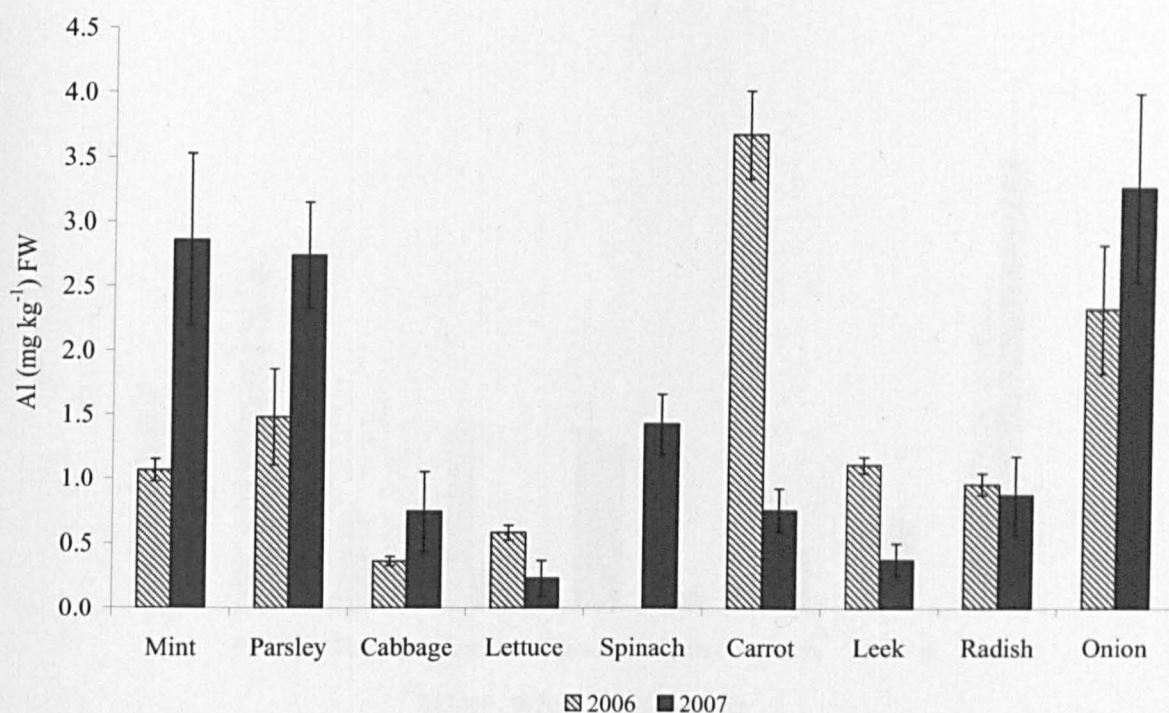


Figure 6.1: Aluminium concentration in edible portions of vegetables grown in waste-amended Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Manganese

Manganese is an essential element for plant nutrition, and uptake is controlled metabolically, in a mechanism similar to Ca^{2+} and Mg^{2+} (Kabata-Pendias, 2001). Uptake of Mn ranged from 0.31 mg kg^{-1} (FW) (cabbage, 2007) to 14.13 mg kg^{-1} (FW) (onion, 2007) (Figure 6.2). There were differences seen between 2006 and 2007 results, with radish and onion showing higher Mn uptake in 2007, but for all other vegetables higher uptake was seen in 2006. Manganese concentrations were similar to those reported by Kabata-Pendias (2001), who reported levels in of $1.1 - 2.6 \text{ mg kg}^{-1}$ (FW), $0.1 - 4 \text{ mg kg}^{-1}$ (FW) and $0.15 - 1.5 \text{ mg kg}^{-1}$ (FW) in cabbage, lettuce and carrots respectively. The 2007 results were comparable to US averages for spinach, cabbage and lettuce (US FDA, 2006).

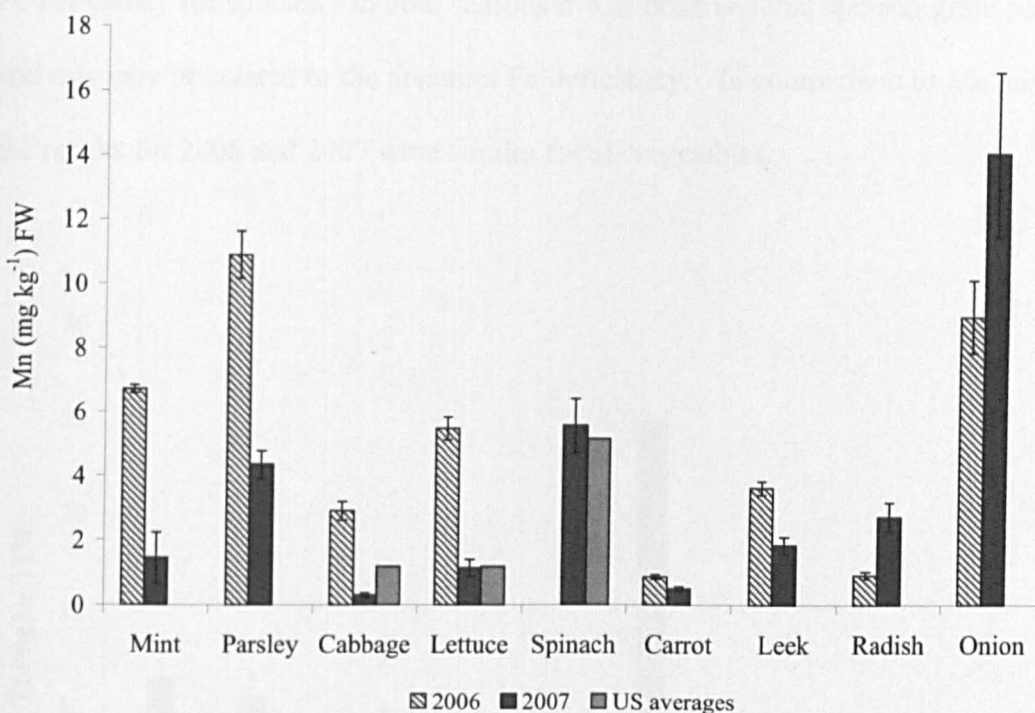


Figure 6.2: Manganese concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. US average data shown for cabbage, lettuce and spinach taken from US FDA (2006).

Iron

The uptake of Fe by plants is metabolically controlled, and Fe can be taken up as Fe^{3+} , Fe^{2+} or Fe chelates (Kabata-Pendias, 2001). There are many recognised metabolic functions of Fe, including involvement in the mechanisms of photosynthetic electron transfer, reduction of nitrites and sulphates, chlorophyll formation and nucleic acid metabolism. Iron concentrations ranged from 3.23 mg kg⁻¹ (FW) (lettuce, 2007) to 11.5 mg kg⁻¹ (FW) (mint, 2007) (Figure 6.3).

Average vegetable Fe concentrations as reported by the US Food and Drug Administration (US FDA, 2006) correspond well with the results of the current study for cabbage and lettuce, but far exceed the results for spinach, indicating a possible

Fe deficiency for spinach. In both seasons it was observed that spinach grew poorly, and this may be related to the apparent Fe deficiency. In comparison to Mn and Al, the results for 2006 and 2007 were similar for all vegetables.

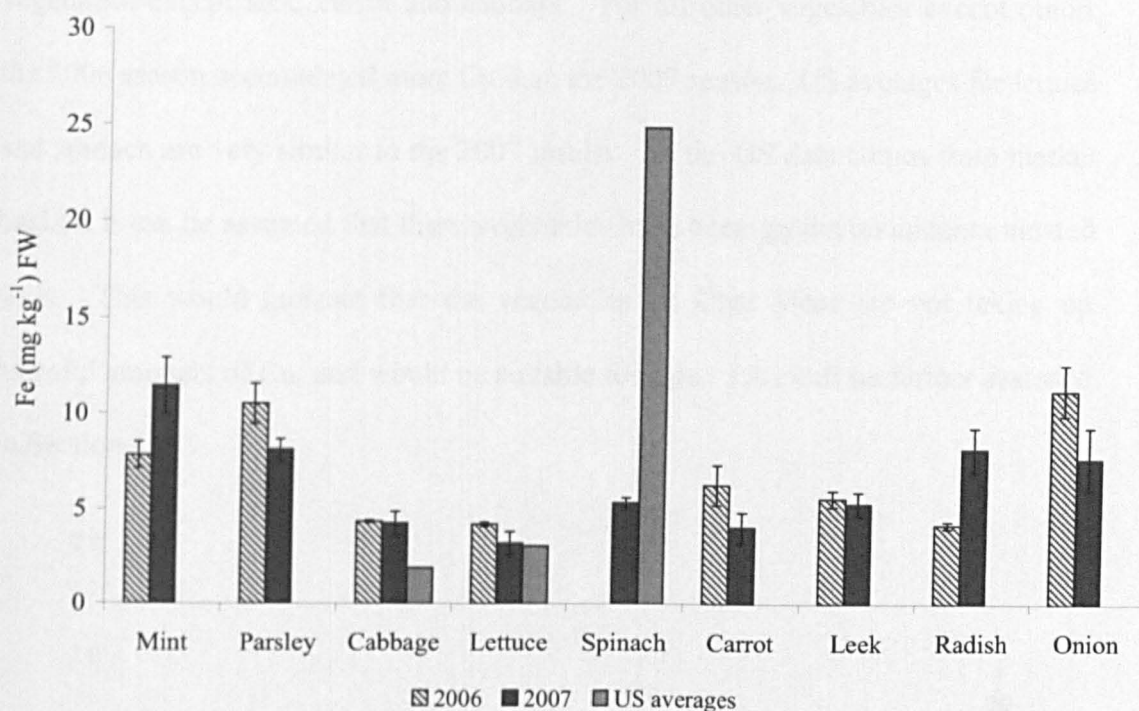


Figure 6.3: Iron concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. US average data shown for cabbage, lettuce and spinach taken from US FDA (2006).

Copper

Copper has many functions in plant physiology including significant roles in photosynthesis, respiration, carbohydrate distribution, nitrogen reduction and fixation, protein metabolism, cell wall metabolism and the production of DNA and RNA (Kabata-Pendias, 2001). Copper concentrations in vegetables grown on

contaminated soil from Chat Moss ranged from 0.27 mg kg⁻¹ (FW) (lettuce, 2007) to 1.84 mg kg⁻¹ (FW) (onion, 2007) (Figure 6.4).

There were large differences seen between the 2006 and 2007 seasons for all vegetables except leek, carrot and cabbage. For all other vegetables except onion, the 2006 season accumulated more Cu than the 2007 season. US averages for lettuce and spinach are very similar to the 2007 results. As the US data comes from market baskets it can be assumed that these vegetables have been grown on uncontaminated soils. This would indicate that the vegetables on Chat Moss are not taking up harmful amounts of Cu, and would be suitable for sale. This will be further assessed in Section 6.4

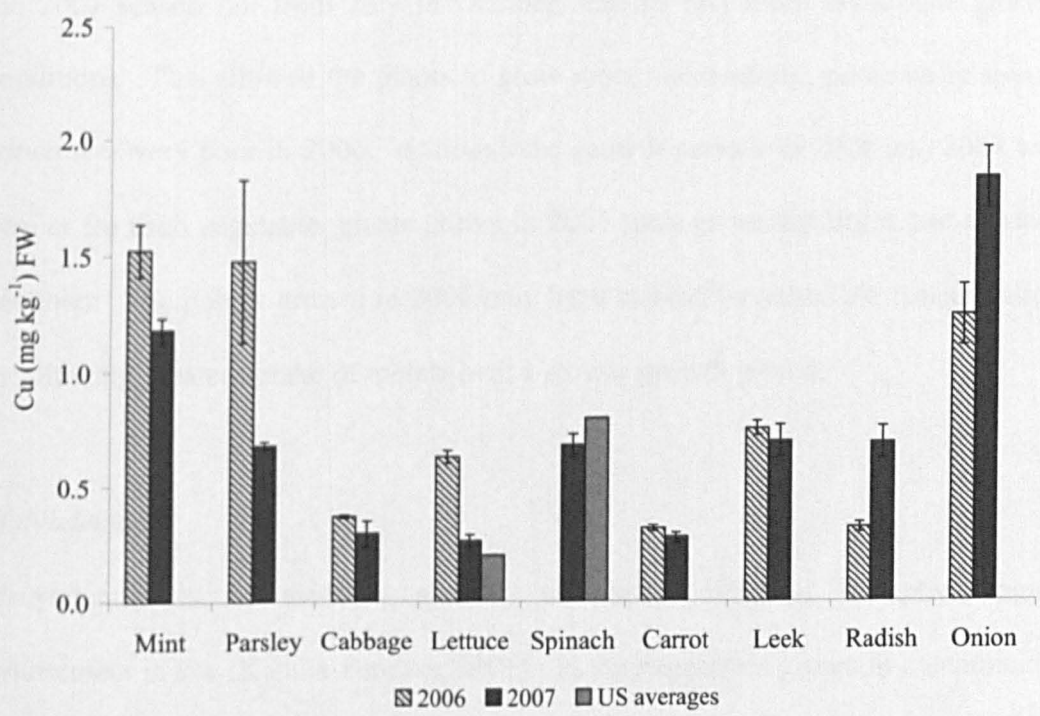


Figure 6.4: Copper concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. US average data shown for lettuce and spinach taken from US FDA (2006).

Zinc

Zinc is an essential element for plant metabolism, and is involved in enzyme function (Kabata-Pendias, 2001). It has been reported that Zn uptake is linear with concentration in nutrient solution and soils (Kachenko & Singh, 2006). Zinc uptake in vegetables grown in contaminated soil from Chat Moss ranged from 1.71 mg kg⁻¹ (FW) (carrot, 2007) to 75.1 mg kg⁻¹ (FW) (onion, 2007) (Figure 6.5).

When compared to US averages for cabbage, lettuce and spinach, it can be seen that Zn uptake in the vegetables exceeded the US averages. It was also observed that vegetables grown in the 2006 season, with the exception of onion and carrot, showed higher Zn concentration. The 2006 season ran from October to December, whereas the 2007 season ran from July to October, and so had more favourable growing conditions. This allowed the plants to grow more successfully, particularly spinach which was very poor in 2006. Although the growth periods in 2006 and 2007 were similar for each vegetable, plants grown in 2007 were generally larger and appeared healthier. The poorer growth in 2006 may have caused increased Zn concentrations by allowing greater uptake of metals over a slower growth period.

Molybdenum

Molybdenum is an essential element in plants, although the physiological requirement is low (Kabata-Pendias, 2001). In the vegetables grown in contaminated Chat Moss soil, uptake ranged from 0.07 mg kg⁻¹ (FW) (carrot, 2006) to 7.35 (FW) (lettuce, 2007) (Figure 6.6).

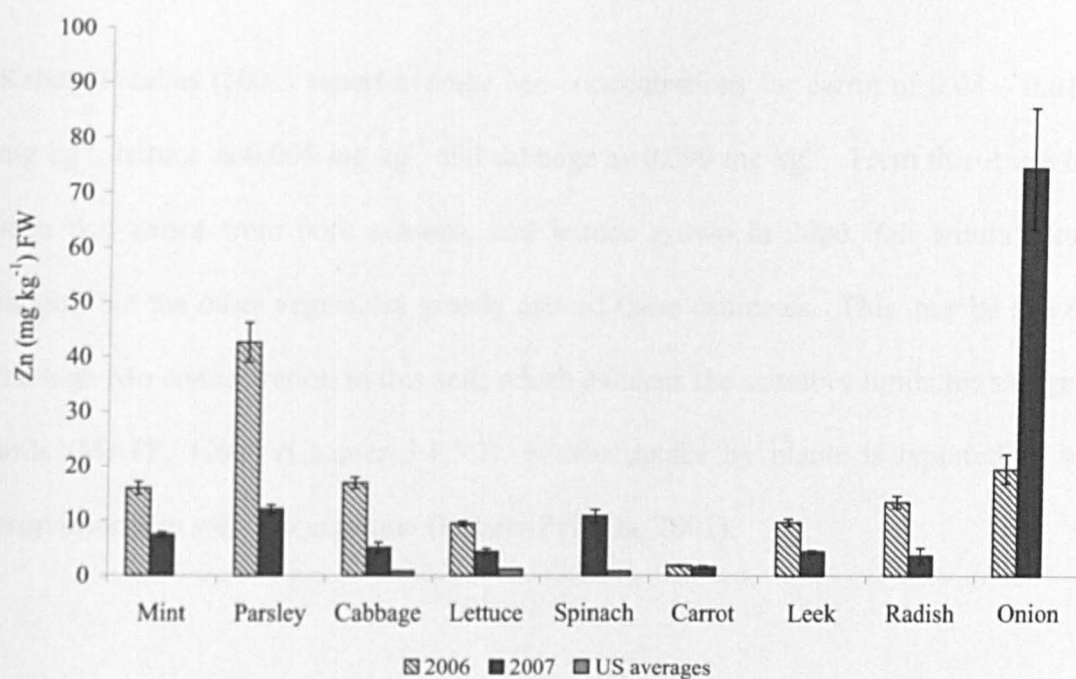


Figure 6.5: Zinc concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. US average data shown for cabbage, lettuce and spinach taken from US FDA (2006).

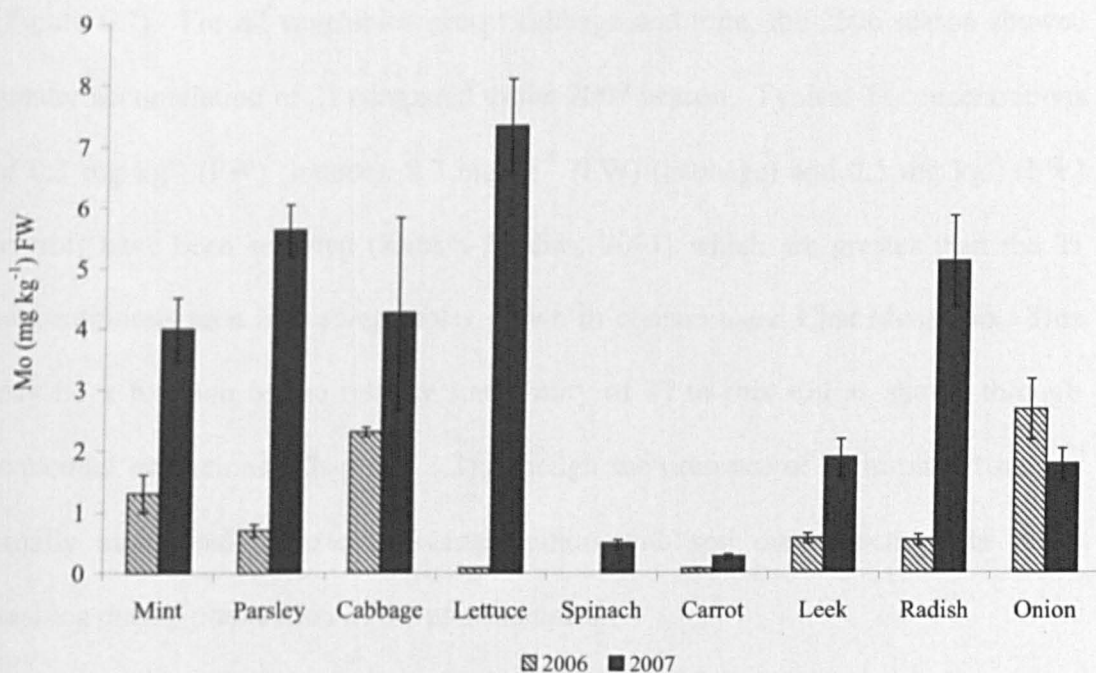


Figure 6.6: Molybdenum concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Kabata-Pendias (2001) report average Mo concentrations for carrot of 0.08 – 0.015 mg kg⁻¹, lettuce as 0.005 mg kg⁻¹ and cabbage as 0.099 mg kg⁻¹. From this it can be seen that carrot from both seasons, and lettuce grown in 2006, fall within these ranges; but the other vegetables greatly exceed these estimates. This may be due to the high Mo concentration in this soil, which exceeds the statutory limits for sludged soils (MAFF, 1998) (Chapter 3.1.3.3), as Mo uptake by plants is reported to be proportional to soil concentration (Kabata-Pendias, 2001).

6.3.2 Non-essential plant elements: Ti, V, Cr, Co, Ni, As, Se, Cd, Cs, Ba, Pb

Titanium

Titanium concentrations in plants grown on soil from Chat Moss ranged from 0.000557 mg kg⁻¹ (FW) (cabbage, 2006) to 0.047 mg kg⁻¹ (FW) (carrot, 2006) (Figure 6.7). For all vegetables except cabbage and mint, the 2006 season showed greater accumulation of Ti compared to the 2007 season. Typical Ti concentrations of 0.3 mg kg⁻¹ (FW) (lettuce), 0.7 mg kg⁻¹ (FW) (cabbage) and 0.5 mg kg⁻¹ (FW) (carrot) have been reported (Kabata-Pendias, 2001) which are greater than the Ti concentrations seen in the vegetables grown in contaminated Chat Moss soil. This may be a function of the relative immobility of Ti in this soil as shown through sequential extractions (Chapter 4.3.3) although the presence of Ti in plant tissue is usually interpreted as external contamination with soil dust which might resist washing during preparation of the plant samples.

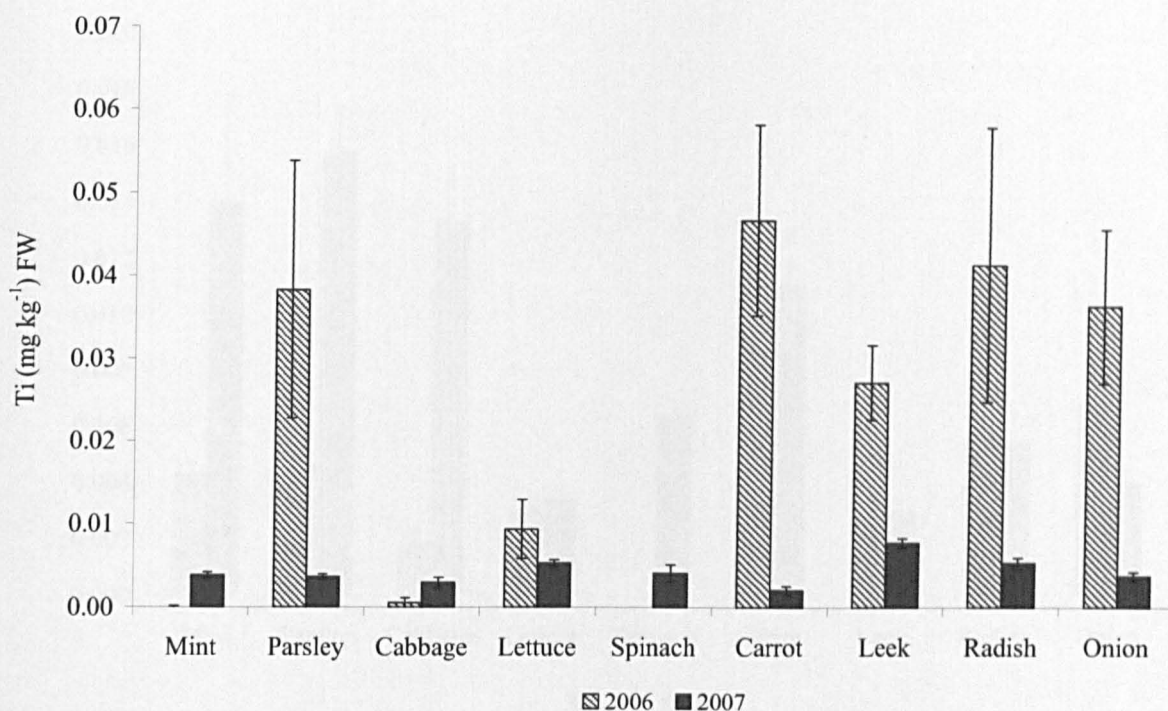


Figure 6.7: Titanium concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Vanadium

Vanadium has been shown to be essential for algal photosynthesis, but there are no clear functions in plant physiology. Vanadium concentrations in plants grown in contaminated Chat Moss soil ranged from 0.0018 mg kg⁻¹ (FW) (cabbage, 2006) to 0.0157 mg kg⁻¹ (FW) (parsley, 2007) (Figure 6.8). Average V concentration in vegetables has been reported to range from 5.3 µg kg⁻¹ FW (lettuce) to 8.8 µg kg⁻¹ FW (carrot) (Kabata-Pendias, 2001), which is within the range seen for vegetables grown in Chat Moss soils.

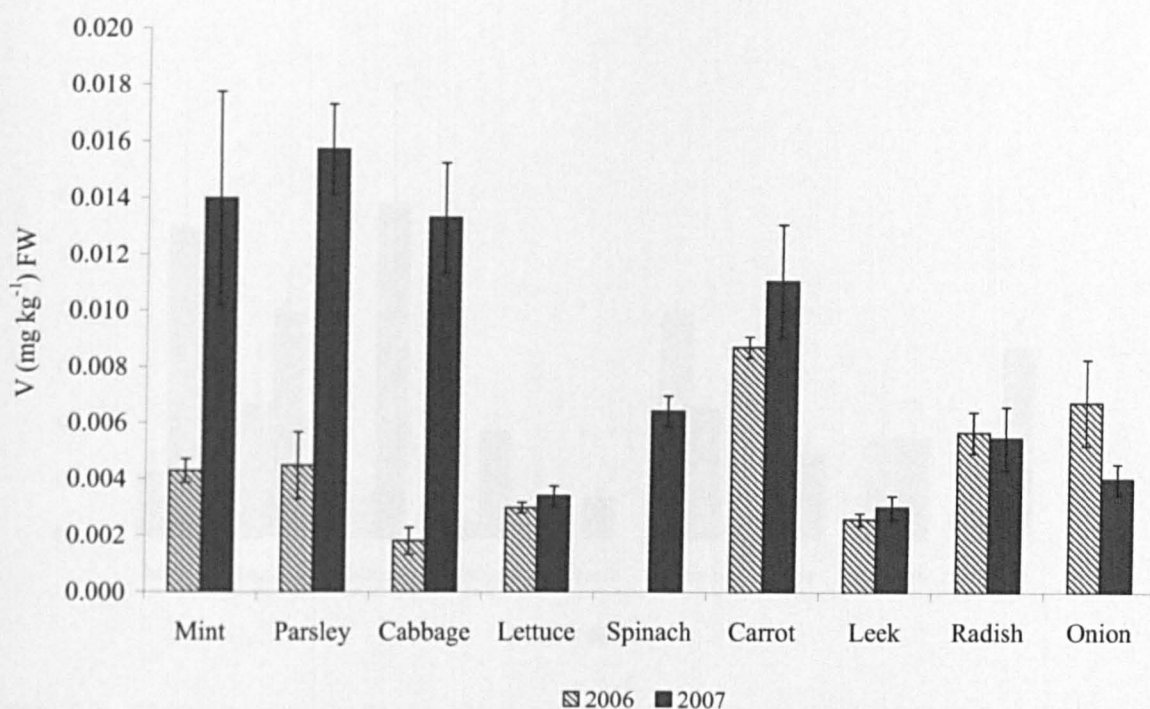


Figure 6.8: Vanadium concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Chromium

Chromium concentration in vegetables grown on Chat Moss soils ranged from 0.0153 mg kg⁻¹ (FW) (lettuce, 2006) to 0.293 mg kg⁻¹ (FW) (cabbage, 2007) (Figure 6.9). Chromium concentrations of 0.008 mg kg⁻¹ (FW) have been reported in lettuce (Kabata-Pendias, 2001) which is similar to the concentration seen in the lettuce and cabbage from the 2006 season. For all vegetables except spinach, carrot and radish the 2007 season showed greater accumulation of Cr than 2006. Uptake of Cr by plants is controlled by soluble Cr content in soils (Kabata-Pendias, 2001). Sequential extractions showed that 39% of Cr in the Chat Moss soil was present in the organic fraction (Chapter 4.3) which has the potential to become solubilised, which may explain the relatively high Cr concentrations in the vegetables.

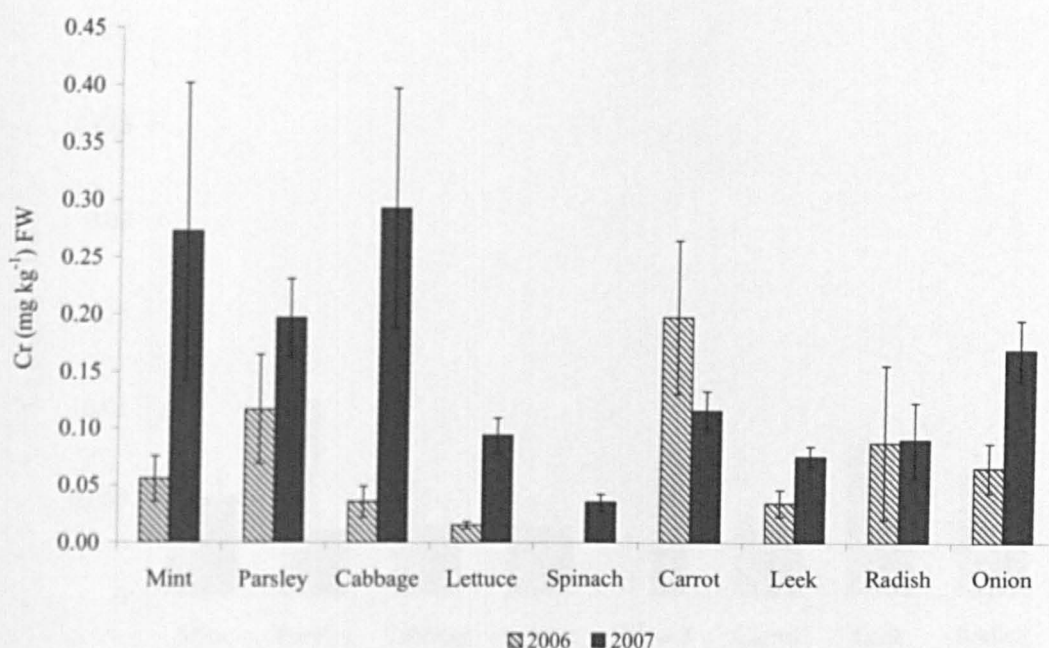


Figure 6.9: Chromium concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Cobalt

Cobalt is essential for algae but there is no known function in higher plants. Cobalt concentrations in vegetables grown on Chat Moss soil ranged from 0.00349 mg kg⁻¹ (FW) (parsley, 2007) to 0.0225 mg kg⁻¹ (FW) (onion, 2007) (Figure 6.10). When compared to known concentrations of Co in cabbage (3.6 – 8 mg kg⁻¹ FW), lettuce (1.9 – 6.8 mg kg⁻¹ FW) and carrot (3 – 4.4 mg kg⁻¹ FW) (Kabata-Pendias, 2001) the Co concentration in the vegetables grown on Chat Moss soils were very low. Cobalt is taken up by plants as organic complexes, and uptake is strongly controlled by soil conditions, which indicates that under the conditions of this experiment and the Chat Moss soil, Co was not generally available for plant uptake.

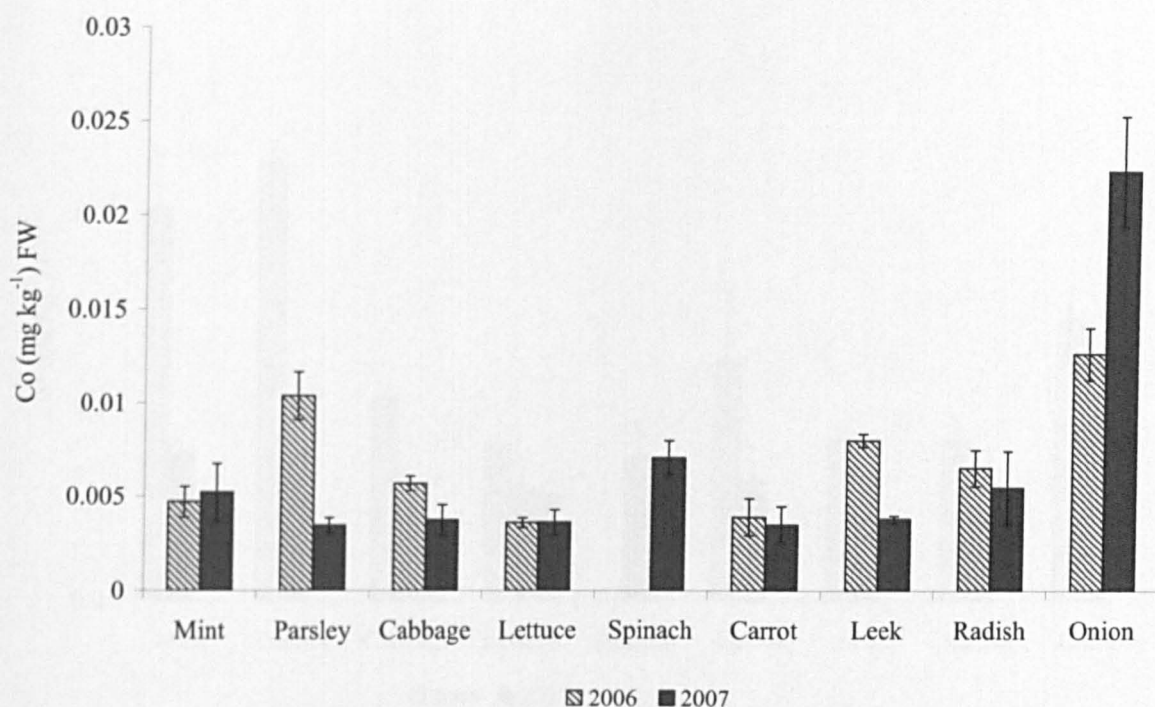


Figure 6.10: Cobalt concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Nickel

Nickel concentrations ranged between 0.0883 mg kg⁻¹ (FW) (cabbage, 2007) to 0.455 mg kg⁻¹ (FW) (parsley, 2006) (Figure 6.11). Nickel concentrations in vegetables have been reported to range from 0.01 mg kg⁻¹ (FW) (lettuce) to 0.05 mg kg⁻¹ (FW) (cabbage) (Kabata-Pendias, 2001). Nickel uptake was similar to US averages (US FDA, 2006), particularly for lettuce.

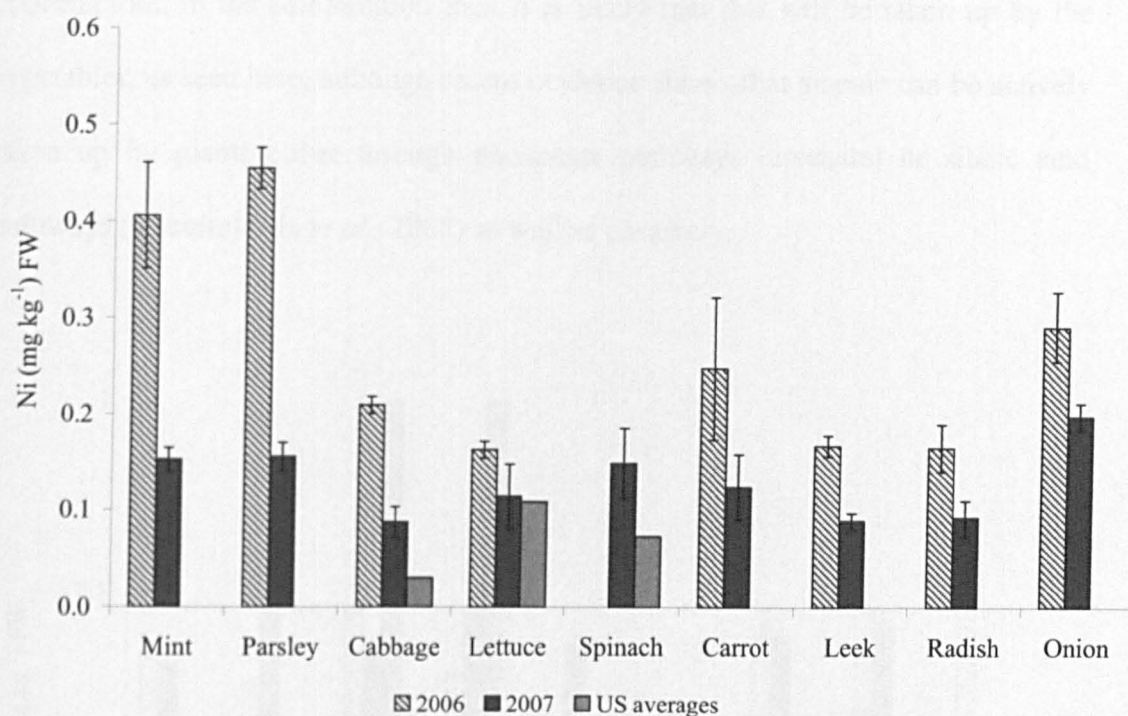


Figure 6.11: Nickel concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. US average data shown for cabbage, lettuce and spinach taken from US FDA (2006).

Arsenic

Arsenic is a constituent of most plants, but there is little known about its biochemical role. Arsenic concentrations in the vegetables grown on Chat Moss soil ranged from 0.00677 mg kg⁻¹ (FW) (onion, 2007) to 0.116 (FW) (onion, 2006) (Figure 6.12). When compared to US and UK average As concentrations (US FDA, 2006; UK FSA, 2002), it can be seen that the Chat Moss vegetables show much higher levels of As in the plant tissues. This corresponds with the levels of As in soil solution collected from the same soil during anaerobic incubation (Chapter 5), which showed levels of As in excess of the Safe Drinking Water Limits as set by the World Health Organisation (WHO, 2008). One of the main mechanisms for the uptake of As by vegetables is passive absorption with water flow, therefore if there is high As

concentration in the soil solution then it is likely that this will be taken up by the vegetables, as seen here, although recent evidence shows that arsenic can be actively taken up by plants either through phosphate pathways (arsenate) or silicic acid pathways (arsenite) (Ma *et al.*, 2008) as well as passively.

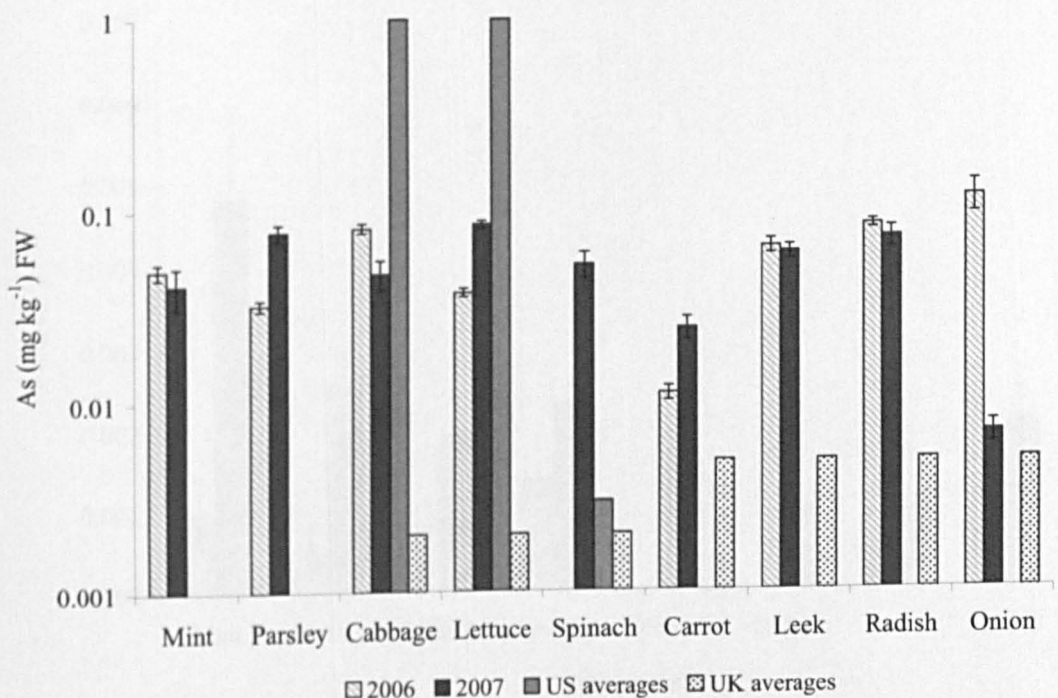


Figure 6.12: Arsenic concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. US average data shown for cabbage, lettuce and spinach taken from US FDA (2006), UK average data shown for cabbage, lettuce, spinach, carrot, leek, radish and onion taken from UK FSA (2002).

Selenium

Selenium concentrations in vegetables grown in contaminated Chat Moss soils ranged from 0 mg kg⁻¹ (FW) (carrot, 2006) to 0.00483 mg kg⁻¹ (FW) (mint, 2007) (Figure 6.13). For all vegetables, the 2007 season showed greater accumulation of Se than the 2006 season. A positive linear correlation has been reported between Se concentration in soils and plants (Kabata-Pendias, 2001), indicating that soil Se

concentration is the controlling factor for plant uptake. Selenium concentrations in vegetables have been reported as $7.2 \mu\text{g kg}^{-1}$ (FW) (parsley), $2.4 \mu\text{g kg}^{-1}$ (FW) (lettuce), $7.3 \mu\text{g kg}^{-1}$ (FW) (onion) and $6.1 \mu\text{g kg}^{-1}$ (FW) (carrot) (Pappa *et al.*, 2006), which are in the same range as the vegetables grown in Chat Moss soil.

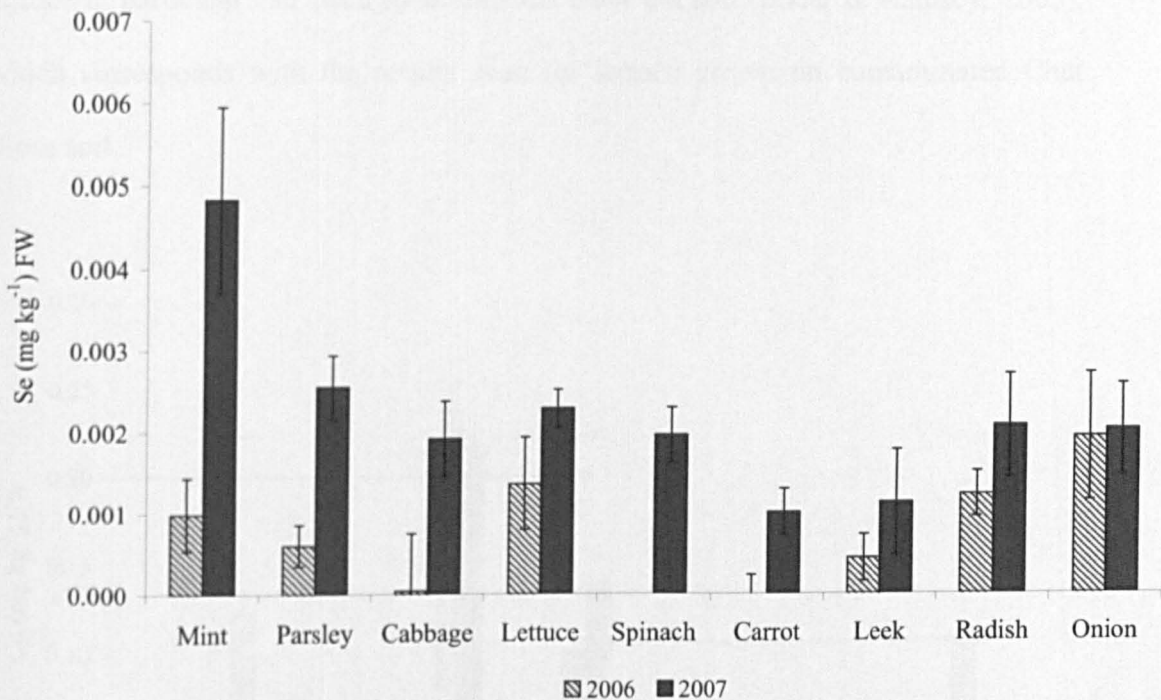


Figure 6.13: Selenium concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Cadmium

Cadmium is a non-essential element for plant metabolism, but it is effectively absorbed by leaf and root systems (Kabata-Pendias, 2001). Cadmium concentrations in the vegetables grown in soil from Chat Moss ranged from 0.007 mg kg^{-1} (FW) (mint, 2007) to 0.238 mg kg^{-1} (FW) (lettuce, 2006) (Figure 6.14).

Limits have been placed on Cd concentration in vegetables by the European Union (EU, 2006), and these limits were exceeded by lettuce grown in both seasons, indicating that these vegetables would not be suitable for sale. The risk posed by these vegetables to human health will be further discussed in Chapter 6.4 using Hazard Quotients. It has been found in other studies that leafy vegetables, and lettuce in particular can strongly absorb Cd from the soil (Podar & Ramsey, 2005), which corresponds with the results seen for lettuce grown on contaminated Chat Moss soil.

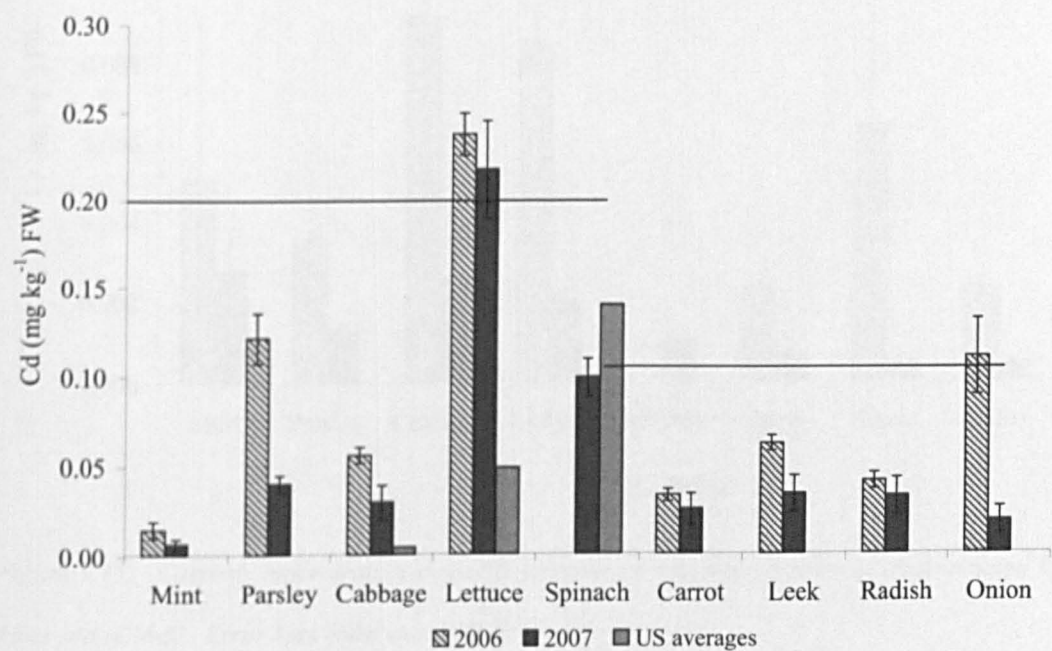


Figure 6.14: Cadmium concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. Horizontal lines show EU limits for Cd in green vegetables (0.2 mg kg^{-1}) and root vegetables (0.1 mg kg^{-1}). US average data shown for cabbage, lettuce and spinach taken from US FDA (2006).

Caesium

Caesium concentrations ranged from 0.0005 mg kg⁻¹ (FW) (leek, 2006) to 0.0092 mg kg⁻¹ (FW) (cabbage, 2006) (Figure 6.15). Caesium concentrations in vegetables have been shown to range from 0.2 – 3.3 µg kg⁻¹ (FW) (Kabata-Pendias, 2001), and the vegetables grown on Chat Moss soil fall at the lower end of this range.

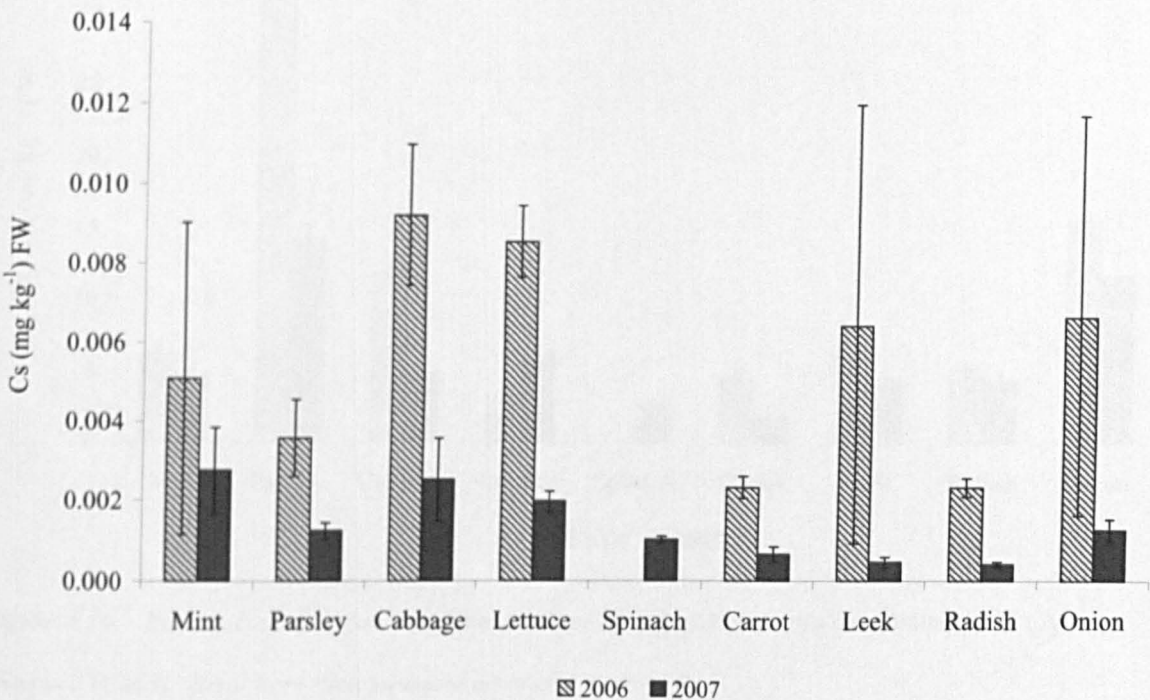


Figure 6.15: Caesium concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Barium

Barium concentrations in vegetables grown in contaminated soil from Chat Moss ranged from 1.8 mg kg⁻¹ (FW) (carrot, 2007) to 31.4 mg kg⁻¹ (FW) (parsley, 2006) (Figure 6.16). Typical Ba concentrations in vegetables range from 0.5 mg kg⁻¹ (FW) (carrot) to 1.3 mg kg⁻¹ (FW) (cabbage) (Kabata-Pendias, 2001), which is much lower than the concentrations seen in these Chat Moss grown vegetables. It has been

reported that Ba uptake can increase in acid soils (Kabata-Pendias, 2001) which could explain the increased uptake in these vegetables, which were grown in acid soils.

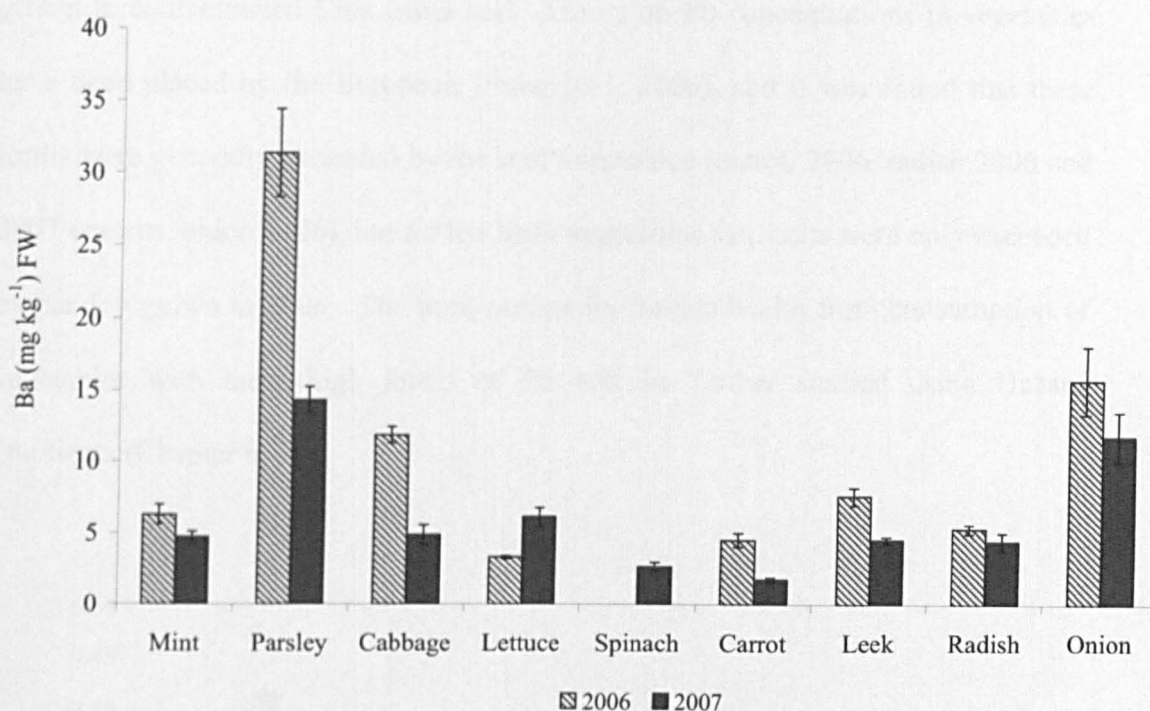


Figure 6.16: Barium concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates.

Lead

Lead is known to occur naturally in plants but there are no essential roles in metabolism of lead. Lead contents in vegetables grown in contaminated Chat Moss soils ranged from 0.038 mg kg⁻¹ (FW) (cabbage, 2007) to 0.415 mg kg⁻¹ (FW) (parsley, 2006) (Figure 6.17). Typical lead concentrations in vegetables were measured as 0.009 – 0.012 mg kg⁻¹ (FW) (carrot), 0.001 mg kg⁻¹ (FW) (lettuce) and 0.016 (FW) (cabbage) (Kabata-Pendias, 2001), and 0.013 mg kg⁻¹ (FW) (spinach) (US FDA, 2006). These concentrations are consistently lower than the Pb concentrations observed in vegetables grown in contaminated Chat Moss soil, most

likely due to the high lead content of the soil (Chapter 3.1.3.3). It was shown using stable lead isotope dilution that ~ 50% of the total Pb concentration was labile, which means it would be present in soil solution and potentially available for plant uptake (Chapter 4.4), this could explain the higher Pb concentrations seen in vegetables grown in contaminated Chat Moss soil. Limits on Pb concentrations in vegetables have been placed by the European Union (EU, 2006), and it was found that these limits were generally exceeded by the root vegetables (carrot, 2006, radish 2006 and 2007 seasons, onion 2006), but for the leafy vegetables the limits were only exceeded by parsley grown in 2006. The implications for human health from consumption of vegetables with these high levels of Pb will be further studied using Hazard Quotients (Chapter 6.4).

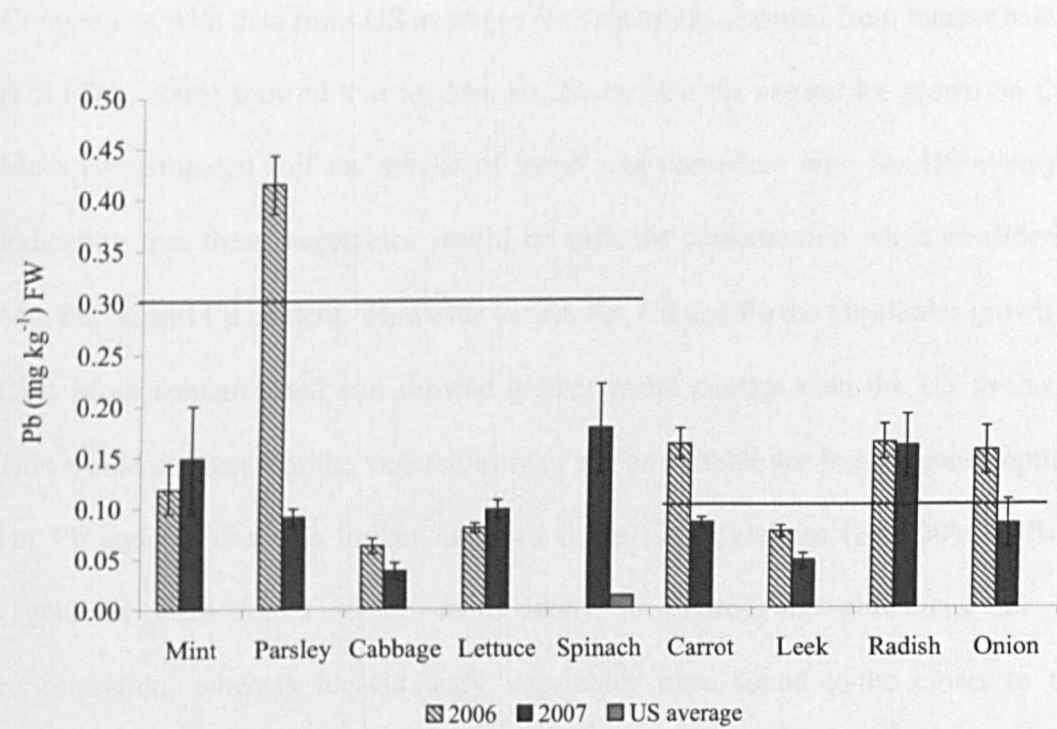


Figure 6.17: Lead concentration in edible portions of vegetables grown in contaminated Chat Moss soil (CM-3). Error bars show standard error of 5 replicates. Horizontal lines show EU limits for Pb in green vegetables (0.3 mg kg^{-1}) and root vegetables (0.1 mg kg^{-1}). US average data shown for spinach taken from US FDA (2006).

Vegetables grown on contaminated soil from Chat Moss showed variable uptake of metals, with variation seen between vegetables, metals and season. For example, spinach grown in 2006 showed accumulation of Zn, Cd, Co and a deficiency of Fe compared to the 2007 season (data not shown). This indicated a possible synergistic relationship between Zn, Cd and Co and an antagonistic relationship with Fe. Synergistic relationships between Cd and Zn particularly in lettuce uptake has also been reported, supporting the results seen here (Podar & Ramsey, 2005), however this could also simply indicate that high concentrations and high plant uptake of Cd, Zn and Co coincide in these soils.

Comparison with data from US averages for vegetables sampled from market baskets (US FDA, 2006) showed that for Mn, Fe, Ni and Cu the vegetables grown on Chat Moss contaminated soil the uptake of metal was consistent with the US averages, indicating that these vegetables would be safe for consumption when considering Mn, Fe, Ni and Cu content. However for Zn, As, Cd and Pb the vegetables grown on Chat Moss contaminated soil showed greater metal content than the US averages. This would suggest that the vegetables may not be suitable for human consumption. For Pb and Cd this was further assessed using EU guidelines (EU, 2006). Root vegetables were found to be more likely to exceed the guidelines for Pb concentration, whereas for Cd leafy vegetables were found to be closer to the guideline limits. This agrees with the known behaviour of Cd and Pb in vegetables, with Cd found to accumulate in leafy vegetables (Podar & Ramsey, 2005; Kachenko & Singh, 2006) and Pb found to accumulate in root vegetables (Finster *et al.*, 2004). One of the main factors affecting plant uptake of metals is often reported as pH

(Wang *et al.*, 2006) which may explain the relatively high metal concentration in the plant tissues of vegetables grown on contaminated Chat Moss soils, as the slightly acidic pH (~6) would aid in metal uptake. The variability in metal uptake both in terms of metal and species show that risk assessments cannot be generalised by total soil metal content, but that bioavailability and crop must be considered (Kachenko & Singh, 2006). For this reason Hazard Quotients were used to assess the risk to human health from consumption of vegetables grown on contaminated Chat Moss soils.

6.4 Implications of metal uptake by vegetables for assessment of risk to human health

Hazard Quotients were used to assess the risk to human health from consumption of vegetables grown on Chat Moss (Section 1.4.2). Hazard Quotients were calculated for Ni, Cr, As, Mn, Zn, Se, Sr, Mo, Cd, Ba and Pb using Reference Dose values from IRIS (USEPA, 2009) and selected references (Table 6.2).

Table 6.2: Reference dose values used to calculate Hazard Quotients of vegetables grown in contaminated Chat Moss soil (CM-3).

Element	RfD (mg kg ⁻¹ d ⁻¹)	Source
Ni	0.02	USEPA IRIS
Cr	0.003	USEPA IRIS
As	0.0003	USEPA IRIS
Mn	0.14	USEPA IRIS
Zn	0.3	USEPA IRIS
Se	0.005	USEPA IRIS
Sr	0.6	USEPA IRIS
Mo	0.005	USEPA IRIS
Cd	0.00036	CLEA (2009)
Ba	0.2	USEPA IRIS
Pb	0.0035	Hough <i>et al.</i> , (2004)

Any Hazard Quotient greater than 1 represents a potential risk to human health, and as seen from Tables 6.3 and 6.4, only Cd and Mo exceeded this value. For Mo, HQ's greater than 1 were achieved in the 2007 season for parsley (1.67), cabbage (1.49), lettuce (1.69) and radish (2.14), although for the 2006 season, all HQ's were lower than 0.6 (radish). For Cd, HQ's greater than 1 were calculated for lettuce grown in both seasons, which agrees with the findings of Podar & Ramsey (2005) of lettuce being an accumulator of Cd.

Table 6.3: Hazard Quotients for ingestion of trace elements in vegetables grown on waste-amended soil from Chat Moss (CM-3; Section 2.1) in 2006 assuming a 70 kg adult consuming 200 g fresh vegetables daily. Reference doses used were from the USEPA-IRIS database and Hough et al., (2004).

	Mo	Cd	As	Mn	Ni	Zn	Ba	Pb	Sr	Se	Cr
Mint	0.311	0.0490	0.197	0.0571	0.0242	0.0631	0.0377	0.0405	0.00603	2.35x10 ⁻⁴	4.42x10 ⁻⁵
Parsley	0.208	0.497	0.161	0.115	0.0335	0.210	0.231	0.175	0.00903	1.76x10 ⁻⁴	1.15x10 ⁻⁴
Cabbage	0.526	0.178	0.311	0.0237	0.0120	0.0642	0.0678	0.0203	0.0107	8.51x10 ⁻⁶	2.71x10 ⁻⁵
Lettuce	0.0374	1.56	0.296	0.0927	0.0193	0.0745	0.0397	0.0542	0.00674	6.43x10 ⁻⁴	2.41x10 ⁻⁵
Carrot	0.0432	0.307	0.122	0.0206	0.139	0.0215	0.0756	0.154	0.00289	0	4.40x10 ⁻⁴
Leek	0.184	0.282	0.349	0.0425	0.0138	0.0537	0.0621	0.0352	0.00716	1.44x10 ⁻⁴	3.77x10 ⁻⁵
Radish	0.193	0.207	0.493	0.0120	0.0150	0.0825	0.0476	0.0840	0.00666	4.44x10 ⁻⁴	1.06x10 ⁻⁴
Onion	0.603	0.346	0.434	0.0726	0.0165	0.0746	0.0883	0.0499	0.0122	4.35x10 ⁻⁴	8.86x10 ⁻⁵

Using Hazard Quotients it could be seen that there was little risk to human health from consumption of the vegetables grown on Chat Moss in the 2006 or 2007 seasons, with the exception of Mo and Cd which showed some potential risk, in particular lettuce for Cd which may not be suitable for cultivation on these soils. This indicated that while the historic waste disposal on Chat Moss resulted in

elevated heavy metal concentration in the topsoil (Chapter 3.1.3.3) the metals were not present in a highly bioavailable form. However under different conditions such as increased rainfall, the plant uptake of metals may increase due to increased solubility and bioavailability of metals as demonstrated in Chapter 5, which could lead to higher Hazard Quotients. It should also be considered that the Hazard Quotients were calculated for adult consumption, and that the risk may be greater for a child due to reduced body weight, although this may be mitigated by the reduced intake of vegetables by children.

Table 6.4: Hazard Quotients for ingestion of trace elements in vegetables grown on waste-amended soil from Chat Moss (CM-3; Section 2.1) in 2007 assuming a 70 kg adult consuming 200 g fresh vegetables daily. Reference doses used were from the USEPA-IRIS database and Hough et al., (2004).

	Mo	Cd	As	Mn	Ni	Zn	Ba	Pb	Sr	Se	Cr
Mint	0.966	0.145	0.171	0.0134	0.00931	0.0303	0.0293	0.0526	0.00481	1.22x10 ⁻³	2.14x10 ⁻⁴
Parsley	1.67	0.166	0.383	0.0458	0.0115	0.0593	0.106	0.0384	0.00715	7.50x10 ⁻⁴	1.95x10 ⁻⁴
Cabbage	1.69	0.139	0.324	0.0953	0.00648	0.0171	0.0356	0.0122	0.00747	5.22x10 ⁻⁴	7.16x10 ⁻⁵
Lettuce	0.232	1.41	0.409	0.0926	0.0190	0.0858	0.0317	0.0667	0.00771	8.98x10 ⁻⁴	5.47x10 ⁻⁵
Spinach	0.699	0.531	0.0451	0.191	0.0192	0.472	0.113	0.0956	0.0132	7.62x10 ⁻⁴	2.15x10 ⁻⁴
Carrot	0.180	0.682	0.274	0.0118	0.0206	0.0189	0.0300	0.159	0.00378	7.04x10 ⁻¹	4.95x10 ⁻⁴
Leek	0.607	0.157	0.327	0.0215	0.00740	0.0254	0.0372	0.0952	0.00503	3.63x10 ⁻⁴	8.27x10 ⁻⁵
Radish	1.49	0.163	0.280	0.00391	0.00790	0.0307	0.0449	0.0853	0.00605	6.88x10 ⁻⁴	5.34x10 ⁻⁴
Onion	2.14	0.356	0.477	0.0372	0.00890	0.0236	0.0427	0.0444	0.00780	7.57x10 ⁻⁴	1.17x10 ⁻⁴

6.5 Conclusions

Heavy metal concentrations in nine types of vegetables and herbs grown on historically contaminated soil from Chat Moss were measured and the results used to

assess the risk to human health from a return of the study area to horticultural production. It was found that, compared to US data for market vegetables (US FDA, 2006), the produce grown on Chat Moss showed slightly higher levels of Zn, As, Cd, Pb but there was no increase in Mn, Fe, Ni and Cu compared to US averages. The US data was collected on vegetables from market baskets, which is taken as an indication of fitness for consumption as it is likely that they were not grown on contaminated soils. The European Union limits on Pb and Cd content of vegetables (EU, 2006) were exceeded by lettuce, spinach and onion for Cd and parsley, carrot, radish and onion for Pb. This broadly suggests that root vegetables grown on Chat Moss may be harmful due to Pb accumulation while green leaf vegetables may present some risk due to Cd uptake. It is known that lettuce strongly accumulates Cd (Podar & Ramsey, 2005) so this may not be an appropriate crop to grow on Chat Moss. To further assess the risk to human health, Hazard Quotients were calculated for a number of elements. Only Cd and Mo were shown to be potentially harmful in the vegetables grown in contaminated soil from Chat Moss with lettuce again showing potentially harmful uptake of Cd. There were large differences in metal uptake seen between the two experimental seasons, which may indicate that growing conditions such as temperature and light affect the uptake of heavy metals and represents a source of uncertainty in the assessment of risk from pot trials.

Overall, the risk assessment showed that it should be reasonably safe to grow most vegetables on Chat Moss. However, it may be useful to increase the use of lime as it has been shown that Cd and many other heavy metals are more bioavailable at lower pH (Podar & Ramsey, 2005; Wang *et al.*, 2006; Mocko & Waclawek, 2004) and the organic Chat Moss soils are probably particularly prone to progressive reduction in

pH due to ongoing oxidation reactions. To reduce the risk from metals such as Pb and Cd, variety selection could be used to choose a variety that does not take up large concentrations of metals from soils, although there is little information available on the effect of variety selection on metal uptake. It has been shown that carrot and pea cultivars show significant variation in metal uptake but no variation between cultivars was observed for spinach or lettuce (Alexander *et al.*, 2006). Further work in this field of cultivar selection would be invaluable for minimising risk of metal uptake from vegetables grown in contamination soils such as Chat Moss and urban allotments. It could be recommended to farmers that vegetable and herb crops should be safe to grow on Chat Moss, with the exception of lettuce which showed potentially harmful uptake of Cd.

Chapter 7: Conclusions

7.1 The nature and extent of the contamination of Chat Moss and Halsall Moss

Through the GBASE survey conducted by the BGS, two areas of metal-contaminated fenlands in NW England were discovered; these were Chat Moss west of Manchester and Halsall Moss north of Liverpool (Breward, 2003). Historical research identified these areas as disposal sites for urban waste from the two cities over a period of several hundred years. In the case of Halsall Moss, the waste was mainly organic in the form of human and animal manures, and in the case of Chat Moss the waste was a mixture of organic and mineral wastes, ranging from manures to steelworks waste. Chat Moss was purchased by the Manchester Corporation in 1895 for use as a waste disposal site to alleviate growing waste generation by the city population, but also to reclaim the peat for agricultural purposes. During drainage, the waste from Manchester was incorporated into the moss to reduce loss of soil volume as the peat dried out. The earliest waste used was nightsoil, which has been defined as “ashes mixed with the contents of privies and the scrapings of the streets” (Coney, 1995) and would have been mainly organic in nature, similar to the wastes incorporated in Halsall Moss. As waste disposal continued on Chat Moss, mineral wastes such as street sweepings, garbage and clinkers were increasingly abundant. Over the 65 years of waste disposal, 529 kt of privy midden waste, 429 kt of nightsoil and 402 kt street sweepings was disposed of on Chat Moss. In total, up to 1.92 Mt of waste was incorporated into the soil, which corresponds to 1890 t ha^{-1} . The Chat Moss estate is recorded as being 1013 ha meaning that 39% of the topsoil of Chat Moss today is

composed of waste materials, with average topsoil considered to be 5000 t ha⁻¹. This calculation assumes that the waste incorporated into Chat Moss was dry, if a moisture content in the waste of 30% is assumed, then the proportion of soil composed of waste materials is 27%.

Little data was available on the waste disposed at Halsall Moss, which was a more informal process, with individual farmers bringing city manures to the farms when returning from markets. Evidence for this practise exists from 1571 (Coney, 1995) and anecdotal evidence showed that this continued until recent years. The waste collected from Liverpool for disposal on Halsall Moss was limited to manures for improvement of the soil.

Field evidence on Chat and Halsall Mosses supported the historical findings, with pottery, slag and coal fragments all visible in the soil at Chat Moss, while only pottery was visible at Halsall Moss. SEM studies confirmed the presence of Fe oxides, coal and pottery in the soils, further supporting the historical evidence. All sites on Chat Moss and Halsall Moss showed elevated heavy metal concentrations in topsoils, accompanied by pH increase and LOI decrease generated by soil reclamation, waste disposal and farming practices such as liming.

To further link the historical research with the contamination seen on the mosses today, Pb source apportionment was used which identified a mixture of Pb ore, UK coal and petrol-derived Pb as the sources of lead in Chat Moss soil. This linear array of contamination sources was also found by Weiss *et al.*, (1999a) in a study of ombrotrophic bogs from Switzerland, who also found it difficult to identify a single

source of contamination. The combination of lead sources identified in Chat Moss soils was in agreement with the historical evidence of waste sources from Manchester.

Principal Component Analysis also highlighted elemental associations often found in industrial waste, and the combination of trace element profiles, historical research, Pb isotope analysis, Scanning Electron Microscopy and Principle Component Analysis showed that past land use had resulted in elevated trace element concentrations in the topsoil.

However the levels of metals measured in the soils of Chat Moss were not in agreement with the original GBASE survey data, which showed much higher levels of contamination. The average topsoil lead concentration of contaminated sites on Chat Moss as measured by GBASE was 1985 mg kg^{-1} , whereas the average as measured by the current study was 378 mg kg^{-1} . This may be related to the size of the sample areas, with the GBASE study sampling over a much larger area than the current study. There were also differences in sample preparation with the GBASE samples sieved to $<150 \mu\text{m}$ which may have caused an overestimation of the metal concentration in the soils. The samples for the GBASE survey were also ashed, which at an organic matter content of ~60% would have caused artificial concentration of metals into the non-ashed residue. This suggests that the original GBASE survey may need to be revisited.

Using the Soil Guideline Values (SGV) published by the Environment Agency (Environment Agency, 2002a; 2002b; 2009a; 2009b) and data from the current study,

only arsenic and cadmium were in breach of the guideline values based on allotment use of the land. The SGV for arsenic places a limit of 43 mg kg^{-1} for allotment land use, and site CM-3 showed As levels of 45 mg kg^{-1} . For cadmium, the SGV is 1.8 mg kg^{-1} , which is the concentration of Cd at site CM-3. For all other SGV's (Se, Ni, Cr and Pb) the levels on Chat Moss were within the limits.

In many cities, particularly in developing countries, the use of urban organic waste as soil amendment is widespread. Due to the potential hazards of this material such as biological contamination from poorly treated wastewater, it was suggested that fresh salad crops such as cucumber, lettuce, tomato, parsley and mint should not be grown where wastewater is used for irrigation (FAO, 2007). It was also reported that crop contamination from heavy metals in peri-urban farming would be minimal, as heavy metal concentration is rarely high enough to be toxic. However mitigation strategies such as processing crops to remove heavy metals or liming to immobilise heavy metals have been proposed (FAO, 2007). Chat and Halsall Mosses can be used as historical proxies for modern day peri-urban farming practices, to assess the long-term impact to soils and crops of urban waste disposal on agricultural soils. Elevated heavy metal concentrations in topsoils have been identified over 50 years since the end of waste disposal, which shows that contamination of the soil can be a lasting problem. The total amount of lead introduced to the soil through waste disposal was calculated. Assuming an average topsoil depth (40 cm) to represent 5000 t ha^{-1} and the Chat Moss estate to be 1013 ha, the total weight of topsoil was assumed to be 5.065 Mt. With an average Pb content of the contaminated sites of 379 mg kg^{-1} , and the Pb concentration of the control sites of 221 mg kg^{-1} , the lead assumed to derive from waste disposal was 157 mg kg^{-1} . This resulted in a lead weight in the topsoil of

the Chat Moss estate (1013 ha) of 795 tonnes derived from waste disposal. The same calculation was also carried out for iron, which showed 46 kt was derived from the waste. Historical records showed that 1.92 Mt of waste was disposed of on Chat Moss, as the dominant forms of waste were nightsoil and privy midden waste (958 kt) and these were less likely to host metal contaminants. The main metal-bearing forms of waste were most likely street sweepings and clinkers, which amounts to 640 kt of waste. Coal will also have been an important metal-bearing phase, but this would be included in privy midden waste, dust, sweepings and clinkers, and cannot be quantified. The estimated 640 kt of metal-bearing waste would seem to be in agreement with the calculation of Fe and Pb content of the soils today, indicating that there has been minimal loss of metals from the soils and that the historical records were correct. However this calculation is very simple, a more detailed assessment of the metal budget of the Chat Moss soil could be carried out with more detailed historical records and an assessment of the original metal content of the waste forms.

7.2. Reactivity of metal contamination on the mosses

The reactivity of lead was investigated through a novel stable isotope dilution technique using ^{204}Pb , which showed ~65% reactivity of lead in Chat Moss contaminated soils (site CM-3). This was high when compared to soils of other contamination histories, with sewage sludge amended soil showing 13% Pb lability, minespoil contaminated soil showing 31% lability and a soil contaminated with petrol-derived lead showing 52% lability. The high lability seen in the Chat Moss soil corresponded with findings of other researchers (Tongtavee *et al.*, 2005; Degryse *et al.*, 2007), and also corresponded to sequential extraction data of potentially reactive phases in Chat Moss soil, which showed that 73% of the total soil lead was

hosted in phases which could be potentially reactive (exchangeable, carbonate-bound, Fe/Mn oxide-bound and organically-bound). Sequential extractions showed that most metals were divided between the organic, Fe/Mn oxide and residual phases in the Chat Moss soils, with no difference in fractionation observed between Chat Moss control and Chat Moss contaminated soils. This suggests the dominant influence of soil characteristics over contaminant origins on fractionation of metals in Chat Moss soils.

Chat Moss soils have a high flooding potential due to the wetland origin of the soils and poor natural drainage. During an experiment which simulated a long-term (21 week) flooding event, redox potential decreased and Dissolved Organic Carbon (DOC) increased, which caused an increase in soil solution concentration of many metals. All metals except Cd were strongly influenced by either redox potential or DOC fluctuations, which corresponded with other studies (Grybos *et al.*, 2007; Charlatchka & Cambier, 2000), and highlights the potential for heavy metal mobilisation in Chat Moss soils during flooding. It should also be considered that drought conditions may cause heavy metal mobilisation due to drought-induced acidification (Tipping *et al.*, 2003), as many heavy metals are increasingly soluble at low pH.

Arsenic, lead, manganese and molybdenum all exceeded World Health Organisation drinking water guidelines at redox potentials commonly seen in agricultural soils. The Environmental Quality Standards for fresh water (Environment Agency, 2009c) were also exceeded by arsenic, iron, copper, lead and zinc during the course of the experiment, which indicates a potential risk to ecosystem health from trace metal

release during flooding events. Whilst a 21 week flooding event may seem extreme, the redox potential reached during the experiment (~200 mV) is a realistic topsoil redox potential during wet conditions, which shows that the mobilisation of elements seen during the experiment may be mirrored by conditions in the field.

7.3. Bioavailability of metal contamination on the mosses

Peri-urban farming is important worldwide. It is defined as the growing of plants and the raising of animals for food and other uses within and around cities and towns, and related activities such as the production and delivery of inputs, processing and marketing of products (FAO, 2007). Peri-urban farming takes place in the urban periphery, and uses urban resources such as land, labour, urban organic wastes and water (FAO, 2007). It is estimated that 15-20% of the world's supply of vegetables and meat are produced through urban and peri-urban farming (Pasquini, 2006), and the increased demand in the UK for locally sourced food with a reduced carbon footprint means a return to market gardening on Chat Moss has been suggested by local farmers. Several government policies support the local production of fruit and vegetables in the UK, including economic prosperity through sustainable farming, improving access and awareness of fruit and vegetables, enabling and encouraging healthy diets for disadvantaged and vulnerable people, dynamic and sustainable social enterprise and reconnecting the consumer with the countryside (Report of the Working Group on Local Food, 2003). A report by the Policy Commission (2002) stated

“We believe that one of the greatest opportunities for farmers to add value ... is to build on the public's enthusiasm for locally-produced food or food with a clear regional provenance”.

This highlights the economic and social drivers for vegetable production on Chat Moss.

The soil contamination and metal mobility observed through sequential extractions, simulated flooding and stable isotope dilution show potential risk for plant uptake of the metals and contamination of the food chain. However, plant uptake studies using nine vegetables and herbs (mint, parsley, lettuce, cabbage, spinach, carrot, leek, onion and radish) grown in contaminated Chat Moss soils showed minimal contamination by heavy metals, with little risk to human health as assessed by Hazard Quotients or EU limits. This was surprising considering the high lability of Pb (as shown by stable isotope dilution) and high solubility of As, Pb, Mo, Mn, Fe, Cu and Zn which all exceeded safe drinking water guidelines and freshwater environmental quality standards. Similar levels of plant uptake were observed in Indian soils irrigated with wastewater, with similar levels of heavy metal soil contamination to Chat Moss (Chary *et al.*, 2008), however in this case the Hazard Quotients showed significant risk, possibly due to different criteria used in calculating the HQ. Minimal uptake of heavy metals by wild and crop plants grown in sewage sludge treated soils was also observed by Kidd *et al.*, 2007, where it was shown that the plants were able to retain the metals in roots to prevent them moving to other tissues.

Differences were observed between green and root vegetables, for example Cd was concentrated in green vegetables whereas Pb was concentrated within root vegetables. This pattern has been observed by other studies (Podar & Ramsey, 2005; Finster *et al.*, 2004). However differences between vegetables were also observed for all metals. This has implications for risk assessments where no distinction

between vegetable species is made, for example the DEFRA/EA CLEA assessment for Cd, As, Ni and Se. A single transfer factor (TF) is given for all green vegetables, and one for all root vegetables. As shown by the vegetable trial with Chat Moss soil, uptake varies significantly between vegetable types. It is also shown in other studies that Cd for example is accumulated by lettuce (Podar & Ramsey, 2005), which would suggest a single transfer factor to calculate risk of Cd uptake by green vegetables would not be accurate. Using the transfer factor for Cd (0.052) and the concentration in contaminated soils from Chat Moss (1.8 mg kg^{-1}), the predicted concentration of Cd in green vegetables would be $0.0936 \text{ mg kg}^{-1}$ (FW). This exceeds the level of Cd measured in mint and cabbage, but is less than the concentration seen in parsley, lettuce and spinach, which highlights the potential inaccuracy of using a single transfer factor to predict metal uptake of vegetables.

The limited plant uptake observed may be due to the presence of calcium oxalate in the soil, which was identified by scanning electron microscopy. Calcium oxalate is known to be exuded by plants in response to heavy metal stress, especially crop plants, as it is known to bind heavy metals in an immobile form (Jarosz-Wilkolazka & Gadd, 2003). During soil digestions, these calcium oxalates would most likely be broken down, liberating the heavy metals, which would normally be in a non-bioavailable form. This may be shown by the large fractionation of metals into organic and residual phases during sequential extractions.

Minimal uptake of heavy metals by vegetables grown in Chat Moss soil indicate that a return to market gardening would not be hazardous to health with the potential exception of lettuce, which was found to accumulate Cd. To minimise this risk, liming could be used, or careful selection of varieties that do not accumulate Cd,

however studies have shown that there is no significant difference in Cd uptake by different cultivars of lettuce (Alexander *et al.*, 2006).

An investigation into the re-introduction of horticulture to Chat Moss using the GBASE data and SGV's would show that roughly 25% of sites on Chat Moss exceed the soil guideline values for arsenic, chromium, nickel and lead. This could lead to the assumption that these sites would be unsuitable for horticulture. However as seen from the plant uptake studies, Hazard Quotients showed minimal uptake and risk to human health from plant contamination by these elements. Hazard Quotients calculated from the soil-to-plant transfer factor given by the Soil Guideline Values and the GBASE data for As show no risk from green vegetables grown on these soils ($HQ = 0.26 - 0.27$) (Figures 7.1 and 7.2), in agreement with the study data ($HQ = 0.21 - 0.27$), although the variation seen in measured Hazard Quotients between different vegetables (Chapter 6.4) was not seen through the GBASE data. This highlights the need for a complete assessment of risk rather than simply considering the total soil metal concentration, including studying the risk for individual vegetable types rather than a generalised assessment of risk.

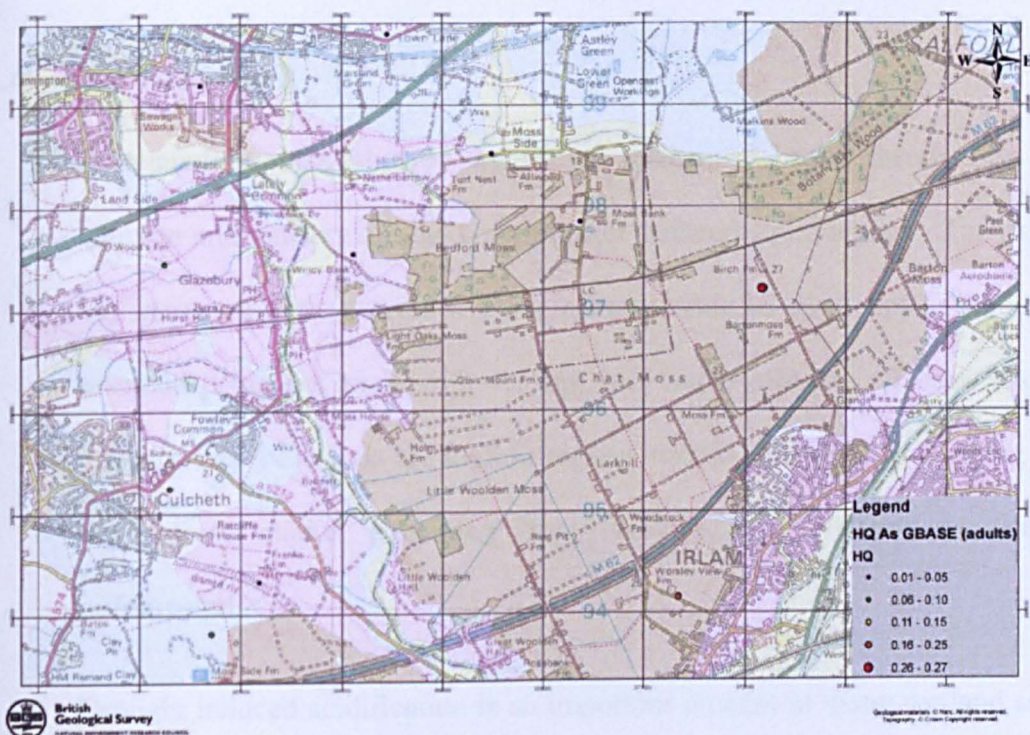


Figure 7.1: Hazard Quotients for arsenic risk (adults) calculated using GBASE data and SGV transfer factors.



Figure 7.2: Hazard Quotients for arsenic risk (children) calculated using GBASE data and SGV transfer factors.

7.4 Further work

- Simulated flooding showed significant release of heavy metals into soil solution under heavy rainfall conditions or reduced soil drainage. The risk of the increased heavy metal solution concentration to plant uptake could be assessed using pot trials with varying soil water contents. This would be important as these soils are high in organic matter and prone to flooding and the risk to market gardening from flooding events should be further investigated.
- Drought induced acidification is an important process in many wetland soils. The effect of this on heavy metal mobility and solubility should be assessed to understand the risks to market gardening from drought conditions which may occur periodically.
- Investigation of variation in metal uptake by different cultivars of vegetables would give a useful insight into potential mitigation strategies for market gardening on contaminated soils, so that cultivars with minimal uptake could be used.
- Field trials of vegetable crops to test the validity of the pot experiments.

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