

**Lead Minerals in Soils Contaminated by Mine-waste:
Implications for Human Health.**

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the degree of Doctor of Philosophy.

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**This thesis is dedicated to the memory
of Lionel Sion, who will always be
remembered for his immortal words
"***** College, let's go for a cruise."**

ABSTRACT

The influence of the solid speciation of lead in soils on human bioavailability has been investigated in a number of areas of the U.K., including soils contaminated by mine-waste from the village of Winster in Derbyshire,

A study of lead levels in garden soil, housedust and on the hands of young children in Winster, a village closely associated with the historic mining of galena (PbS), indicate that high concentrations of lead in garden soils (Geometric mean = 7,140 µg/g) are transferred to the child via the soil-dust-hand-mouth pathway. However, blood lead concentrations of children aged 1-8 yrs. (Geometric mean = 9.4 µg/dl) are within normal U.K. ranges.

Investigation of the solid speciation of lead in soils from Winster and other areas of the U.K., including London garden soils and a motorway roadside soil used a density separation technique to separate lead-bearing grains from the soil matrix. Grains were identified and classified using an SEM/EDX technique. Elemental analysis of the high density soil fraction allowed the relative proportions of lead-bearing grains to be expressed as a percentage of total soil-lead. An amorphous form of the lead phosphate, pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), was found to be a common constituent of the lead-bearing solid phase. It is particularly abundant in soils from Winster village, where it represents in excess of 50% of the total soil-lead.

Pyromorphite is believed to have formed in these soils as the end-product of the weathering of lead compounds, in accordance with thermodynamic predictions. It has an extremely low solubility in acidic environments which approximate to conditions in the human stomach. Thus, the substantial amounts of pyromorphite present in Winster soils contributed to a low bioavailability of soil-lead to humans. This accounts for the unexceptional blood lead concentrations found in children living in the mining village, despite the evidence of an elevated intake of lead. It is unlikely that pyromorphite in urban and roadside soils contributes to a reduced human bioavailability of soil-lead as only a small amounts of pyromorphite are present in these soils.

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SYMBOLS AND ABBREVIATIONS

Chemical Symbols

ΔG°_f	Standard Gibb's Free Energy of Formation (25°C, 1 atm)
K_{sp}	Solubility Product (25°C, 1 atm.) <i>i.e.</i> $K_{sp} = \{M^{n+}\} \{L^{n-}\}$
K_s^*	Solubility Product involving protonated ligand (25°C, 1 atm) <i>i.e.</i> $K_s^* = \{M^{n+}\} \{HL^{(n-1)-}\}$
M	An unspecified metal
L	An unspecified ligand
ΣM	Total concentration of metal M
$\Sigma_{dis} M$ or $\Sigma_{dis} L$	Total aqueous concentration of metal M or ligand L
$\{M^{n+}\}$ or $\{L^{n-}\}$	Activity of metal species M^{n+} or ligand species L^{n-} in solution

Mathematical Symbols/Abbreviations

n	no. of samples
G.M.	Geometric Mean
G.S.D.	Geometric Standard Deviation
Mean or μ	Arithmetic Mean
S.D. or σ	Standard Deviation
log	Logarithms to Base 10

Units of Measure

bar	unit of pressure equal to 0.987 atmospheres
atm.	atmospheric pressure
a.l.s.	above sea level
s.g.	specific gravity
A	Ampere
V	Volt

General Abbreviations

AAS	Atomic Absorption Spectrophometry
CEC	Cation Exchange Capacity
DIW	De-ionised Water
EDX	Energy Dispersive X-ray Spectrometry
IAP	Ion Activity Product
ICPAES	Inductively Coupled Plasma Atomic Emission Spectrometry
IEP	Iso-Electric Point
JCPDS	Joint Committee on Powder Diffraction Standards
NBS	National Bureau of Standards
PVP	Polyvinylpyrrolidone
SEM	Scanning Electron Microscope/Microscopy
SOM	Soil Organic Matter
WDX	Wavelength Dispersive X-ray Spectrometry
XRD	X-ray Diffraction

CHAPTER 1: INTRODUCTION

Lead is one of the seven metals of antiquity. Its long history of usage by man has resulted in the widespread distribution of this element throughout the surface environment. The acute toxicity of this metal has long been established, but recent public health concerns have centred on the long-term, low level, environmental exposure of young children to lead which may impair intellectual development. The soil-dust-hand-mouth pathway has been shown to be an important route of environmental lead to young children. Therefore, the U.K. Government, in line with other governments of developed countries is currently considering guidelines on the maximum permissible concentration of lead in soils (Simms, 1986; Simms and Beckett, 1987; ICRCL, 1987).

The quantity of literature on lead in the environment is voluminous. Because of public concern, many studies have been undertaken, especially on the distribution and transport of lead within the biosphere. However, little is understood of the geochemical behaviour of lead in soil and how this might affect human bioavailability (uptake through the gut) of ingested soil-lead. It is this aspect of lead geochemistry in soils that is addressed in this thesis.

Stumm *et al.* (1983) published an article entitled "From environmental analytical chemistry to ecotoxicology - a plea for more concepts and less monitoring and testing". This study attempts to respond to this plea by presenting a concept: that of weathering of lead compounds in soil and the implications for human health.

The thesis is in two parts focusing on Winster, a village closely associated with historic mining activities. The first part, the Winster Lead Study, investigates the sources and pathways of lead to young children living in the village. The second part, the Solid Speciation Study, concerns the solid speciation of lead in soils in the vicinity of the village and results are interpreted in terms of the bioavailability of soil-lead. In addition, the solid speciation of lead in soils from other parts of the U.K., representing a range of sources and ages of lead contamination, are also examined enabling a comparison to be made with the solid speciation of lead in Winster. This allows conclusions to be drawn on the origin of lead minerals in Winster soils.

The two parts of the thesis are developed concurrently. Chapter 2 describes the background to the Winster Lead Study whilst Chapter 3 describes the background to the Solid Speciation Study. Sampling, methodology and results chapters (Chapters 4, 5 and 6 respectively) are arranged in two parts corresponding to the two studies. The two parts are discussed together in Chapter 7; conclusions and recommendations for further work are stated in Chapter 8.

CHAPTER 2: LEAD AND MAN

Lead (symbol Pb from the Latin "plumbum") is a dense (11.342 g/cm^3 at 25°C) metallic element and has been termed a "heavy metal", a group of elements which includes copper mercury, cadmium and zinc. It has been used extensively by man since early civilisation despite its known toxicity.

2.1 Lead in History

Lead was one of the first metals to be smelted in ancient times. The common lead ore, galena (PbS) is easy to smelt, requiring only a modest temperature which could be achieved in a camp fire. The substitution of silver (Ag) for lead (up to 10 wt.% Ag in galena) made lead ores potentially very valuable. The oldest known piece of lead dates back to 6500 B.C. and was discovered in Turkey. Ancient lead workings have been found in many parts of the world including Britain, Central Europe, the Middle East (including Mesopotamia), the Far East and China. These workings are mostly open cast, no shafts from this period have been identified. (Nriagu, 1983.)

It is not clear when mineral deposits were first worked in Britain. Lead was definitely being produced by the late Bronze Age as it was used to lower the melting point of this metal and had become an important metal by the Iron Age. The Roman invasion of Britain is thought to have been prompted by reports of the country's great mineral wealth. Within six years of the Roman occupation of Britain, lead was being produced for export. Pre-Roman and important Roman areas of lead workings are located in Wales, Derbyshire and the Mendip Hills. Lead ore deposits are present at shallow depth in these areas and would have been easily worked from the surface. Lead was extracted from galena (PbS) by roasting to PbSO_4 followed by reduction to Pb using CaCO_3 as a

flux. (Nriagu, 1983.)

During the Middle Ages, lead was treated with suspicion and prejudice. Much of the scientific effort of this era was directed towards the attempt to transmute lead into gold (Au). In the twelfth and thirteenth centuries the demand for lead increased and many of the old Roman mines were opened and reworked. By the seventeenth century Britain was producing considerable amounts of lead both for the home market and export to the continent. During the Industrial Revolution in the latter half of the eighteenth century new mining techniques developed and productivity increased in response to an increased demand for lead. (Smith, 1986.)

In the latter half of the eighteenth century and the beginning of this century, lead mining in Britain grew less important as lead imports from abroad became cheaper. At present, very small quantities of lead are mined, mostly as a by-product of other minerals *e.g.* fluorite.

2.1.1 Historical Uses of Lead

Lead found widespread commercial applications in the ancient world. It is malleable, dense, resistant to corrosion and has a low melting point. These properties made lead one of the most important industrial minerals in Greek and Roman times despite its lack of glamour and lustre. The Romans used lead to such an extent that sometimes lead is referred to as a "Roman Metal". The principal uses of lead were for: nonferrous alloys; pewter and solder; coinage; glass; glazes and enamels; plumbing; stationery; roofs, gutters and downspouts; burial of the dead; vases, vessels and kitchenware; statuettes and figurines; ship building and other naval purposes; standard weights; projectiles in warfare; pigments; medicinal purposes; and food preservatives and colorants. Many of these ancient uses of lead are still utilized today. (Nriagu, 1983.)

With the fall of the Roman civilisation lead usage decreased until the Middle Ages when lead became an important metal once more. Its principal uses were similar to ~~those~~ of Roman times but it was not used to a large extent in food preparation. In the seventeenth century lead was extensively used in the roofing and plumbing of large country houses, leading to an renewed demand for lead. With the Industrial Revolution

many new uses of lead were created. One of the most important uses was in the manufacture of sulphuric acid. Lead was also used as plates in storage batteries and as ammunition in the form of lead. Many of the modern uses of lead (as described in Section 2.2.2) were invented during this period. (Smith, 1986.)

2.1.2 Lead Poisoning in History

The toxic properties of lead have been known since ancient times and lead poisoning is perhaps one of the earliest occupational diseases. Chronic lead poisoning or "plumbism" was common in lead workers from Ancient times until the end of the nineteenth century when risk-control measures were introduced. (Nriagu, 1983.)

In lead mines the incidence of plumbism depended on the type of ore and personal hygiene of the worker. The low incidence of plumbism in men who worked with galena ores is related to the insolubility of PbS (see Section 4.8.2). Where the more soluble Pb-carbonate ore was exploited, lead poisoning was more prevalent. The smelting of lead ore gave the greatest risk of occupational exposure. Fumes from lead smelting were notoriously toxic and throughout history lead smelters have been sited away from areas of habitation. However, lead poisoning of workers was not restricted to the mining and smelting industry. Workers who used lead in other industries such as painting, plumbing, roofing, sculpturing, pewterware making, shipbuilding, enamelling and pottery glazing also suffered from lead poisoning. (Willies, 1974; Nriagu, 1983.)

Non-occupational exposure to lead has also prevailed throughout history. Lead poisoning from the cosmetic use of lead compounds by Egyptians, Asians and Chinese in ancient times was probably widespread. Exposure from lead in drinking water caused by lead piping may have been important in certain areas, as it is today. The contamination of fermented beverages with lead was fairly widespread but especially prevalent in Greco-Roman times. Indeed, it has been suggested that lead poisoning of the Roman oligarchy from excessive use of lead in food, drink and plumbing was one of the principle causes of the fall of the Roman Empire (Gilfillan, 1965). However, many reasons have been suggested to explain the collapse of Rome and it is possible that lead exposure was only a minor cause.

The toxicity of ingested lead compounds has been documented since the 2nd century B.C. Nicander (quoted by Nriagu, 1983) described the symptoms arising from the ingestion of lead carbonate (white lead). He mentions constriction of the palate and gums, pallor, asperity of the tongue, singultus, colic, a very dry cough, palsy, nausea, ocular disturbances and torpor. However, it is not clear to what extent lead poisoning in humans was recognised. There are many ancient descriptions of ailments showing the above symptoms but these could be due to a number of diseases in addition to lead poisoning. The correct diagnosis of lead poisoning was therefore problematic and cause of the ailment often not recognised in Ancient times, although it was widely known that lead was toxic.

Since Ancient times epidemics of chronic lead poisoning associated with specific causes have been described (Smith, 1986). Chronic lead poisoning has become less frequent, especially during this century, as precautions began to be taken against excessive occupational and non-occupational lead exposure.

2.2 Lead in Modern Society

Lead is widely used in the developed world. The United States, Europe and Japan account for approximately 85% of refined lead consumption, equivalent to 3.3 million metric tons in 1980 (Robinson, 1978).

2.2.1 Uses of Lead

The following brief descriptions of the modern uses of lead are taken from a review by Urbanowicz (1986), except where indicated.

The major uses of lead are in the storage battery, paint, petrol, the building industry and as a solder.

- ***Storage batteries*** provide the largest outlet for lead. Plates are made of lead oxides, massicot (PbO), minium (Pb_3O_4) and plattnerite (PbO_2) and immersed in sulphuric acid to form an electric cell.

- The use of ***lead in paint*** has been summarised by Davies (1983a):

"White lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) and red lead (Pb_3O_4) were used as pigments by the Greeks. Basic lead carbonate is still in use in white paint for exterior use and was the only white pigment until ZnO started to replace it later last century. From about 1920 onwards TiO_2 , BaSO_4 and CaSO_4 were used to replace white lead and in the 1930,s CaCO_3 was also introduced into paint formulations. Lead silicates produce durable films and can replace white lead. Red lead is a useful rust inhibitor and therefore a good primer for iron and steel structures. Formulations containing chromates and lead compounds produce colours ranging across the spectrum from red to blue-green. Normal lead chromate (PbCrO_4) is a brilliant yellow and is extensively used in street markings. There is also a wide variety of less frequently used pigments based on compounds of lead cyanamide, titanate, chloride, fluoride, antimonate and phosphosilicate and also flake metallic lead."

The use of lead in paint is currently being phased out as recommended by the Royal Commission on Environmental Pollution (RCEP, 1983) because of the high lead content of these paints (up to 66 wt.%). However, these paints are still used on the outsides of buildings and in shipping. Modern paints often contain small amounts of organic lead as a drying agent.

- Tetra-ethyl lead (TEL) is added in small quantities to ***petrol*** as an "anti-knock" agent, allowing engines to operate at higher compression ratios. A phased reduction of the lead content in petrol took place in the U.K. during the 1970's and was followed by a substantial decrease in January 1986. In addition, unleaded petrol is being increasingly used resulting in a decline of this use of lead.

- The resistance of lead to corrosion and its malleability is utilized in the **building industry**. Lead is used in two forms: as a sheet for roofing and as a pipe for plumbing. Lead has traditionally been used to waterproof parts of buildings where rainwater may seep through *e.g.* flashings around the base of chimneys. This use of lead continues and the roofs of many modern buildings contain lead. In contrast, the use of lead for plumbing has diminished since 1945 when cheaper alternatives such as copper and plastic became available.

- Lead and lead alloys (commonly with tin) are commonly used as low temperature **solders**, especially in the electronics industry. Lead solder has also been used in the canning of foodstuff although this practice is declining rapidly as it contributes significantly to the dietary intake of lead by humans.

Other uses of lead include sheathing of telephone and power cables; bearings for moving mechanical parts; X-ray shielding in the fields of atomic energy and medicine; ammunition in the form of lead shot; lead weights *e.g.* for fishing and in the manufacture of printing blocks. Products in which lead has not been specifically used but a component in the manufacture contained lead, may also contain lead. *e.g.* Food and beverages may contain amounts of lead from production processes or solder in containers and caps.

For economic reasons, a large proportion of lead waste from batteries, roofing, plumbing and cable sheathing is recovered and recycled in secondary lead smelters. However, lead used in paint and petrol cannot be recovered effectively and significant amounts of lead are released to the environment from these sources (see Sections 2.4.1 and 2.4.2).

2.2.2 Toxicology of Lead

The human health effects of lead have been intensively investigated in recent years. Much of the work has aimed to link adverse health effects with the level of lead exposure. The commonest measure of exposure is blood lead concentration, which reflects recent exposure. Other human materials such as bone, teeth and hair can give evidence

of lead exposure over a period of time (Rutter, 1983).

Occupational exposure in lead-using industries has been reduced by the implementation of stringent precautions and regulations; blood lead concentrations of lead-workers are regularly monitored to prevent undue exposure. Consequently chronic lead health effects have become progressively less frequent and serious. However, the threshold level of exposure, at which adverse health effects are initiated, is currently the subject of much controversy (*e.g.* Kazantzis, 1988).

The long term, non-occupational exposure of children to environmental lead has caused much concern recently. Whilst amounts of lead are too small to cause classical symptoms of lead poisoning, it is thought intellectual development may be impaired. Recent studies on the neuropsychological effects of lead in children include those by Landsdown (1986); Landsdown *et al.* (1986); Harvey (1986); Harvey *et al.* (1988); MRC (1985, 1988). The results of these studies are not conclusive but there does appear to be an adverse effect of elevated blood lead concentrations on intelligence/attainment. The uncertainty arises from a number of confounding variables such as socio-economic status and the "caretaking" environment of the child which are related to blood lead concentrations in children and their intelligence and attainment (Urbanowicz *et al.*, 1987; Ernhart *et al.*, 1988).

Very young children of pre-school age have been identified as the population group most at risk from exposure to environmental lead (DoE, 1978; DHSS, 1980). Children's blood lead typically peaks at approximately 2 years of age, although this peak is small or absent in children with little access to the general environment *e.g.* hospitalised children (Duggan, 1983; RCEP, 1983). Also, it has been shown that children's blood lead concentrations are generally higher than those of their mothers (Duggan, 1983). This suggests the existence of an important pathway of lead uptake affecting children but not adults (Duggan, 1983). This has led to the concept of a soil-dust-hand-mouth pathway providing an important route of lead into young children. This pathway is discussed in Section 2.3.1.

2.3 Pathways of Lead to Young Children

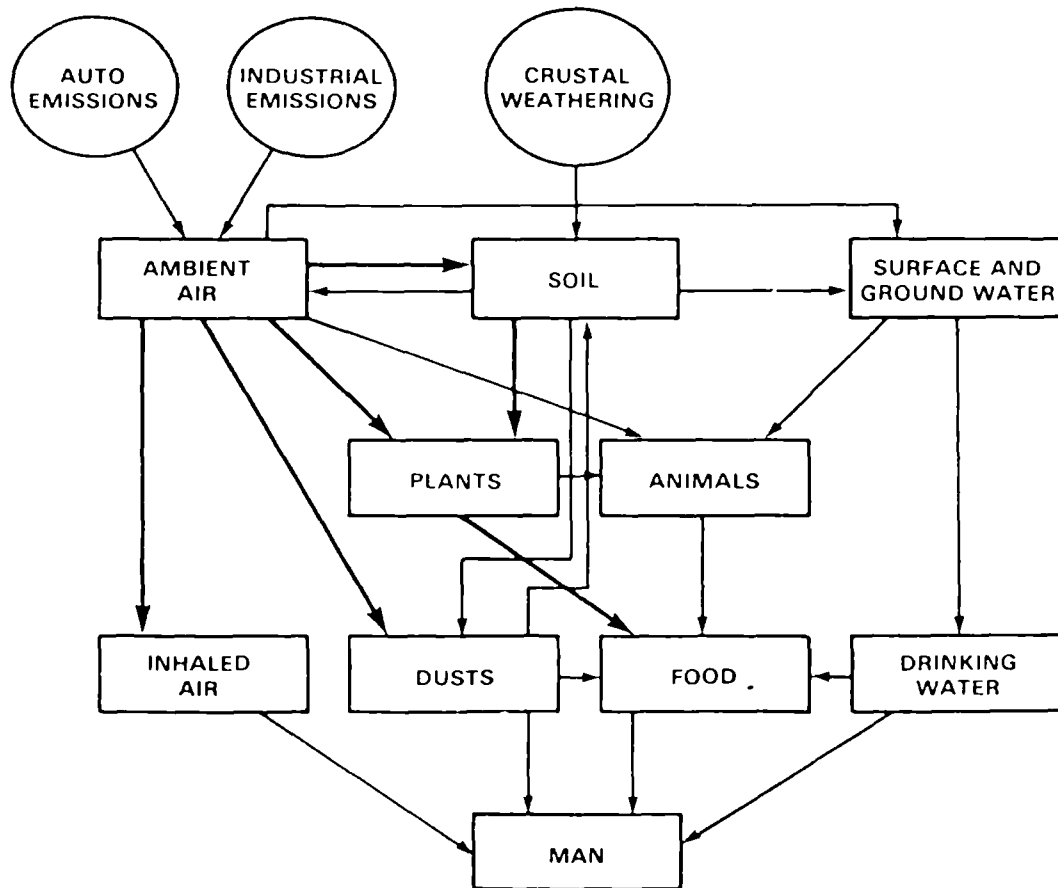


Figure 2.1 Pathways of lead exposure from the environment to man.

The major pathways of lead to man are shown in Figure 2.1. Many of these pathways are interconnected and the resulting flow chart is quite complex. However, from Figure 2.1 it can be ascertained that the major immediate sources of lead in man are: inhaled air, food, drinking water and dust. Dust includes external dust (roadside dusts or streetdusts) and internal dust (housedust). For the purposes of discussing pathways of lead to young children, external dust can be regarded as equivalent to soil, whilst housedust

or indoor dust (often referred to as simply dust) represents a specific stage along the pathway.

Two British studies have considered the relative importance of these different pathways of lead to young children; one by the Royal Commission (1983) in their review of lead in the environment and the other by Davies *et al.* (1990) based on surveys undertaken in Birmingham. Both concluded that housedust accounts for over half of a young child's daily uptake of lead (Table 2.1). Housedust is ingested by hand-to mouth activity and is not considered an important pathway of lead to adults (RCEP, 1983).

Table 2.1 Relative contribution of air, dietary and dust lead to the daily lead intake and uptake of a young child				
Source	Percentage of child's daily lead intake		Percentage of child's daily lead uptake	
	Royal Commission (RCEP, 1983)	Birmingham Study (Davies <i>et al.</i> , 1990)	Royal Commission (RCEP, 1983)	Birmingham Study (Davies <i>et al.</i> , 1990)
INHALATION				
Air Lead	2.4	2.3	3.2	3.1
INGESTION				
Dietary Lead	26.4	34.6	26.2	34.3
Dust Lead	71.1	63.1	70.6	62.6

2.3.1 The Soil-Dust-Hand-Mouth Pathway

Young children inadvertently ingest soil and dust by hand to mouth activity. It has been estimated that a young (≈ 2 yr. old) child touches something (moveable or fixed) approximately 15 times a minute; an identical rate was obtained for objects (or parts of the body) touching the mouth area or going into the mouth (Harvey *et al.*, 1985). Children may even purposefully eat soil or dust, the habit known as pica.

The amount of lead on the hands of children is related to dust lead concentration in both the outdoor environment (Duggan *et al.*, 1985) and the indoor environment (Davies *et al.*, 1990). However, there is uncertainty regarding which environmental

measure of lead best reflects children's exposure to lead. Gallacher *et al* (1984) showed children's hand lead to be an important contributor to blood lead concentrations whilst Davies *et al.* (1990) found lead loading (the amount of lead per m² = dust lead concentration x mass of dust per m²) to be a better indicator of children's exposure to lead than the amounts of lead on children's hands. Laxen *et al.* (1987a) found housedust lead concentration to be a more useful predictor of blood lead than lead loading (hand lead was not considered). Despite the uncertainty surrounding predictors of blood lead concentrations, there is good evidence that household dust is ingested by hand-to-mouth activity and makes a significant contribution to blood lead concentrations in children.

Several authors *e.g.* Duggan (1983), Duggan and Inskip (1985) and Elwood (1986) have associated a rise in children's blood lead concentration with an increase in garden soil and housedust lead concentrations (see Section 2.5.3). Lead in soil may contribute to children's blood lead levels by two pathways. Household dust may contain substantial amounts of soil, especially garden soil, that has been carried into the home on shoes, clothes *etc.* (Culbard *et al.*, 1985). In addition, children are directly exposed to soil in the outdoor environment where they may ingest soil by hand-to-mouth activity.

Thus, the ingestion of soil and dust via hand-to-mouth activity is an important pathway of lead into young children. This implies that soils and dusts are important sources of lead.

2.4 Lead in Soils and Dusts

The physical transportation of lead in the terrestrial environment is limited. Lead-rich particles tend to be dense as lead is a heavy metal and so have a short residence time in the atmosphere (Francis *et al.*, 1970; Nriagu, 1978). Hence, lead released into the atmosphere will be deposited onto the surface of soils. Downward leaching of lead in soils is negligible in most cases as lead is only slightly soluble in water and strongly bound to solid soil phases, notably organic matter which concentrates in surface horizons (Nriagu,

1978; Section 2.4.2; Chapter 3). Therefore, lead has a long residence time in soil and acts as a sink for lead in the terrestrial environment.

External dusts, such as roadside or street dusts also act as a sink for lead in the absence of soil. External dusts contribute to lead concentrations in housedusts in a similar fashion to soil *i.e.* human transportation on shoes, clothes *etc.* (see Section 2.3.1). In this study external dusts are considered together with soils as a potential source of lead to humans.

2.4.1 Sources and Compounds of Lead

Additions of lead to the environment are from both natural and anthropogenic sources. Present day anthropogenic lead emissions to the atmosphere (and hence to the surface environment in general) are at least an order of magnitude greater than emissions from natural sources (Nriagu, 1979). Natural sources include forest fires and volcanic emissions where lead is released to the atmosphere and subsequently deposited (Nriagu, 1978). The major anthropogenic sources of lead are: paint, vehicle exhaust, coal-ash, mining and smelting which are added to soil and dusts by various pathways. Lead may be added to soils (or road/street dusts) and housedusts by atmospheric deposition and/or dissipation by humans.

(a) Paint

As noted in Section 2.2.2, lead has been used extensively in paint formulations. The main compounds of lead used in paint are: basic lead carbonate ($2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$); lead oxide, minium (Pb_3O_4); lead silicates and chromates. Less frequently used lead compounds include cyanamide, titanate, chloride, fluoride, antimonate and phosphosilicate. Metallic lead is also used in paints.

Lead paint flakes from unkempt paintwork and redecoration may transgress into housedusts or, if external, into garden soil. Paint factories where lead pigments have or are being used may also be regarded as sources of lead contamination in soils and dusts.

(b) Vehicle emissions

Lead is released to the atmosphere from the exhausts of vehicles using leaded petrol. Vehicles represent a mobile source of lead, causing widespread contamination (Nriagu, 1978; Section 2.4.2). The decline in use of leaded petrol suggests that the importance of this source is declining. However, lead has a long residence time in soils so vehicle emissions still represent an important source of lead in the surface environment.

Lead is primarily emitted from vehicle exhausts as soluble lead bromides and chlorides but it has been shown (Ter Haar and Bayard, 1971) that these bromochlorides rapidly convert to lead oxide (PbO_x), carbonate (PbCO_3), oxycarbonate (PbO.PbCO_3) and possibly hydrocerussite ($2\text{PbCO}_3.\text{Pb(OH)}_2$). Ter Haar and Bayard (1971) also showed that in contact with SO_3 in the atmosphere, vehicle-emitted lead halides convert to lead sulphates and oxysulphates (PbSO_4 and PbO.PbSO_4). Other studies (Biggins and Harrison, 1978; 1979) of airborne lead particles have identified $(\text{NH}_4)_2\text{SO}_4.\text{PbSO}_4$ which is thought to be an intermediate compound in the conversion of vehicle-emitted lead halides to PbSO_4 . The conversion of vehicle-emitted lead halides to other salts in soils and dusts is discussed in detail in Sections 3.6.5 and 3.7.5.

(c) Coal ash

Coal ash has not received much attention as a source of lead although its extensive use in households, especially historically, could represent a major source of lead contamination. Lead would be released to the atmosphere via smoke from chimneys and added to soils by the dumping of coal ashes. Davies (1983a) estimated that lead is enriched in coal by a factor of 21 with respect to the crustal abundance of lead. Lead would be present as an impurity in coal, probably replacing iron in pyrite (FeS) which is common in coal.

(d) Mining and smelting

Lead has been mined and smelted since the earliest civilisations (see Section 2.1). Contamination from mining and smelting generally causes intense localised pollution in contrast to the widespread low level contamination caused by paint, vehicle emissions and coal ash.

Lead was once an important British export and was both mined and smelted in

Britain (Section 2.1); nowadays extremely little lead is mined. In contrast, Britain is still a significant refiner of lead, mostly by secondary smelting (the re-smelting of lead rich materials *e.g.* batteries). Present-day smelters operate under strict environmental regulations and emit low levels of atmospheric lead (*e.g.* Darley Dale Smelter, Section 4.2.3). Nevertheless, smelters are significant point sources of lead contamination.

Mining and smelting are important historic sources of lead in the environment. Historic mining and smelting practices were extremely inefficient and mostly operated with little environmental control. As a result, large amounts of lead were released to the environment. The long residence time of lead in soils means that contamination from these sources is still present today, even in areas where mining and smelting ceased several centuries ago.

Contamination from historic mining practices is mainly due to old mine-spoil tips and ore-washing processes. Old lead mine spoil tips contain ore that was not extracted; dust from these tips caused (and still causes in areas where tips are not fixed by vegetation (Davies and White, 1981)) more widespread contamination. Effluent from ore-washing contained fine particles of lead ore which settled in alluvium downstream from ore-washing sites. Contamination from historic smelters is due to airborne emissions produced while the smelter was operational and old slag heaps. Airborne emissions were a considerable source of contamination from historic smelters because of their inefficiency; the toxic properties of these fumes were notorious and are well documented (Section 2.2.1). Most of the lead in these fumes settled in the immediate vicinity of the smelter contaminating the surrounding area. Slag heaps contain lead rich residues from smelting and unsmelted ore. Again, wind dispersal of these tips produced more widespread contamination and still does in areas where tips are not vegetated (Harper *et al.*, 1987).

Contamination from mining was mainly in the form of the major lead ore, galena (PbS) but secondary ores of lead, notably cerussite (PbCO₃) were important locally. Lead emissions from present day smelters have been shown (Foster and Lott, 1980) to consist of lead sulphate (PbSO₄) and oxysulphate (PbO.PbSO₄). Although many designs of smelter have used over the centuries, the basic method of producing lead from ore has not changed. Therefore, historic smelters would have emitted lead in the same chemical form as present day smelters.

(e) Miscellaneous sources

Miscellaneous sources of lead include storage batteries (lead metal and lead oxides); lead weights for fishing (lead metal) and lead solder (alloy with other metals *e.g.* tin) which may be kept in the home or disposed of in gardens or waste tips. Commercial garages are significant local sources of lead (see section 2.4.2), presumably from spillage of unburnt leaded fuel. The chemical form of lead from this source is therefore likely to be tetra-ethyl lead.

2.4.2 Lead Concentration in U.K. Soils and Housedusts

Lead is present throughout the cosmos and therefore occurs naturally in soils. However, the concentrations of lead in many soils have been influenced by the activities of man; widespread contamination from industrial or urban processes has raised lead concentrations above normal or background levels (Nriagu, 1978). The Wolfson Geochemical Atlas of England and Wales (Webb *et al.*, 1978) identified several areas of raised lead concentrations in stream sediments (which are associated with soil lead concentrations). The major areas of raised lead concentrations were cities *e.g.* London, Birmingham; industrial conurbations *e.g.* Cardiff, the Avonmouth smelter complex near Bristol and historic lead mining and smelting areas in Derbyshire, Wales and the Mendip Hills. These historic mining and smelter areas are called geochemical "hotspots" because of their very high lead concentrations. The immobility of lead in soil is starkly demonstrated by these areas where high lead concentrations still persist even though mining and smelting operations ceased over 100 years ago.

No background values of lead in housedusts are available as housedust cannot be considered to be naturally occurring. However, lead in housedust does show considerable variation and is dependent on numerous factors. The relationship between garden soil lead concentrations and housedust lead concentrations is interesting as an inverse to the normal relationship is shown in geochemical "hotspot" areas, as will be discussed in Sections 2.4.2(c) and (d).

(a) Uncontaminated soils

Lead is present in all soils. Nriagu (1978) reported average lead concentrations in uncontaminated soils of 14 µg/g for England, 42 µg/g for Wales, and 30 µg/g for Scotland. Davies (1983b) suggested an average normal lead content in soils of 42 µg/g and values greater than 110 µg/g should be regarded as anomalous.

Reaves and Berrow (1984) examined the surface and vertical distribution of total lead in rural Scottish soils. Lead concentrations in organic soils were generally higher and more variable than those in mineral soils. Lead was also enriched in surface horizons where soil organic matter (SOM) content is greatest. This indicates an affinity of SOM for lead which would contribute to the downward immobility of lead. The geochemistry of lead in soil is discussed in detail in Chapter 3.

(b) Roadside soils

It is now generally accepted that surface lead concentrations in roadside soils are elevated due to lead emitted by vehicle exhaust. Nriagu (1978) summaries the voluminous literature written on the subject of lead contamination of roadside soils. He concludes:

- Lead concentration in roadside soils is related to traffic density and the mode of operation of vehicles; a higher percentage of lead in automobile exhaust is discharged from fast flowing traffic than in slow moving traffic *e.g.* city driving.
- There is a curvilinear decrease in soil lead concentration with distance from the road. The effect of traffic is generally limited to 100 m either side of the road with the majority of lead deposited within the first 10-20 m.

Lead concentrations in U.K. roadside soils and dusts have been reported as 245 µg/g and 296 µg/g for soil, 660 µg/g and 1570 µg/g for dust along a rural section of motorway; 6,190 µg/g (soil) and 2,540 µg/g (dust) for major rural roads (Harrison *et al.*, 1981).

(c) Urban Soils and Housedusts

Results from a national survey of the metal content of U.K. urban soils and dusts conducted by Culbard *et al.* (1988) are summarised in Table 2.2. Lead concentrations in urban soils are higher than those reported for rural, uncontaminated soils which reflects the effects of human habitation. Increased lead concentrations have been found in soils and dusts from households located near commercial garages and waste land (demolition sites and tips) and households bordering on roads (Davies *et al.*, 1990).

Table 2.2 Lead concentrations in U.K. garden soils and housedusts (Culbard <i>et al.</i> , 1988)			
<i>Location and sample type</i>	<i>n</i>	<i>Geometric Mean (µg/g Pb)</i>	<i>Range (µg/g Pb)</i>
<i>All study locations less hotspots</i>			
Housedust	4,638	561	5-36,900
Garden soil	4,126	266	13-14,100
<i>London Boroughs</i>			
Housedust	683	1,010	5-36,900
Garden soil	578	654	60-13,700

Both housedust and garden soil lead concentrations increase with house age (Thornton *et al.*, 1985; Davies and Thornton, 1987; Davies *et al.*, 1987;). This is thought to arise from the increased use of leaded paint in older houses and a longer history of soil contamination from bonfires and fossil fuels residues (Thornton *et al.*, 1985). Elevated concentrations of lead were reported for seven London boroughs (see Table 2.2) which are thought to reflect the city's long history and its large population and traffic density (Culbard *et al.*, 1988).

Lead concentration in housedust is significantly related to garden soil concentrations (Culbard *et al.*, 1988); housedust lead concentrations are higher than those in garden soil, on by an average factor of 2 (see Table 2.2). This enrichment of lead in

housedusts implies an important internal source of lead. This source is thought to be leaded paint as housedust lead concentrations are significantly increased by the presence of leaded paint (Culbard *et al.*, 1988) and instances of redecoration (Culbard *et al.*, 1988; Davies *et al.*, 1990). Supporting evidence also comes from a study by Rundle and Duggan (1986) who showed that the increase in lead concentrations in playground dusts during external redecoration of schools were due to the dispersion of leaded paint flakes. Although the above study refers to the external environment, a similar situation can be envisaged inside the home.

(d) Soils and housedusts in geochemical "hotspot" areas

As stated previously, the Wolfson Geochemical Atlas of England and Wales (Webb *et al.*, 1978) identified Derbyshire, North Wales and the Mendip Hills as the main areas containing land contaminated by historic mining and smelting practices. It has been estimated that some 4,000 km² of agricultural land in England and Wales is contaminated with lead from this source (Thornton, 1987). Contaminated areas in Derbyshire form the major study area of this thesis and are considered separately in Section 2.6.

Values of up to 2,900 µg/g Pb have been found in alluvial plains downstream of a historic mining area in Ceredigion, Wales; caused by the direct injection of mine effluent into rivers during the nineteenth century (Alloway and Davies, 1971a). Apparently uncontaminated soils contained higher lead concentrations than control samples, illustrating the effect of aerial pollution from historic smelting. In a different part of Wales (Halkyn Mountain in North Wales) lead concentrations of up to 6,944 µg/g have been found in soils associated with historic mining sites (Davies and Roberts, 1975; 1978). Garden soil and dust samples from the nearby village of Halkyn showed elevated levels of lead. Geometric means of 1,127 µg/g Pb (soil) and 340 µg/g Pb (housedust) have been reported (Davies *et al.*, 1985). Soil lead concentrations were higher than those of housedusts, the reverse of the situation in urban areas *e.g.* London. This a classic illustration of a "hotspot" situation and implies a strong external source of contamination, *i.e.* historic mining. It is this source of contamination which raises housedust lead concentrations when it is transported into the home.

In the Mendip Hills concentrations of 47,200 µg/g and 45,800 µg/g Pb have been recorded in soil samples from old lead spoil tips at Velvet Bottom, near Charterhouse

(Tills and Alloway, 1983; Gregson and Alloway, 1984). The nearby village of Shiphams was a centre for zinc mining although significant quantities of lead were also mined. Geometric mean lead concentration for Shiphams garden soil has been reported as 2,000 µg/g and for housedust as 786 µg/g (Thornton, 1988). Again, garden soil lead concentrations are higher than housedusts due to the importance of mining contamination in the external environment.

Summary

Many soils and dusts in the U.K. contain elevated concentrations of lead because of man's activities. Contamination due mainly to the use of leaded petrol can be seen in roadside soils and dusts. The effects of human habitation are seen in urban areas where widespread, low level contamination has resulted from the use of lead in paint and fuel and from the dispersal of waste products *e.g.* coal ash. Historic mining and smelting has caused intense localised pollution which persists in soils (and hence housedusts) to the present day.

2.5 Exposure of Young Children to Lead

The commonest method of measuring exposure is analysis of venous blood samples, which reflects current or recent exposure. However, it is difficult to make comparison between different blood lead studies because of variability in analytical accuracy and precision and because of the variation of blood lead with age in young children (Section 2.3). Blood lead concentrations have been falling in recent years (Elwood, 1986) at an estimated rate of 4% per annum since the early 1970's (DoE 1990). This coincides with the reduction of lead content in petrol, paint and food. During the same period, analytical instrumentation has greatly improved the accuracy of blood lead determinations. Therefore, only recent analyses of children's blood lead are reported here, as older analyses may not accurately reflect exposure.

2.5.1 Urban/Heavily Trafficked Areas

Analyses of children's blood lead in inner-city areas have produced geometric means of 10.7 µg/dl (age 6-9 yr.) for Edinburgh (Laxen *et al.*, 1987a) and 11.7 µg/dl (age 1-3 yr.) for Birmingham (Davies *et al.*, 1990). The higher blood lead concentrations found in the later study (Davies *et al.*, 1990) reflect the age differences between sample sets. Strehlow and Barltrop (1987) examined blood lead concentrations in children aged 5-7 yr. living in urban and rural areas over a period of three years. Geometric means of 7.4 to 8.3 µg/dl Pb were reported for London and 6.4 to 6.8 µg/dl Pb for Suffolk and were found to be significantly different for each year. Children (age 6-7 yr.) attending schools situated on heavily trafficked roads have reported geometric mean blood lead concentrations of 7.3 µg/dl (DoE, 1990), approximately equal to children living in London.

2.5.2 Geochemical "Hotspot" Areas

Blood lead analyses have also been reported for children living in geochemical "hotspot" areas. Recent analyses for a village in Derbyshire form part of this study and are reported in Section 6.3.2, previous analyses are referred to in Section 2.6.1. Gallacher *et al.* (1984) reported elevated blood lead concentrations (mean = 22.6 µg/dl) in young children aged 1-3 yr. living in an old mining area of Wales. However, the same study reported mean blood lead concentrations in children living along heavily trafficked roads as 16.6 µg/dl. The most likely explanation for the comparably high concentrations found throughout the Gallacher *et al.* (1984) study is the use of capillary blood samples which are not strictly comparable to the venous blood samples reported above. Nevertheless, blood lead concentrations in children living in the old mining areas were significantly different to those living in a control village remote from industry, heavy traffic and lead mining.

Blood lead concentrations (G.M. = 8.9 µg/dl) have also been reported for children aged 1-16 yr. living in the village of Shipham (Strehlow and Barltrop, 1988). These blood lead concentrations were virtually identical to those in a nearby control village

uncontaminated by historic mining. However, the age span of children sampled is very large and it is possible that this has masked differences in blood lead concentrations in young children where the soil-dust-hand-mouth pathway is thought to be important (Section 2.3.1).

2.5.3 Exposure Models

Several authors have attempted to quantify the increase in blood lead concentration associated with an increase in soil and dust lead concentrations. In some studies, the parameter δ has been calculated. δ is the increment in blood lead concentration (in $\mu\text{g}/\text{dl}$) per 1,000 $\mu\text{g}/\text{g}$ increase in dust or soil lead concentration and assumes a linear relationship.

Duggan (1983) and Duggan and Inskip (1985) suggested that on average $\delta \approx 5$, in close agreement with the value of $\delta \approx 4$ suggested by Elwood (1986). Duggan (1983) reported that the value of δ varied between 1 and 10 $\mu\text{g}/\text{dl}$ per 1,000 $\mu\text{g}/\text{g}$ and was higher for industrial sources of lead than from lead derived from historic mining activities. The values of δ reported above are mean or median values derived from numerous published studies, ^{see table 2} between which there is considerable variation in the ages of children sampled which could influence δ . Despite this weakness, δ indicates the nature of the relationship between soil and dust and blood lead concentrations.

Other authors have defined the increase in blood lead concentration associated with increasing soil and dust lead concentrations from single studies. Multiple regression analysis incorporating drinking water and household dust estimates δ at 1.9 $\mu\text{g}/\text{dl}$ per 1,000 $\mu\text{g}/\text{g}$ rise in dust lead concentration for Edinburgh children with a median population blood lead of 10.1 $\mu\text{g}/\text{dl}$ (Laxen *et al.*, 1987a). This estimate of δ is considerably lower than those based on literature reviews and a response curve (Laxen *et al.*, 1987a) shows that the relationship is not linear.

Davies *et al.* (1990) produced a regression model based on the Birmingham study:

$$\log\text{PbB } (\mu\text{g}/\text{dl}) = 0.55 + 0.10\log X_1 + 0.14\log\text{PbW } (\mu\text{g}/\text{l})$$

Table 2.3 Summary of studies conducted outside the U.K. relating increments in blood lead concentrations with increases in soil and dust lead concentrations.

Study	Lead in Environmental Samples ¹		Lead in Children's Blood			δ^2
	Soil (Pb $\mu\text{g/g}$)	Dust (Pb $\mu\text{g/g}$)	n	Age (yrs.)	Blood Lead ¹ ($\mu\text{g/dl}$)	
Angle and McIntire (1982), Omaha, NE, USA.	81-339	211-479	831	1-18	23-30	6.8
Bornschein <i>et al.</i> (1989) Telluride, CO, USA.	178	281-567	94	<6	6	2.2
Milar and Mushak (1982) Raleigh, NC, USA.	--	250-3000	47	1-4	18-44	9.0
Phillips <i>et al.</i> (1989) Herculaneum, MO, USA.	70-2,258	170-2,080	229	1-5	7-22	2.2
Rabinowitz and Bellinger (1988) Boston, MA, USA.	702 (7-13,240)	--	195	0.5-2	6	0.9
Reeves <i>et al.</i> (1982) Auckland, NZ.	24-842	--	195	1-3	12-19	5.0
Roels <i>et al.</i> (1980), Belgium.	--	112-2560	148	10-14	9-25	3.5
Stark <i>et al.</i> (1982) New Haven, CT, USA.	230-1330	160-630	153	0-1	27	2.2
			334	2-3		2.0
			439	4-7		0.6
Walter <i>et al.</i> (1980), Silver Valley, ID, USA	400-7500	--	860	1-9	21-66	1.1

¹ Means of soil, dust and blood lead concentrations are given for the low and high lead areas used in the estimation of δ ; otherwise, range of individual results are given in parenthesis.

² δ is the increment in blood lead concentration per 1,000 $\mu\text{g/g}$ increase in dust or soil lead concentration.

References for Table 2.3

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where PbB is blood lead concentration, X_1 is the dust lead loading multiplied by the rate for hands touching all objects (see Section 2.3.1), PbW is the water lead concentration. This version of the model is slightly simplified as a minor factor, S (whether either of the child's parents smoked) is not taken into account.

These models relating lead exposure to soil and dust lead concentration indicate the expected increment in blood lead concentrations with an increase in soil and dust lead concentration.

2.5.4 Summary

Thus, children living in inner-city areas or attending schools situated on heavily trafficked roads have an increased exposure to lead compared to those living in rural areas. However, it is not clear whether elevated soil and dust lead concentrations from historic mining and smelter sources are reflected in children's blood lead concentrations, although quantitative models suggest an elevation in blood lead concentration of approximately 5 µg/dl per 1000 µg/g increase in soil or dust lead concentration.

2.6 Lead in Derbyshire

Some 250 km² of land in Derbyshire is contaminated with lead from historic mining and smelting practices (Webb *et al.*, 1978; Colbourn and Thornton, 1978; Thornton and Webb, 1979). Analyses of a peat profile from Derbyshire together with radiocarbon age determinations (Fig. 2.2) show that peaks in the lead content of peat coincide with the rise of the Derbyshire lead industry (Lee and Tallis, 1973). Lead mining mostly occurred in the Derbyshire Peak District, a national park in Derbyshire. The mining history of the area is well documented (*e.g.* Ford and Rieuwerts, 1983) and is described in Section 4.1.1.

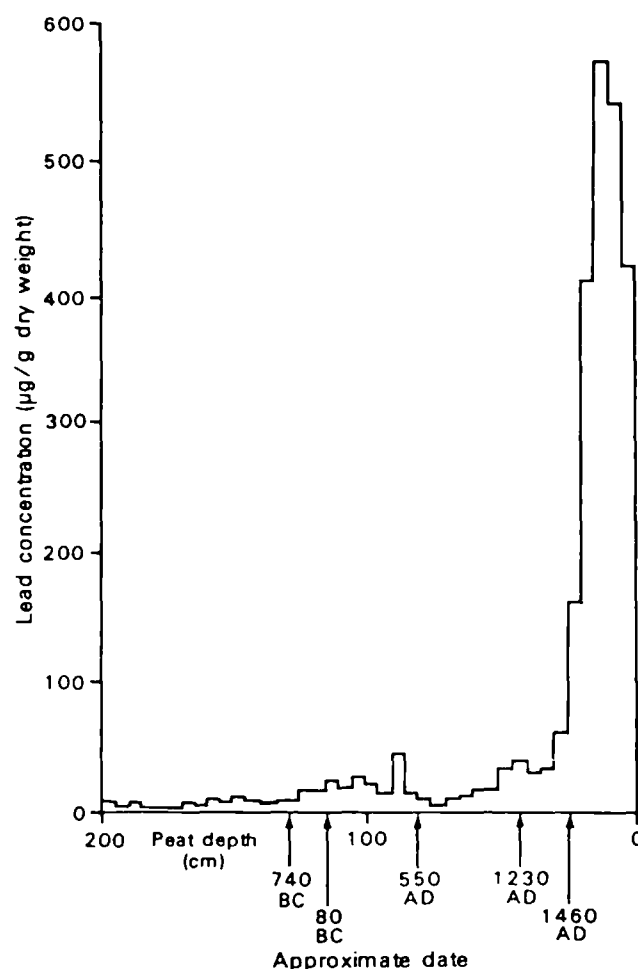


Figure 2.2 Lead analysis of a peat profile from Derbyshire (Lee and Tallis, 1973).

2.6.1 Lead Concentrations of Soils and Dusts

The national survey of Culbard *et al.* (1988) identified the villages of Elton, Youghreave and Winstar (known as the Derbyshire mining villages) as having the highest lead concentrations out of all of the 53 towns and villages sampled in the U.K. Geometric mean lead concentrations of 5,160 µg/g for garden soil and 1,870 µg/g for housedust were reported in these village communities closely associated with past mining activities. In common with other "hotspot" areas (Section 2.4.2), soil lead concentrations are higher than housedust lead concentrations due to the importance of external lead contamination.

2.6.2 Exposure of Young Children to Lead

An investigation of lead exposure in the local population of these Derbyshire mining villages was conducted by Barltrop *et al.* (1974, 1975). Geometric mean blood lead concentrations of 25.0 µg/dl with a maximum concentration of 45 µg/dl Pb were reported for 2 year old children (Barltrop *et al.*, 1975). These blood lead concentrations were considered elevated but within the normal U.K. range (for the 1970's); no adverse health effects were apparent.

Barltrop *et al.* (1975) put forward two reasons why blood concentrations were not grossly elevated. One suggestion was that lead in soil and dusts constituted only a minor source of lead in young children. However, it has since been established that lead in soil and dust does make a substantial contribution to lead concentration in the blood of young children (Section 2.3.1). The second suggestion was that the chemical form and source of the lead may influence the bioavailability of lead in dust and soil to humans. This idea is supported by works of Barltrop and Meek (1975) and Chamberlain *et al.* (1978) who found that the bioavailability of PbS (the chemical form of the lead ore, galena) was less than other lead compounds (see Section 3.8 for a fuller discussion).

2.7 Summary and Aims of Winster Lead Study

The history of lead and man has been described. Lead has been used by man since the earliest civilisations and is widely used in modern society, despite its well known toxicity. Although chronic cases of lead poisoning are uncommon in present times, there is concern over the long term environmental exposure of lead to young children which may impair intellectual development. Environmental lead is transferred to the child via the soil-dust-hand-mouth pathway which is an important route of lead exposure for young children.

Lead is present in all soils but the concentration of lead in many soils and

housedusts has increased as a result of man's activities. The relationship between increases in soil and housedust lead concentrations and the associated rise in blood lead concentrations of young children can be quantified and is known as δ .

Historic lead mining and smelting activities caused intense localised pollution of soil which is still present today because of the long residence time of lead in soil. High concentrations of lead in soil may be transferred to children living in close proximity to mine-waste by the soil-dust-hand-mouth pathway. However, it is not clear whether elevated soil and dust lead concentrations from historic mining sources are reflected in children's blood lead concentration and it has been suggested that the bioavailability of lead in soils derived from mine-waste may be less than those from other sources.

The aim of the Winster Lead Study is to assess the quantity of lead along the soil-dust-hand-mouth pathway to young children in the Derbyshire mining village of Winster closely associated with historic lead mining activities. Together with information on the lead exposure of young children living in this village, this allows a comparison of the human bioavailability of lead in mine-waste contaminated soils and housedust with that of typical urban soils and housedusts.

CHAPTER 3: GEOCHEMICAL BEHAVIOUR OF LEAD IN SOIL

Lead is a material different from all other materials, a metal which you feel is tired, perhaps tired of transforming itself and that does not want to transform itself anymore: the ashes of who knows how many other elements full of life, which thousands upon thousands of years ago were burned in their own fire.

Primo Levi, 1975

In this chapter, the geochemical behaviour of lead in the soil is described with emphasis on the solid phase. The formation of lead phosphates in soil is theoretically predicted and the lack of evidence for these phosphates discussed. The bioavailability of soil-lead to plants and humans is considered with reference to the influence of soil lead minerals. This chapter forms the background to the investigation into the solid speciation of lead in soils described in Chapters 5 and 6.

3.1 General Properties of Lead

Lead (Pb) has an atomic number of 82 and atomic weight of 207.19. There are four stable isotopes of lead (mean natural abundances are given in brackets): ^{204}Pb (1.5%), ^{206}Pb (23.6%), ^{207}Pb (22.6%) ^{208}Pb (52.3%) which are daughter products of the natural uranium and thorium radioactive decay series. It is the largest of the Group IV-A elements, having the electron configuration $6s^2 4f^{14} 5d^{10} 6p^2 [\text{Xe}]$. The $6s^2$ electron pair are

firmly held by the nucleus so the chemistry of lead is dominated by the reactivity of the $6p^2$ electron pair. Hence, the divalent oxidation state [Pb(II)] predominates. However, Pb(IV) compounds do form *e.g.* Pb_3O_4 and PbO_2 but only with strongly electronegative ligands *e.g.* F and O which are not themselves oxidised by Pb(IV).

Goldschmidt (1954) classified elements on the basis of their mineralogical occurrence within the earth. Lead was classified as predominately chalcophile (associated with sulphides) but exhibited some characteristics of the siderophile group (metallic). Neibor and Richardson (1980) classified heavy metals into an oxygen seeking class, a nitrogen/sulphur seeking class and a borderline class related to their solution chemistry and atomic properties. Lead was placed in both the nitrogen/sulphur seeking class and borderline class.

Thus, lead can exhibit characteristics belonging to various geochemical groups but is predominately associated with sulphur.

3.2 Distribution of Lead within the Soil

3.2.1 Introduction

Soil is a dynamic, heterogeneous system comprising inorganic and organic material in solid, aqueous and gaseous phases. Soil is formed at the surface of the earth, between the lithosphere and atmosphere and constitutes a vital part of the biosphere. Essentially, soil is a weathering complex formed from bedrock (the parent material). Primary minerals, unstable at the earth's surface, are broken down to form more stable secondary minerals. The formation of soil is influenced by many factors including climate, geology, topography, biological organisms and time.

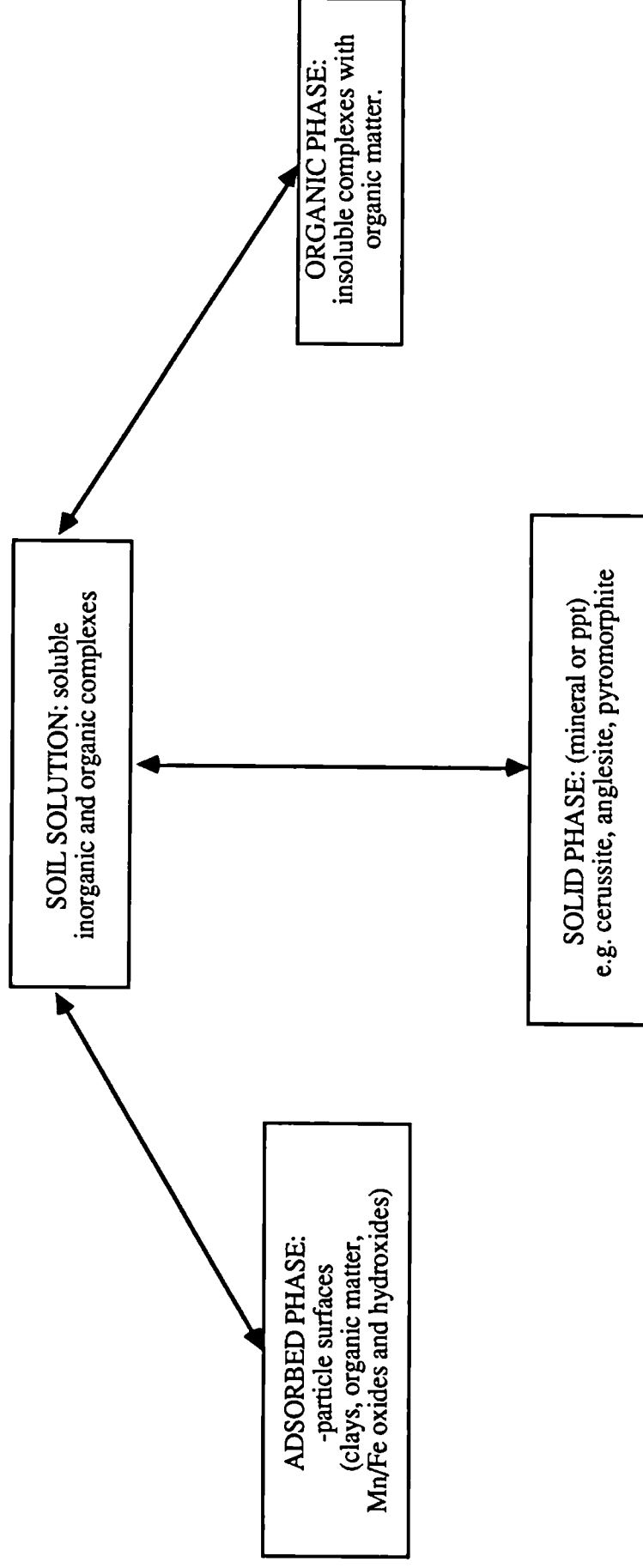


Figure 3.1 Geochemical behaviour of lead in soil

The geochemical behaviour of lead in soils can be discussed in terms of the following soil phases:

- soil solution
- the surfaces of clay minerals and iron/manganese oxides¹
- organic matter
- solid (primary and secondary minerals)

The general behaviour of heavy metals can be described in terms of their distribution between these phases; ions entering the soil solution *e.g.* from the chemical weathering of primary minerals may be adsorbed onto the surfaces of clay minerals, iron/manganese oxides or organic matter, chelated with organic matter or precipitated to form an inorganic solid (Fig. 3.1).

3.2.2 Sequential Extraction Techniques

Because the physical determination of metal partitioning between these phases is difficult, selective chemical leaching techniques have been developed to characterise phases on the basis of their chemical reactivity. Sequential extraction techniques such as the scheme of Tessier *et al.* (1979) have proved the most successful in characterising metal distribution in sediments (Valin and Morse, 1982). The method of Tessier *et al.* (1979) which was originally intended for aquatic sediments, distinguishes six fractions representing 1) soluble, 2) exchangeable (adsorbed but will enter soil solution upon cation exchange), 3) carbonate, 4) iron/manganese oxide, 5) organic and 6) residual (mineral) phases. Each fraction and associated metal content are successively taken into solution by a series of partial chemical extractions. These fractions are not perfectly differentiated by the technique; there is a certain amount of overlap between fractions and extraction efficiency varies with sediment type (Valin and Morse, 1982). Results obtained by this technique should therefore be interpreted with caution, especially when soils (or media

¹The term oxides applying to iron and manganese includes hydrated and non-hydrated oxides.

other than sediments are used as the extraction material. Nevertheless, the method provides a useful indicator of the distribution of heavy metals between soil phases.

3.2.3 Critical Evaluation of Sequential Extraction Techniques

Several authors have performed the Tessier *et al.* (1979)⁷⁹ sequential extraction scheme on U.K. soils. Harrison *et al.* (1981) examined roadside soils and streetdusts collected from urban areas and heavily trafficked rural roads in and around Lancaster whilst Gibson and Farmer (1984, 1986) followed a slightly modified extraction scheme on urban soils and streetdusts from Glasgow. Streetdusts are similar to soils and are considered to behave in an identical fashion to soils for the purposes of this discussion. The Gibson and Farmer (1984, 1986) scheme differentiates between lead adsorbed by manganese oxides (easily reducible) and those of iron (moderately reducible). Elliot (1989) carried out a comparative study of Derbyshire soils collected from lead mine-waste sites in Winster and lead smelter sites at Stone Edge following the scheme of Tessier *et al.* (1979). The results from these studies are summarised in Table 3.1.

Extraction data for the urban samples from Glasgow and Lancaster studied by Gibson and Farmer (1984, 1986) and Harrison *et al.* (1981) (Table 3.1) show similar partitioning of lead between fractions but the Derbyshire samples exhibit a somewhat different partitioning. If the carbonate-bound and residual fraction are considered together to represent lead held in the inorganic solid phase, roughly half of the lead present in the Lancaster and Glasgow samples is held in this phase. In the Derbyshire samples, however, only one third of lead resides in the solid fraction and extremely little is present in the residual fraction (less than 5%).

Table 3.1 Mean chemical partitioning (percent of total) of lead in Glasgow and Lancaster soils and streetdusts and heavily contaminated Derbyshire soils										
					Chemical fraction					
	n	Range of total Pb concentration (µg/g)	Mean Pb concentration (µg/g)	pH range	1 Easily exchangeable	2 Carbonate-bound	3 Easily reducible (MnO bound)	4 Moderately reducible (FeO bound)	5 Organically bound	6 Residual (mineral lattice)
<i>Urban soils</i>										
Glasgow soil ¹	397	22-1,990	216	4.3-7.1	2	11	0	51	19	17
Glasgow streetdust ²	60	35-1,750	1,884	6.5-7.5	13	28	5	27	14	13
Lancaster soil ³	4	245-6,190	--	6.5-7.5	1	26		44	12	17
Lancaster streetdust ³	6	660-2,540	148.3	6.9-8.4	1.5	43		38	7.5	10
<i>Derbyshire soils</i>										
Contaminated by mining ⁴	9	471-21,670	7,176	5.7-7.2 ⁵	4.5	27		37	28	3.4
Contaminated by smelting ⁴	9	345-30,260	13,144	4.0-6.6 ⁵	21	29		21	25	4.0

¹ Gibson and Farmer (1986). The reducible fraction is differentiated into two phases by this extraction scheme.

² Gibson and Farmer (1984), same extraction scheme as Gibson and Farmer (1984).

³ Harrison *et al.* (1981).

⁴ Elliot (1989).

⁵ From Merry (1988); an almost identical soil sample set.

Gibson and Farmer (1984, 1986) found that the percentage of lead in the residual fraction decreased and the percentage in the exchangeable fraction increased slightly as the total lead concentration increased. Thus, the extremely high total lead concentrations found in Derbyshire soils could explain the reduced proportion of lead in the residual fraction (Table 3.1). Gibson and Farmer (*op. cit.*) reported that the reduction of lead in the residual fraction was a product of inputs of lead from polluting sources. This may be true in the urban situation where lead is at least partly present as soluble halides from vehicle emissions (see Section 2.4.1(b)). However, in Derbyshire lead contamination has arisen because of the addition of largely insoluble lead-rich solids which would lead to a rise in the amount of lead in the residual fraction.

An alternative explanation is that lead minerals in Derbyshire soils (almost certainly containing lead sulphide) are partially digested by one or more of the reagents used during the extraction process. For instance, the large quantities of lead in the organically bound fraction of Derbyshire samples could represent galena solubilised by the oxidising agents used in this extraction. This would imply that the low values of residual lead are a manifestation of the fractionation scheme being applied to a non-equilibrium soil containing minerals not usually found in the surface environment. If this is the case, then an increased amount of mineral lead would report in non-mineral phases. Because of these uncertainties, it would be unwise to place anything more than a casual inference on the extraction data from Derbyshire soils.

In his comparative study, Elliot (1989) attributed the difference in proportion of exchangeable lead between smelter site and mine-waste samples (Table 3.1) to the mineralogy of the polluting source and reduced pH of the smelter samples. He asserted that lead in the sample sites would be present as lead sulphate (Section 2.4.1) which is more soluble than galena (PbS), the major constituent of mine-waste (Section 2.4.1). Relative solubilities of lead minerals are discussed in Section 3.8. The solid speciation of lead in these Derbyshire samples is investigated as part of this study and is further discussed in Chapters 5 and 6.

In all of the above studies, lead is strongly associated with the iron and manganese oxide fraction agreeing a similar study on stream sediments by Tessier *et al.* (1982). The majority of this lead is present in the moderately reducing fraction (representing iron oxides) of Gibson and Farmer (1984, 1986). Organic matter assumes moderate importance,

although the association with lead is greater in soils than streetdusts because of the increased organic content in soils (Gibson and Farmer, 1986). The carbonate fraction has a greater significance in Lancaster than Glasgow as a result of the higher pH (Gibson and Farmer, 1986). A negligible amount occurs in the exchangeable fraction.

3.2.4 Summary

It appears from sequential extraction studies that lead in soils and streetdusts is often strongly associated with iron oxides. If the carbonate and residual fractions are summed to represent the mineral phase this becomes an important group, although the importance of the carbonate phase varies with pH. Of less importance is organic matter and extremely little lead is present as an exchangeable cation on mineral surfaces.

3.3 Lead in the Soil Solution

Although very small amounts of soil lead are present in the soil solution, the aqueous speciation of lead is important as it affects adsorption reactions and mineral formation and solubility. However, it is extremely difficult to determine the chemical speciation of solutes analytically so much of our understanding of the behaviour of lead in waters comes from thermodynamic predictions.

3.3.1 Concentration of Lead in Soil Solutions

The amounts of lead found in soil solutions are very low, generally of the order of around 0.001 µg/l. Commonly, this accounts for <1% of total soil lead and contributes to the low mobility of lead in soils. There is evidence to suggest that many of the reported high concentrations of lead in soil solutions are in fact the result of lead being present in

a colloidal, not solvated form (Shaw *et al.*, 1984).

The concentration of lead in soil solutions has been determined in a number of studies. Mean concentration in saturation extracts of 68 soils from California, USA was 0.005 $\mu\text{g/l}$ with a range of <0.01-0.30 $\mu\text{g/l}$ and median of <0.01 $\mu\text{g/l}$ (Bradford *et al.*, 1971). Shaw *et al.* (1984) reported a concentration of 0.64 $\mu\text{g/l}$ in a saturation extract of heavily contaminated ($\Sigma\text{Pb} = 46,700 \mu\text{g/g}$) mine spoil from Derbyshire. Tills and Alloway (1983) and Gregson and Alloway (1984) extracted soil solutions from soils spanning a wide pH range (3.9-7.4) and reported lead concentration ranges of 0.09-12.37 $\mu\text{g/ml}$ and 0.7-23.0 $\mu\text{g/ml}$ respectively. Both concluded that the amount of lead in solution was not correlated with total soil lead. Soil solution lead concentrations appear to be primarily dependent on pH (Tills and Alloway, 1983) with higher levels occurring at low pH.

3.3.2 Aqueous speciation of lead

Lead in natural waters may be present as a free cation or complexed with inorganic or organic ligands. The aqueous speciation of lead is complex but advances in chemical thermodynamics involving the determination of stability constants² for lead species have enabled the prediction of dominant lead species over a wide range of conditions.

(a) Inorganic speciation

Lead is abundant as the free cation (Pb^{2+}) only at low pH in the absence of inorganic complexing agents such as SO_4^{2-} , NO_3^- , OH^- , Cl^- , HCO_3^- , CO_3^{2-} and HPO_4^{2-} or H_2PO_4^- (Lindsay, 1979). Surface and groundwaters are considered to be oxidising or transitional environments and S^{2-} is only stable in more reducing fluids (Fig. 3.2) so lead sulphide complexes are not considered here. PbSO_4^0 has received little attention in the literature although its formation is possible at low pH (Sposito, 1983) and at $\{\text{SO}_4^{2-}\} > 10^{-3} \text{ M}$ (Lindsay, 1979). Below $\{\text{NO}_3^-\} = 10^{-2} \text{ M}$ the PbNO_3^+ complex is negligible and it is suggested that $\{\text{NO}_3^-\} \approx 10^{-3}$ in soils (Lindsay, 1979).

² A stability constant is defined as the equilibrium constant (K_{st}) for the reaction $\text{ML}_{n-1}(\text{aq}) + \text{L}(\text{aq}) \rightleftharpoons \text{ML}_n(\text{aq})$.

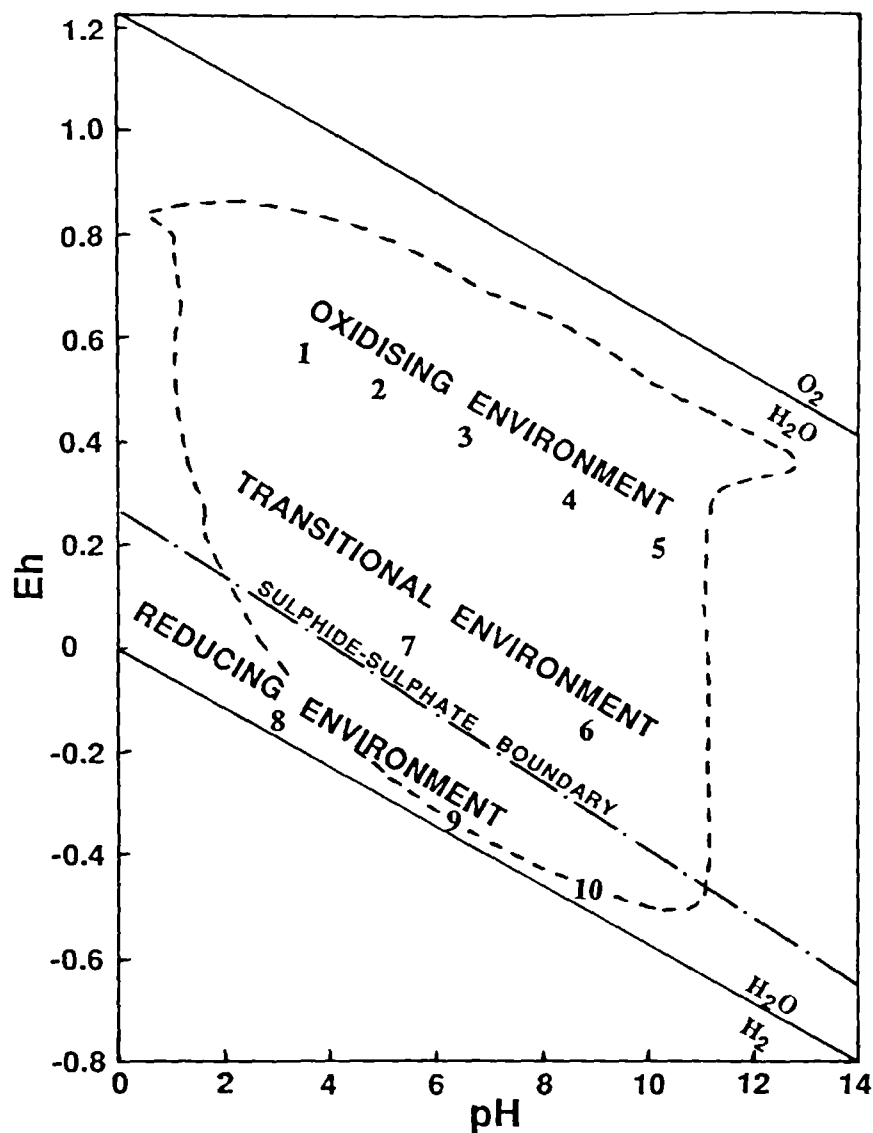


Figure 3.2 Eh-pH diagram of natural surface environments at 25°C, 1 bar (Brookins, 1988). The upper and lower stability limits of water are indicated by *solid lines*. The *dashed line* represents the range of natural Eh-pH measurements. The *dash-dot line* marks the sulphide-sulphate boundary which separates oxidising, sulphate-bearing waters above this boundary from reducing sulphide (as H_2S or HS^-)-bearing waters below. Oxidising, transitional and reducing environments are indicated. Specific environments are (*numbers on figures*): 1 mine waters; 2 rain; 3 streams; 4 normal ocean water; 5 aerated saline water residues; 6 ground waters; 7 bog waters; 8 water-logged soils; 9 euxenic marine waters; 10 organic rich, saline waters.

Hahne and Kroontje (1973) considered the systems Pb-O-H and Pb-Cl-H₂O over the whole pH range. At pH 6.2 in the Pb-O-H system, there is a change in predominance from Pb²⁺ to Pb(OH)⁺ with increasing pH. Polynuclear [Pb(OH)_n⁽²⁻ⁿ⁾⁺] complexes *e.g.* Pb(OH)₂⁰ are not thought to be important at the low lead levels found in natural waters (Hem, 1976; Rickard and Nriagu, 1978), although may be present in considerable amounts at pH>10 (Hahne and Kroontje, 1973).

In the Pb-Cl-H₂O system Pb-Cl complexes start to become significant at chloride concentrations of 10^{-1.2} M (Hahne and Kroontje, 1973). This is above the concentration found in most surface soils and ground waters: for example, Bradford *et al.*⁽¹⁹⁷¹⁾ reported a mean of 12.6 meq/l (≡ 10^{-1.9} M) and Griffin and Jurinak (1973) reported a mean of 10^{-2.9} M in saturation extracts from surface soils (0-15 cm) in Utah, USA. Saline soils may contain high levels of aqueous chlorine but such soil types are uncommon in the U.K. and therefore not considered here. Thus, Pb(OH)⁺ would be expected to predominate over Pb-Cl complexes in most soil solutions.

In the presence of carbonate, there is competition between hydroxide and carbonate ligands for lead. Using the stability constants given by Bilinski and Stumm (1973), Hem (1976) calculated that PbCO₃⁰ would be the predominate lead complex at pH 6 to pH 9 down to a Σ_{diss}CO₃ of 10^{-3.5} M/l. Below pH 6, PbHCO₃⁺ would logically form and below ΣCO₃=10^{-3.5} M/l Pb(OH)⁺ would predominate. The pH and Σ_{diss}CO₃ at which Pb(OH)⁺ would convert to PbHCO₃⁺ is not clear. Also, there is some confusion regarding carbonate complexes of lead. It is possible that Pb(CO₃)₂²⁻ forms in soil solutions (Bilinski and Stumm, 1973) but there is considerable uncertainty regarding the value of the stability constant. However, (Rickard and Nriagu, 1978) acknowledge that even if the constant given by Bilinski and Stumm (1973) is grossly inaccurate, carbonate complexes dominate in alkaline oxic water systems in contact with a carbonate source, either solid phase or atmospheric CO₂.

Little is known about the formation of lead-phosphate complexes. Nriagu (1972) suggested that PbH₂PO₄⁺ and PbHPO₄⁰ may be important lead species in natural water systems. Lindsay (1979) considered PbH₂PO₄⁺ complex to be insignificant whilst PbHPO₄⁰ increased in importance above pH 7.

(b) Organic speciation

Numerous organic substances can form stable complexes with lead and appreciable amounts of these may be present in natural waters. A review of organic matter in soils by Stevenson and Ardakani (1972) lists amino acids, organic acids, polyphenols, peptides, proteins and polysaccharides as generally forming soluble complexes with metals. This list comprises organic species known to exist in living organisms which have not undergone reaction in the soil to form complex polymers (humic and fulvic acids). Humic acid (high molecular weight) forms mostly insoluble complexes with metals (see Section 3.5) but fulvic acid (low molecular weight) complexes are generally water soluble (Stevenson and Ardakani, 1972).

Schnitzer and Skinner (1967) determined stability constants for several metal-fulvic acid complexes at pH 5.0 and found them to decrease in the order:



All stability constants were found to increase with increasing pH. This is due to the association of metal ions mainly with the carboxyl (-COOH) and phenolic (-OH) functional groups in fulvic acids which become increasingly ionized, especially COOH, with increasing pH (Schnitzer and Skinner, 1967).

The importance of organo-lead complexes is demonstrated by a simple aqueous model involving a chelating agent, nitrilotriacetate (NTA) (Rickard and Nriagu, 1978). The PbNTA complex was calculated to be the dominant lead species below pH 6 at NTA concentrations as low as 10^{-7} M. However, above pH 6 inorganic complexes were dominant. Lead acetate complexes have been proposed as a mechanism for the transport of lead in low temperature hydrothermal systems (Manning, 1986).

Summary

In the pH range of most soils (approximately pH 5-9) the aqueous speciation of lead will be dominated by inorganic complexes especially $\text{Pb}(\text{OH})^+$, PbHCO_3^+ , PbCO_3^0 and possibly $\text{Pb}(\text{CO}_3)_2^{2-}$ and PbHPO_4^0 . Lead will only be present as a free cation in acidic soils in the absence of organic complexes which may dominate at these low pH values.

3.3.3 Determinations of Lead Speciation in Soil Solutions

1;H)e

There is relatively little literature documenting determinations of lead speciation in soil solutions, presumably because of the analytical difficulties involved. The following studies have apportioned aqueous lead species indirectly on the basis of charge or molecular weight.

A speciation study by Tills and Alloway (1983), distinguished between positively charged (cationic), negatively charged (anionic) and organic forms of lead. Lead was predominately cationic in acidic soils but in an alkaline, calcareous soil from Velvet Bottom, Mendip Hills, a large proportion of solution lead was neutral which the authors suggested indicated the predominance of PbCO_3^0 . An anionic species, thought to be PbHCO_3^- was also present in small concentrations in the Mendip soil. In highly organic soils with soil organic matter (SOM) >20% and low pH (4-5), organically complexed lead accounted for over 13% of the total lead solution concentrations (Tills and Alloway, 1983).

Gregson and Alloway (1984) used gel permeation chromatography studies to determine the proportion of organically complexed lead in soil solutions. With the exception of one acidic sample (pH=4.4), lead was associated with organic matter of low molecular weight indicative of fulvic acid in all soil solution samples. This association increased with increasing pH. The authors suggest that this increase of lead associated with organic matter is related to increased stability constants for lead-organo complexes at higher pH, in agreement with the work of Schnitzer and Skinner (1967) and the considerations of Bloom (1981). At high pH (>6.1) lead was also associated with organic matter of high molecular weight. This could be due to the formation of a soluble humic acid complex or a complex with an organic compound known to exist in living organisms.

Summary

Determinations of lead speciation in soil solutions indicate that predictions from theoretical considerations of the aqueous speciation of lead are broadly correct. However, without a definitive analytical technique, the aqueous speciation of lead cannot be accurately assessed.

3.4 Adsorption of Lead in Soil

Adsorption in soils is the adhesion of ions or molecules to the surface of soil solids. The ions are bound by electrostatic (or coulombic) forces. The ability of a soil to adsorb cations (positively charged ions or complexes) is known as the cation exchange capacity and can be experimentally determined. Colloidal (<2 μm diameter) particles are largely responsible for adsorption due to their large surface area to volume ratio. Lead is adsorbed from solution onto the surfaces of clay minerals, iron and manganese oxides and organic matter but the mechanisms of interactions are poorly understood and this has led to some confusion in the literature.

3.4.1 Adsorption Mechanisms

Several different mechanisms are thought to be involved in the adsorption of metal ions although they are fundamentally driven by the attraction of opposite charges; namely a charge on the adsorbed ion or complex and a charge on the absorbing surface. Many authors have distinguished between specific adsorption which is irreversible and cation exchange which is reversible (*e.g.* Raffaldi *et al.*, 1976; Sposito, 1984; Alloway, 1990). Generally, specific adsorption occurs when relatively low concentrations of cations interact with a particle to form what is known as an inner-sphere complex where there is direct contact between cation and particle. Cation exchange occurs at higher cation concentrations by the formation of outer-sphere complexes where the adsorbed cation retains its solvation shell resulting in indirect contact between cation and particle (Sposito, 1984).

Little is known about the nature of surface bonds and it is often difficult to distinguish between specific adsorption and cation exchange from experimental data. There is evidence to suggest that the same mechanism applies to both types of adsorption (Quirk and Posner, 1975) and no distinction will be made between the two types in this study.

(a) Clay minerals

Clay minerals invariably have charged structures due to structural imperfections in the lattice or ion substitutions. Cations in clays are usually substituted by ions of a lesser valence which results in a net negative charge. A further charge results from edge effects along the mineral surfaces. These charges are permanent and not affected by pH. (Gast, 1977)

(b) Iron/manganese oxides

Oxides, such as those of iron and manganese display a pH dependent charge. According to the goethite (α -FeO.OH) model of Quirk and Posner (1975), this is due to the chemical adsorption of water at the surface of the oxide. The result is a net positive charge at low pH $[\text{Fe}(\text{OH}_2)(\text{OH}_2)]^+$, a net negative charge at high pH $[\text{Fe}(\text{OH})(\text{OH})]^-$ and a point at which no charge exists $[\text{Fe}(\text{OH})(\text{OH}_2)]^0$. The pH at which zero charge occurs is known as the iso-electric point (IEP) and is specific to a given compound.

(c) Organic matter

Organic matter contributes considerably to the cation exchange capacity (CEC) of a soil. In a review of the literature, Bloom (1981) considers the interaction of metals with organic matter. He recounts that adsorption sites are provided mainly by the carboxyl (-COOH) and phenolic (-OH) functional groups of humic acids. (See also Section 3.5.)

3.4.2 Adsorption Models

Lagerwerff and Brower (1973) found that the adsorption of lead could be described by a Gapon type equation which relates to columbic charges between metal and surface. However, many other authors *e.g.* Zimdahl and Skogerboe (1977); Harter (1979, 1983); Gerritse *et al.* (1984); Elliot ^{*et al.*} (1986) have found excellent correlations with a Langmuir type equation. The Langmuir adsorption isotherm involves the concept of a maximum adsorption sites resulting in a decrease in adsorption as surface metal concentration increases. Forbes *et al.* (1976) found that heavy metal adsorption on goethite was not only related to pH but also to the existing surface charge. Their data fitted an equation based

on a Langmuir type isotherm that included the adsorption of H^+ or OH^- better than the traditional Langmuir isotherm as it allowed for binding energy changes as the surface charge varied.

In summary, most studies have found that adsorption data fits a Langmuir type equation. The important feature of this equation is that it involves an adsorption maximum which is reached asymptotically.

3.4.3 Adsorption of Lead by Soil Constituents

The most popular technique for studying adsorption of lead in soils is to add lead in solution form (usually nitrate or chloride) to a soil sample and then leave to equilibrate for a period of 24-48 hours *e.g.* Zimdahl and Skogerboe (1977). The soil or supernatant (or both) are then analysed for lead. The solution need not contain only lead; many authors have used solutions containing one or more metals in addition to lead to investigate competitive adsorption *e.g.* Lagerwerff and Brower (1973), Bittell and Miller (1974).

Soil can generally immobilise high amounts of lead added as a solution (Harter, 1979; Zimdahl and Skogerboe, 1977). For instance, Hem (1976) predicted that sediments having the same properties as synthetic halloysite (an amorphous 1:1 clay) would be able to adsorb 90% of lead present within a concentration range of 10-1,000 mg/l at pH 6-8 (lead was assumed not to precipitate). It is difficult to ascertain whether immobilised lead is adsorbed or precipitated. For example, a method similar to that described above has been used to determine mineral solubility equilibria (Santillan-Medrano and Jurinak, 1975). This complexity is discussed in terms of the kinetics of mineral formation in Section 3.7.3.

Many of the experiments in the literature have used dilute solutions of lead. At these levels precipitation is not likely to be a factor controlling lead in solution (Jones and Jarvis, 1981). Where large quantities of lead have been added to soils, precipitation has been considered but found to be of secondary or negligible importance (Harter, 1979, 1983; Zimdahl and Skogerboe, 1977).

Statistical regression analysis indicates that the main agents responsible for

adsorption of lead in soils are clays and organic matter (Soldatini *et al.*, 1976; Zimdahl and Skogerboe, 1977). As clay minerals and SOM are two of the main contributors to soil CEC, this leads to a correlation of lead adsorption and CEC. Soldatini *et al.* (1976) also found no correlation of lead adsorption with quantity of manganese oxides agreeing with the findings of Gibson and Farmer (1984, 1986) reported in Section 3.2.

Several authors have reported that the adsorption of lead and other heavy metals increases with increasing pH *e.g.* Zimdahl and Skogerboe (1977); Harter (1979, 1983); Gerritse *et al.* (1984); Elliot *et al.* (1986). This is thought to be at least partly due to the increased ionization of iron and manganese oxides suggested by Quirk and Posner (1975) and discussed in Section 3.4.2. However, as clay minerals and SOM are considered the main agents responsible for adsorption and very little of the pH variation can be assigned to the clay minerals (Jones and Jarvis, 1981), some mechanism involving SOM must account for increased adsorption at high pH. Harter (1983) found that SOM was important as a source of pH dependent cation retention. His conclusions are supported by Stevenson and Ardakani (1981) who considered that the increased affinity of SOM to adsorb metals at higher pH_λ^{is} due to increased ionization of the carboxyl and phenolic groups.

(a) *Hydrolysis of lead*

Adsorption of heavy metals in soils increases markedly with pH in the region corresponding to the first hydrolysis of the cation (Jones and Jarvis, 1981). This is defined by the reaction $M^{n+} + OH^- \rightleftharpoons MOH^{(n-1)+}$ with equilibrium constant K_1 . For lead, Pb^{2+} and $Pb(OH)^+$ are present in equal concentrations at pH ($\equiv pK_1$) 6.2 although the transition in predominance from Pb^{2+} to $PbOH^+$ takes place over a pH range, approximately from pH 5 to pH 8 (Hahne and Kroontje, 1973). The hydrolysed ion is more easily adsorbed than the free cation (Elliot^{et al.}, 1986; Harter, 1983) but the reasons for this are uncertain. Harter (1983) predicted an approximate increase of 60% in the adsorption of lead between the range pH 6-8 based simply on the difference in charge between the divalent cation and univalent complex. Quirk and Posner (1975) and Forbes *et al.* (1976) consider further that partial hydrolysis is an essential part of the adsorption mechanism of metals onto oxides. Therefore, the greater the degree of hydrolysis of a cation, the more favourable adsorption becomes. The pK_1 value for the hydrolysis of lead also has important consequences on the order of heavy metal preferential adsorption sequences (see below).

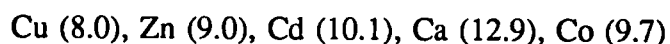
Hydrolysis promoted at the surface of an oxide is thought to be responsible for the adsorption of lead onto the positively charged surface of goethite at pH values as low as pH 4-5; similar effects are noted for other heavy metals (Quirk and Posner, 1975; Forbes *et al.*, 1976).

(b) Competitive adsorption

Adsorption is a competitive process. Bittell and Miller (1974) reported that Pb^{2+} would be preferentially adsorbed by a factor of 2 or 3 over Cd^{2+} and Ca^{2+} in a clay system comprising kaolinite, illite, montmorillonite. Lagerwerff and Brower (1973) studied the exchange reactions of Pb^{2+} with Al^{3+} and Ca^{2+} at various salinity levels (determined by NaCl concentrations) in kaolinitic, montmorillonitic and illitic soils. Aluminium was favoured over Pb^{2+} but Pb^{2+} was favoured over Ca^{2+} . Elliot *et al.* (1986) found that lead successfully competed against Cu, Zn and Cd (the adsorption of Zn and Cu being much less than Pb and Cd) in acidic mineral soils and soils containing 2-4% SOM. Forbes *et al.* (1976) found the following sequence described the adsorption of heavy metals onto goethite:



This competition does not only arise from the suitability of ionic charge and radius. The preferential adsorption sequences discussed above can be related to the pK_1 values of the metals. The lower the pK_1 value, the greater the affinity of the metal to be adsorbed (Quirk and Posner, 1975; Forbes *et al.*, 1976; Elliot *et al.*, 1986). Quirk and Posner (1975) and Forbes *et al.* (1976) suggest that pK_1 indicates the ease of cation hydrolysis and so the lower the value, the less energy required to bind the metal. Thus, the greater affinity of lead for adsorption over most other heavy metals is related to its low pK_1 value (6.2), which is lower than those of other divalent metals considered here:



(data from Baes and Mesmer, 1976).

3.4.4 Summary

Lead in solution is immobilised quickly and efficiently by soil. The main process is thought to be adsorption onto the surfaces of clay particles and organic matter. Lead successfully competes against many other cations to be adsorbed, which is related to its relatively low pK_1 .

3.5 Organic Matter

Soil organic matter (SOM) has considerable influence over the mobility of heavy metals in soils (Bloom, 1981; Ram and Verloo, 1985). It is thought that the association of lead with SOM is largely responsible for the accumulation of lead in the upper 5 cm of the soil, where organic matter is present (see Section 2.4.2(a)). Lead can form very stable organic complexes (Stevenson and Ardakani, 1972; Ram and Verloo, 1985).

Soil organic matter can be classified into 2 main groups: (1) biochemicals of types known to occur in living organisms, and (2) a series of complex polymers formed by secondary synthesis reactions. Compounds included in the first group form largely soluble complexes whilst the second group includes humic and fulvic acids. Fulvic acid complexes are mostly soluble whilst those of humic acid are not. This is only a general rule as both may form soluble and insoluble complexes. (Stevenson and Ardakani, 1972)

Soluble organic lead complexes were discussed in Section 3.3 and only lead associated with solid organic matter is considered here which is mostly held in humic acid complexes.

Szalay (1964) described lead as a "huminophilic" element because it was sorbed by humic acids in laboratory studies. Bloom (1981), citing the work of Stevenson (1976), stated that lead has a high bonding strength with humic acid. The bonding strength is less than that of Cu but very much greater than that of Fe, Ni, Co, Zn, Mn and Ca. Metal ions are largely bound by the carboxyl and phenolic function groups as they are in fulvic acids

(Bloom, 1981). Increased ionization of these groups with increasing pH leads to a greater degree of binding at high pH (Stevenson and Ardakani, 1972).

The exact nature of the interaction between cations and binding sites has been the subject of recent controversy. It is extremely difficult to distinguish between adsorbed lead and bound or chelated lead from experimental data as adsorption takes place on the same sites as binding. Bloom (1981) proposed that most divalent cations are bound in outer-sphere complexes whereas chelation necessarily involves an inner-sphere complex. This is analogous to the difference between specific adsorption and cation exchange on mineral surfaces discussed in section 3.4. The high binding strength of lead, however, led Bloom (1981) to suggest that lead is held in an inner-sphere complex, possibly partially hydrated. This would imply that the large amounts of lead associated with organic matter in the adsorption experiments of Zimdahl and Skogerboe (1977) and Harter (1983) may in fact be bound rather than adsorbed as stated.

3.6 Solid Phase

For lead to be held in the mineral phase of soil, it must form chemical bonds with inorganic anions. Thus, fixing of lead by the solid phase is distinguished from adsorption where ions are held by electrostatic forces and from organic complexation. Lead may be held in the lattices of primary and secondary minerals as a minor constituent, substituting for cations of similar radius or as a major constituent, contributing substantially to the overall mass of the mineral.

3.6.1 Lead substitution in Minerals

The ionic radius of Pb^{2+} is between 1.18 and 1.32 Å (Wedepohl ^{*et al.*}, 1969). Pb^{2+} commonly substitutes for a number of cations in minerals: K^+ (radius: 1.33 Å), Sr^{2+}

(radius: 1.12-1.27 Å), Ba²⁺ (radius: 1.34-1.43 Å) and even Ca²⁺ (radius: 0.99-1.06 Å) and Na²⁺ (radius: 0.95-1.0 Å) though their radii are considerably smaller than Pb²⁺ (Wedepohl ^{et al.} 1969). Similarly, these cations can substitute for Pb²⁺ in minerals where lead is a major constituent.

(a) Substitution in primary minerals

Primary minerals originate from the parent rock material, normally the underlying strata. Usually, the parent rock formed at temperatures and pressures vastly different from those currently found in the surface environment and are therefore in a state of disequilibrium. Primary minerals in soils have been incorporated by physical weathering processes but have not yet chemically weathered to form secondary minerals.

Sposito (1983) has compiled lists of the principal modes of occurrence of trace metals in primary and secondary minerals. In primary minerals, lead is often present substituted for potassium in feldspars and micas, for calcium in feldspars, pyroxenes and phosphates, and for iron and manganese in oxides. Feldspars contain an average of 50-100 µg/g Pb and micas 30-40 µg/g Pb (Wedepohl ^{et al.} 1969). Plagioclases (calcium feldspar) and amphiboles (similar to pyroxenes) contain on average 20 µg/g and 15 µg/g Pb respectively by substitution with Na⁺ and Ca²⁺ (Wedepohl ^{et al.} 1969). Pb²⁺ can also substitute for Ca²⁺ in CaCO₃, the major constituent of limestone, up to an atomic Pb:Ca ratio of at least 1:8.5 (Palache *et al.*, 1951).

(b) Substitution in secondary minerals

Lead can co-precipitate with secondary soil minerals such as manganese oxides and the clay minerals illite and smectite (Sposito, 1983). This has probably caused confusion in the adsorption experiments discussed in Section 3.4.3 as these soil constituents have also been cited as important in the adsorption of lead.

3.6.2 Lead Minerals - Eh-pH Diagrams

There are some 240 lead minerals known to exist in the earth's crust. However, only very few of them are important in the surface environment. Eh-pH diagrams are of

considerable use in predicting which lead minerals will be stable under varying conditions of oxidation/reduction and acidity/alkalinity. Equilibria between compounds in a defined system are plotted on a graph with pH as the X-axis and Eh as the Y-axis. Stability fields of minerals in the system are thus shown as functions of Eh and pH. The major limitation of most Eh-pH diagrams is that equilibria are drawn for pure compounds. In natural systems there would usually be some solid solution which may affect the equilibria but this is not generally shown on Eh-pH diagrams. Other limitations are that they are drawn at a fixed temperature and pressure and for a fixed solution composition. This can largely be overcome by drawing diagrams for the required conditions *e.g.* Fig. 3.3 is drawn for 25°C and 1 bar pressure, approximating to conditions at the Earth's surface.

(a) The Pb-S-C-O-H system

The conventional Eh-pH diagram for Pb is shown in Fig. 3.3. This was first presented by Garrels and Christ (1965) and has been subsequently cited by many authors since *e.g.* Krauskopf (1979); Brookins (1988). It shows equilibria among lead compounds in water in the presence of CO₂ and S *i.e.* in the system Pb-S-C-O-H. Changes in $\Sigma_{\text{diss}}\text{CO}_3$ and $\Sigma_{\text{diss}}\text{S}$ alter the diagram very little, provided concentrations are within the normal ranges found in natural solutions (Krauskopf, 1979). Galena has a large stability field even if dissolved sulphur is as low as 10⁻⁵ M (Garrels and Christ, 1965). A reduction in $\Sigma_{\text{diss}}\text{CO}_3$ causes Pb(OH)₂ to become stable in place of cerussite but carbonate levels in soils are generally high enough (above atmospheric CO₂) for cerussite to be the more stable mineral (Lindsay, 1979). The Garrels and Christ (*op. cit.*) Eh-pH diagram shows the chief minerals actually observed in the natural environment, emphasising the practical use of such diagrams.

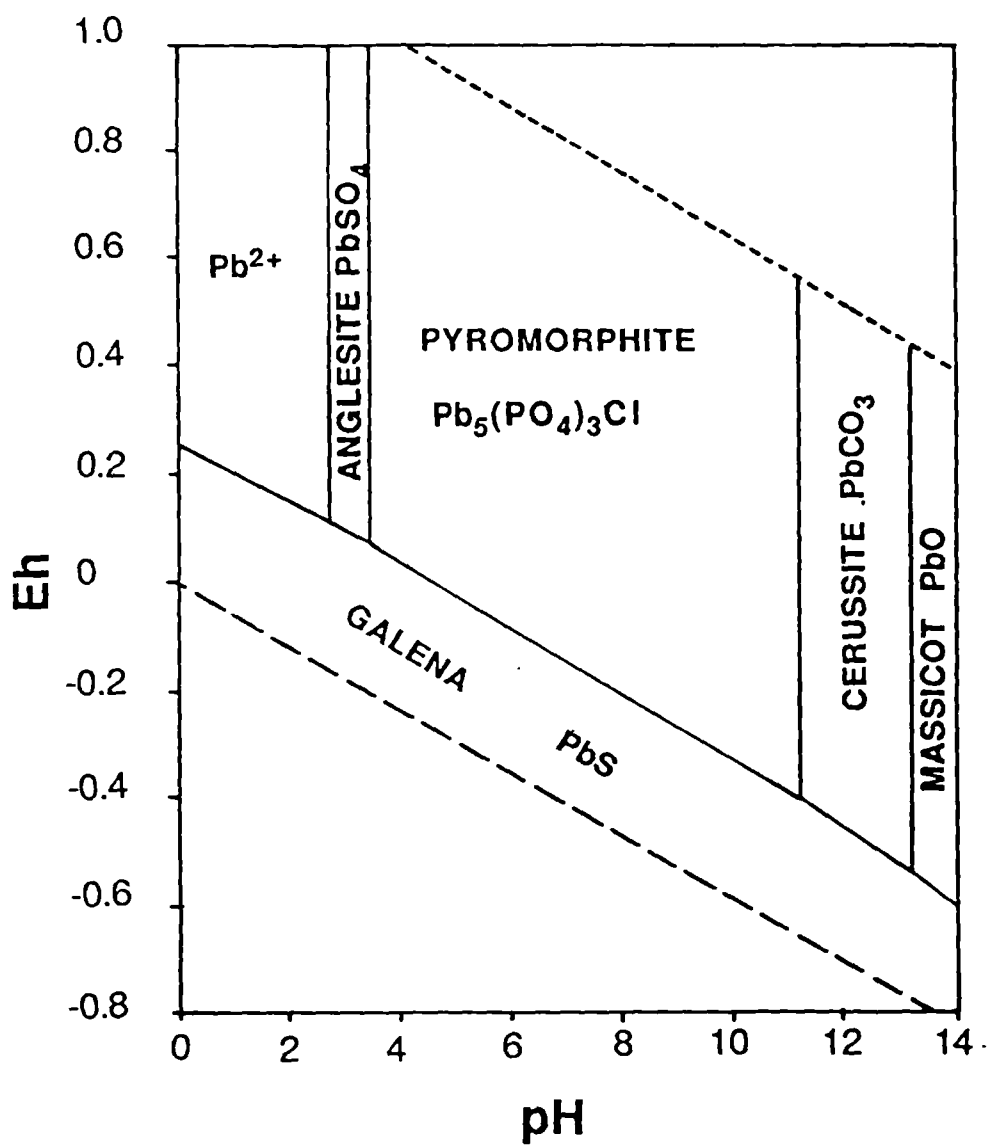


Figure 3.4 Eh-pH diagram for the system Pb-S-P-C-O-H-Cl at 25°C, 1 atm (Nriagu, 1974). *Dashed lines* indicate the stability limits of water. $\sum_{\text{diss}}\text{S}=10^{-3}$ M, $\sum_{\text{diss}}\text{CO}_3=10^{-2}$ M, $\sum_{\text{diss}}\text{P}=10^{-6}$ M, $\sum_{\text{diss}}\text{Cl}=10^{-3}$ M, $\{\text{Pb}^{2+}\}=10^{-6}$.

The Eh-pH diagram of natural surface environments (Fig. 3.2) shows that soils in equilibrium with ground waters would be oxidising and would lie above the sulphide/sulphate boundary within the range pH 3-10. Therefore, either anglesite (PbSO_4) or cerussite (PbCO_3) would be expected to be in equilibrium with the soil solution, precipitating or dissolving depending on the Pb^{2+} , CO_3^{2-} and SO_4^{2-} activity in the soil solution. Another important feature shown by the diagram is that galena (PbS) would be expected to be thermodynamically unstable in a soil environment. It is most likely to oxidise to either anglesite or cerussite depending on whether the pH is above or below pH 6, although at high pH and Eh galena may weather to hydrocerussite or a lead oxide.

(b) The Pb-S-P-C-O-H-Cl system

Nriagu (1974) has constructed an Eh-pH diagram for lead minerals in the system Pb-S-P-C-O-H-Cl which is presented in Fig. 3.4. The difference between the two Eh-pH diagrams is striking. The inclusion of phosphorus and chlorine in the system produces a large stability field of chloropyromorphite (usually referred to in geological literature as simply pyromorphite), $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ in the oxidised area of the diagram above the sulphide/sulphate boundary. This agrees with early work by Jowett and Price (1932) which suggested that the formation of chloropyromorphite could be geologically important.

3.6.3 Lead Phosphates

In a series of papers and articles by Nriagu (1972, 1973, 1974, 1984) and Rickard and Nriagu (1978) the role of lead phosphates in soils, sediments and natural waters is considered in a thermodynamic framework. Possible phosphates in the system Pb-P-O-H-Cl are: $\text{Pb}(\text{H}_2\text{PO}_4)_2$, PbHPO_4 , $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_4\text{O}(\text{PO}_4)_2$ and $\text{Pb}_5(\text{PO}_4)_3\text{X}$ (X = halide ion, OH^- , NO_3^-). In this system, chloropyromorphite is by far the most thermodynamically stable and insoluble lead phosphate over the Eh and pH range encountered in natural systems (Nriagu, 1973). It has a ΔG_f° ³ of -3791.5 kJ/mol (-906.2 kcal/mol) calculated from an

³ ΔG_f° is Gibb's Free Energy of Formation; the more negative the free energy of formation of a compound, the more stable the compound.

experimentally determined solubility product (Nriagu, 1973). It may, however, hydrolyse to lead oxide or hydroxide at high pH (Nriagu, 1973). PbHPO_4 , $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_4\text{O}(\text{PO}_4)_2$ and $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ will convert to chloropyromorphite in the presence of chloride ions (Jowett and Price, 1932) and it is unlikely that $\text{Pb}(\text{H}_2\text{PO}_4)_2$ forms in normal surface environments (Nriagu, 1973).

Another lead phosphate mineral which Nriagu (1974, 1984) considers may form in soils is plumbogummite, $\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$. Plumbogummite has an estimated ΔG°_f of -5109.0 kJ/mol (-1225.7 kcal/mol), according to a model comprising formation reactions written in terms of simple oxides and hydroxides (Nriagu, 1984). The stability fields of chloropyromorphite and plumbogummite have been shown to dominating strongly over those of cerussite and anglesite on phase stability diagrams (Nriagu, 1974, 1984).

The preferential precipitation of plumbogummite over chloropyromorphite from soil solution is favoured by lower lead concentrations, higher pH (> 6 or 7) and higher phosphorus and aluminium concentrations. Other secondary lead phosphates which may form in soils include hinsdalite ($\text{PbAl}_3(\text{PO}_4)(\text{OH})_6\text{SO}_4$) and corkite ($\text{PbFe}_3^{3+}(\text{PO}_4)(\text{OH})_6\text{SO}_4$). These minerals are stable in alkaline environments at particularly low phosphorus concentrations (Nriagu, 1984). Lead can form several phosphates with other metals e.g. tsumebite ($\text{Pb}_2\text{Cu}(\text{PO}_4)(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) and dewindtite ($\text{Pb}(\text{UO}_4)(\text{PO}_4)_2(\text{OH})_4 \cdot 8\text{H}_2\text{O}$) (Nriagu, 1984). These require a high concentration of other metals e.g. copper and uranium above the range normally encountered in the surface environment and are not considered here.

3.6.4 Geological Analogy

Lead-bearing solid phase formation in soils is geochemically mimicked by the oxidation of sulphide ore deposits. Both processes occur over similar Eh and pH ranges, although elemental concentrations may be somewhat different.

Anglesite and cerussite are extremely well known as oxidation products of galena (Palache *et al.*, 1951; Read, 1971), as implied by the Eh-pH diagram of Garrels and Christ (1965) in Fig. 3.3. Other common lead-bearing secondary minerals include oxides (e.g. minium, Pb_3O_4); mixed carbonates, sulphates, oxides and chlorides (e.g. hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$; leadhillite, $\text{PbSO}_4(\text{CO}_3)_2(\text{OH})_2$; phosgenite, $\text{Pb}_2\text{CO}_3\text{Cl}_2$) and the

pyromorphite series (Read, 1971).

The oxidising products of galena in sulphide deposits in Leadhills, Scotland have been documented by Temple (1955/1956). A common sequence is the weathering of galena to anglesite followed by weathering to cerussite or hydrocerussite. These minerals are themselves often replaced by chloropyromorphite and polysphæit (a calcium rich variety of chloropyromorphite, see below). Hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$) and vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$) are recorded but rare. These pyromorphites are considered to be the end products of the weathering sequence.

(a) Pyromorphite

The pyromorphite series consists of three isostructural end members: pyromorphite (or more properly chloropyromorphite), $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ and the arsenic and vanadium analogues mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ and vanadinite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ respectively (Read, 1971). Palache *et al.* (1951) does not include vanadinite as an end member of the pyromorphite series but is reported as a vanadian rich variety. Palache *et al.* (1951) state that a full solid substitution between mimetite and chloropyromorphite exists but mimetite is considerably less common than chloropyromorphite; a complete solid substitution between chloroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) does not exist but calcium is reported as frequently substituting for lead up to Ca:Pb 1:2.1 (wt.% oxide). This calcium-rich variety of chloropyromorphite is called polysphæit (Palache *et al.*, 1951).

It has been shown that many variations on the basic pyromorphite formula, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ are possible. Limited solid substitution of Ca for Pb, exchange of As and V for P and OH for Cl may take place. The As and V rich members of the mineral suite are rare and unlikely to be important in soils because As and V are generally present in quantities far less than phosphorus (Bowen, 1966), although no detailed thermodynamic studies have been undertaken on their stability relative to chloropyromorphite. Similarly, OH replacement of Cl is rare because chloropyromorphite is thermodynamically more stable. Any hydroxypyromorphite formed in a soil would be expected to convert to chloropyromorphite in the presence of low concentrations of chloride ions. Limited Ca substitution for Pb however, is common and may be important in soils. Indeed, Rickard and Nriagu (1978) and Nriagu (1984) suggest that a mineral between the end members chloropyromorphite-hydroxyapatite will form in soils. Thus, the form of pyromorphite

most likely to be important in soils is chloropyromorphite containing amounts of calcium. The term pyromorphite will henceforth be adopted to describe chloropyromorphite with or without calcium substitution. Whilst not strictly accurate, it is more in keeping with geological and other literature.

(b) Plumbogummite

Plumbogummite ($\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) has also been reported as a mineral. Although rarer than chloropyromorphite, plumbogummite has been observed as pseudomorphs after chloropyromorphite (Palache *et al.*, 1951). This observation supports the suggestion of Nriagu (1974) that plumbogummite is thermodynamically stable with respect to chloropyromorphite. Again, Ca substitution for Pb is common and Rickard and Nriagu (1978) and Nriagu (1984) suggest that a mineral with a composition between the end members plumbogummite and crandallite ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) will form in soils.

3.6.5 Identification of Lead Minerals in Soils and Streetdusts

Numerous studies on the identification of the solid phases containing lead in soils and dusts have been conducted (*e.g.* Olson and Skogerboe, 1975; Biggins and Harrison, 1980; Linton *et al.*, 1980; Hopke *et al.*, 1980 and Mattigod *et al.*, 1986). Lead is usually present at trace levels in soils so lead compounds make up a minute proportion of the soil solid, impeding identification of the lead-bearing phase in soils.

(a) Preconcentration techniques

The above mentioned authors have overcome this problem by employing preconcentration techniques. Preconcentration is largely achieved by density gradient separation. Lead compounds are amongst the densest components of soil and so fall into the heaviest fraction. Further preconcentration can be achieved by magnetic separation (lead being a non-magnetic element) either before (Linton *et al.*, 1980; Biggins and Harrison, 1980) or after (Olson and Skogerboe, 1975) density separation. The resulting lead rich fraction can then be analysed by X-ray diffraction (XRD) *e.g.* Olson and Skogerboe (1975), Biggins and Harrison (1980); and/or scanning electron microscopy

(SEM) associated with energy dispersive X-ray spectrometry (EDX) *e.g.* Linton *et al.* (1980), Mattigod *et al.* (1986). A modification of this preconcentration technique and subsequent examination of the solid lead-bearing phase is followed in this study and described in Chapter 5.

All the above studies found lead to be concentrated in the $>3.3\text{g/cm}^3$ non-magnetic fraction. However, significant amounts were found in all density fractions from ≤ 1.5 to $>3.3\text{ g/cm}^3$ and in both the magnetic and non-magnetic fractions (where applicable). This may represent the association of lead with the lighter soil components or imperfect separation due to physical trapping of lead minerals by lighter grains.

(b) Lead compounds in urban soils and dusts

The solid lead-bearing phase in highway and urban soils from the United States and streetdusts from Lancaster and other U.K. cities have been studied using XRD by Olson and Skogerboe (1975) and Biggins and Harrison (1980) respectively. Only crystalline material can be examined using this technique which accounts for only 50% of the lead present in the preconcentrated material (Olson and Skogerboe, 1975) and a few per cent of total soil lead (Biggins and Harrison, 1980).

The following compounds were reported in the soils and streetdusts of the above studies: PbS , Pb^0 , Pb_3O_4 , $\text{PbSO}_4\cdot(\text{NH}_4)_2\text{SO}_4$ and PbSO_4 as major components and $\text{PbO}\cdot\text{PbSO}_4$ and $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ as minor or trace components. PbS was found only on a lead ore transportation route (Olson and Skogerboe, *op. cit.*), where galena is probably the main component of ore. Pb^0 was found in vehicle parking areas in both the U.K. and the U.S. It is thought to arise from the cold starting of vehicles (Biggins and Harrison, *op. cit.*). Pb_3O_4 was found in Lancaster streetdusts and was attributed to leaded paint (Biggins and Harrison, *op. cit.*). $\text{PbSO}_4\cdot(\text{NH}_4)_2\text{SO}_4$ was only found in Lancaster and was thought to represent an intermediate compound in the conversion of lead halides to PbSO_4 as it transforms to PbSO_4 on leaching with water (Biggins and Harrison, *op. cit.*; Section 2.4.1).

Both investigations concluded that PbSO_4 was the most frequently observed crystalline compound and that this forms from the conversion of lead bromochloride emitted by vehicles. Supporting evidence is afforded by the studies of Ter Haar and Bayard (1971) and others (Section 2.4.1(a)) who found that lead was primarily emitted from vehicle exhaust as bromochloride but rapid conversion to lead salts including lead

sulphate occurred in the atmosphere. It is therefore possible that a large proportion of this transformation occurs in the atmosphere by reaction with SO_3 rather than in the soil environment.

Both authors suggest that further reaction in the soil is possible. Further weathering, possibly of vehicle emissions (Ter Haar and Bayard, 1971) is thought to account for the presence of $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, although it is also possible that this represents unweathered paint (Biggins and Harrison, 1980). This is in accordance with the Eh-pH diagram of Garrels and Christ (1965) which predicts that PbSO_4 would be unstable in Lancaster streetdust, previously reported to have a pH range of 6.5-7.5 (Harrison *et al.*, 1981). No explanation has been found in either study to account for the presence of $\text{PbO} \cdot \text{PbSO}_4$ but it is likely to have formed from in a similar manner to PbSO_4 .

Linton *et al.* (1980) identified exclusively PbSO_4 by XRD in U.S. streetdusts. SEM/EDX analysis revealed lead bearing particles of automotive origin (identified by morphology) associated with Fe and Br. Al, Ca, K, Na, Mg, Si and Zn were also associated with these particles, although not consistently. The association of lead with iron accounts for the presence of lead bearing particles in magnetic fractions (Linton *et al.*, 1980). The association of lead with this wide range of elements can not be readily explained but may represent adhesion of lead-bearing particles to soil constituents. Paint chips showed a strong association of lead and titanium, but no X-ray diffraction pattern for this type of particle was identified.

(c) Lead compounds in mine-waste soil

Mattigod *et al.* (1986) identified leadhillite, $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ by XRD analysis on mine-waste soils from the vicinity of Shipham, U.K. Shipham is a historic mining village in the Mendips, Somerset where Zn ore was mined together with lesser amounts of lead ore. The chemical form of the ores is not stated but has been reported elsewhere (Gough, 1967) as predominately sulphides. Leadhillite was enhanced in finer grained fractions and SEM/EDX analysis revealed an anhedral morphology (Mattigod *et al.*, 1986), implying that it is a secondary rather than primary mineral. Galena was not identified by XRD which is interesting as it implies that the mineral has completely oxidised. This would have occurred over the past 150 years, since mining ceased in 1850.

The Eh-pH diagram of Garrels and Christ (1965) does not consider the mixed

phase leadhillite. If represented, it would probably form a field between anglesite and cerussite.

(d) Evidence for lead phosphate formation in soils

Plumbogummite is reported to have been identified in Indian soils by Sarma and Krisha Murti (1969/1970). A method involving HF digestion of soils was employed to preconcentrate phosphates (not digested by HF) sufficiently to allow identification by XRD. However, this method has been shown to contain serious errors as residues from blank samples (presumably containing very little lead) yield XRD spacings that are very similar to plumbogummite (Campbell *et al.*, 1972), resulting in erroneous identification. Hence, the findings of Sarma and Krisha Murti (*op. cit.*) may simply be an artefact of the technique.

Nriagu (1974, 1984) reported the presence of plumbogummite in Canadian soils adjacent to a highway but does not give a method of analysis. If the same method as Sarma and Krisha Murti (*op. cit.*) was used, this may also be an erroneous finding. Therefore, these studies cannot be regarded as conclusive evidence of the formation of plumbogummite in soils.

Norrish (1975) has reported the presence of hinsdalite ($\text{PbAl}_3(\text{PO}_4)(\text{OH})_6\text{SO}_4$) in Pb-rich lateritic soils from Australia. SEM X-ray maps are presented which show the association of lead with Al, P, S and Ba. The presence of barium cannot be satisfactorily explained and quantitative analysis indicates that the specimen is not a pure mineral. The possibility of an aggregate with BaSO_4 can not be eliminated. The X-ray maps, however, do imply that lead phosphates may be present in soils.

Further circumstantial evidence for lead phosphate formation in soils comes from a study by Santillan-Medrano and Jurinak (1975). Data from experiments where solution lead was added to soils, was plotted on diagrams representing equilibrium solubilities of various lead minerals. $\{\text{Pb}^{2+}\}$ was found to be regulated by lead hydroxide up to a pH of approximately 6.6. Above this pH, $\{\text{Pb}^{2+}\}$ was controlled by lead phosphate, although it was not possible to identify the dominant soil phase and the phosphates considered ($\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_4\text{O}(\text{PO}_4)_2$ and $\text{Pb}_5(\text{PO}_4)_3\text{OH}$) have similar solubilities. Pyromorphite was not considered because there was a negligible amount of chlorine in the system and plumbogummite was also not considered. Once again, the study implies that lead

phosphates could be important in soils. However, care must be taken when interpreting this type of experiment as many authors have described adsorption using data from similar experiments (*e.g.* Zimdahl and Skogerboe, 1977; Harter, 1983; Section 3.4.3).

3.6.6 Summary

Lead is present in the solid phase of soil in both primary and secondary minerals. Eh-pH diagrams are useful in predicting secondary lead minerals that are in equilibrium with the soil. Lead-phosphates have been predicted to be stable in soils and this is supported by geological evidence indicating that lead-phosphates form and are stable in the surface environment. However, no conclusive observations of these minerals have been made, despite numerous studies on the identification of the solid phase of lead in soils and dusts. This apparent contradiction is addressed in the following section.

3.7 Equilibrium, Kinetic and Solubility Considerations

3.7.1 Introduction

On the basis of thermodynamic predictions and geological evidence, it would be reasonable to expect pyromorphite or possibly plumbogummite to form in soils. However, no conclusive observations of these minerals have been made, despite numerous studies on the identification of the solid phase of lead in soils and dusts (Section 3.6). It is suggested that this paradox can be solved by considering equilibrium, kinetic and solubility aspects of the soil system and their relation to lead phosphate formation.

The situation is complicated by the controversy surrounding which is the principal soil constituent responsible for the fixation of lead when added in solution. As discussed in Section 3.4.3, two essentially similar experiments with similar results, one by Harter

(1983) and one by Santillan-Medrano and Jurinak (1975) have discussed their data in different terms. Harter (1983) considered the fixation of lead to be due to adsorption, whilst Santillan-Medrano and Jurinak (1975) considered that solid phase formation was responsible. The timescale of mineral formation lends the argument towards adsorption but precipitation remains a possibility.

3.7.2 Thermodynamic Models

It is very hard to distinguish between adsorption and precipitation on a macroscopic scale. Quantitative thermodynamic models have been developed in an attempt to identify the geochemical controls on lead concentration in natural waters. Hem (1976) presents a simple model of adsorption involving a synthetic clay of known CEC in an aquatic environment. In this model it is possible to consider solid phase formation as the precipitation of PbCO_3 (pyromorphite is rejected as a solid because it has not been identified in any natural aqueous system). However, in the subsequent calculations, Hem (*op. cit.*) assumed that lead was not precipitated and concluded that the vast majority of lead in the system would be adsorbed onto the clay.

SOILCHEM

Sposito and Mattigod (1980) developed a computational chemical equilibrium model to describe trace element behaviour in soils known as *GEOCHEM*. An upgraded version of *GEOCHEM* is now available called *SOILCHEM* (Sposito and Coves, 1988), in which the model for metal adsorption is improved. *SOILCHEM* is able to calculate the speciation of chemical elements among the aqueous, solid and adsorbed forms in the soil. There are 3 types of calculations:

- (i) metal-ligand interaction, which determines aqueous speciation;
- (ii) ion activity product (IAP), which defines mineral-solution equilibria;
- (iii) surface complexation, which models the interactions of aqueous trace elements with the surfaces of organic and inorganic solids.

For each of the above groups there is a set of mole balance equations. Certain characteristics of a soil *e.g.* CEC, solute concentrations are entered into the program which

then runs through a series of iterations until all equations are satisfied. The result is a list of the percentage distribution of each metal and ligand between aqueous species (free ions and complexes), solid phases and adsorbed forms.

The advantage of this computer model is that multi-component equilibria can be calculated very quickly, calculations which would otherwise take days. This means the interactions of *e.g.* a metal with an exhaustive number of ligands can be calculated with ease. Many of these interactions will prove insignificant but it is important that they are considered.

A meritorious attribute of the *SOILCHEM* program is flexibility. The program can consider mixed solid phases, redox reactions or simply mineral solubility equilibria. Many characteristics of a soil can either be fixed or calculated *e.g.* pH, CO₂, ionic strength. Similarly, solids can either be allowed to form or imposed on a system.

However, *SOILCHEM* has limitations. It is a model and must be treated as such. It cannot predict soil reactions absolutely and the data must be interpreted with a good understanding of the model. The results produced by *SOILCHEM* can never be better than the thermodynamic data it contains. Whilst the thermodynamic data file in *SOILCHEM* is comprehensive and contains data from recent compilations, these are subject to errors and inconsistencies. One major limitation of the *SOILCHEM* is the absence of a model for organic chelation of metals. However, *SOILCHEM* is being constantly updated and improved. Whilst the problem of modelling organic chelation has not yet been addressed, this may be possible in the future. The program demonstrates enormous potential to become a powerful tool in the study of trace element equilibria in soils but at present its use is limited. A simple solubility computation using *SOILCHEM* is described in Section 3.7.4.

3.7.3 Kinetics and Disequilibrium

Thermodynamics and considerations of chemical equilibria enable predictions to be made on the state of an element or substance at equilibrium. The soil is a constantly changing environment where equilibrium is probably never actually reached. However, chemical reactions always proceed towards equilibrium, never away from it. Thus,

equilibrium relationships provide the key to predict which reactions can and cannot occur in soils. (Lindsay, 1981)

Lead phosphates may not be present in the solid phase because soils are not in equilibrium. Kinetics of mineral formation are slow. Analogy with geological mineral formation gives a time scale of the order of years, even 10's to 1000's of years. This is in contrast to adsorption reactions which take place on a time scale of a few days (*e.g.* Zimdahl and Skogerboe, 1977). Precipitation, however, in a non-crystalline form may be rather more rapid than mineral formation but an estimate of the time scale is not available. Mattigod *et al.* (1981) consider the time scales of different soil processes in their admirable review of factors affecting the solubility of trace metals in soils. Similarly, West (1981) considers the time scales involved in mineral weathering and adsorption on the supply of trace elements to plants via the soil solution. Both these reviews conclude that mineral-solution equilibria could take a long time (of the order of years) to establish. Unfortunately, elsewhere in the literature there is scant consideration of the kinetics of mineral formation/dissolution.

Qualitative model

Any unstable lead compound in soil, however insoluble, will gradually weather to a more stable state. This is generally thought to be carried out by a process of dissolution, although other models have been suggested (Krauskopf, 1979). Upon dissolution, lead would be available for adsorption, chelation with organic matter or solid phase formation.

Adsorption involves the formation of physical bonds; the nature of bonding in organic matter chelation is uncertain but is essentially physical or quasi-chemical (Section 3.5; Bloom, 1981) and the solid phase involves the formation of chemical bonds. Chemical bonds are far stronger than physical bonds so the solid phase is likely to be more thermodynamically stable than either the adsorbed or chelated phase. However, the kinetics of adsorption and (presumably) chelation are such that they will take place initially even though the solid phase is likely to be more thermodynamically stable.

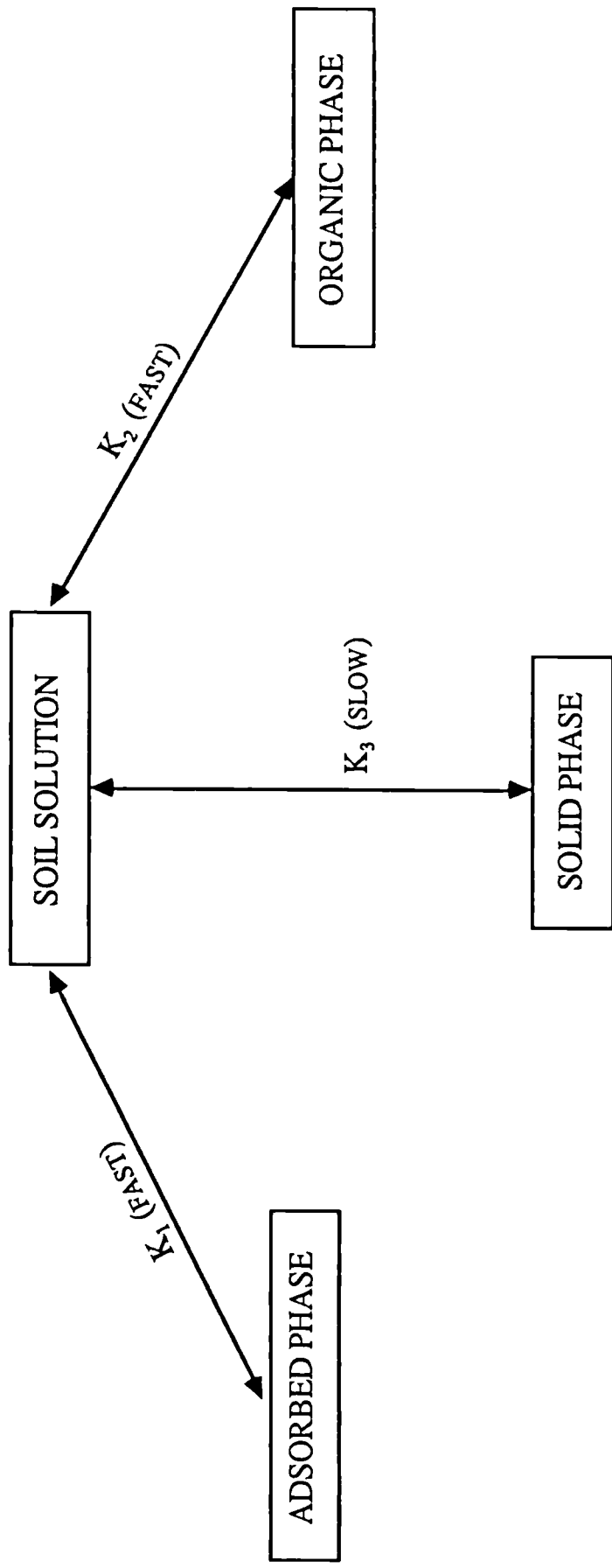


Figure 3.5 Kinetics of mineral formation in soils. K_1 , K_2 and K_3 are equilibrium constants; the relative speed with which equilibrium is attained is indicated. After Sparks (1989) and West (1981).

It is possible to imagine several processes competing for lead in the soil solution. This is shown diagrammatically in Fig. 3.5 which is essentially a simplified qualitative interpretation of the *SOILCHEM* model. Adsorption (K_1) and chelation (K_2) establish equilibria with the soil solution quickly, whereas the solid-solution (K_3) equilibrium is slow to establish. At equilibrium, all phases will be in equilibrium with the soil solution and the whole system can be said to be in equilibrium *i.e.* the solid phase will be in equilibrium with the adsorbed and chelated phases and vice versa. This equilibrium is expected to favour solid phase formation as this is the most thermodynamically stable.

However, solid phase formation will only occur if there is enough of the specified element in the soil. Else, a solid phase will not form and lead's geochemical behaviour in soil will largely be governed by adsorption, chelation and/or co-precipitation with other minerals. Mattigod *et al.* (1981) and Jones and Jarvis (1981) both state that precipitation is not important at trace levels (<1 wt.%) as adsorption/desorption reactions control the activity of trace metals in solution. Many authors (Section 3.6.5) have identified lead as a solid phase in soils and dusts where lead is present in concentrations <1 wt.% and reported that the solid, crystalline phase accounts for a very small fraction of the total lead. However, in highly contaminated soils lead is not a trace element but a major element and therefore solid phase formation could be important.

Summary

Experimental evidence suggests that an amount of lead added to a soil in either solution or unstable solid form will initially be largely taken up by adsorption or chelation. Thermodynamics predicts that if enough lead is present then, with time, most of this lead will form a stable solid phase and much less will be held in the adsorbed or chelated phases. The elemental activities required for the precipitation of lead phosphates are considered in the next section.

3.7.4 Solubility

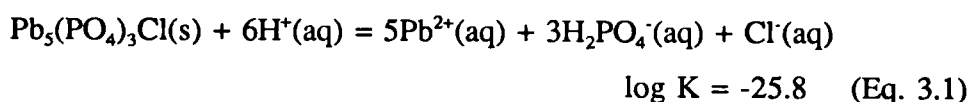
Assuming precipitation does occur, $\{\text{Pb}^{2+}\}$ will be controlled by the least soluble mineral present (Sposito (1981). Theoretical mineral-solution equilibria studies by Lindsay (1979) show that, over the pH range of most soils pyromorphite is the least soluble lead mineral; less soluble than lead oxides, sulphates and carbonates, although plumbogummite was not included in the study. (Solubilities of lead minerals are discussed in terms of the bioavailability of lead in Section 3.8.) Lindsay (1979) suggests that pyromorphite is capable of "buffering" $\{\text{Pb}^{2+}\}$, maintaining it between approximately 10^{-6} M at pH 4 and 10^{-12} M at pH 8-9.5. Solubility decreases with increasing pH and varies according to which phosphate mineral controls $\{\text{HPO}_4^{2-}\}$ or $\{\text{H}_2\text{PO}_4^-\}$.

However, it is possible that the formation of pyromorphite in soils will be limited by the availability of phosphorus or chlorine and plumbogummite by the availability of aluminium and phosphorus. It is unlikely that chloride concentrations will limit pyromorphite formation as chlorine is virtually ubiquitous in the surface environment and the stoichiometry of the pyromorphite formula requires relatively little chlorine [$\text{Pb:P:Cl} = 5:3:1$ (molar) and $\approx 29:2.5:1$ (wt.%)]. The average phosphorus content in soils is given as 650 $\mu\text{g/g}$ (Bowen, 1966) although higher values are expected in cultivated soils as phosphorus is added in the form of fertilizer. Aluminium is generally present in appreciable quantities as primary or secondary aluminosilicates, the average content being 71,000 $\mu\text{g/g}$ (Bowen, 1966). However, these elements may not be available in sufficient quantities for mineral formation and may restrict the formation of pyromorphite or plumbogummite. This aspect of lead phosphate formation is explored by considering solubility equilibria.

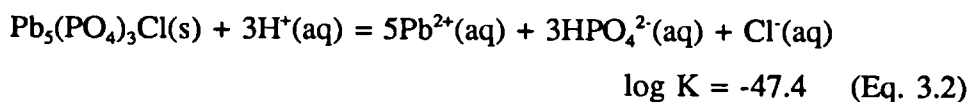
Solubility equilibria calculations

Stoichiometric equations can be written for the precipitation/dissolution of pyromorphite or plumbogummite in terms of constituent aqueous species. From equilibrium constants for these equations, the activities of the aqueous species required for mineral formation can be calculated. Rickard and Nriagu (1978) consider this aspect of Pb phosphate formation using the following chemical equilibria:

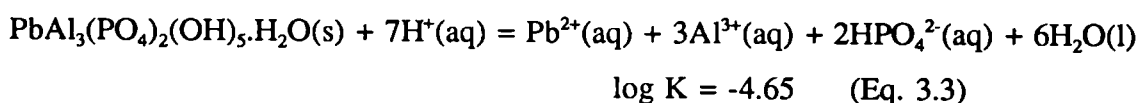
for pyromorphite at pH<7,



at pH>7,



and for plumbogummite at pH>7,



The two different pyromorphite equations are written for pH values above and below pH 7 as this corresponds to the change in the dominant aqueous phosphorus species from H_2PO_4^- to HPO_4^{2-} (Lindsay, 1979). Rickard and Nriagu (1978) only consider plumbogummite formation in an alkaline environment as this is the environment in which it is most likely to form.

Rickard and Nriagu (*op. cit.*) consider that if $\{\text{Pb}^{2+}\}=10^{-10}$ M and $\{\text{Cl}^-\}=10^{-3}$ M, then at pH 6 $\{\text{H}_2\text{PO}_4^-\}\geq 10^{-2.9}$ M for pyromorphite to form. At pH 8 $\{\text{HPO}_4^{2-}\}$ is only required to reach 10^{-7} M for pyromorphite to precipitate. It is suggested that $\{\text{HPO}_4^{2-}\}=10^{-6}$ M at this pH, indicating that pyromorphite will form in alkaline soils. For plumbogummite at pH 8, if $\{\text{HPO}_4^{2-}\}=10^{-6}$ M and $\{\text{Pb}^{2+}\}=10^{-10}$ M then $\{\text{Al}^{3+}\}$ required for plumbogummite formation is $\approx 10^{-13}$ M (Rickard and Nriagu, *op. cit.*). The authors estimate $\{\text{Al}^{3+}\}$ to be approximately 10^{-11} M at this pH making the formation of plumbogummite feasible.

As lead concentration increases, the $\{\text{HPO}_4^{2-}\}$ required decreases and pyromorphite can therefore form at lower pH values. Nriagu (1984) considers that pyromorphite is the most stable mineral in neutral to acid environments at $\{\text{HPO}_4^{2-}\}$ as low as 10^{-12} M and $\{\text{Pb}^{2+}\}=10^{-6}$ M.

This approach has serious limitations. Whilst Pb^{2+} may be the dominant species below pH 6, under alkaline conditions (Eq. 4.2 and 4.3) the aqueous speciation of Pb is expected to be dominated by PbCO_3^0 and Pb(OH)^+ (as discussed in Section 3.3.2). These lead species are not considered in the above equations and may have considerable

influence on the solubility of pyromorphite and plumbogummite. Uncertainties are also introduced by lack of knowledge of elemental activities in the soil solution as acknowledged by Rickard and Nriagu (1978).

Computational models, such as *SOILCHEM* (described in Section 3.7.3) can predict the activities of free ions more accurately by considering the interactions of a metal with many ligands, rather than simply estimating the percentage of free aqueous ions and complexes. These have a far greater potential to estimate the feasibility of mineral formation than simple approaches such as the one outlined above.

In conjunction with Professor G. Sposito (pers. comm., 1990) a simple *SOILCHEM* computation (not involving adsorption) with concentrations set at $\Sigma_{\text{diss}} \text{Pb}^{2+} = 10^{-3} \text{ M}$, $\Sigma_{\text{diss}} \text{SO}_4^{2-} = 10^{-3} \text{ M}$, $\Sigma_{\text{diss}} \text{CO}_3^{2-} = 10^{-3} \text{ M}$, $\Sigma_{\text{diss}} \text{PO}_4^{3-} = 10^{-5} \text{ M}$ and $\Sigma_{\text{diss}} \text{Cl}^- = 10^{-2} \text{ M}$ was run at pH values of 1, 7 and 11. At pH=1, $\text{PbSO}_4(\text{s})$ controlled $\{\text{Pb}^{2+}\}$. At higher pH, pyromorphite did form, but was limited by phosphorus concentration. All of the phosphorus in the system became bound with pyromorphite and then PbCO_3 precipitated. The concentration of lead used in this computation is several orders of magnitudes higher than would reasonably be expected in a soil solution so this situation may not arise in the natural environment. However, the computation does show that lead has a strong affinity to form pyromorphite with phosphorus.

Whilst both these approaches are subject to limitations, they suggest that the formation of both pyromorphite and plumbogummite is generally feasible in soils.

Summary

The solubility aspect of lead phosphate formation is inconclusive due to lack of data, which is a problem common to many solubility calculations. However, it seems likely that the elemental activities expected to be encountered in soil solutions are sufficient for the precipitation of pyromorphite and plumbogummite. It is clear that phosphorus has a strong affinity for pyromorphite but its affinity for plumbogummite is unknown. Indeed, Nriagu (1974) suggested that pyromorphite would control $\{\text{P}\}$ rather than hydroxyapatite $[(\text{Ca}_5\text{PO}_4)_3\text{OH}]$ when $\{\text{Ca}^{2+}\}/\{\text{Pb}^{2+}\} < 10^6$.

3.7.5 Discussion of Literature

Nriagu (1974; 1984) and Rickard and Nriagu (1978) discuss the formation of lead phosphates in soils from the transformation of lead-rich automobile emissions. It is assumed that as lead has such a short residence time in the atmosphere, it would be deposited in roadside soils in its primary form *i.e.* bromochlorides (Ter Haar and Bayard, 1971; Section 2.4.1(a)). These lead compounds are soluble and hence would be reactive in the soil environment. Reaction schemes are proposed for the reaction of these soluble lead compounds with phosphates in the soil to form largely insoluble lead phosphates including pyromorphite and plumbogummite.

However, the work of Olson and Skogerboe (1975), Biggins and Harrison (1980) and others (Section 3.6.5) suggests that soil PbSO_4 is formed from automotive lead. In Section 3.6.5 it was suggested that this transformation occurred in the atmosphere by reaction with SO_3 . The precipitation of PbSO_4 from atmospheric vapour containing dissolved Pb and SO_3 is a plausible reaction and Ter Haar and Bayard (1971) suggest that automotive lead compounds react rapidly with the atmosphere (Section 2.4.2(a)). Therefore, it is likely that the soluble automotive lead compounds have largely reacted to form less soluble PbSO_4 before deposition in roadside soils and are therefore not as reactive as assumed by Nriagu (*op. cit.*).

Olson and Skogerboe (1975) and Biggins and Harrison (1980) both suggest that further weathering of PbSO_4 in soils is possible and there is some tentative evidence for this in their work (Section 3.6.5). However, as indicated above, the kinetics of mineral formation are slow and it may take many years for unstable PbSO_4 to form detectable levels of stable lead phosphates. Therefore, whilst automotive lead in roadside soils may react to form lead phosphates as discussed by Nriagu (*op. cit.*), lead phosphates should be regarded as the end product of the weathering sequence which includes metastable compounds such as PbSO_4 .

A further consideration is the analytical technique employed by Olson and Skogerboe (1975), Biggins and Harrison (1980) and Mattigod *et al.* (1986). XRD was employed which only detects crystalline compounds. Olson and Skogerboe (1975) and Biggins and Harrison (1980) suggest that only 50% of the lead in the preconcentrated fraction can be accounted for by this technique. This implies that there is an important

non-crystalline solid phase component of lead. Although no suggestions of its composition are given it is possible that some of this could be an amorphous lead phosphate, not detectable by XRD.

If only small quantities of lead phosphates are expected in soils where lead has been recently added (*e.g.* automotive lead) as a result of the slow formation of lead phosphates in soils, individual grain analysis by SEM/EDX would be able to detect lead phosphates better than XRD. Grains examined by Norrish (1975) indicated the presence of lead phosphates in soils but those examined by Linton *et al.* (1980) did not.

3.7.6 Summary

There are two possible explanations for the lack of identification of lead phosphates in soils:

- (i) lead phosphates do form in soils but slowly so they are only present in small quantities and may be amorphous.
- (ii) lead phosphates do not form in soils, although thermodynamically predicted. Either elemental activities in solution are too low for the precipitation of lead phosphates, thermodynamic data is inaccurate or soil kinetics prevents their formation.

3.8 Bioavailability of Soil-Lead

"Bioavailability" is a rather ambiguous term. The bioavailability of an element can be taken to mean its availability to be taken up by plants or its availability to humans and animals via ingestion. The bioavailability of soil-lead in each case is governed by different processes. Plant and human bioavailability can be related to the geochemical behaviour of lead in soil discussed in earlier sections of this chapter; the bioavailability of soil-lead to animals however, is complex and largely influenced by bacterial digestion of soil in the

stomachs and is beyond the scope of this discussion.

Plants are thought to gain most of their nutrients from the soil solution. In a review of soil-plant relationships, West (1981) considers that the concentrations of elements ~~is~~ ^{are} buffered by cation exchange but ultimately controlled by mineral solubility. Thus, lead minerals present in the soil will influence the bioavailability of lead to plants.

In contrast to plant-available lead, the availability of ingested soil-lead to humans is determined by acid digestion in the stomach and subsequent absorption through the walls of the intestine. The acid solubility of soil-lead minerals will influence the extent to which lead is solubilised in the stomach (and hence available for subsequent adsorption in the intestine).

3.8.1 Bioavailability to Plants

There are numerous reviews of lead availability to plants *e.g.* Zimdahl and Arvik (1973); Zimdahl and Koeppe (1977); West (1981) and only a brief summary of the salient features of plant uptake of lead are given here.

Many authors have attempted to predict the uptake of lead and other elements from soil by the use of single chemical extractants *e.g.* EDTA (Davies and Roberts, 1975); 1 M NH_4COOH_3 (Maclean *et al.*, 1969). These extractants are chosen as they are thought to remove fractions which are easily solubilised *i.e.* the exchangeable fraction.

The amounts of lead in plants are generally small, of the order of a few hundredths of a $\mu\text{g/g}$ to a few $\mu\text{g/g}$ (Zimdahl and Arvik, 1973). Soil uptake has been found to be reduced by an increase in pH or the addition of phosphate or lime (Maclean *et al.*, 1969; Miller and Koeppe, 1970; Zimdahl and Foster, 1976). In a survey of urban soils and vegetables, Moir and Thornton (1990) found that <1% of vegetables contained lead in amounts exceeding the current U.K. statutory limit for saleable food (1 $\mu\text{g/g}$ fresh weight).

Many authors have concluded that there is no significant translocation of lead from roots to leaves (Zimdahl and Koeppe, 1977). Malone *et al.* (1974) found lead phosphate deposits in corn roots, preventing the translocation of lead into the aerial part of the plant. Lead associated with foliage is mostly due to residues from soil splash or aerial deposition of atmospheric lead (Zimdahl and Koeppe, 1977).

3.8.2 Bioavailability to Humans

It has been shown earlier (Section 2.3.1) that the ingestion of soil and dust is an important pathway of lead to young children. The bioavailability of ingested soil-lead to humans is therefore of considerable importance in assessing the health risks associated with this element.

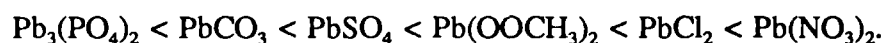
There have been several studies on the bioavailability of ingested lead which are reviewed by Chaney and Mielke (1986). These have shown that the availability of lead in ingested soil and dust will be dependent on a number of factors: particle size, nutritional factors and chemical species.

Baltrop and Meek (1979) found that absorption of lead from rat gut increased with decreasing particle size and that particle size would be an important influence on bioavailability for particles below 100 μm diameter. This is thought to relate to the amount of surface area open to acid attack in the stomach.

Heard *et al.* (1983) found lead uptake to be greatly reduced by the simultaneous ingestion of food. It was also found that the presence of calcium and phosphorus reduced lead uptake, although the combination of calcium and phosphorus had more effect on lead absorption than calcium did alone. The authors suggest that lead is co-precipitated in an insoluble form with the formation of a calcium phosphate.

Indirect work on the bioavailability of ingested dust has been conducted by Gibson and Farmer (1984). 0.007 M hydrochloric acid was used as a chemical extractant simulating stomach acidity. Data indicated that an average of 41% of ingested lead would be available for absorption.

It is argued that solubility does not equate with bioavailability (Chaney and Mielke, 1986). This is supported by the findings of Holt *et al.* (1987) who fed solution lead with several different anions to rats. Absorption was inversely correlated with the formation constant for the ion pair. Absorption increased in the order:



Nevertheless, these *in vitro* experiments indicate the amounts of acid-soluble lead that would be available for absorption.

3.8.3 Influence of Lead Minerals on the Bioavailability of Soil-Lead to Plants and Humans

In this section, the influence of lead minerals on the bioavailability of soil-lead to plants and humans is discussed. The solubility of lead minerals in water (K_{sp}) is assumed to determine the bioavailability of lead to plants, whilst the acid solubility of lead minerals (K^*) is assumed to determine bioavailability to humans. Solubilities of lead minerals thought to be important in soils (discussed in Section 3.7.4) are listed in Table 3.2. The bioavailability of lead to both soils and plants is influenced by a number of factors such as pH and the amount of lead in the exchangeable fraction (discussed in Sections 3.8.1 and 3.8.2). Only one factor is considered in isolation here and so is not a definitive guide to soil-lead bioavailability.

Table 3.2 Solubilities of lead minerals at 25°C, 1 atm ¹		
Mineral	Reaction	Equilibrium constant
Anglesite	$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$	$\log K_{sp} = -7.72^2$
Cerussite	$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-}$	$\log K_{sp} = -12.8$
	$PbCO_3 \rightleftharpoons Pb^{2+} + HCO_3^-$	$\log K^* = 4.65$
Galena	$PbS \rightleftharpoons Pb^{2+} + S^{2-}$	$\log K_{sp} = -28.1$
	$PbS + H^+ \rightleftharpoons Pb^{2+} + HS^-$	$\log K^*_{a1} = -15.1$
	$PbS + 2H^+ \rightleftharpoons Pb^{2+} + H_2S$	$\log K^*_{a2} = -8.14$
Pyromorphite	$Pb_5(PO_4)_3Cl \rightleftharpoons 5Pb^{2+} + 3PO_4^{3-} + Cl^-$	$\log K_{sp} = -84.4$
	$Pb_5(PO_4)_3Cl + 6H^+ \rightleftharpoons 5Pb^{2+} + 3H_2PO_4^- + Cl^-$	$\log K^* = -25.8$
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O \rightleftharpoons Pb^{2+} + 3Al^{3+} + 2PO_4^{3-} + 5OH^- + H_2O$	$\log K_{sp} = -99.3^3$
	$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O + 7H^+ \rightleftharpoons Pb^{2+} + 3Al^{3+} + 2HPO_4^{2-} + 6H_2O$	$\log K^* = -4.65$

¹ Data from Rickard and Nriagu (1978) unless noted.

² There is no net chemical reaction between anglesite and H^+ .

³ Nriagu (1984).

From Table 3.2 it can be seen that galena, pyromorphite and plumbogummite have low solubilities (both in water and acid) in comparison to other lead minerals. Lead chloride and bromide (emitted by vehicle exhausts, Section 2.4.1) are not included in the table as they are relatively soluble lead salts.

(a) Influence of lead sulphide (galena)

The bioavailability of mine-waste lead is based on the assumption that galena constitutes the bulk of the lead-bearing solid phase. However, it is later shown in this study (Chapters 6 and 7) that this assumption is not valid for historic mine-waste.

Bioavailability to plants

Alloway and Davies (1971b), Davies and Roberts (1975) and Davies and Ginnever (1979) have grown radishes and other vegetables in areas of mine-waste contaminated soil. EDTA extractable levels of soil-lead were generally low in the contaminated areas and a 30 fold increase in soil lead concentration gave rise to an increase of only 2.3 fold in root crops (Davies and Ginnever, 1979). However, Davies and Roberts (1978) found that ≈60% of radishes grown in Welsh soil contaminated with mine-waste exceeded the current U.K. statutory limit of lead concentration in saleable food. Similar results were reported by Alloway and Davies (1971b), also in Wales.

Whilst these studies imply that mine-waste derived lead has a low bioavailability to plants, very little work has been done on the bioavailability of soil galena to plants. In Section 3.3.1 it was concluded that lead concentrations in soil solutions were not dependent on total soil lead concentration. Therefore, whilst galena has a low solubility in water (see K_{sp} in Table 3.2) no conclusions on the influence of galena on the bioavailability of soil-lead to plants can be made.

Bioavailability to humans

A comprehensive literature review by Steele *et al.* (1990) has evaluated the impact of mine-waste derived lead in soil on human blood lead concentration (an indicator of lead exposure (see Section 2.2.2)). They conclude that the contribution to blood-lead from this source is less than that from smelter, vehicle or paint sources. The authors suggest that this may be due to mine-waste particles being of a large size and/or lead sulphide

being absorbed less than other compounds.

Chamberlain *et al.* (1978) found less percentage uptake of ^{203}Pb when in the form of PbS than PbCl_2 . Barltrop and Meek (1975) examined the absorption of different lead compounds relative to lead acetate in rats. These included PbCl_2 , PbS , $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$, PbO and Pb . Basic lead carbonate had the highest percent absorption which the authors suggest reflects the greater solubility of this compound in gastric juice. PbS absorption was significantly lower than lead acetate whilst absorption of the other compounds was similar to lead acetate.

From these studies, it appears that galena does have a reduced bioavailability to humans which reflects its low acid solubility (Table 3.2).

(b) Influence of lead phosphates (pyromorphite and plumbogummite)

Lead phosphates appear to have a considerable influence on the bioavailability of soil-lead, to both plants and man.

Bioavailability to plants

Lead uptake by plants was shown to be reduced by the addition of phosphate or lime and lead phosphate deposits in corn roots prevent the translocation of lead into aerial parts of the plant (Section 3.8.1). The low solubility of lead phosphates in natural waters (Table 3.2 and Section 3.7.4) implies that their presence would reduce the amount of lead available to buffer lead activity in the soil solution, thus contributing to a reduced bioavailability.

Bioavailability to humans

The acid solubility of pyromorphite is low (Table 3.2) markedly lower than that of other lead minerals. Plumbogummite, however, is basic in character and so acid solubility is relatively high. Hence, the presence of pyromorphite (but not plumbogummite) in soil would therefore be expected to contribute to a reduced bioavailability of soil-lead to humans.

It was shown in Section 3.8.2 that precipitation of lead with a calcium phosphate inside the body is thought to reduce lead bioavailability (Heard *et al.*, 1983) and the formation of a lead phosphate ion pair reduces intestinal absorption (Holt *et al.*, 1987).

Further implication that pyromorphite is important in controlling the bioavailability of lead to humans comes from the early work of Jowett and Price (1932) who suggested that pyromorphite may form in human blood.

It is estimated that 95% of the total body burden of lead resides in the bone (Moore, 1986) which is composed of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and has an apatite structure (Neuman and Neuman, 1953). It is interesting to note that pyromorphite has an identical apatite structure, (Palache *et al.*, 1951). This suggests that the substitution of calcium for lead in pyromorphite (Section 3.6.4(a)) is analogous to the substitution of lead for calcium in bone. The structure of plumbogummite is also hexagonal. It is not known if this is an apatite structure (Palache *et al.*, 1951) but a similar analogy could apply.

Hence, it appears that the presence of pyromorphite in soils would contribute to a reduced bioavailability of soil-lead to humans; the presence of plumbogummite, however, may increase the bioavailability of soil-lead.

3.8.4 Summary

Lead has a low availability to plants and translocation from the roots to the aerial parts of the plant is limited. Lead in soil and dust, however, is considerably more available to humans. It is suggested that urban derived lead is more bioavailable than mine-waste derived lead because of the presence of galena in mine-waste soils. However, the influence of galena on the bioavailability of soil-lead to plants is uncertain. Lead phosphates can exert a strong influence on reducing the bioavailability of lead to plants and humans, although plumbogummite would be fairly soluble in the human stomach. Furthermore, there is circumstantial evidence to show that lead phosphates or lead-calcium phosphates are important in controlling the movement of lead within both plants and the human body.

3.9 Summary and Aims of Solid Speciation Study

The geochemical behaviour of lead in soils has been described. Thermodynamic considerations have shown that lead phosphates are capable of forming in soils and could have considerable influence on the bioavailability of soil-lead to both plants and humans. No conclusive evidence of their existence has so far been reported; this may be due to slow mineral formation.

The aim of the Solid Speciation Study is to determine nature of the lead-bearing solid phase in soils from the Winsters area, Derbyshire which have been contaminated by historic mining activities (see Section 2.6.1). The solid speciation is discussed in terms of its influence on the bioavailability of lead in these soils to humans.

In addition, the solid speciation of lead in a number of other U.K. soils is determined. These spoils represent different sources of lead contamination and different lengths of time since contamination. Comparison of the solid speciation of lead in Winsters soils with these other U.K. soils allows the origin and formation of lead minerals in Winsters soils to be discussed.

CHAPTER 4: STUDY AREAS AND SAMPLING LOCATIONS

Sampling was undertaken in several parts of the U.K. but was concentrated in the main study area, the village of Winster in the Derbyshire Peak District.

Two sets of samples were collected. The first set constitutes the Winster Lead Study and consists of garden soil and housedust samples together with handwipe and blood samples from local children in Winster. These samples are analysed for total lead to evaluate the sources and pathways of lead to young children in the village. The second sample set consists of bulk soil samples. Several of these samples were collected from lead mine-waste sites in the area surrounding Winster and also from other areas in Derbyshire and various parts of the U.K. The solid speciation of lead in these samples is identified (Chapters 5 and 6) and its influence on the human bioavailability of soil-lead discussed (Chapter 7).

This chapter describes the main study area of Winster in Derbyshire, sampling methodology of the Winster Lead Study and site descriptions of bulk soil samples collected for the Solid Speciation Study. The experimental procedures followed on these samples are described in the following chapter, Chapter 5.

4.1 Derbyshire Peak District

The Derbyshire Peak District is situated in the Southern Pennines, Central England and has a temperate climate. The scenery is dominated by bleak high hills and moorland in the north (the Derbyshire Pennines) and lower rolling hills in the south (the Derbyshire Dales). Figure 4.1 shows the location of towns and sampling areas in Derbyshire.

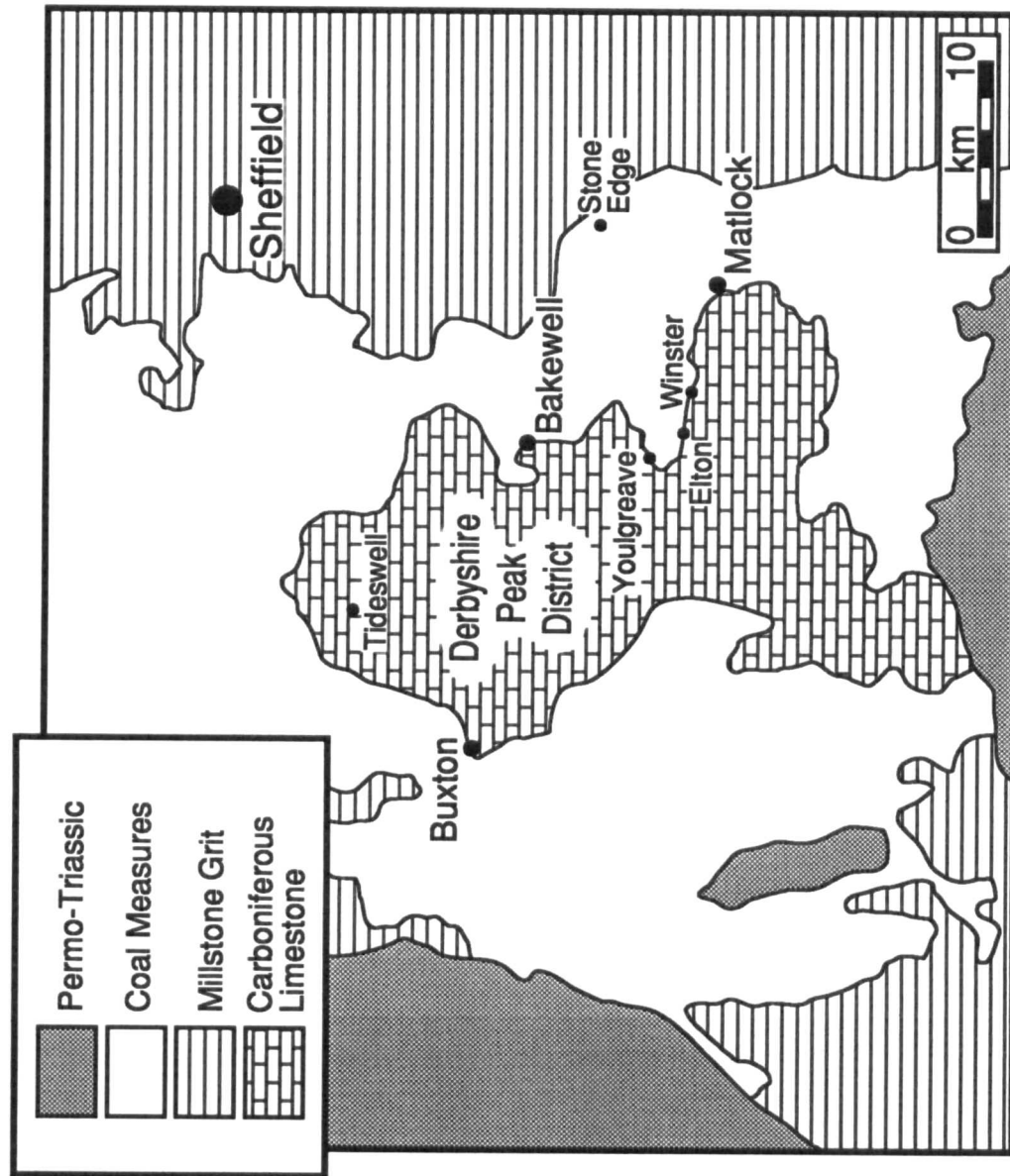


Figure 4.1 Simplified geological map of the South Pennines showing sample localities in Derbyshire

4.1.1 Geology, Mineralisation and Lead Mining History of the Peak District

The following summary of the geology and mineralisation of the Derbyshire Peak District is taken from the Geological Survey 1:50,000 map, Bakewell (Sheet SK26) and the Geological Survey memoir of this region (Edwards and Trotter, 1954); the history of lead mining in the Peak District is recapitulated from a detailed portrayal compiled by Ford and Rieuwerts (1983).

The geology of the Derbyshire Peak District is dominated by a thick sequence of Carboniferous Limestone overlain by the Millstone Grit Series. Contemporary volcanic activity has resulted in the occurrence of basaltic tuff and lava horizons throughout the limestone and to a lesser extent in the Millstone Grit. Dolerite sills later intruded these sediments in the late Carboniferous-early Permian periods. Galena, sphalerite, barite and fluorite ($\text{PbS-ZnS-BaSO}_4\text{-CaF}_2$) mineralisation took place intermittently from late Carboniferous to Jurassic periods, peaking in the Permian (Ineson and Mitchell, 1973). This mineralisation occurs mostly in the limestone but small pockets of mineralisation have been found in the Millstone Grit. Some areas of limestone have been altered to dolomite as a result of downward percolation of magnesium-rich waters during the Permian or Triassic periods. During the Cretaceous period, these sediments underwent gentle upwarping along a N-S elongated axis to form the Derbyshire Dome, resulting in the outcrop pattern shown in Figure 4.1.

Mineral veins in the limestone have been worked principally for lead ore (galena) which has been mined in Derbyshire since the Roman occupation of Britain. Traditionally, ore was transported east away from the limestone mining areas to forested hills overlying Millstone Grit where it was smelted. Here, wood could be used as fuel for fires which would be aided by hill breezes. Mining practices were generally crude and small scale until the early eighteenth century when Industrial Revolution technology was applied to the lead industry. The most intensive and productive era of lead mining followed until the industry collapsed in the latter half of the nineteenth century. A few lead mines remained open during the early part of this century until the last Derbyshire lead mine, Millclose mine in Darley Dale near Winster, closed in 1938.

Other minerals have also been mined in the Pennines. Whilst subordinate to galena, Zinc ore (sphalerite, ZnS) has been important locally. The oxidised zones of veins contain

cerussite (PbCO_3), known as "white ore"; pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$); smithsonite (ZnCO_3) and witherite (BaCO_3) which are alteration products of the original sulphides. Cerussite and smithsonite have been mined in some parts of the Peak District along with calcite, barite and witherite. A variety of fluorspar called "Blue John" has been mined as a decorative stone.

4.2 Winster Village

Winster (GR SK242605) (population ≈ 670) lies on a north facing slope at a height of 250 m a.s.l. It is situated in the southern Peak District, south of the A6 road running between Matlock and Bakewell. It is one of the three Derbyshire mining villages identified by Culbard *et al* (1988) in their U.K. heavy metal survey (see Section 2.6.1). The other two villages (Elton and Yougholgreave) are nearby (Fig. 4.1), but Winster was chosen as the main study village because of its convenient population size.

4.2.1 Geology and Mineralisation of the Winster Area

The geology and mineralisation of the Winster area is summarised in Figure 4.2. A basaltic horizon outcrops in the southernmost part of this area which lies within dolomitised Monsal Dale Limestone which underlies the southern part of the village. Bedding dips northwards at $10\text{--}20^\circ$, at a steeper angle than the topographical slope. Thus, moving northwards the geology passes through dolomitised Eyam Limestone up into the overlying Longstone Mudstone. The boundary between Eyam Limestone and Longstone Mudstone runs E-W along the Winster Main Street (Fig. 4.2). The mudstone lies to the north of this boundary and forms a valley containing a stream, being softer and less pervious than the surrounding lithologies. Kinderscout Grit (the lowest part of the Millstone Grit Series) forms the hill rising on the opposite side of the valley to Winster.

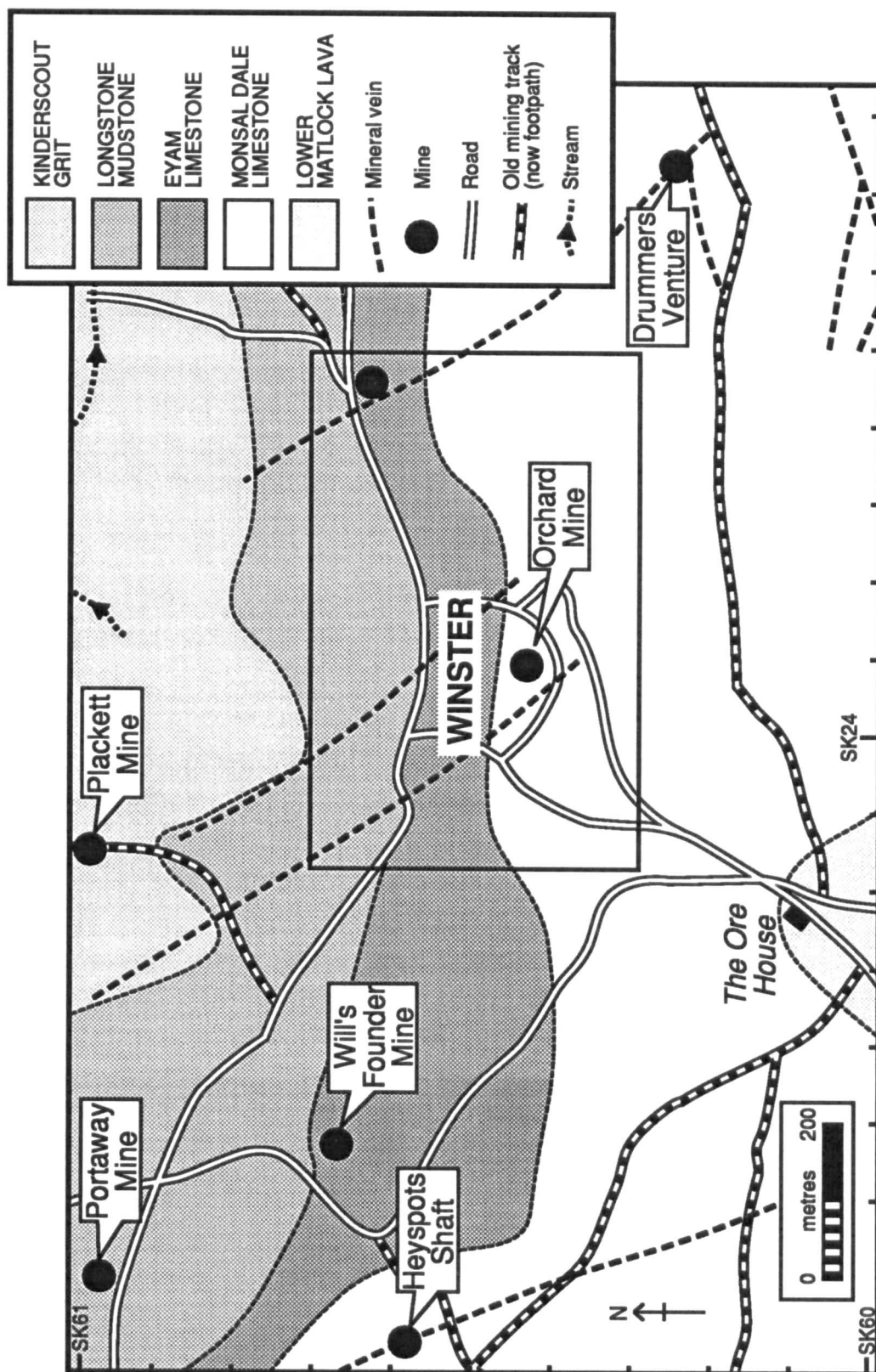


Figure 4.2 Geology and mineralisation of the Winster area
Detail of Winster village (boxed area) is shown in Figure 4.4

Three major near-surface mineral veins run through Winster village, becoming deeper northwards. The veins have been worked principally for galena with sphalerite as a by-product. Other lead ores found in this region are cerussite and pyromorphite. Cerussite has been mined in small quantities at Mosey Mere Mine (GR 60222383) to the south-west of Winster. Pyromorphite is rare but has small quantities have been found in the Winster area (Cotter-Howells and Giddens, 1990)

4.2.2 Lead Mining History of Winster

The history of lead mining of Winster is a classic example of industrial boom-and-crash. Family or small partnership working was the mode from medieval times until the eighteenth century when larger scale workings became more common. The smaller mines, however, continued to be worked and many houses had direct access to a lead mine. Portaway, Drummers Venture, Plackett Mine, Will's Founder Mine and Orchard Mine were all large mines in the Winster area (Fig. 4.2). Ore was mostly washed on site using water pumped up from the mines. It was then transported to Winster village where it was sold or stored in the Ore House (see Fig. 4.2) before transportation to the Matlock area for smelting.

Winster prospered greatly from the lead mining industry and grew into a bustling market town from a small village. Fine eighteenth century town houses dominate the centre of the village, built as the village rapidly expanded. Hamlets developed around Winster, notably a large settlement called Islington situated to the west of the village. Small settlements also developed around Plackett and Portaway Mines. In common with other mining areas, many of these houses were built on land directly surrounding the mine or mines so mining took place in close proximity to many of the houses dating from this era.

Winster was one of the first settlements to prosper from lead mining because the ore was readily accessible. The industry declined dramatically during the late eighteenth century, earlier than most other lead mining areas in the Peak District because most of the accessible ore had been worked and the expense involved in working deeper mines made them uneconomical, especially since accessible ore was still plentiful in other Peak

District areas. Many of the mines closed although a few continued to be worked. Some of the spoil heaps from these closed mines were reworked during a brief expansion of the industry in the late nineteenth century.

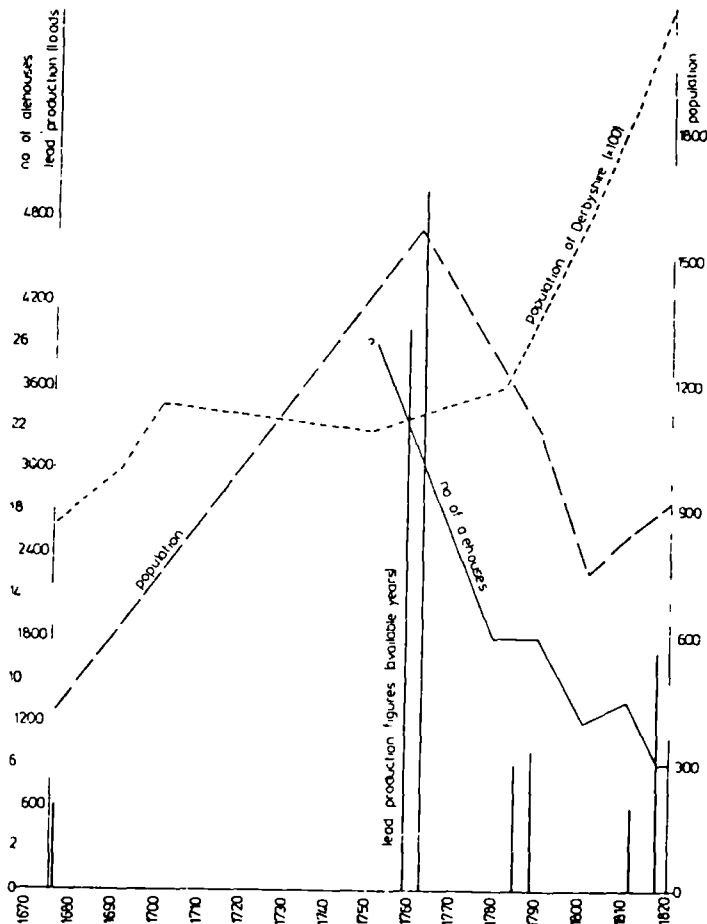


Figure 4.3 Comparison of population, lead production and public houses in Winster, 1676-1817 (Heaney, 1982)

Heaney (1982) showed a remarkable correlation between lead production population and number of ale houses in Winster (Fig. 4.3). At the peak of lead production in the 1760's there were 24 ale houses in the village. The decline of the lead mining industry lead to a sharp decrease in the population of Winster and by the end of the eighteenth century there were only 7 or 8 ale-houses (Heaney, 1982). The settlements at Portaway and Plackett Mines and the hamlet of Islington became uninhabited and only scattered ruins of these can now be seen.

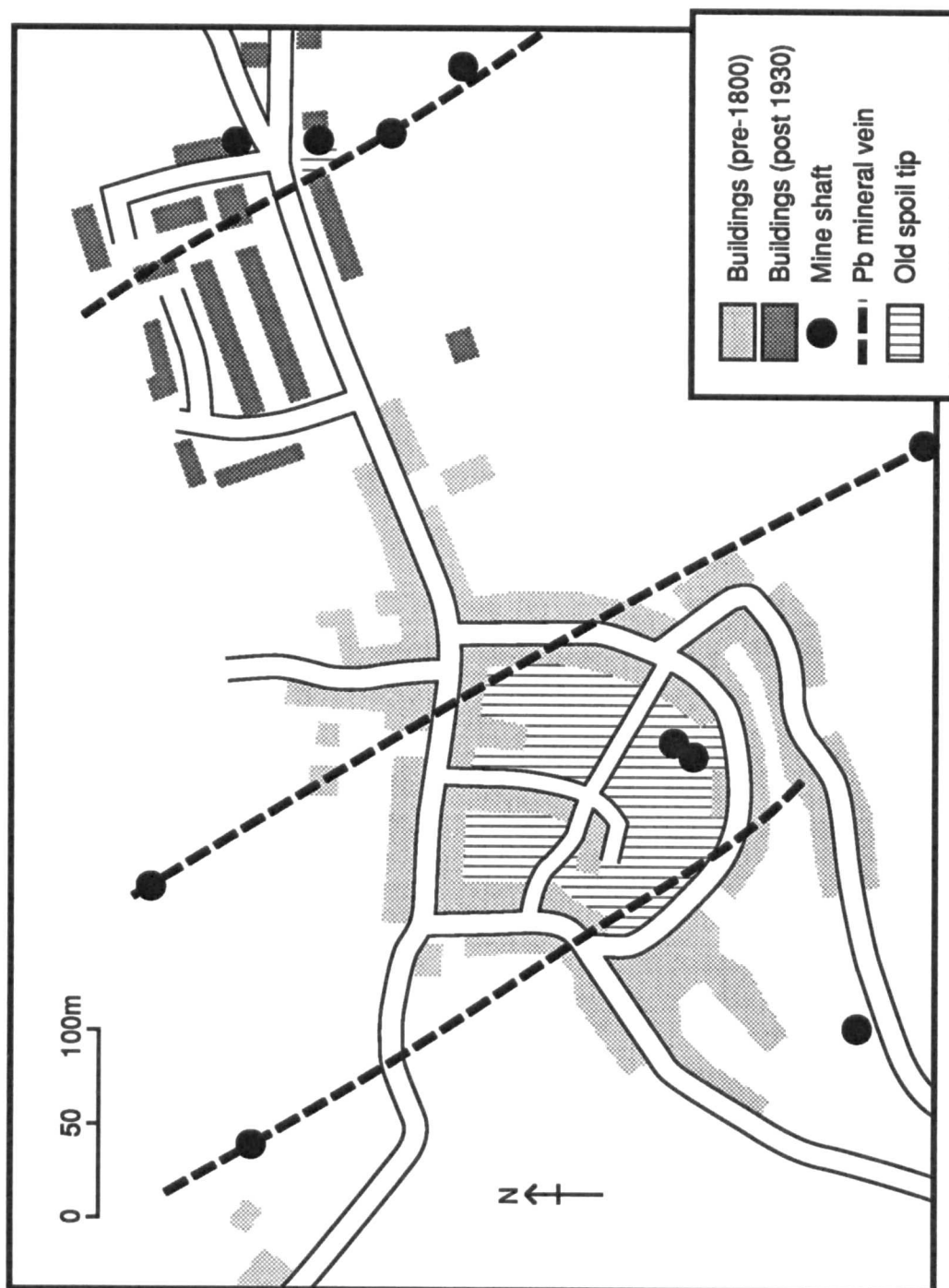


Figure 4.4 Sketch map of Winster village

Figure 4.5



Figure 4.5 Photograph of the centre of Winster village. The central grassed hillock of mine spoil from the now disused Orchard Mine is clearly shown. This hillock forms the gardens of many of the surrounding houses.

4.2.3 Present Day Winster Village

Figure 4.4 is a simplified map of Winster village showing housing and mining features. The village has an unusual form due to its rapid expansion and subsequent decline and can be divided into two parts (Fig. 4.4). The central part of the village comprises eighteenth century housing whilst newer housing has been built on the eastern periphery of the village. This newer housing is mostly post-Second World War as very little building took place between the decline of the lead mining industry and the latter half of this century. The older houses form an irregular array almost completely enclosing a central hillock of mine spoil (from Orchard Mine, see Fig. 4.5) which forms the gardens of many of the surrounding houses. Very little evidence of past mining activities is present in the orderly rows of the newer houses.

Most of the land surrounding Winster is pasture used for grazing. Old mine workings are abundant and show characteristic features. Pre-industrial workings appear as hollows in the ground, known as bell-pits. Later workings are seen as several small grassed hillocks giving the land a "hummocky" appearance. Usually, one or more of these hillocks contains a (now capped) mine shaft at the centre. Present day footpaths and bridleways in the Winster area are often old tracks which ran between the mines and the (now renovated) Ore House (Fig. 4.2).

Present day extractive industry

At present, old spoil heaps are being intermittently reworked for fluorspar at two sites near Winster. Small amounts of galena are extracted as a by-product of this operation.

In Darley Dale, approximately two miles to the north-east of Winster, there is a secondary lead smelter on the site of Millclose Mine. This smelter represents a potential point source of lead pollution in the Winster area. However, atmospheric deposition of lead is monitored closely and is reported to be negligible (DDDC, 1988).

4.2.4 Hartington - the Control Village

It was necessary to select a control village for the Winster Lead Study which represents background concentrations of lead in Derbyshire in the absence of historic lead mining activities.

The village of Hartington (GR SK128604) is situated in a valley 10 km to the west of Winster (Fig. 4.1). It is at a height of 225 m a.s.l. and has a population size similar to that of Winster. It was chosen as a control because the village lies on mineralised Monsal Dale Limestone but neither mining nor smelting have taken place in the immediate vicinity. Lead concentrations in samples from this village are compared with those in samples from Winster (Chapter 6).

4.3 Sampling - PART I: WINSTER LEAD STUDY

Soil and dust samples were collected in January 1988; handwipe samples in May 1988 and venous blood samples in September 1989. Tap water was not sampled as part of this study but Winster samples are reported to have a mean value of 5 µg/l for the year 1989/1990 (Severn Trent Water, 1991), well below the current EEC directive maximum of 50 µg/l (EEC, 1986).

4.3.1 Household Samples

41 households within Winster village were sampled at random (Fig. 4.6), together with 4 farmhouses in close proximity to the village. In addition, 5 households within the control village of Hartington were sampled. Samples of housedust and garden soil were collected from each household.

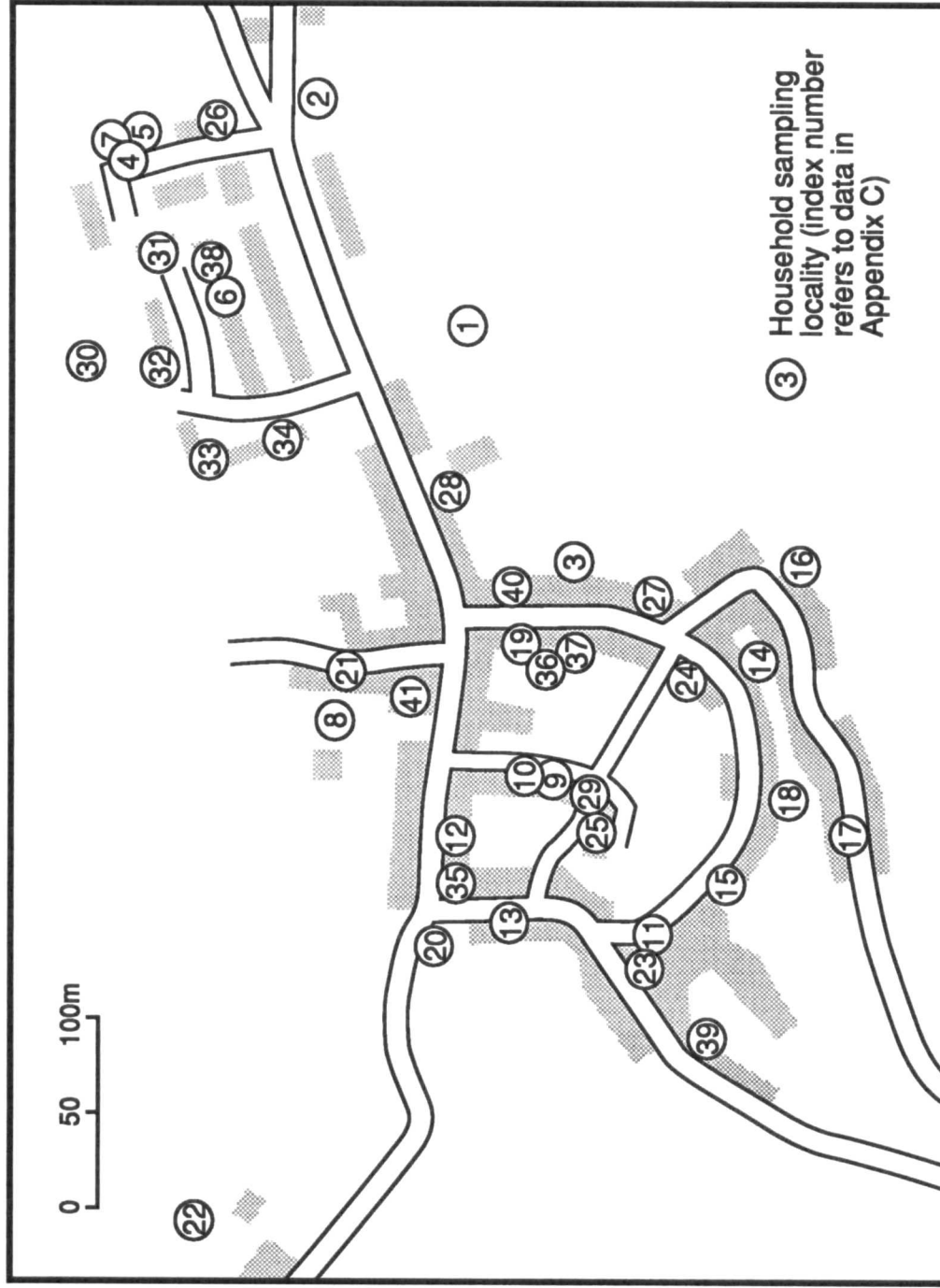


Figure 4.6 Household sampling localities in Winster village

4 m² of each householder's living room carpet was vacuumed and the dust collected in a filter thimble inserted into the vacuum nozzle (Watt *et al*, 1983). This method allowed dust loading and hence dust lead loading (the amount of lead per m²) to be calculated. Soil samples comprised 25 (0-5 cm) depth subsamples of exposed earth.

To evaluate sample variability, 4 duplicate housedust samples were taken during the same week and 4 duplicate soil samples 5 months later.

4.3.2 Handwipe Samples

The quantity of lead present on the hands of ten young (1-2½ yr. old) Winsters children attending playgroup was determined using the handwipe technique of Davies and Watt (1986). The sampler's hands were first washed and wiped, then each child's pair of hands were wiped with a total of 3 wet-wipes which were placed in a self-sealing plastic bag and retained for analysis. Repeat samples were taken from two children on different days during the same week to evaluate sample variability.

4.3.3 Blood samples

Venous blood samples were taken from ten children aged 1-8 yr. by a local practitioner and analysed at the Trace Element Unit, Southampton General Hospital.

4.4 Sampling - PART II: SOLID SPECIATION STUDY

Bulk soil sample locations from the Winster area and selected parts of the U.K. were chosen to reflect lead contamination from a variety of sources resident in the soil for differing periods of time. All soils are considered oxidising (see Fig. 3.2, Section 3.3.2(a)) as they are in contact with the atmosphere. Even the subsoil *DVS922*, which is not in contact with the atmosphere would represent a transitional rather than reducing environment if in equilibrium with ground waters (see Fig. 3.2). However, microenvironments within the soil may vary in oxidising potential. A list of samples is given in Appendix J for reference throughout the study.

For each soil sample site, a small area (30 cm x 30 cm) was deturfed if the site was grassed. Approximately 1 kg of soil was then collected from each site using a stainless steel trowel and placed in a self-sealing plastic bag for transportation back to the laboratory.

A small tufted plant producing star shaped white flowers in May/June was found growing at several of the sampling locations and was identified as *Minuartia verna*, also known as leadwort or spring sandwort. It is heavy metal tolerant, containing up to 7,740 µg/g Pb dry weight and has been found in historic lead mining areas in Derbyshire and the Mendips in Somerset, notably on disturbed ground *e.g.* spoil tips (Shimwell and Laurie, 1972).

4.4.1 Winster Samples

The following sites were chosen as they represent highly contaminated soil derived from lead mine-waste (with the exception of *WSG923* which is a stream sediment). Soils in the area are silty or silty-clay loams which have been identified as brown earths belonging to either the Lulsgate (calcareous) or Nordrach (non-calcareous) series (Curtis *et al.*, 1976)¹. Sampling locations are shown in Figure 4.7.

¹ Reference should also be made to the 1:250,000 coloured series soil map of England and Wales (1987), Midland and Western England (Sheet 3), Soil Survey and Land Research Centre, Silsoe Campus, Bedfordshire, U.K.

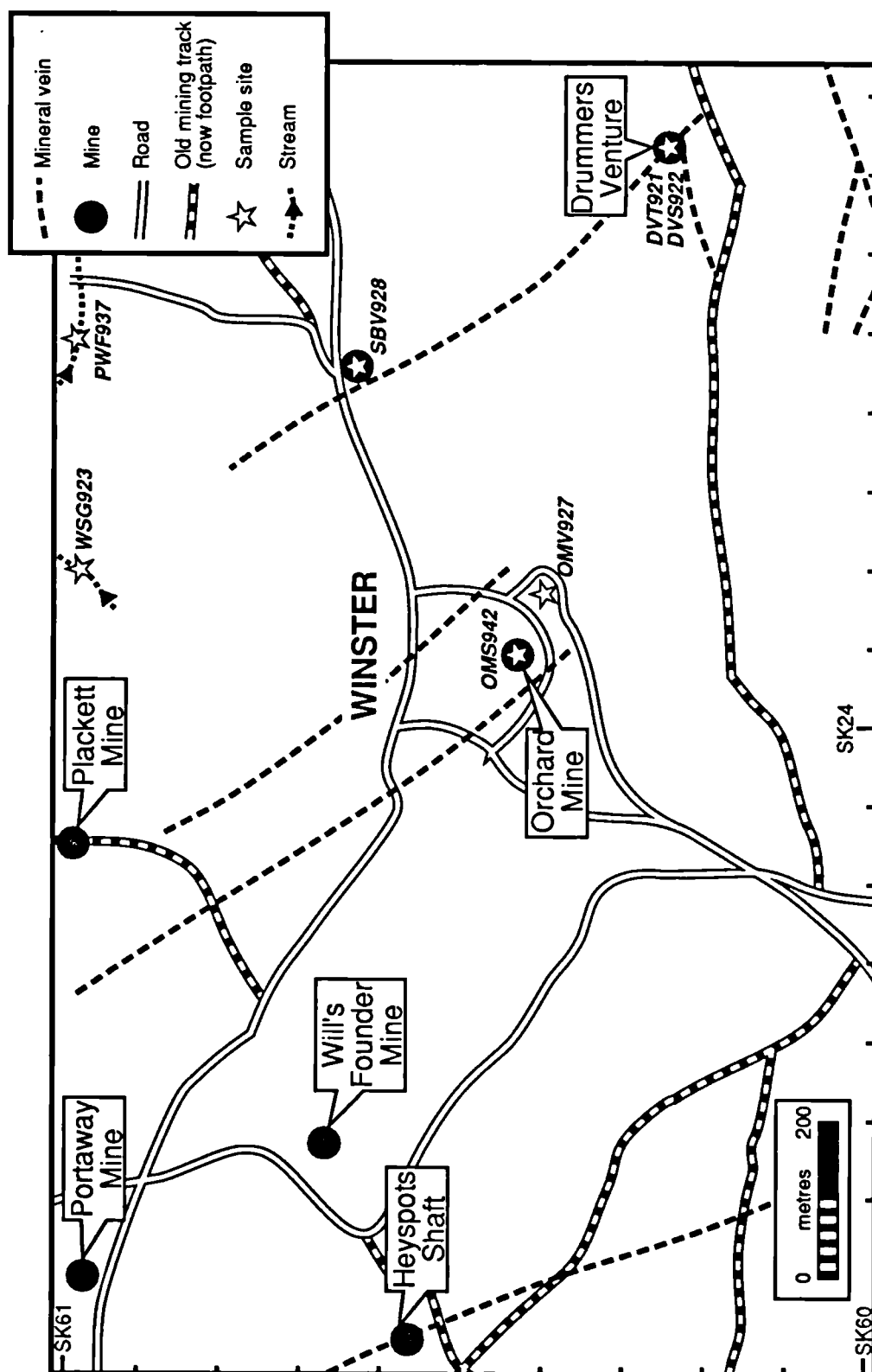


Figure 4.7 Soil sampling sites in the Winster area

- **Drummers Venture (GR SK24606035)**

Samples: DVT921 (topsoil)
DVS922 (subsoil)

This location lies on the hill to the south of Winster village. The site consists of a large number of hillocks and shafts, indicating that this area was once the scene of extensive lead mining. The ground is now entirely grassed over and used for grazing. One topsoil (0-5 cm) sample and one subsoil (10-15 cm) sample were taken from a grassed hillock near a mine adit. The soils were well drained brown silty-loam and both contained calcite. The subsoil appeared redder than the topsoil due to the lack of organic matter.

- **Painter's Way Farm (GR SK24436098)**

Sample: PWF937

This sample location is situated by Painter's Way farm near the stream running to the north of Winster area. A small hillock of grassed mine-waste is present near the stream, the surrounding land being pasture. One topsoil (0-5cm) sample was taken of the mine spoil. The soil was a brown silty-loam and contained calcite.

- **Orchard Mine-Site (GR SK24086043)**

Sample: OMS942

This site lies in the centre of Winster village and mine-spoil from this disused mine now forms a large grassed hillock (see Figure 4.5). This wasteland is used for recreational purposes by local children. One top-soil sample (0-5 cm) was taken of this mine-waste soil which was a well drained brown silty-loam containing calcite.

- **Ore Washing Site (GR SK24186097)**

Sample: WSG923

This sample location is in the stream that runs to the north of the village. Ore from the nearby mine shaft was washed at this point in the stream. *Minuartia verna* was found growing near the mine shaft. One stream sediment was taken from the fast flowing mid point of the stream using a stainless steel trowel. The sediment consisted almost entirely of gravel in which calcite was abundant.

- **Vegetable Garden Soil I (GR SK24146040)**

Sample: OMV927

This household lies in the eighteenth century part of the village. A lead vein runs very close to the house and the garden has been formed from mine-waste. One topsoil (0-5cm) sample was taken from the vegetable plot in this garden. The soil was dark brown and peaty due to the regular addition of compost. No calcite was visible.

- **Vegetable Garden Soil II (GR SK24436064)**

Sample: SBV928

This household lies in the modern part of the village. The garden consists of a grassed hillock with a vegetable plot in the centre, surrounding an old mine shaft. One topsoil (0-5cm) sample was taken from this vegetable plot. The soil was a brown silty-loam and contained calcite.

4.4.2 Derbyshire Soils

Samples were taken from areas in Derbyshire other than Winster to allow comparison of the solid speciation of lead in differing soils. Four samples were selected from different areas in the Derbyshire Peak District: one historic smelter site, one old industrial site and two lead mine-waste sites. The smelter site represents an ancient source of lead, but from smelting rather than mining. It also overlies different geology. The industrial site also represents an ancient source of lead contamination, but not directly derived from mining or smelting. The two lead mine-waste sites represent a similar source of lead to Winster but the underlying limestone is not dolomitised.

- **Tideslow Farm (GR SK15457791)**

Sample: TF943

This site was chosen because previous work by Colbourn (1976) and Elliot (1989) found high concentrations of lead (up to 50,000 µg/g) in topsoils at this location. The farm is in the north of the Derbyshire Peak District, near Tideswell (see Fig. 4.1). The area overlies undolomitised Monsal Dale Limestone. A shallow vein known as Tideslow Rake runs through the farm. This is part of a major vein in the area which has been worked periodically since the Roman occupation of Britain. Mineral statistics (Burt *et al.*, 1981) show that the vein was last worked in the latter half of the last century although this was a smaller scale operation than previous workings. The vein is at shallow depth so has been worked mostly from the surface giving rise to a long stretch of hummocky ground. *Minuartia verna* was observed growing on spoil from the rake. The mine-waste is mostly grassed over, although bare patches of gravel are present. This land is used for occasional pasture.

One topsoil sample (0-5 cm) was taken from a grassed area of this hummocky ground. The soil was a well drained brown silty-loam, similar to soils collected from the Winster area and contained calcite.

- **Hollow Farm (GR SK21786370)**

Sample: HF945

This farm lies between Winster and Youlgreave and lies on undolomitised Monsal Dale Limestone. Lead mine shafts are present at the centre of several small hillocks which are used for pasture. There is no recorded history for these particular mine workings but it is likely to be similar to that of the Winster mines. *Minuartia verna* was observed growing near the shafts.

One topsoil (0-5 cm) sample was taken from the side of one of these hillocks. The soil was similar to those collected from the Winster area *i.e.* a well drained brown silty-loam and contained calcite.

- **Stone Edge Smelter Site (GR SK33466691)**

Sample: SE952

This location lies approximately 7.5 km NNE from Matlock (see Fig. 4.1). Millstone Grit forms the underlying strata. The site is dominated by a tall, square chimney. This recently restored chimney is part of the lead smelting complex that operated on this site between *c.*1750 and *c.*1840 (Ford and Rieuwerts, 1983). The isolation of this site reflects the toxicity of the fumes given off by this process. Large heaps of slag and furnace debris once occupied the area north of the chimney. These heaps have largely been removed although remnants can still be seen and *Minuartia verna* now grows on these remnants. Taylor (1968), Merry (1988) and Elliot (1989) found high concentrations of lead (up to 30,000 µg/g) in topsoils from this vicinity. The area is now open heather moorland and not used for grazing.

One topsoil (0-5 cm) sample was taken from the remnants of a slag heap approximately 5 m north of the chimney. The soil was dark brown and peaty, contained no calcite but pieces of grey vesicular slag were seen.

- **Via Gellia Industrial Site (GR SK28435756)**

Sample: VGWH941

This site is located in a wooded valley (the Via Gellia) which runs south of Winster towards Matlock. The valley follows a basaltic horizon in the limestone and contains a sizeable stream. There are many small industrial sites along this valley, most are very old and many now disused. A large lead paint industry was based here from c.1700-c.1850 as supplies of water and lead were plentiful. As the British lead industry collapsed, many of these factories either closed or were converted for use in other industries *e.g.* cotton.

The sampling site lies on the boundary between Monsal Dale Limestone and a dolerite intrusion. It is not in the close vicinity of lead veins or old mine workings but is known to have once been associated with the lead paint industry. It is unclear, however, if the site was used for another purpose after the collapse of lead mining until its eventual closure c.1850 (Willies, pers. comm., 1989). The site comprises several derelict buildings, now mostly grassed over with tree cover. The remnants of an old wheel house can be seen, once powered by the nearby stream which overlies the impervious dolerite.

One bulk topsoil sample (0-5 cm) was taken from soil formed on the inside of a derelict building. The soil was bark brown and peaty.

4.4.3 Other U.K. Soils

Soils were collected from areas within the U.K. other than Derbyshire to represent different soil environments and different sources of lead to Winster, allowing the solid speciation of lead in soils to be discussed in a broader context. Areas in the U.K. where bulk soil samples were taken include M1 roadside, London and the Mendip Hills in Somerset.

10) Mendip Hills, Somerset.

Samples: CHBP953
CHMS960

The Mendip orefield was selected as a sample location as it has a similar geology, mineralisation and mining history to the Derbyshire Peak District. Both orefields comprise mineralised Carboniferous Limestone although the cap rock is dolomitised conglomerate in the Mendips and Millstone Grit in Derbyshire; the structure and degree of faulting also differs (Ford, 1976). Soils from the area are clay loams and have been identified as calcareous brown earths belonging to the Wrington series (Findlay, 1965; Curtis *et al.*, 1976).

Samples were collected from an extensive area of gruffy ground called Velvet Bottom, near Charterhouse. This land is the site of historic lead mining, dating back to the Roman occupation of Britain. Work was mostly carried out from the surface as veins are at shallow depth (Gough, 1967). This location overlies Black Rock Limestone and Burrington Oolite, which belong to approximately the same coral-brachiopod zone as Monsal Dale Limestone in Derbyshire, implying similar conditions and time of deposition.

The area is now mostly grassed over and conserved as a SSSI. A historical study of the Charterhouse mining district by Stanton and Clarke (1984) has revealed that areas of eighteenth century mine spoil were reworked in the mid nineteenth century. Using their guide, it was possible to sample mine-waste spoil tips from known ages. One topsoil sample (0-5 cm) was taken from a nineteenth century ore washing pond or buddling pond (CHBP953) ^{from} an eighteenth century spoil tip (CHMS960).

• M1 Roadside Soil (GR TL5113207)

Sample: MIS934

This sample site is located on the M1 motorway approximately 8km north of the M1/M25 junction, a section of the motorway bearing heavy traffic. Roadside soil at this

locality will contain lead of automotive origin that has accumulated since the opening of the M1 motorway in 1959. The underlying geology consists of Cretaceous chalk although roadside soil has probably been affected by motorway construction. The land has been left fallow and vegetation comprises long grasses.

One topsoil sample (0-5 cm) was taken from the grassed verge of the southbound carriageway. The soil was a brown clay-loam; no calcite was visible.

• London Garden Soils

<i>Samples: Hammersmith and Fulham -</i>	<i>83/072</i>
	<i>83/279</i>
	<i>83/279</i>
<i>Westminster -</i>	<i>88/015</i>
	<i>88/177</i>

Topsoils (0-5 cm) from gardens in the London Boroughs of Hammersmith and Fulham and Westminster were collected in 1982-1984 as part of a national reconnaissance survey on metals in urban dusts and soils undertaken by the Applied Geochemistry Research Group, Imperial College, London (Culbard *et al.*, 1988). Five samples from houses built between 1870-1919 with garden soil lead concentration >1,000 µg/g were recovered from storage; three are from the borough of Hammersmith and Fulham and two are from the borough of Westminster. The source of lead in these soils is not definitely known but is probably from various origins including paint, vehicle and household waste. London Clay underlies these sampling locations although these urban soils have probably been modified by the addition of compost and extraneous material such as building rubble.

4.5 Summary

Garden soil and housedust samples together with handwipe and blood samples from local Winsters children form the basis of the Winsters Study. Analysis of these samples for total lead is described in Part I of the following chapter, Chapter 5. Bulk soil samples from the vicinity of Winsters village and other areas of the U.K. form the basis of the Solid Speciation Study. The determination of the solid speciation of lead in these soils is described in Part II of Chapter 5.

CHAPTER 5: METHODOLOGY

In this chapter the experimental procedures performed on the samples described in Chapter 4 are presented in two parts. Part I corresponds to the Winster Lead Survey and Part II to the Solid Speciation Study. The results from these analyses are given in Chapter 6.

PART I - THE WINSTER LEAD STUDY

Garden soil, housedust and handwipe samples were analysed for total lead content. These samples, together with blood lead concentrations give information on the transfer of lead to young children in Winster.

5.1 Sample Preparation

5.1.1 Soil and Housedust Samples

Soil and housedust samples were dried at 60°C. Housedusts were passed through a 1 mm sieve to remove carpet fibres whilst soils were disaggregated, sieved to <2 mm and ground to a fine powder in a "Tema" mill.

Soils and housedusts were then prepared for total element analysis following the method of Thompson and Walsh (1989). 0.25 g of sample was digested in 5 ml of 4:1 concentrated nitric-perchloric acid and taken to dryness over 24 hours (1 hour at 50°C,

3 hours at 150°C, 18 hours at 180°C). On cooling, samples were leached for 1 hour at 60°C in 2 ml of 5M hydrochloric acid (HCl), mixed and made up to a final volume of 10 ml with de-ionized water (DIW). This resulted in a solution matrix of 1 M HCl which is the matrix upon which calibration for the inductively coupled plasma atomic emission spectrometer (ICPAES) is based in the Imperial College Geology Department.

5.1.2 Handwipe Samples

Handwipes were prepared for total lead analysis following the method of Davies and Watt (1986). Each set of handwipes were digested in 20 ml warm (40-60°C) concentrated nitric acid and taken to dryness once the solutions became clear by boiling at 80°C. The residues were leached in 2 ml of 5M HCl and made up to a final volume of 10 ml with DIW.

5.2 Sample Analysis and Analytical Quality Control

Determinations of total lead concentration in soil, housedust and handwipe samples were performed using instrumental analysis. Errors arise in analysis from geochemical variation between sub-samples, sample preparation procedure and instrument noise (Thompson and Howarth, 1976). The use of quality control methods to assess the exactness of ICPAES determinations has been outlined by Thompson and Walsh (1989). In this study these quality control methods are extended to other analytical techniques such as flame atomic absorption spectrophotometry (AAS) and later to the density separation procedure and classification scheme in the Solid Speciation Study (see Sections 5.4.4 and 5.5.1 (c)).

Results from quality control standards for the Winster Lead Study are presented in Section 6.1, for the household samples in Section 6.2 and for hand and blood lead in

Section 6.3.

5.2.1 Soil and Housedust Samples

Solutions from soil and housedusts were analysed in three batches using an ARL 34000 ICPAES, calibrated using blank and standard 1M HCl solutions. The instrument allows the simultaneous analysis of 25 elements in solution but only lead was of interest in this study. When solution lead concentrations were above the calibration range ($>100 \mu\text{g/ml}$), progressive dilution with 1M HCl (by a factor of 10 each time) brought lead concentration to within calibration limits.

Throughout the analysis a data quality control programme (after Thompson and Walsh, 1989) was adhered to which is routinely implemented by the Imperial College Geology Department. Each batch contained at least 10% duplicate pairs, 5% "house" soil reference materials (characterised by previous analysis) and 5% reagent blanks inserted at random positions within the batch.

5.2.2 Handwipe Samples

Lead in the 10 handwipe samples was determined in one batch by a Perkin-Elmer 5000 AAS, calibrated using blank and standard 1M HCl solutions.

An extensive quality control programme (after Davies and Watt, 1986) was implemented.

The batch contained:

- 3 reagent blanks, with no wipes
- 3 procedural blanks, each comprising 1 unused wipe
- 3 wipes spiked with known amounts of PbCl_2 solution (10, 20 and 50 μg Pb; each amount duplicated)
- 2 flasks containing only 10 μg Pb in solution.
- 2 wipes spiked with in-house dust reference material
- 1 wipe spiked with NBS Reference Material 1648-Urban Particulates.

5.2.3 Blood Samples

The concentrations of lead in blood were analysed by Dr. H.T. Delves at the Trace Element Unit, Southampton General Hospital using flame AAS as described by Delves (1970). Protocol for controlling the accuracy of blood lead analyses was similar to that described in the U.K. Blood Lead Monitoring Programme 1984-1987 (DoE, 1990).

PART II - SOLID SPECIATION STUDY

Preliminary investigation of Winster mine-waste soils by scanning electron microscopy (SEM) with X-ray spectroscopy indicated the presence of three major minerals: galena, cerussite and pyromorphite (Section 6.7.1). The aim of this study was to determine the relative proportions of these minerals in soils. A method was devised whereby lead bearing grains were separated from the soil matrix by a density separation technique and classified using SEM combined with X-ray spectroscopy. Elemental analysis of density separates by ICPAES enabled a quantitative determination of the amount of total soil-lead present as lead minerals to be made using the following equation:

$$\text{Wt.\% of total-soil lead present as pyromorphite} = \frac{\text{Wt.\% of total soil-lead held in solid phase}}{\text{Wt.\% of lead in solid phase present as pyromorphite}} \times$$

and similarly for the galena, cerussite and iron-rich classes. (Eq. 5.1)

To test if these minerals were crystalline, X-ray diffraction was employed.

The results of these analyses (Chapter 6), together with information on the basic properties of the soils allows inferences to be drawn on the formation of these minerals in soils (see Chapter 7).

5.3 Total Element Concentrations and Soil pH

5.3.1 Total Elemental Concentrations

A portion of the air dried soil (<2 mm) was ground to a fine powder and a 0.25 g aliquot digested in acid according to the method described in Section 5.1.1. The resulting solutions were analysed in one batch for total elemental concentrations by ICPAES. The calibration and quality control procedure are as described in Section 5.2.1. Lead and phosphorus were the elements of interest for these samples and their total concentrations are given in Section 6.4.1.

5.3.2 Soil pH

The pH of soils is important in this study as the thermodynamically stable solid phase of lead changes with pH (see Section 3.6.2). The pH of air dried soil (<2 mm) was measured following the method described by Avery and Bascomb (1974). 10 g of soil was mixed with 25 ml DIW and left to stand for 10 minutes. The pH of the suspension was measured using a calomel electrode previously calibrated with buffer solutions at pH 4.0, 7.0 and 9.2. 2 ml of 0.125M CaCl_2 were then added and mixed with the suspension. A further reading taken after a 10 minute standing period.

The use of CaCl_2 is thought to mask small differences in salt content without displacing a large fraction of the H^+ ions (McLean, 1982) and therefore gives a truer measurement of pH.

Soil pH values obtained from both methods are listed in Section 6.4.2.

5.4 Density Separation Procedure

Lead has a high relative atomic weight (hence the term "heavy metal"; Section 3.1) and so forms minerals which are heavier than those of most soil grains. Separations of soils in di-iodomethane (called a heavy liquid because of its high density, s.g.=3.32), have had success enriching lead-bearing grains in the high density fraction (*e.g.* Olson and Skogerboe, 1975; Biggins and Harrison, 1980; Mattigod *et al.*, 1986). However, these authors have reported extremely little of the total soil lead in the high density fraction and it is suggested that the process is inefficient (an approximation of 50% efficiency was given by Biggins and Harrison, 1980). As part of this study a density separation procedure which would maximise efficiency was devised combining methods described in the literature.

5.4.1 Introduction

The aim of the following method is to efficiently separate heavy minerals from soils. It is based on the heavy liquid separation technique developed for crushed rock by Henley (1977) but with certain adaptations for use with soil.

Henley's (1977) method involves centrifugal separation of material in a heavy liquid (di-iodomethane) yielding "floats" and "sinks". A density gradient spanning the specific gravity range of the light minerals is created by introducing a lighter, miscible fluid into the top of the heavy liquid. On centrifugation, each of these light minerals positions itself at a level corresponding to its density in the gradient and not as a discrete, compact layer entraining heavy minerals as in uniform density separations. The essential requirement of the gradient is the spreading of the light minerals, the precise profile of the gradient is not critical. (Henley, 1977)

Tests performed by Henley (1977) showed that separation efficiency was improved by repetition of the procedure. Vast improvement in efficiency was reported after three density separation stages, a fourth separation did not greatly improve efficiency. Therefore, three density separation stages are considered optimum.

5.4.2 Adaptions to Henley's (1977) Method

- Henley (1977) used N,N- dimethylformamide as a dilutant for the density gradient. However, this compound is highly toxic so chloroform was used as a substitute.
- Each sample was introduced to a solution of polyvinylpyrrolidone (PVP) in absolute ethanol before addition of the heavy liquid to prevent flocculation of soil grains. The use of PVP as a suspending agent for fine grains in a non-aqueous medium has been recommended by Francis *et al.* (1972) and successfully used by Mattigod and Ervin (1983), Essington (1984) and Mattigod *et al.* (1986).
- Ultrasound was used for 10 minute periods at several stages of the density separation procedure. This was required to encourage the separation of aggregates in which clay minerals may have adhered to lead-bearing grains, which would cause them to report to the low density fraction.
- The cumulative "sinks" from the operation were purified using a simplified density separation procedure to separate any low density grains entrained in the high density fraction.

5.4.3 Separation Method

(a) Sample preparation

Approximately 10 g of sample was hand ground using a pestle and mortar to a powder of <150 µm. This grain size was considered small enough to separate sizeable aggregates but large enough to prevent excessive adhesion of grains on the surfaces of glassware. In addition, no further grinding was necessary for any of the subsequent analyses on the density separates.

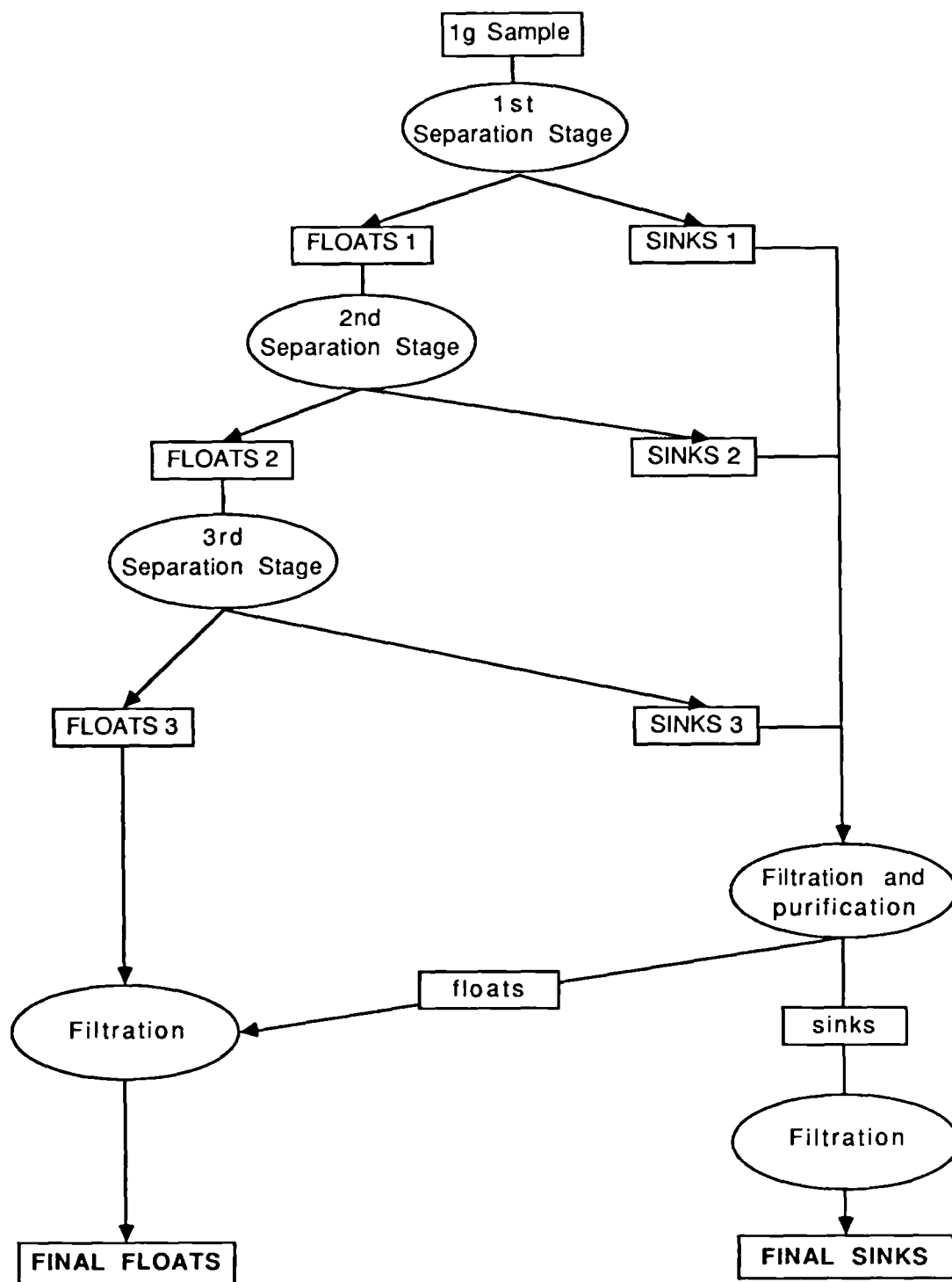


Figure 5.1 Flow chart outlining the density separation procedure.

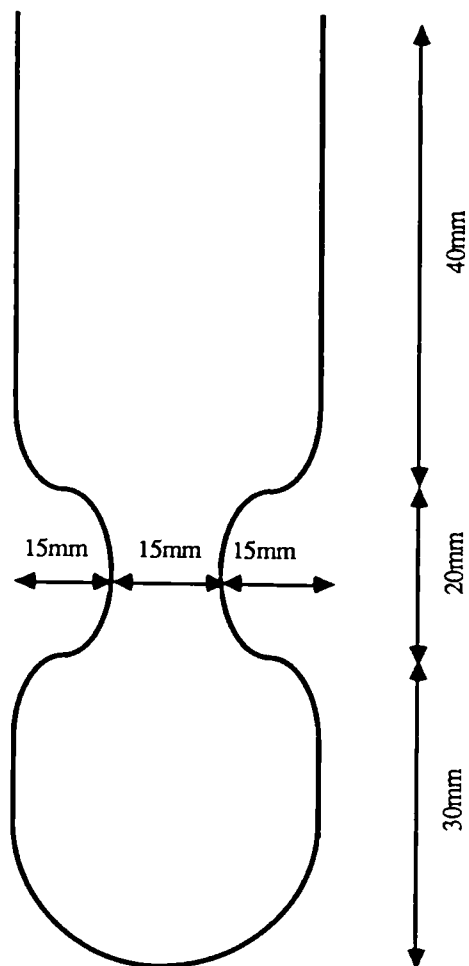


Figure 5.2 Shape and approximate dimensions of density separation tube.

(b) Procedure

A flow chart giving an outline of the method is presented in Figure 5.1. Two separations from the same soil sample were carried out simultaneously in paired separation tubes, allowing each separation to be duplicated. The following method description applies to a single separation.

A 1 g sample of soil was introduced into a necked separation tube (Fig. 5.2) via a glass weighing boat and dispersed in a solution of 20 wt.% polyvinylpyrrolidone (PVP) in absolute ethanol with the use of ultrasound. The exact concentration of PVP is not critical, only that the solution is strong enough to disperse the soil grains. Di-iodomethane was added to the tube and the mixture subjected to further ultrasound. A small amount of chloroform (≈ 2 ml) was introduced to the interface of the heavy liquid and PVP/ethanol solution. The tube was then rotated gently in the hands causing mixing of the liquids, hence creating a density gradient. The mixture was then subjected to centrifugal separation at 2,500 r.p.m. for 30 minutes which separated the soil into two density fractions, "floats" (low density) and "sinks" (high density).

A plunger was then inserted into the tube constriction (Fig. 5.3), preventing liquids and solids migrating from the top of the tube to the bottom and vice-versa. The "floats" were transferred to a fresh tube ready for the next separation stage whilst the "sinks" were collected on a filter (see below).

The density separation procedure was carried out a total of three times. The "sinks" from each density separation were collected on one filter whilst the "floats" were collected by filtration (see below) at the end of the last separation (see Fig 5.1).

The cumulative "sinks" were purified by a simplified version of the density separation procedure. They were removed from the filter, introduced into a fresh separation tube and dispersed in PVP/ethanol solution using ultrasound. Di-iodomethane was added and the mixture centrifuged as before. No chloroform was used in this purifying sequence as little material was present. The plunger was inserted into the tube and the additional "floats" added to the cumulative float residue. (see Fig. 5.1). The purified "sinks" were collected on a separate filter.

Material was removed from dried filters and carefully transferred to a preweighed polypropylene container which was subsequently reweighed to determine the mass of the two separates. These masses are reported in Section 6.5.

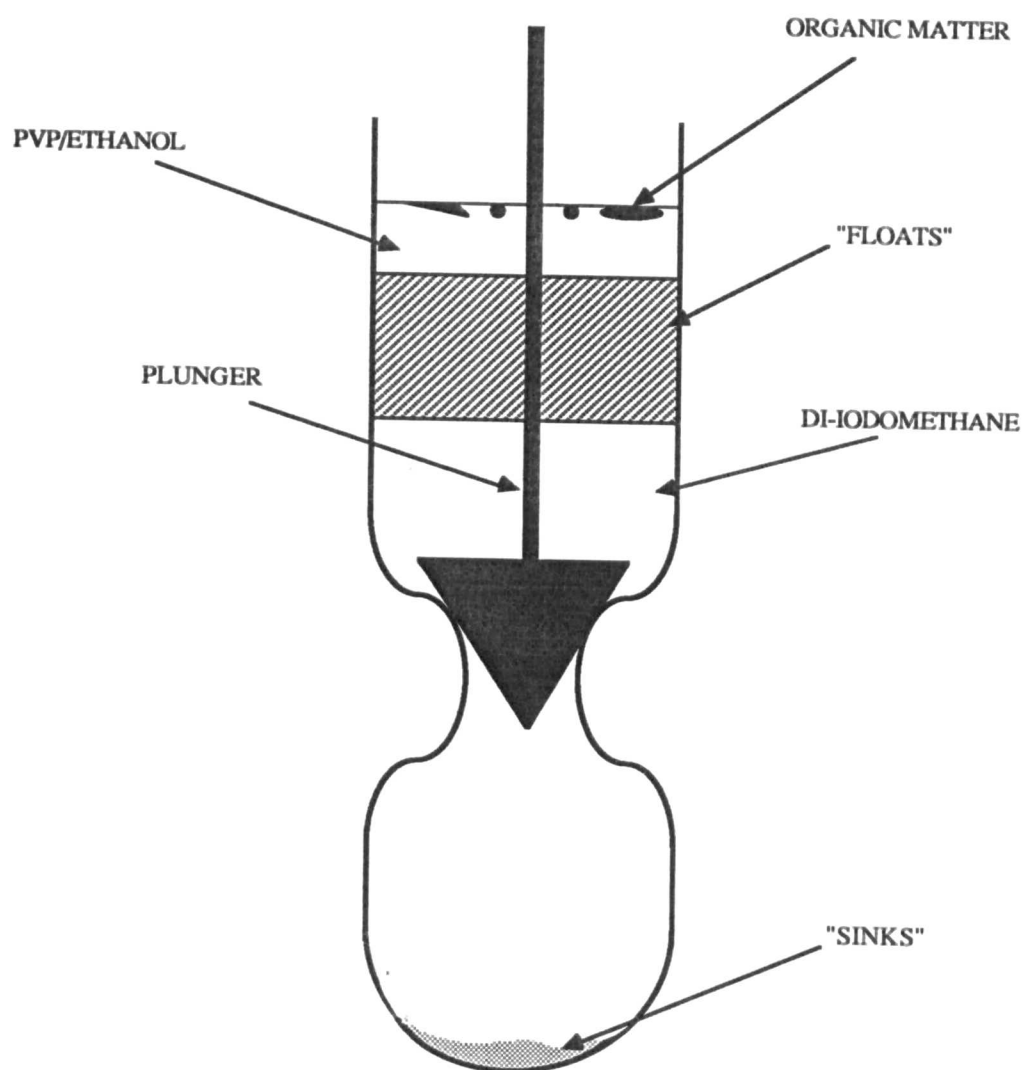


Figure 5.3 Separation of "floats" and "sinks". The plunger is inserted into the tube constriction to segregate the density fractions.

(c) Filtration

Two 3-piece glass/PTFE vacuum filtration apparatus was used, one 47 mm diameter for the high density fraction and one 90 mm diameter for the low density fraction. Whatman glass microfibre filters were found to be the most suitable although they did trap some of the very fine grains within the filter.

All residues were washed thoroughly with absolute ethanol to remove traces of the heavy liquid. Filters were pre-weighed and subsequently reweighed after the residue had been collected and transferred to polypropylene containers. This enabled the amount of material trapped (and therefore lost) in the filters to be calculated.

(d) Di-iodomethane recovery

The filtrates from the density separations containing di-iodomethane were placed in a separating funnel with large volumes of DIW. The mixture was vigorously shaken and then allowed to stand overnight. The di-iodomethane formed a lower layer which was collected.

The collected di-iodomethane was filtered and warmed gently at 40-50°C to evaporate off any remaining chloroform. Di-iodomethane is decomposed by light causing iodine to be liberated and the liquid to darken. The liquid was clarified by shaking with a little dilute potassium hydroxide solution which absorbed the released iodine (Allman and Lawrence, 1972). The di-iodomethane was run out the bottom of the funnel, its density checked with the use of density beads, and poured into a bottle ready for re-use.

5.4.4 Methodology Quality Control

Di-iodomethane is a heavy liquid commonly and successfully used for heavy mineral separation (*e.g.* Olson and Skogerboe, 1975; Essington, 1983; Mattigod and Ervin, 1984; Mattigod *et al.*, 1986). It is an polar organic liquid and is unlikely to affect the solid speciation of lead.

Insignificant quantities of lead are dissolved by the heavy liquid. Preliminary experiments indicated that lead contained in the heavy liquid was below the detection limit of flame AAS (*i.e.* <50 µg/l). Olson and Skogerboe (1975) reported that the total

amount of lead present in di-iodomethane following separation was less than 1 µg. Although slightly greater amounts of solubilised lead than that reported by Olson and Skogerboe (1979) might be expected through the use of chloroform (an efficient organic solvent) and recycling, this is unlikely to affect the separation of lead bearing grains from soil.

Blanks, standards and duplicates

To ascertain the efficiency of the method a "standard" soil (known as *DS-STD*) was made up from a soil (<2 mm) with low total lead content (52 µg/g by ICPAES analysis). Ground mineral samples of galena, cerussite and pyromorphite (the major minerals identified in mine-waste soils, see Section 6.7.1) were added to this soil (10 wt.% each). This standard soil was saturated with water, stirred and left to soak for 24 hours to allow the minerals to assimilate with the soil. It was then air-dried and ground to <150 µm. Total lead and phosphorus concentrations were determined by ICPAES using the method described in Sections 5.1.2. and 5.2.1.

The density separation was performed twice on *DS-STD* and twice on a soil uncontaminated by lead (known as *BLK*), although this blank soil proved to have a relatively high lead content of 424 µg/g (by ICPAES analysis). In addition, one sample (*OMS942*) was separated twice, the duplicate separation known as *OMS942D*.

5.5 Analysis of Density Separates

Because two separations of the same sample were carried out simultaneously, the density separation procedure resulted in two "sinks" (S1 and S2) and two "floats" (F1 and F2) for each sample. This meant that there was enough material for several different analyses to be performed on the heavy fraction. This was especially important in the case of the London soils as extremely little material was present in the high density fraction (see 6.5.2; Appendix E).

For each sample, half of S2 (or all if required) was used to make sections for SEM analysis. The remaining half of S2 and half of S1 (or simply S1 if inadequate amounts of material were available) were analysed together with F1 and F2 for total lead and phosphorus concentrations. For selected samples, the remaining half of S1 was analysed by X-ray diffraction (XRD).

5.5.1 Elemental Concentration

Elemental concentrations of lead and phosphorus were determined in both density fractions by ICPAES following the acid digestion procedure given in 5.1.1. Analysis was performed in two batches; quality control procedure and calibration were as described in Section 5.2.1. F1 and F2 from each sample together with S1 and (if possible S2) were analysed for lead and phosphorus concentrations. These concentrations are reported in Section 6.6.

5.5.2 Scanning Electron Microscopy with X-Ray Microscopy

Sample grains from the heavy density separate were sprinkled on a glass slide, polished and coated with a thin layer of carbon in preparation for SEM analysis. This gave a cross-section through the sink material suitable for quantitative analysis when viewed under the scanning electron microscope (SEM). A JEOL 733 Superprobe interfaced with a Link Analytical AN10000 Analyser was used for all SEM analysis.

Introduction

The principle of scanning electron microscopy coupled with X-ray dispersive spectroscopy (also called electron microprobe analysis) for the analysis of materials has been fully discussed in several texts (*e.g.* Reed, 1971). Essentially, electron bombardment is used to generate X-rays and secondary electrons within the sample; electrons are also deflected (back-scattered) by the sample. Images of the sample can be generated from both types of resultant electrons. Secondary electrons are used to create an image of the

sample surface at high magnification whilst back-scattered electrons give an image whose brightness is roughly proportional to the mean atomic number of the sample.

From the wavelength and intensity of the lines in the X-ray spectrum, elements with atomic number > 11 present can be identified and their concentration calculated (usually with the aid of computer software). Energy dispersive X-ray spectroscopy (EDX) can analyse the spectrum simultaneously whilst wavelength dispersive X-ray spectrometry (WDX) selects one wavelength at a time.

(a) Quantitative Analysis

Lead-bearing grains were located using SEM back-scattered electron imaging. Lead-bearing grains gave the brightest images among the grains present and so were easily detected.

Grains were analysed by EDX at 15 kV employing a counting time of 100 seconds; machine calibration was performed with a cobalt standard. Analysis of galena was possible by EDX as the quantitative programme, *ZAF-4/FLS* (Link Analytical, 1983) is able to distinguish between the Pb-M α^1 and S-K α^1 lines which have very close energies and cannot be differentiated by visual inspection of the spectrum. The EDX "windows" in in following sections (Sections 5.5.2(b) and (c)) were set by visual inspection of the spectrum so alternative methods of X-ray detection (such as WDX used in Section 5.5.2(b)) or correction factors (such as those in Section 5.5.2(c)) were necessary in galena analysis other than by *ZAF4/FLS* because of the overlap between the sulphur and lead lines.

The analysis of cerussite proved problematic as X-ray spectroscopy cannot analyse for light elements such as carbon or oxygen; this is later discussed along with the results of this analysis in Section 6.7.1.

(b) Image analysis

Two mixed phase grains were subjected to X-ray mapping which indicates the relative abundance of elements but is not quantitative. In this technique, X-rays are collected at each pixel (a point on the screen) as the electron beam scans across a field of view. These X-rays were detected by EDX with the exception of galena (PbS) where WDX was used (see Section 5.5.2(a) above). In EDX analysis, the X-rays were counted

through a predefined set of regions ("windows") of the spectrum, known as a window file. Each window was 9 channels wide (20 eV per channel) and was positioned at the centre of an expected element peak. With WDX no such window file was necessary as WDX is monochromatic. The result of X-ray mapping is a set of maps of a field of view, one for each element (or window), showing the relative number of X-ray counts from each pixel point. X-ray maps are presented in Figure 6.4, Section 6.7.2.

(c) Classification of lead-bearing Grains

The aim of the following method was to determine the proportion of different lead-bearing grains in the high density soil fraction.

Introduction

The use of an automated image analysis program, *DIGISCAN/FDC* (Link Analytical, 1984) linked to the SEM together with particle characterisation software, *MIDAS* (Link Analytical, 1990) has been developed at Environmental Geochemistry Research, Imperial College to classify urban lead-bearing grains. Comprehensive reviews of this technique have been given by Watt and Johnson (1987) and Watt (1990).

Method

The method can be split into two parts: (i) the collection of X-rays from lead-bearing grains (*DIGISCAN/FDC*) and (ii) correction of X-rays and classification of grains (*MIDAS*).

(i) *DIGISCAN/FDC* searches for lead-bearing grains using the principle of back-scattered electron signal strength described in Section 5.5.1(a). Visual examination of a digitised image of a field of view containing lead-bearing grains allowed a threshold signal strength to be selected such that the computer analysed only those pixels which pertain to lead-bearing grains (see Fig. 5.4). A grid of points (spanning all or half of the material on the slide) was generated to control automated analysis. All automated runs used identical operating conditions (given in Appendix A) to ensure comparability. Optimum magnification was variable, between 100x and 200x but is taken into account by the *DIGISCAN/FDC* program.

Figure 5.4

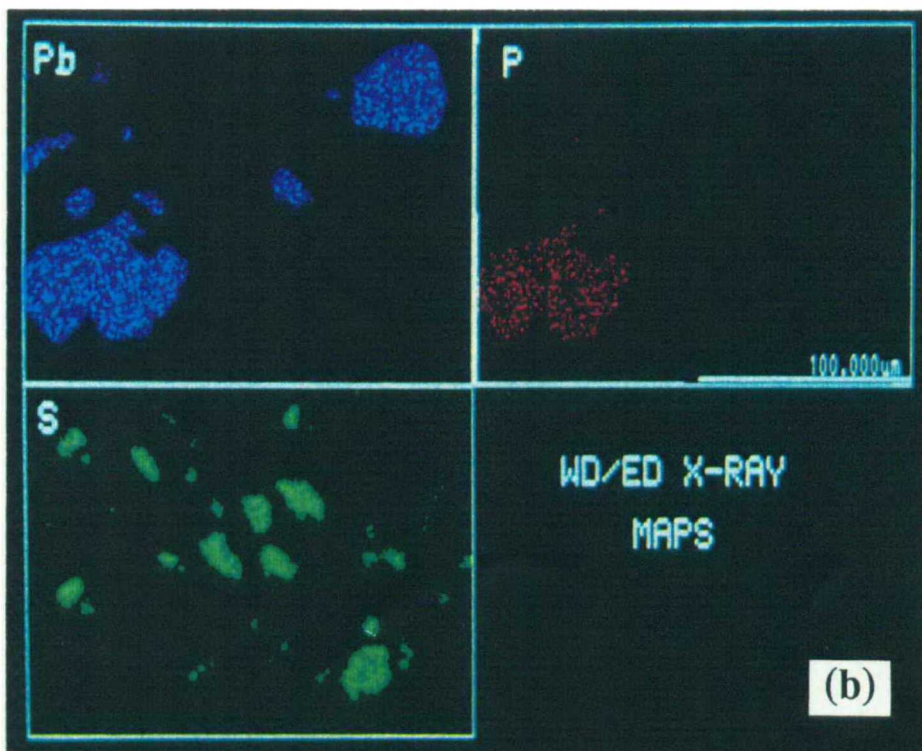
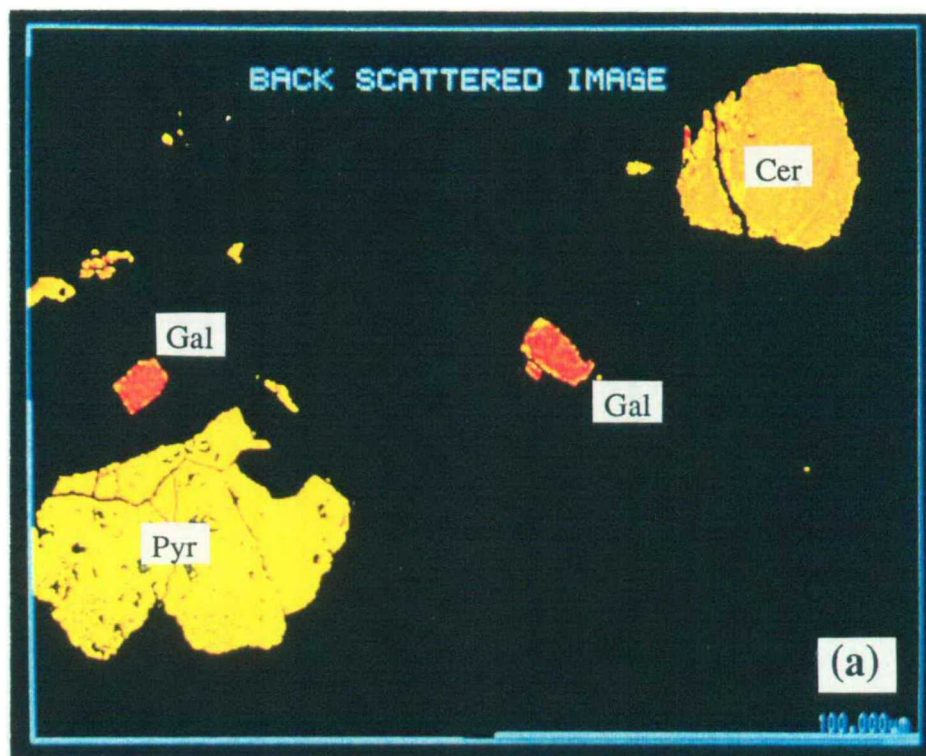
Figure 5.4: Use of SEM image analysis to set the threshold back scattered electron signal for automated analysis.

The following photographs are of one field of view in the high density fraction of a Winster mine-waste sample (*DVS922*).

Opposite Plate

(a) Back scattered electron image shows the presence of lead-bearing grains. Gal=galena, Pyr=pyromorphite, Cer=cerussite.

(b) X-ray maps (see Section 5.5.1(a)) show the association of lead and sulphur in galena grains; lead and phosphorus in pyromorphite and the absence of any elemental association in cerussite. Other sulphur bearing grains are mostly barite (BaSO_4).



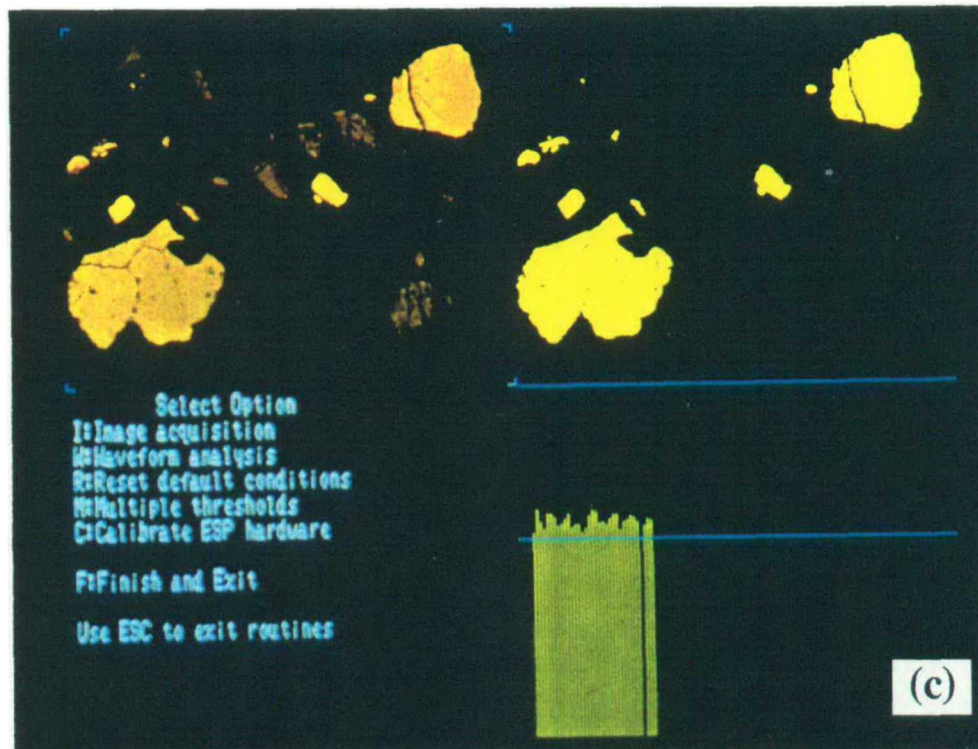


Figure 5.4(c) The threshold level of the back scattered electron image is set using the Link Analyser. The digitised image (top left) shows the presence of non lead-bearing grains but the threshold image (top right) shows only lead-bearing grains. Waveform analysis of the back scattered electron signal (bottom right) assists setting of the threshold level (indicated by horizontal lines).

For each grid point the computer scanned across the field of view noting the location of each pixel above the threshold level. All touching pixels in a feature were summed to give a two dimensional area. The beam was then driven back to each feature in turn for the collection of X-rays. A summary form of the resulting X-rays was stored as number of counts in windows corresponding to a predefined window file (as described in Section 5.5.1(b)). The *DIGISCAN/FDC* window file (listed in Appendix A) comprised 19 windows: 15 element windows and 4 background windows. Background windows were equally spaced throughout the spectrum but were defined in areas away from characteristic X-ray peaks for the analysed elements.

(ii) The raw X-ray data was then transferred into *MIDAS* where background and peak overlap corrections were made. All elements were corrected for background X-ray counts (using the method described by Watt (1990) but the only significant overlap which required correcting was between lead and sulphur. These corrections were performed using a *MIDAS* window file, essentially a computational matrix which is presented in Appendix A.

A classification scheme was developed from analysis of crushed mineral samples of galena, cerussite and pyromorphite for use with *MIDAS*. This scheme is given in Appendix A and originally involved only three elements: lead, sulphur and phosphorus. The inclusion of a large number of elements in the *DIGISCAN/FDC* and *MIDAS* window files allowed the elemental composition of grains to be examined. This resulted in a new class being developed, an iron-rich class which was important in the analysis of London soils (see Section 6.7.3).

Using this classification scheme, lead-bearing grains from the dense fraction of soils were classified as galena, pyromorphite, cerussite, iron-rich or unclassified. Together with area information for each grain, this allowed the relative proportions of these classes to be expressed as a percentage of the total area of lead-bearing grains.

Limitations of the Method

Any automated method is subject to weaknesses. Whilst this method does have important limitations, it is a powerful tool for the classification of grains. The major limitations are:

- Quantitative analysis of grains is not possible by this method as only summary information is stored in the X-ray windows.
- Aggregates of grains or grains containing more than one lead phase generally fall into the unclassified class. Some of these aggregates proved interesting and were further examined by X-ray mapping (see Section 5.1.1(a)).
- Only a very simple classification scheme is used here (Appendix A) which can lead to errors. Potential errors are of considerable importance in the galena and cerussite classes.

The galena class represents lead associated with sulphur. Anglesite (PbSO_4) and leadhillite ($\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$) are both sulphur-bearing lead minerals that have been identified in soils (Section 3.6.5) which would also classify as galena.

For a grain to fall into the cerussite class it is required to contain lead but little or no sulphur, phosphorus or iron (carbon and oxygen cannot be analysed by this method). Thus, hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and oxides/hydroxides of lead would also fall into this class. Furthermore, a lead-bearing grain associated with any other element apart from sulphur or phosphorus (*e.g.* a leaded paint grain associated with titanium) would also classify as cerussite.

Similarly, the pyromorphite class is defined as lead associated with phosphorus which encompasses both pyromorphite and plumbogummite, the two lead phosphates predicted to be thermodynamically stable in soils (Section 3.6.3; Nriagu, 1974, 1984).

These errors are not important for Winster mine-waste soils and the pyromorphite class in all samples, where grains were identified using quantitative analysis and/or X-ray diffraction. However, in non mine-waste soils the cerussite and galena classes may not accurately describe the contents of so-classified grains. The

limitations of the classes are further discussed with the results of the classification scheme in Section 6.7.3.

Quality Control

A classification standard (*SEM-STD*) was formulated with 40 wt.% silica sand and 20 wt.% each of mineral samples of galena, cerussite and pyromorphite. This was analysed in duplicate. The classification of grains in this standard ^{was} ~~were~~ used to define the precision of the scheme.

In addition, 6 samples were analysed in duplicate to evaluate the accuracy of the method. Standards from the density separation (*DS-STD*) (see Section 5.4.3) were also run but there was not enough material in the blank soils (*BLK*) to analyse by this method. The "floats" from three soils with large quantities of lead reporting into the light density fraction: *PWF937 F1*, *OMS942 F1* and *88/015 F1* were also analysed by this method.

5.5.3 X-Ray Diffraction

Selected samples were analysed by X-ray powder diffraction (XRD) techniques. Many standard analytical text books describe the principles of XRD (*e.g.* Lindholm, 1987) but essentially a material is identified on the basis of the reflectance (or diffraction) angle of incident X-rays on lattice planes within the substance. The major limitation of XRD technique is that only crystalline ^{material} can be analysed and amorphous substances cannot be readily detected by this method.

Analyses were performed using a Philips AP1700 automated powder diffractometer with variable geometry divergence slits over a 2Θ range between 5 and 80° , using Cu-K α radiation at 40 kV and 50 mA.

There was not enough material available to allow XRD analysis of London soils but random orientation powder samples made from the heavy mineral fraction (S1) of the following samples were analysed: *DVT921*, *DVS922*, *WSG923*, *OMV927*, *SBV928*, *PWA937*, *OMS942*, *SE952*. A crushed sample of mineral pyromorphite from the study by Cotter-Howells and Giddens (1990) was also analysed. The results of XRD analysis are presented in Section 6.9.

5.6 Summary

Household lead concentrations and the amount of lead on the hands of young Winsters children have been determined using the analytical techniques described above. The results of these determinations, together with blood lead concentrations in Winsters children are presented in Chapter 6 under the heading, Part I - Winsters Lead Study.

Lead-bearing grains in soils have been preconcentrated using a density separation technique. The high density fraction of each soil was subjected to elemental analysis for lead and phosphorus and SEM analysis, where lead-bearing grains were identified and classified. Selected samples were subjected to analysis by XRD technique. Results obtained using these techniques are present in Chapter 6 under the heading, Part II - Solid Speciation Study.

CHAPTER 6: RESULTS

In this chapter the results from analyses described in Chapter 5 are presented; the Winstar Lead Study in Part I and the Solid Speciation study in Part II. These results are discussed in the following chapter, Chapter 7.

PART I - THE WINSTER LEAD STUDY

Here the determinations of lead in household samples and on the hands of young children (as described in Sections 5.1 and 5.2) are presented together with the blood lead concentrations in Winstar children. These results are introduced via assessment of analytical error from the quality control programme described in Section 5.2.

6.1 Analytical Quality Control

Summaries of the analyses of blanks, reference materials and duplicate samples used in the estimation of analytical error of lead determinations in household samples and handwipe samples are given in Appendix B. Thompson and Howarth (1976) and Thompson and Walsh (1989) suggest that where the number of duplicates is less than 50, a plot of duplicate determinations on specially designed quality control charts should be constructed. This allows a pictorial comparison of analytical precision with the expected limits of $\pm 10\%$. However, in this study a numerical estimation of error was required so

mean percentage differences are given.

6.1.1 Analysis of Soils and Housedusts

The quality control data given in Appendix B1 indicate an accuracy (bias) at low lead concentrations ($\approx 15 \mu\text{g/g}$) of +14.6% and at high lead concentrations ($\approx 500 \mu\text{g/g}$) of -4.7%. Both of the reference materials contained lead in amounts considerably less than sample values but this is not thought to introduce any further error as accuracy generally increases towards higher concentrations (Thompson and Walsh, 1989). Precision (reproducibility) is estimated at $\pm 3.2\%$ from analysis of duplicate samples (Appendix B2).

6.1.2 Analysis of Handwipes

The quality control data for handwipes is given in Appendices B3 and B4. Visual inspection of the percentage differences from accepted values (Appendix B4) for analyses of standards suggests that sample values are underestimated as most of these biases are negative although no clear reason for this is apparent. Therefore, accuracy is estimated at -10.9% and precision of $\pm 6.7\%$.

6.1.3 Blood Analysis

Quality assurance reported in the U.K. Blood Monitoring Programme (DoE, 1990) gives a range of analytical bias from $-0.17 \mu\text{g/dl}$ to $+0.14 \mu\text{g/dl}$. Re-analysis of samples gave excellent reproducibility with 95% of differences between $\pm 2.5 \mu\text{g/dl}$ (DoE, 1990). Blood analyses in this study are expected to have similar accuracy and precision as samples were analysed in the same laboratory and a similar quality control programme implemented (see Section 5.2.3).

6.2 Household Lead Levels in Winster and Hartington

A summary of household lead levels in Winster and Hartington (the control village) is presented in Table 6.1 together with data from two previous studies on the Derbyshire mining villages comprising Winster and two similar nearby villages (Elton and Youlgreave; Section 4.2). Geometric means are reported as the data shows a positively skewed distribution. Individual household lead levels are given in Appendix C1.

Table 6.1 Household lead levels in Derbyshire				
	WINSTER	HARTINGTON	DERBYSHIRE MINING VILLAGES	
	Present Study		Barltrop <i>et al.</i> (1975)	Culbard <i>et al.</i> (1988)
<i>Garden Soil</i> (µg/g)				
n	42	5	41	89
G.M.	7,140	631	4,880	5,610
Range	2,370-23,800	197-1660	1,050-28,000	1,180-22,100
<i>Housedust</i> (µg/g)				
n	45	5	41	100
G.M.	1,560	302	1,800	1,870
Range	462-6,240	143-587	420-25,000	606-7,020
<i>Lead Loading</i> ¹ (µg/m)				
n	44	5	--	--
G.M.	275	78.7	--	--
Range	14.2-3,560	25.8-170	--	--

¹ Lead loading (µg/m²) = housedust lead concentration (µg/g) x dust loading (g/m²)

Replicate samples (see Section 4.3.1) indicate a sample variability maximum of 62% for housedust lead concentration, 93% for lead loading (Appendix C2) and 35% for garden soil lead concentration (Appendix C3). These figures are similar to those reported by Laxen *et al.* (1987(b)): +/- 65% for housedust and +/- 81% for lead loading which indicate considerable temporal and spatial variation in household dust lead concentration and lead loading. Soil variability is thought to be a product of the sampling strategy (*i.e.* would be less if more subsamples had been taken) coupled with heterogeneity associated with extremely high lead levels. Mean household lead levels found in Winster are in broad agreement with those from the two previous studies on the Derbyshire mining villages (Table 6.1; Barltrop *et al.*, 1975; Culbard *et al.*, 1988).

Mean garden soil and housedust lead concentrations in Hartington are significantly less than that in Winster at the 99% level (Student's t-test). Lead loading in Hartington is also significantly less than that in Winster at the 95% level (Student's t-test).

For all households in Winster and Hartington, lead concentrations in garden soils are greater than that of the corresponding housedusts (see Appendix C). This effect was enhanced in Winster where mean garden soil lead concentration is 4½ times greater than that of housedust (see Table 6.1). All garden soils in Winster exceeded 2,000 µg/g Pb and 50% of housedusts contained more than 1,000 µg/g Pb with 33% of housedusts exceeding 2,000 µg/g Pb. The four farmhouses (house nos. 42-45 in Appendix C) show similar lead values to households within the village and are not significantly different at the 5% level (Student's t-test). Other work (Cotter-Howells and Thornton, 1991) has shown that lead concentrations in vegetable plot soil are similar to those in garden soils.

Figures 6.1(a) and (b) show the spatial distribution of household lead concentrations in Winster village. Houses in the centre of the village, which are all pre 1800, generally contain greater quantities of lead in both housedust and garden soil than the newer houses to the east of the village centre. This is clearly shown in Table 6.2 where the geometric mean of lead concentrations in older households is double that of newer households. The spatial distribution of lead within Winster village is further discussed in Section 7.1.1.

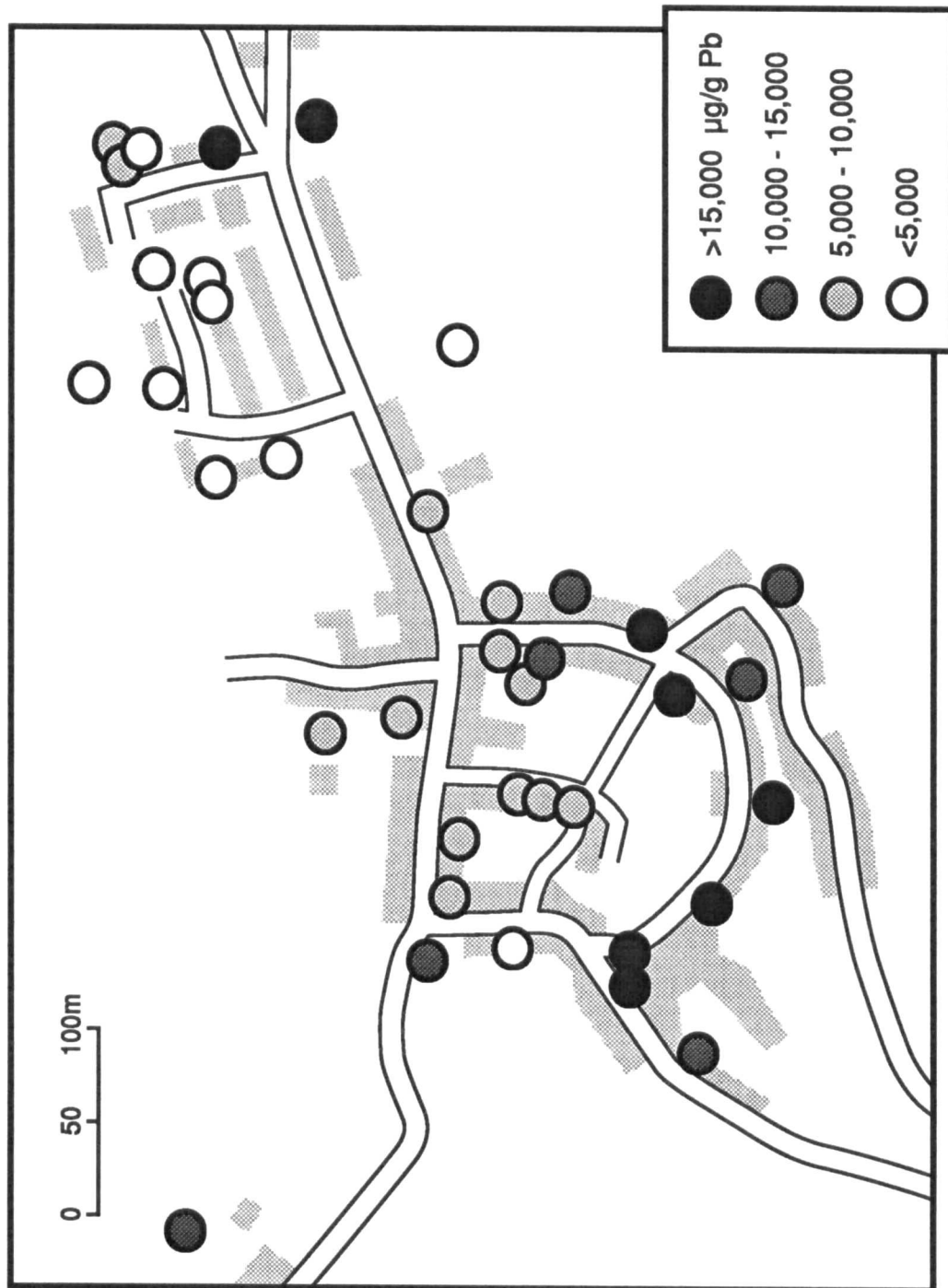


Figure 6.1(a) Distribution of lead in garden soil, Winster village

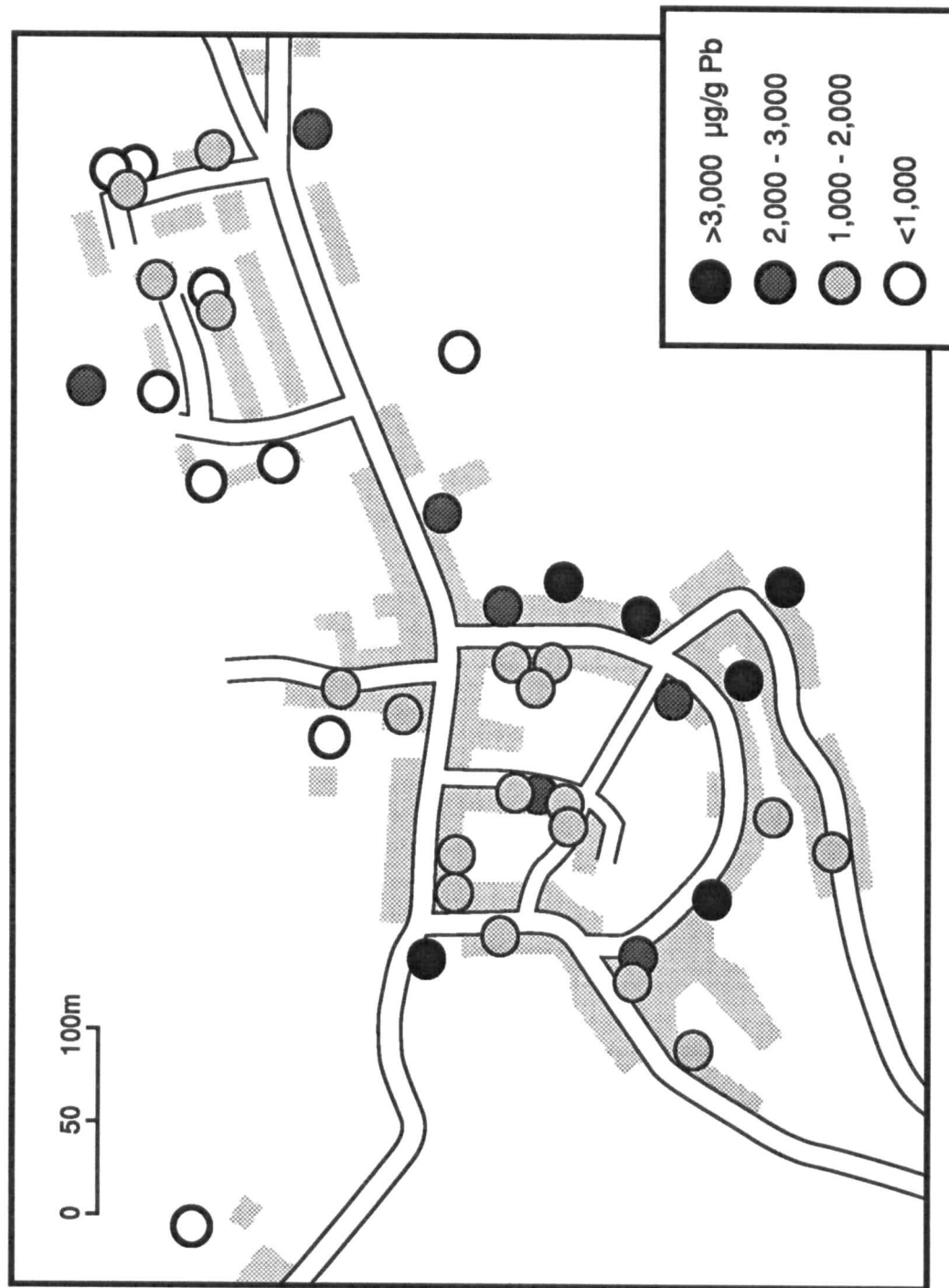


Figure 6.1(b) Distribution of lead in housedust, Winster village

Table 6.2 House age and lead concentration in Winsters			
	n	Geometric Mean (Pb µg/g)	Range
HOUSES <60 YEARS OLD			
Housedust	16	925	462-2,300
Garden Soil	16	4,300	2,370-17,600
HOUSES >60 YEARS OLD			
Housedust	29	2,080	1,100-6,240
Garden Soil	16	9,720	3,920-23,800

6.3 Hand and Blood Lead Concentrations

6.3.1 Lead on the Hands of Young Winsters Children

The geometric mean (range) of lead on the hands of Winsters children aged 1-2.5 yrs is 13.1 (6.60-39.5) µg Pb per pair of hands. Two duplicate samples gave variabilities of 20% and 66% (Appendix C5). This is in agreement with the average geometric coefficient of variation (Kirkwood, 1979) of 34% for hand lead values (with the exception of one outlier of 406.1 µg Pb) reported by Davies and Watt (1986).

6.3.2 Blood Lead Concentration of Winsters Children

Blood sampling in Winsters was limited because of the small population size, prohibiting any rigorous statistical analysis. The overall geometric mean (range) of lead in children's blood (1-8 yrs) is 9.4 (6.2-20.7) µg/dl and 6.9 (6.2-8.3) µg/dl for those aged 1-3 yrs. Typically, children's blood lead reaches a maximum at 2 years (see Section 2.2.2). The apparently anomalous result obtained in the present study is probably caused

by the extremely small sample size ($n=3$).

PART II - SOLID SPECIATION STUDY

In this study, the amount of lead reporting to the high density soil fraction and the apportionment of lead-bearing grains within this fraction are used to estimate the percentage of total soil-lead accounted for by each class of lead-bearing grains. A list of soil samples used in this study is given in Appendix J for reference throughout this chapter.

6.4 Total Elemental Concentrations and Soil pH

Total (or whole) lead and phosphorus concentrations (ΣPb and ΣP) and soil pH were determined in Section 5.3. The results of these determinations are presented in Table 6.3.

Table 6.3 Total lead and phosphorus concentrations and soil pH				
Sample	Pb concentration (µg/g)	P concentration (µg/g)	pH ¹	
			H ₂ O	CaCl ₂
<i>Density Separation Quality Control</i>				
BLK	424	963	--	--
DS-STD	107,700	6,780	--	--
<i>Winster Samples</i>				
DVS921	17,240	2,098	7.67	7.27
DVT922	13,280	1,499	8.41	7.86
PWF937	25,930	2,540	7.74	7.28
OMS942	24,770	1,665	7.63	7.30
WSG923	23,380	2,034	8.00	7.41
OMV927	14,990	3,996	7.67	7.04
SBV928	21,710	4,786	6.81	6.36
<i>Derbyshire Soils</i>				
TF943	27,280	861	8.32	7.61
HF945	11,330	1,674	7.37	6.89
SE952	31,530	885	5.61	5.08
VGWH941	2,713	1,709	7.27	6.91
<i>Other U.K. Soils</i>				
CHBP953	33,390	1,423	7.28	6.79
CHMS960	34,750	1,161	8.31	7.84
MIS934	603	726	7.84	7.53
<i>London Garden Soils</i>				
83/072	2,043	3,121	7.27	6.84
83/126	2,271	2,472	6.05	5.94
83/279	2,123	2,307	6.73	6.34
88/015	12,640	3,926	6.58	6.48
88/177	6,590	2,109	6.71	6.44

¹ Results for pH determinations in both the presence and absence of CaCl₂ are given (see Section 5.3.2).

6.4.1 Total Soil Lead and Phosphorus Concentrations

(a) Analytical quality control

Analytical quality control data for elemental analysis by ICPAES of whole soil samples is summarised in Appendix D. The data indicates a bias for lead of +34.6% at low concentrations ($\approx 15.0 \mu\text{g/g}$) and +3.5% at higher concentrations ($\approx 500 \mu\text{g/g}$). For phosphorus, a bias of -5.0% is present at $P \approx 420 \mu\text{g/g}$ and -1.0% at $P \approx 650 \mu\text{g/g}$. The high bias present at low lead concentrations is probably caused by the extremely high lead concentrations in samples causing a "carry over" effect in the instrumentation which affects the analysis of the low lead concentration reference material. Precision is estimated at $\pm 5.8\%$ for lead and $\pm 2.7\%$ for phosphorus.

(b) Lead

The density separation blank (*BLK*) contains higher concentrations of lead than expected ($\approx 400 \mu\text{g/g}$; see Table 6.3). However, this concentration is lower than all the field samples and so is valid as a blank, representing background lead concentrations in soils. The density separation standard (*DS-STD*) contains exceptionally high levels of lead because it was artificially contaminated with lead minerals (Section 5.4.4).

All Winstar samples, other mine-waste soils (*TF943*, *HF945*, *CHBP953* and *CHMS960*) and the smelter site sample (*SE952*) have lead concentrations in excess of 1 wt.% Pb (*i.e.* $>10,000 \mu\text{g/g}$) indicating the highly contaminated nature of these samples. At these concentrations, lead is considered a major rather than a trace element. Other soils were selected for the Solid Speciation Study because they contain $>1,000 \mu\text{g/g}$ Pb (*i.e.* moderately contaminated soils) except for the motorway roadside soil (*MIS934*) which has a concentration $\approx 600 \mu\text{g/g}$.

(c) Phosphorus

The density separation blank (*BLK*) was not intended as a phosphorus blank. However, its phosphorus concentration is amongst the lowest found in the samples (see Table 6.3). The phosphorus content of *DS-STD* is higher than those of the samples because of the addition of pyromorphite, a lead phosphate.

The phosphorus concentration of most of these soils is above the average worldwide concentration of $\approx 650 \mu\text{g/g}$ reported by Bowen (1966) (see Section 3.7.4). Phosphorus concentrations are highest ($>2,000 \mu\text{g/g}$) in the cultivated soils of Winstar (*OMV927* and *SBV928*) and London garden soils, probably reflecting addition of phosphorus in the form of fertilizer.

6.4.2 Soil pH

In this study the critical pH value is 6.0, the theoretically predicted value below which anglesite is stable and above which cerussite is stable under oxidising conditions in the absence of phosphorus (Fig. 3.3; Section 3.6.2). The effect of adding CaCl_2 is to slightly lower the pH value obtained which is not critical for most samples. However, in sample 83/126 the two pH determinations give pH values either side of 6.0, making it unclear whether anglesite or cerussite would be expected to be thermodynamically stable.

All Winstar mine-waste soils have high pH (CaCl_2 average = 7.43) which reflects the calcareous nature of these samples (see Section 4.4.1). Other mine-waste soils (*TF943*, *HF945*, *CHBP953* and *CHMS960*) have similar pH values. All samples have $\text{pH} > 6$ with the exception of 83/126 (see above) and *SE952* which is acidic (CaCl_2 pH = 5.08).

6.5 Results of Density Separations

In this section, the masses of soil present in the "floats" (high density fraction) and "sinks" (low density fraction) resulting from the density separation procedure described in Section 5.4.3 are presented. A summary of density separation masses (averages of duplicate separations) is given in Table 6.4. Individual results are presented in Appendix E. As each separation was carried out in duplicate, two masses for each sample are reported in Appendix E. The first refers to F1 and S1 (F=floats and S=sinks) and the

second to F2 and S2.

Table 6.4 Masses of density separates ¹		
Sample	Mass of "floats" (g)	Mass of "sinks" (g)
<i>Density Separation Quality Control</i>		
BLK ²	0.0010	0.9829
DS-STD ²	0.2336	0.7129
<i>Winster Samples</i>		
DVT921	0.0492	0.8489
DVS922	0.0615	0.8171
PWF937	0.0541	0.8535
OMS942	0.0806	0.8705
WSG923	0.0805	0.7744
OMV927	0.0404	0.8415
SBV928	0.0614	0.7080 ³
<i>Derbyshire Soils</i>		
TF943	0.0428	0.9206
HF945	0.0971	0.8337
SE952	0.0353	0.8992
VGWH941	0.0041	0.9599
<i>Other U.K. Soils</i>		
CHBP953	0.0066	0.9644
CHMS960	0.0217	0.9600
M1S934	0.0040	0.9206
<i>London Garden Soils</i>		
83/072	0.0060	0.9564
83/126	0.0037	0.9310
83/279	0.0041	0.9540
88/015	0.0047	0.9331
88/177	0.0056	0.9218

¹ Averages of duplicate separations; original mass approximately 1g.

² Average of repeated duplicate separations.

³ Single separation.

6.5.1 Methodology Quality Control

Before separation, *DS-STD* contained 30 wt.% of lead minerals (Section 5.4.4) but in the two separations only 21% and 25% of the original mass reported to the "sinks" (Appendix E), giving an average of 23% (Table 6.4). Therefore, the efficiency of this method probably lies between 60% and 80%, which compares favourably with the estimated 50% efficiency reported by Biggins and Harrison (1980). However, *DS-STD* was artificially contaminated and the efficiency for natural samples may be less. Only a minute amount of high density material was separated from *BLK*, despite its relatively high lead concentration. The exactness (accuracy and precision) of the density separation procedure is further considered using the concentrations of lead and phosphorus in the separates as well as the masses of these quality control standards in Section 6.6.3.

Accuracy is estimated from the summation of the masses reporting to the "floats", "sinks" and left on filters compared to the initial mass and gives an average of $\pm 4.19\%$ (Appendix E). This figure must be interpreted with caution. The amounts of material left on filters is quite substantial (up to 0.05% of the original mass) which is, strictly speaking, lost material although it can be accounted for. However, the vast majority of this material was from the low density separate and does not represent an important loss from the high density separate. Also, some of the filters are thought to contain remnants of diiodomethane, increasing the apparent weight left on filters which would lead to an underestimate of material lost during separation.

Precision (repeatability of the density separation procedure), estimated from the duplicate separations of each sample, gives an average of $\pm 20.4\%$ for "sinks" and $\pm 1.5\%$ for "floats" (Appendix E). Repeat separations of *BLK*, *DS-STD* and *OMS942* gave average masses of duplicates that did not differ more than 10% although precision between duplicates was variable (see Appendix E).

6.5.2 Masses of Density Separates

The mass of the high density ($>3.3 \text{ g/cm}^3$) fraction of the soil is generally very small. Table 6.4 shows typical values for highly contaminated samples ($>1 \text{ wt.}\% \text{ Pb}$ in

whole soil; see Table 6.3, Section 6.4.1) are of the order of 0.005 g (5% of the original mass) and for less contaminated samples approximately 0.0005 g (0.5% of the original mass).

A more meaningful expression of the separation is given by the amounts of total soil-lead and phosphorus reporting to each density fraction which is presented in Figure 6.2 (Section 6.6.3(b)).

6.6 Lead and Phosphorus Content of Density separates

The concentrations of lead and phosphorus in density separates (analysed in Section 5.5.1) are discussed in this section and combined with the masses of density separates to give the amounts of lead and phosphorus in the density separates.

Table 6.5 presents a summary of concentrations of lead and phosphorus in the density separates (averages of duplicate separations). Individual results are presented in Appendix F together with analytical quality control data for ICPAES elemental analysis. Two listings are given for each sample in Appendix F referring to duplicate separations. However, in some samples, notably the London garden soils, it was only possible to analyse one of the sink fractions (S1) as the whole of the other sink fraction (S2) was required for SEM analysis.

6.6.1 Analytical Quality Control

Analyses of reference materials (Appendices F1 and F3) indicate a bias of +40.7% at low lead concentrations ($\approx 15.0 \mu\text{g/g}$) and +0.8% at higher lead concentrations ($\approx 500 \mu\text{g/g}$). For phosphorus, a bias of -5.0% is present at $P \approx 420 \mu\text{g/g}$ and -3.9% at $\approx 650 \mu\text{g/g}$. The high bias present at low lead concentrations is similar to that reported in Section 6.4.1 and is also thought to be caused by the extremely high lead concentrations

in samples causing "carry over" effect, affecting the analysis of the low lead concentration reference material.

Analytical precision is estimated at $\pm 5.2\%$ for lead and $\pm 6.2\%$ for phosphorus from analysis of duplicate samples (Appendices F2 and F4). The precision of the density separation method can be estimated from the percentage differences in lead and phosphorus concentrations between sink and float pairs (Appendix F5). Float pairs give an estimated precision of $\pm 5.6\%$ for lead and $\pm 6.7\%$ for phosphorus. Sink pairs give an estimated precision of $\pm 9.0\%$ for lead and $\pm 10.2\%$ for phosphorus. Float pairs give similar precision to duplicate samples (analytical precision) but sink pairs give a higher error range, probably because of the small masses involved.

6.6.2 Lead and Phosphorus Concentrations in Density Separates

Table 6.5 Lead and phosphorus concentrations in density separates				
Sample	Lead (µg/g)		Phosphorus (µg/g)	
	"Sinks"	"Floats"	"Sinks"	"Floats"
<i>Density Separation Quality Control</i>				
BLK ^{1,2}	4,730	332	5,200	819
DS-STD ²	452,000	31,100	17,000	1,880
<i>Winster Samples</i>				
DVT921	207,000 ³	6,220 ³	24,400 ³	1,010 ³
DVS922	141,000 ³	3,170 ³	16,200 ³	491 ³
PWF937	175,000	15,300	12,700	1,690
OMS942 ²	122,000	12,800	6,320	1,360
WSG923	189,000	4,670	16,200	631
OMV927	152,000 ³	7,340 ³	12,100 ³	3,630 ³
SBV928	129,000 ³	13,800 ³	20,600 ³	4,130 ³
<i>Derbyshire Soils</i>				
TF943	419,000	14,400	9,970	638
HF945	13,400	13,700	261	1,750
SE952	224,000	31,400	1,651	1,100
VGWH941	11,300 ³	2,720	1,700 ³	1,750
<i>Other U.K. Soils</i>				
CHBP953	496,000 ³	32,400	1,700 ³	1,430
CHMS960	609,000	33,000	2,100	1,420
M1S934	16,500 ³	543 ³	1,880 ³	779 ³
<i>London Garden Soils</i>				
83/072	55,700 ³	2,080	3,770 ³	4,420
83/126	44,000 ³	5,350	4,830 ³	4,800
83/279	9,790 ³	2,960	3,490 ³	3,590
88/015	166,000 ³	13,900	1,290 ³	4,470
88/177	60,600 ³	8,590	4,630 ³	2,710

¹ Combined result from the sink pair as extremely small amounts of material available (see Table 6.4).

² Average of repeated duplicate separations.

³ Single analysis.

(a) Lead

The aim of the density separation procedure was to separate lead held in the solid phase from the soil matrix (see Section 3.6). Other phases of soil-lead *e.g.* soil solution (Section 3.2) adsorbed (Section 3.4) or chelated with organic matter (Section 3.5) have much lower densities because of the lighter nature of water, clays, and organic matter. However, lead adsorbed onto iron/manganese oxides will report to the high density soil fraction as these grains have densities $>3.3 \text{ g/cm}^3$. For the purpose of this study, lead associated with iron/manganese oxides is regarded as part of the solid phase, since it can be distinguished by the classification scheme (see Sections 5.5.2(c) and 6.7.3). Therefore, lead present in the high density soil fraction is assumed to be held in the solid phase.

Lead is enriched in the high density fraction of all samples and standards, including the density separation blank (*BLK*). All "sinks" contain $\geq 1 \text{ wt.}\%$ ($=10,000 \text{ }\mu\text{g/g}$) lead and enrichment to $>10 \text{ wt.}\%$ occurs in all Winsters samples (enrichment up to $60 \text{ wt.}\%$), *TF943* (Derbyshire mine-waste soil), Mendip mine-waste soils (*CHBP953* and *CHMS960*), the smelter site sample (*SE952*) and one London garden soil (*88/015*). Hence, lead is a major element in all the high density fraction of samples (even when a trace element in the whole soil). The "sinks" are thus suitable for analysis by SEM (Section 6.7) and XRD (Section 6.9).

The low density fraction of samples also contains lead, in some cases in high concentrations. In the Winsters samples, lead concentrations in the low density fractions are between 0.3 and $1.5 \text{ wt.}\%$. Other samples with high lead concentrations ($>1 \text{ wt.}\%$) in the "floats" are: all Derbyshire and Mendip mine-waste samples (*TF943*, *HF945*, *CHBP953* and *CHMS960*), the smelter site sample (*SE952*) and one London garden soil (*88/015*). All other samples contain $<0.5 \text{ wt.}\%$ Pb in the "floats".

Almost all float fractions with high lead concentrations are from highly contaminated samples. Retention of lead in the low density fraction is mainly due to two factors: (i) lead present in other forms other than the solid phase *e.g.* as ions adsorbed onto clays or organic material (see above) with an average density $<3.3 \text{ g/cm}^3$ and (ii) imperfect separation caused by adhesion of lead-bearing grains to lighter minerals (*e.g.* clays). The presence of a substantial concentration of lead in the float portion of *DS-STD* ($\approx 3 \text{ wt.}\%$) and the knowledge that the separation technique is at best between 60% and

80% efficient suggests that imperfect separation may be a major cause of relatively high lead concentrations in float fractions.

(b) Phosphorus

Whilst phosphorus is a light element (atomic no. 15) enrichment in the high density fraction of soils would be expected if phosphorus was associated with lead in the form of a phosphate *e.g.* pyromorphite or plumbogummite (see Section 3.6.3). Therefore the concentration of phosphorus in the density separates is of interest in this study.

Phosphorus is enriched (>0.5 wt.%) in all sink fractions from Winstar samples and *TF943* (mine-waste contaminated soil, Derbyshire) up to a maximum of 20 wt.% P. This suggests a high density host for phosphorus, possibly a lead-rich host. In contrast to lead enrichment, phosphorus is not notably enriched in the high density fraction from the smelter site sample (*SE952*) or the Mendip mine-waste soils (*CHBP953* and *CHMS960*). In these and other samples phosphorus concentration is approximately the same as that of the "floats" and reflects total soil-phosphorus concentration (Section 6.4.1).

6.6.3 Distribution of Lead and Phosphorus between Density Separates

The amounts of lead and phosphorus in the high and low soil density fractions provide a meaningful expression of the distribution of these elements as they combine both the both the mass of the separates and elemental concentrations in those separates. This allows the proportion of total soil-lead held in the high density soil fraction (representing the solid phase) to be calculated according to the following equation:

$$\begin{array}{l} \text{\% of total soil-lead} \\ \text{present as solid phase} \end{array} = \frac{(\text{mass of "sink" x Pb conc. of "sink"})}{(\text{mass of "sink" x Pb conc. of "sink"}) + (\text{mass of "float" x Pb conc. of "float"})}$$

and similarly for phosphorus.

(Eq. 6.1)

The proportion of total soil-phosphorus reporting to this fraction is important as it demonstrates the presence or absence of an association with lead (see Section 6.6.2(b)). Comparison of the summations of these amounts with the analysed elemental concentrations of whole soils (method described in Section 5.3.1) indicate the combined error of the density separation technique (method described in Section 5.4) and elemental analysis of the separates (method described in Section 5.5.1).

The amounts of lead and phosphorus present in the density separates are obtained by simple multiplication of the mass of each separate (Section 6.5.2; Appendix E) by the concentration of lead or phosphorus in that separate (Section 6.6.2; Appendix F). In Appendix G, these amounts are given for the F1 and S1 separates (see Section 6.5 for definition) of each sample and percentage distributions (calculated from Appendix G) are illustrated in Figure 6.2. No such calculation was feasible on the F2 and S2 separates as elemental concentrations in S2 were not obtained for many samples (see Section 6.6 above).

(a) Estimation of Error

In Appendix G, the amount of lead in "floats" and "sinks" is summed to give a calculated total amount of lead, similarly for phosphorus. This total is compared with the total obtained by ICPAES analysis of the whole soil (Section 6.6.2). The deviation of the calculated total from the analysed total represents the cumulative errors from the density separation procedure and ICPAES analysis.

For lead, the average deviation is +/- 21.3%, comparable with that for phosphorus (+/- 19.2%). Individual results in Appendix G show that in most of the samples the error for lead is broadly similar to that for phosphorus, implying that error is mostly in the density separation procedure rather than analysis. This in agreement with the greater precision obtained for elemental analysis (+/- 5%; see Section 6.6.1) than for the high density soil fractions (+/- 20%; see Section 6.5.1)

BLK1 shows low amounts of lead and phosphorus in the high density fraction. The calculated total for both lead and phosphorus is lower than the analysed total indicating that inter-sample contamination during the separation procedure was not a problem. However, it is thought that contamination is possible in *MIS934* (see 6.6.3(b).

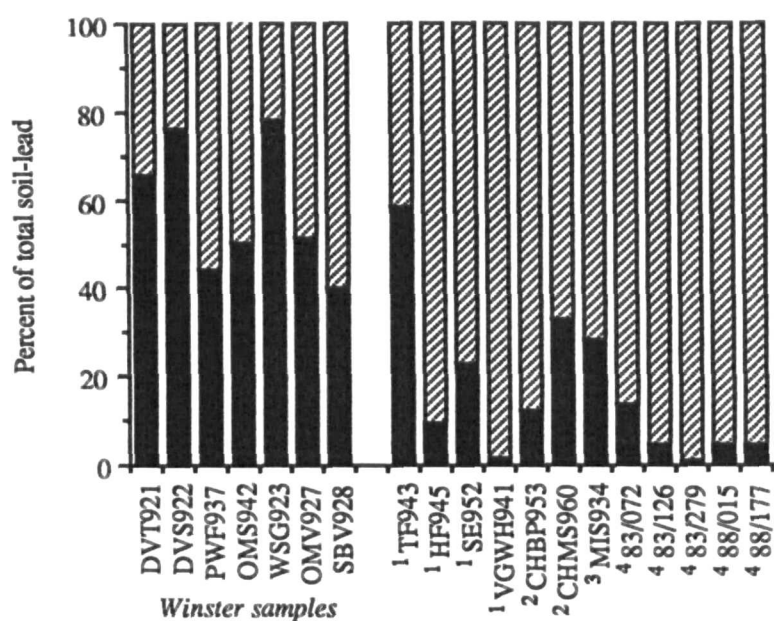
A large proportion of the total lead and phosphorus was present in the high density fraction of *DS-STD1* ($\approx 80\%$). This figure is an estimate of the efficiency of the density separation procedure as, in theory, these values should be close to 100% because this was an artificially contaminated soil (see Section 5.4.4). This assessment of efficiency is slightly higher than that defined by the masses of separates (Section 6.5.1).

(b) Distribution of lead and phosphorus

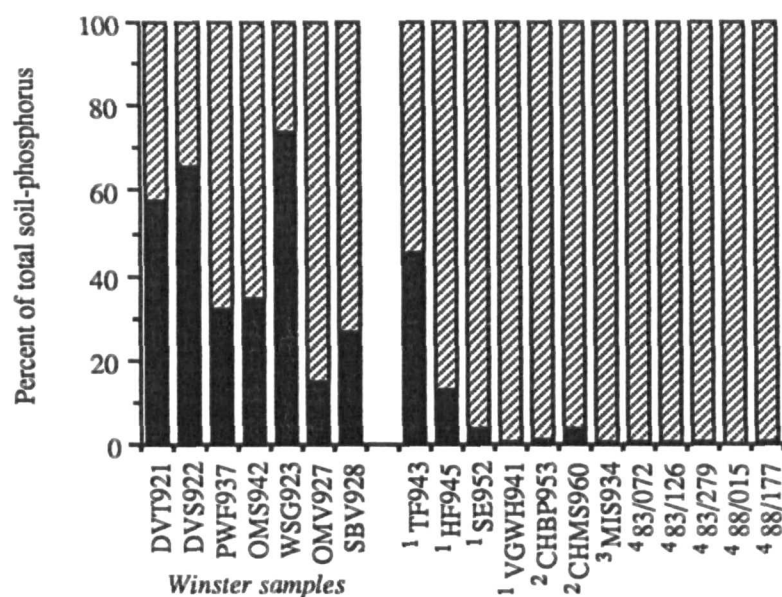
The amount of lead in the sink portion of each sample listed in Appendix G can be expressed as a percentage of the total calculated lead and similarly for phosphorus. These percentages are illustrated graphically in Figure 6.2.

Over 40% of the total soil-lead is concentrated in the high density fractions of the Winstar samples. Other highly contaminated soils (other mine-waste soils, *TF943*, *HF945*, *CHBP953* and *CHMS960*, and the smelter site sample, *SE952*) show less of an enrichment, with between 5 and 30 wt.% of total soil-lead. The high density fraction of moderately contaminated soils (the old industrial site, *VGWH941* and London garden soils) generally contains a low percentage of total soil-lead (10 wt.% or less) implying that other phases of lead in soils are much more important than the solid phase. The one exception is the motorway roadside soil (*MIS934*) which contained ≈ 25 wt.% of total soil-lead in the solid phase. The reason for this is unclear, especially as this sample contained the lowest concentration of soil-lead (see Table 6.3; Section 6.4.1). It could represent contamination by other, highly contaminated soils but this of little consequence as discussed in Section 6.7.1(c).

The patterns of the distribution of lead and phosphorus between density separates for Winstar samples (Fig. 6.2) shows a clear similarity for these two elements indicating an association of lead with phosphorus. The only exception to this is the garden soil sample, *OMS927*, where a relatively small proportion of phosphorus is present in high density separate. This could be indicative of the highly cultivated nature of the soil *i.e.* a substantial amount of total soil-phosphorus may be held as calcium phosphates, the form in which it is commonly added to soils as fertilizer.



(a) Distribution of lead



(b) Distribution of phosphorus

Figure 6.2 Distribution of lead and phosphorus between soil density fractions.

¹ Derbyshire soils; ² Mendip soils; ³ Motorway roadside soil; ⁴ London garden soils.

In other highly contaminated soils, where a considerable proportion of total soil-lead ^{is} present in the high density fraction, the association of phosphorus with lead differs. Comparable proportions of phosphorus and lead are present in the high density soil fractions of *TF943* and *HF945* but a lesser proportions of phosphorus in *SE952* and *CHBP953* and *CHMS960*. Negligible proportions of phosphorus are present in the high density fractions of moderately contaminated soils, comparable with the low percent of total soil-lead reporting to this fraction.

The percentage of total soil-lead reporting to the "sinks" is later used in the calculation of the percentage total soil-lead accounted for by mineral classes defined by SEM analysis (Section 6.8).

6.7 SEM Analysis

6.7.1 Identification and Analysis of Lead-bearing Grains

The lead-bearing grains identified in Winstar samples using the SEM/EDX technique described in Section 5.5.2(a) were galena, cerussite and pyromorphite. No other lead minerals were present. Pyromorphite was also identified in samples from other areas. Galena and cerussite may well be present in some of these other samples (*e.g.* Derbyshire and Mendip mine-waste soils) but were not subject to quantitative analysis as pyromorphite was the mineral of primary interest.

SEM photographs of typical lead-bearing grains encountered in the course of this study are presented in Figure 6.3.

Figure 6.3

Figure 6.3 SEM photographs of lead-bearing grains

The following photographs illustrate the different lead minerals occurring in Winster mine-waste soils and the various pyromorphite morphologies encountered during the course of this study. All photographs are of polished grain mounts from the high density soil fraction. Scale bar is approximately 10 μm .

Plate 1

Secondary Electron Images

These images show morphology and surface features of grains.

- A** Typical euhedral grain of galena showing cubic fracture (*DVS921*), Winster.
- B** Two mixed-phase grains of cerussite and galena in a Derbyshire mine-waste (*TF943*). The two phases are clearly shown in the back-scatter image (photograph **A**, Plate 3).
- C and D** Typical featureless anhedral cerussite grains (*DVS921*), Winster.

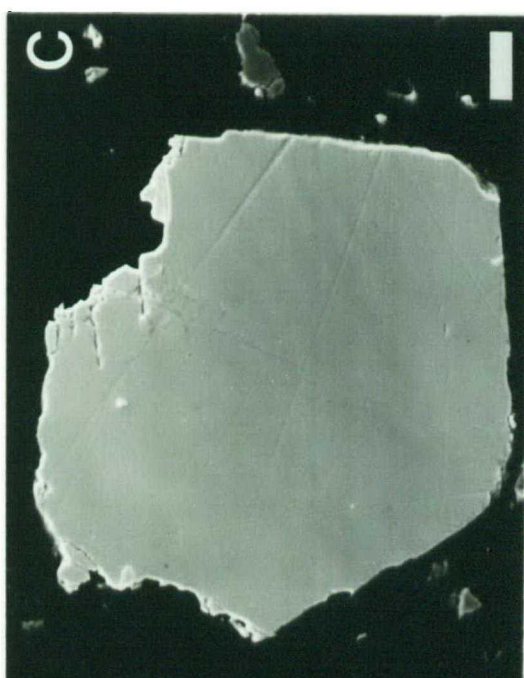
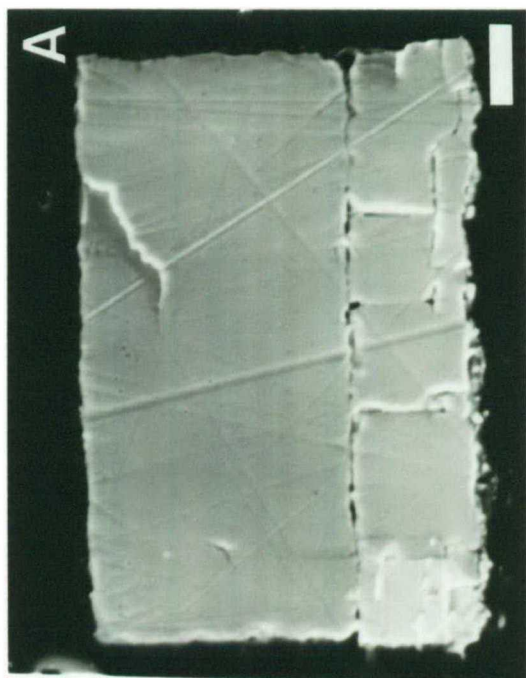
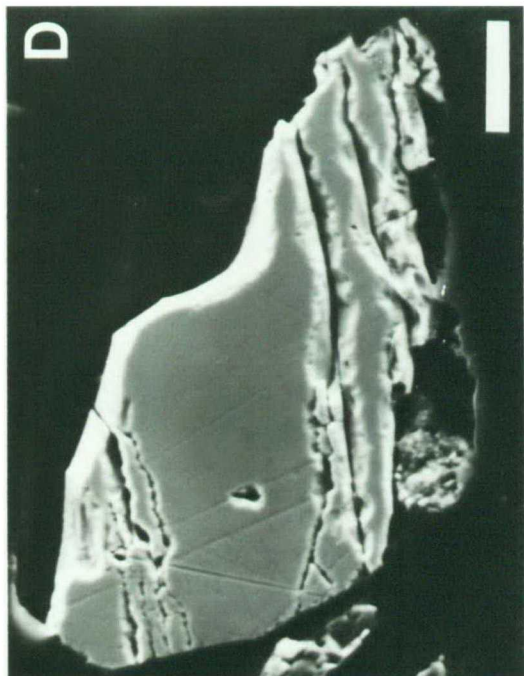
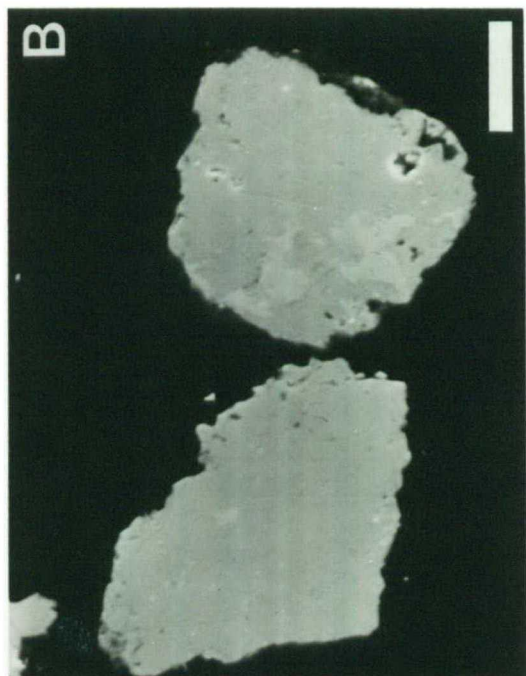


Plate 2

Secondary Electron Images

These photographs show the morphology of pyromorphite in mine-waste and other soils.

A Typical anhedral grain of pyromorphite in mine-waste soil from Winster (*DVS922*)

B Anhedral grain of pyromorphite from the old industrial site, Derbyshire (*VGWH941*).

C Grain of pyromorphite (*VGWH941*) with calcium-rich zones (shown in back-scattered image: photograph **B**, Plate 3).

D Pyromorphite grain from a London garden soil (*83/279*) with a blocky (well formed?) zone in the bottom left of the grain.

E Pyromorphite grain in a London soil showing a central solid core with botryoidal outer zone (*83/279*)

F Pyromorphite in a London soil (*88/015*). Similar to **E** showing a central solid core with botrydoidal outer zone.

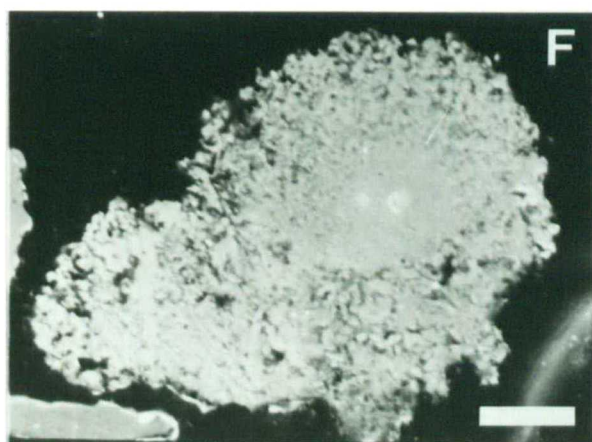
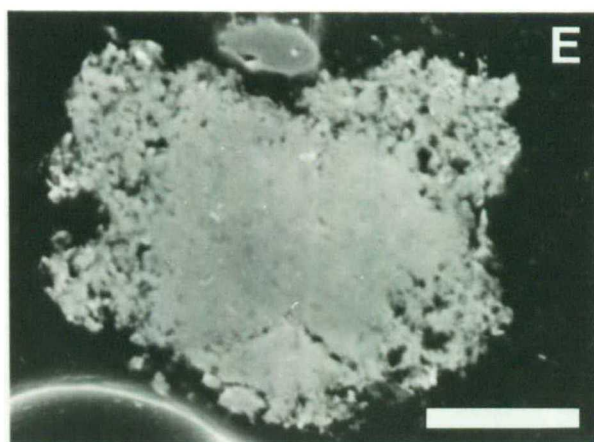
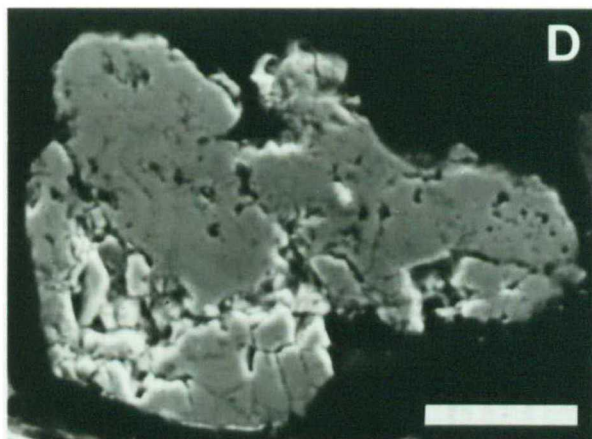
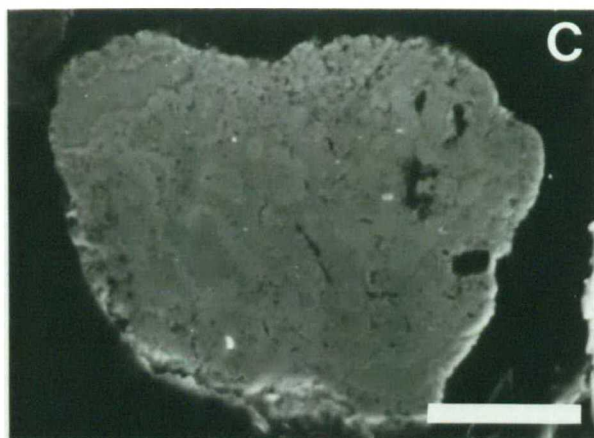
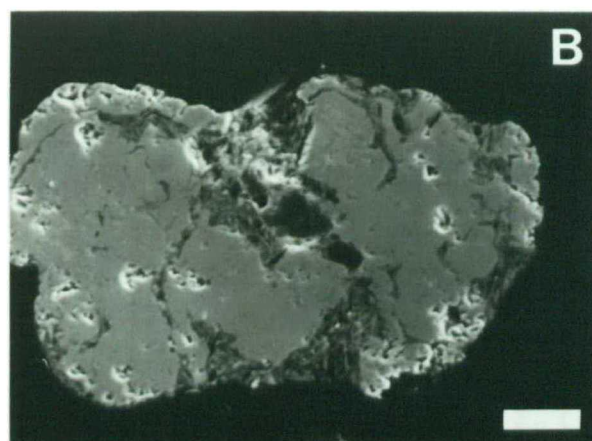
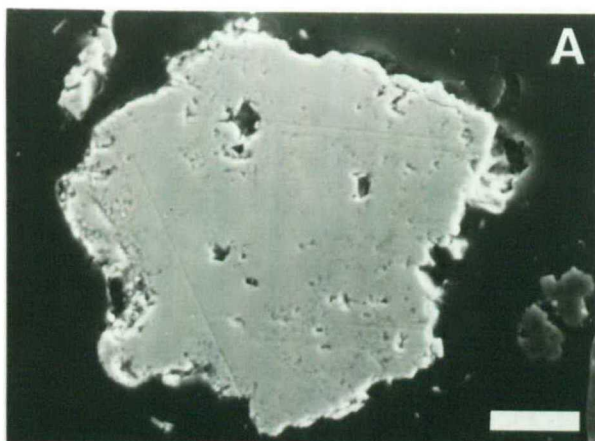


Plate 3

Back-Scatter Electron Images

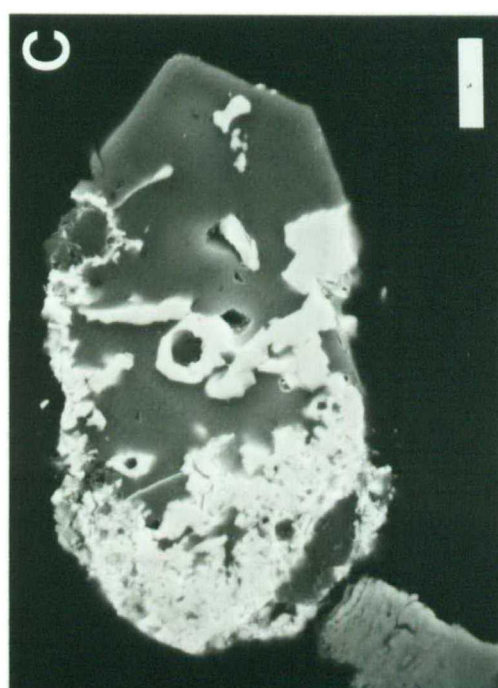
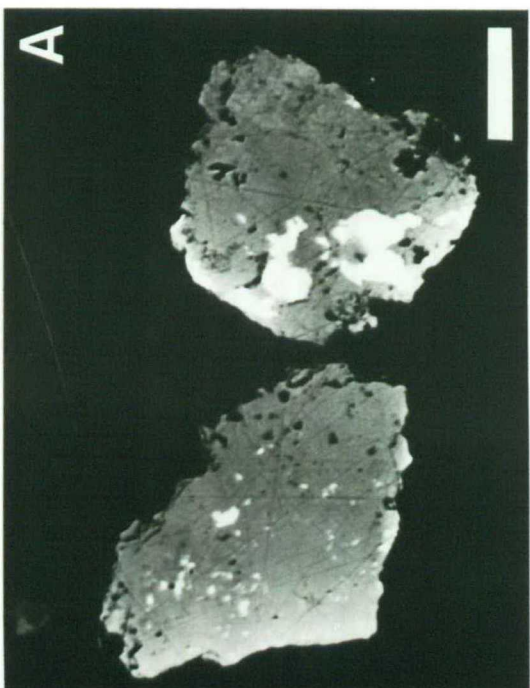
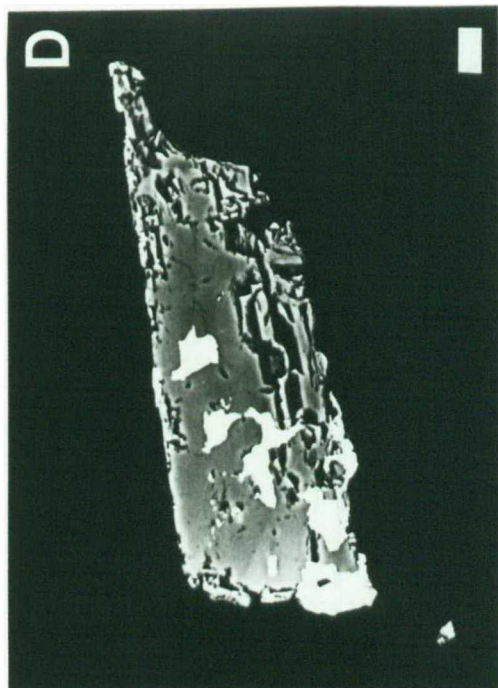
These images emphasise areas of contrasting atomic number (approximately proportional to density).

A Bright areas represent galena cores (inclusions?) of photograph **B** (Plate 1) within the darker cerussite.

B Pyromorphite grain (photograph **C**, Plate 1) showing calcium substitution of lead. Dark areas contain up to 7 wt.% calcium (low atomic number) whilst bright areas (alongside cracks?) are poor in calcium.

C Pyromorphite (bright areas) deposited on a calcite grain in motorway roadside soil (*MIS934*).

D Barite grain in motorway roadside soil (*MIS934*) with deposits (inclusions?) of pyromorphite (bright areas).



(a) Galena in Winsters samples

Galena (PbS) was identified in all the Winsters samples. Typical analyses of unaltered galena grains gave 86.3-86.6 wt.% Pb, 13.4-13.7 wt.% S which is in agreement with values calculated from the empirical formula (86.6 wt.% Pb, 13.4 wt.% S). An example of a typical galena grain showing euhedral cubic facets is presented in Plate 1, Figure 6.3.

(b) Cerussite in Winsters samples

A set of grains present in all Winsters samples, yielded only lead under SEM/EDX analysis which is indicative of several lead compounds. The following evidence strongly suggests that this mineral is cerussite and, in the Winsters samples, is interpreted as such.

The empirical formula of cerussite (PbCO_3) yields a calculated lead concentration of 77.54 wt.%, equivalent to a PbO content of 83.53 wt.%. However, analysis of grains of this mineral in Winsters samples gave values between 77.6 and 81.2 wt.% PbO. Because carbon and oxygen cannot be analysed by this technique, the oxide wt.% does not total 100% so cannot be used to assess the accuracy of analysis. It is unlikely that this mineral could be another lead mineral which also yields only lead under SEM analysis *e.g.* massicot, PbO ; minium, Pb_3O_4 ; hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ as these contain lead in substantially different proportions to the analysed value.

Analysis of a cerussite standard (in addition to the calibration standard) yielded a similar wt.% PbO. This may be used to infer that the mineral identified is cerussite and that instrument calibration may be inaccurate for this mineral. Additional evidence for the presence of cerussite is afforded by the identification of cerussite by XRD in Winsters samples (Section 6.9). Therefore, whilst identification of cerussite by quantitative SEM analysis is not conclusive, it is highly probable that this mineral is cerussite.

Hence, both SEM/EDX and XRD analyses suggest that cerussite was present in Winsters samples. The anhedral morphology of typical homogeneous grains are shown in Plate 1, Figure 6.3. Cerussite was also found in the weathered zone of galena grains (Plates 1 and 3, Figure 6.3; Figure 6.4(a)).

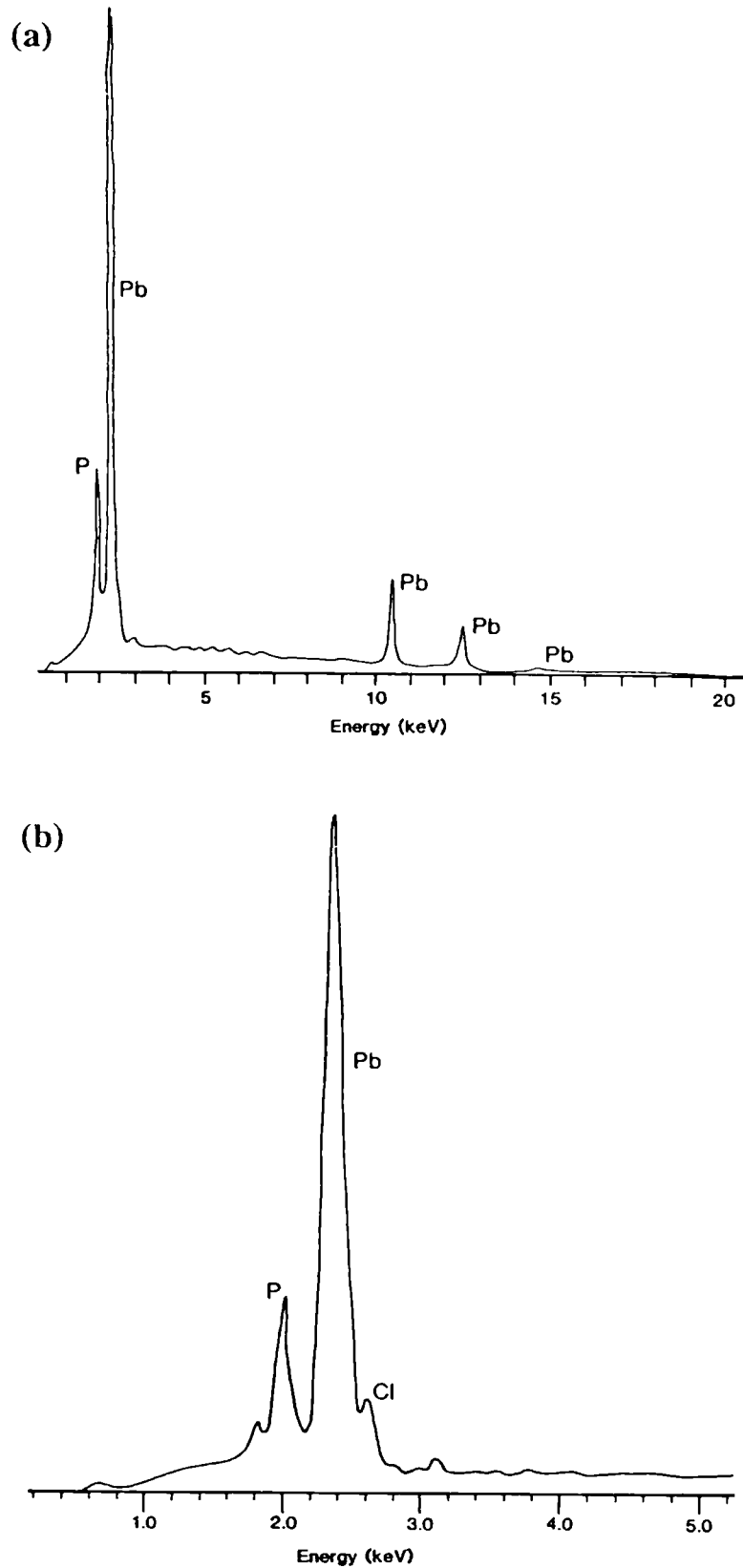


Figure 6.4 SEM/EDX qualitative spectrum of pyromorphite. Lead and phosphorus peaks are shown in (a); the chlorine peak is visible on the expanded scale in (b).

Table 6.6 Electron microprobe analyses of pyromorphite													
	SEM-STD	SEM-STD	DVS922	DVS922	TF943	TF943	VGWH941	VGWH941	MIS934	MIS934	83/126	83/126	83/279
								wt. % oxide					
PbO	84.30	83.54	74.34	73.47	74.26	73.51	84.84	72.23	82.64	72.83	72.92	79.17	72.70
CaO	0.19	0.28	7.06	6.87	6.79	7.52	--	8.14	0.12	6.95	7.79	1.57	6.29
P ₂ O ₅	13.91	13.88	17.23	16.91	17.05	16.82	13.28	17.32	13.98	16.23	18.18	14.12	15.68
Cl	2.94	2.41	2.53	2.65	2.62	2.37	2.56	1.86	2.21	2.17	0.94	2.34	1.74
Rem.	--	0.27	0.36	--	--	0.17	0.61	0.66	--	1.64	0.31	1.01	1.59
Sub-total	101.34	100.38	101.50	99.91	100.73	100.39	101.31	100.21	98.95	99.82	100.14	98.22	98.00
O≡Cl ¹	0.66	0.54	0.57	0.60	0.59	0.53	0.58	0.42	0.50	0.49	0.21	0.53	0.39
Total	100.68	99.84	100.93	99.31	100.14	99.85	100.73	99.79	98.45	99.33	99.93	97.69	97.61
													98.24

Rem. (= Remainder) consists of trace amounts of Fe, Zn and Cd

¹ Correction for oxygen excess due to the presence of a second anion (chlorine) according to the method outlined by Deer *et al.* (1960).

(c) *Pyromorphite*

Pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) was identified by the presence of lead and phosphorus peaks in the EDX spectrum (Figure 6.4) and confirmed by quantitative analysis (Table 6.6). Pyromorphite was present in all Winster samples, one Derbyshire mine-waste soil (*TF943*), soil from the old industrial site in Derbyshire (*VGWH941*), motorway roadside soil (*MIS934*) and all London garden soils. No pyromorphite was identified in the second Derbyshire mine-waste soil (*HF945*), soil from the Derbyshire smelter site (*SE952*) or mine-waste soils from the Mendips (*CHBP953*) and (*CHMS960*). Plumbogummite ($\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) was not present in any of these samples, indicated^{by} the absence of an aluminium peak in the spectrum.

Analyses of pyromorphite from Winster, Derbyshire and London soils are listed in Table 6.6. The proportions of element oxides and chlorine are similar to those given by Palache *et al.* (1951) except that arsenic (a possible substitute for phosphorus, see Section 3.6.4) was not present in any of the grains: vanadium was also absent. Low wt. % totals were obtained for some of the London soils because it was difficult to find a large enough homogenous area within a grain suitable for analysis (see Figure 6.3). Many of the pyromorphite grains contained calcium, substituting for lead up to a Pb:Ca ratio of 2.2:1 (atomic) but more usually 2.7:1. However, none of the mineral pyromorphite grains in *SEM-STD* showed appreciable amounts of calcium (Table 6.6). The amount of calcium substituting for lead varied both from grain to grain within the same sample (Table 6.6) and, in some cases, within the same grain (Plates 2 and 3, Figure 6.3).

Pyromorphite grains from Winster mine-waste soils and soil from the old industrial site, Derbyshire are generally discrete, homogeneous grains contrasting with the incoherent, botryoidal (literally "raspberry like") grains found in London garden soils (Plate 2, Figure 6.3). Pyromorphite in the motorway roadside soil (*MIS934*) was sometimes found as very small grains associated with other mineral grains (Plate 3, Figure 6.3). This implies that even if the large proportion of total soil-lead held in the solid phase is a result of contamination (see 6.6.3(b)), this is of little consequence as the morphology of pyromorphite in this sample is very distinctive and not found in any of the other samples. Therefore, the origin of pyromorphite in *MIS934* soil is not solely from contamination.

Figure 6.5

Figure 6.5 SEM image analysis of mixed phase lead bearing grains

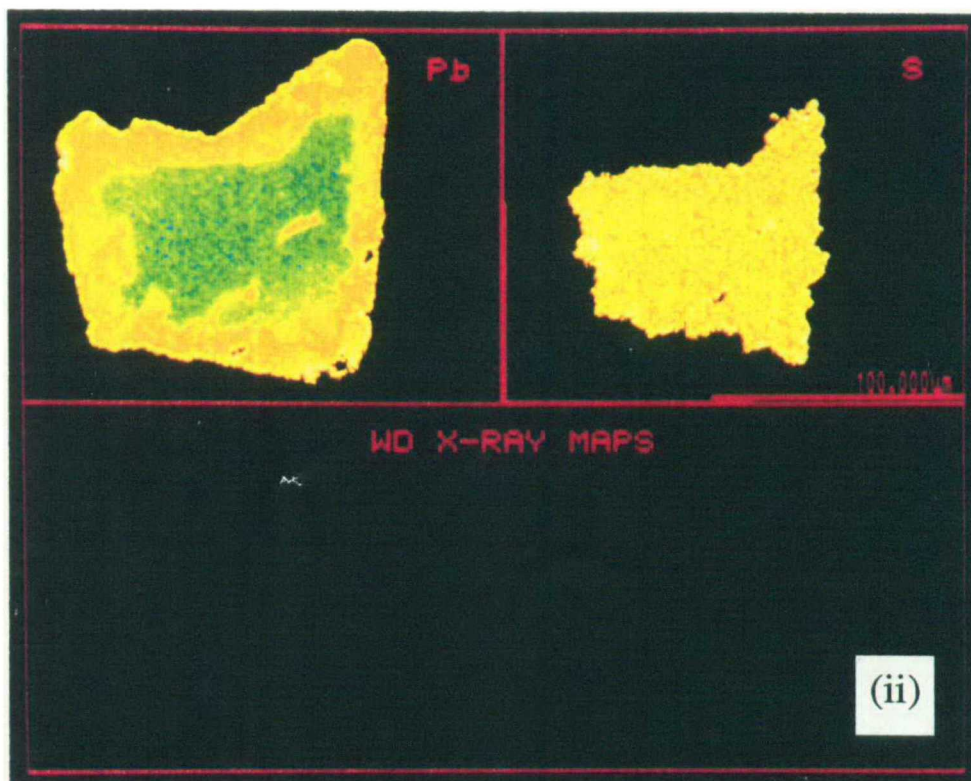
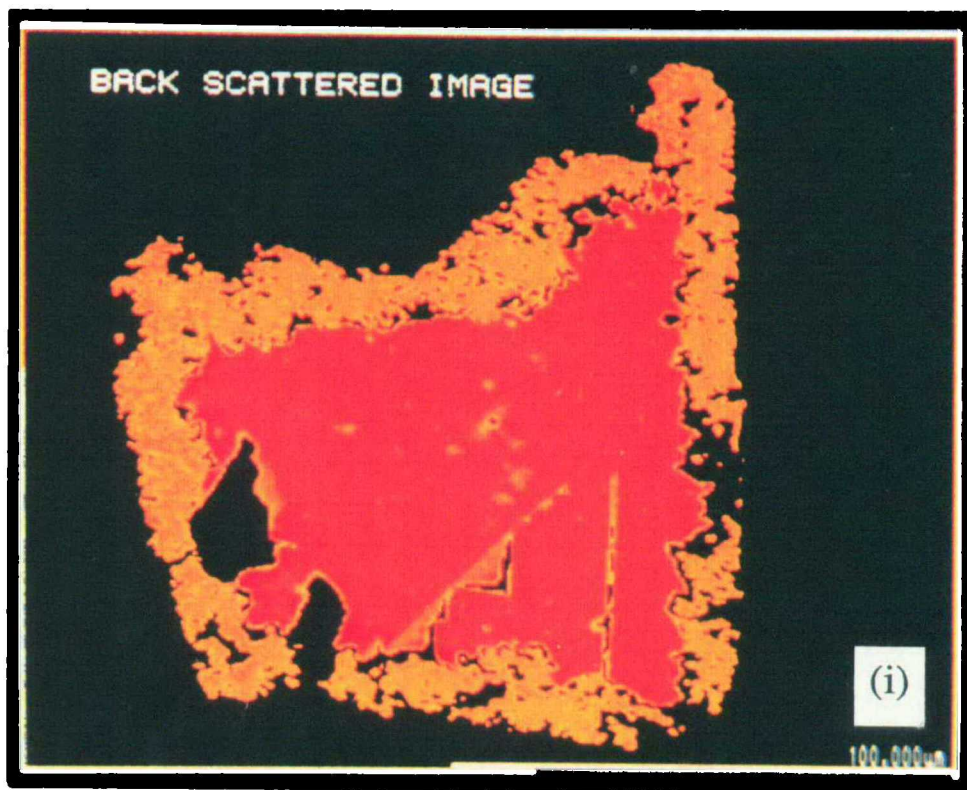
In the following back-scattered images, higher atomic number is indicated by gradation from yellow to red. In the X-ray maps, increase in element concentration is indicated by gradation from yellow, to green, to blue. There is no relationship in apparent concentration between elements or grains.

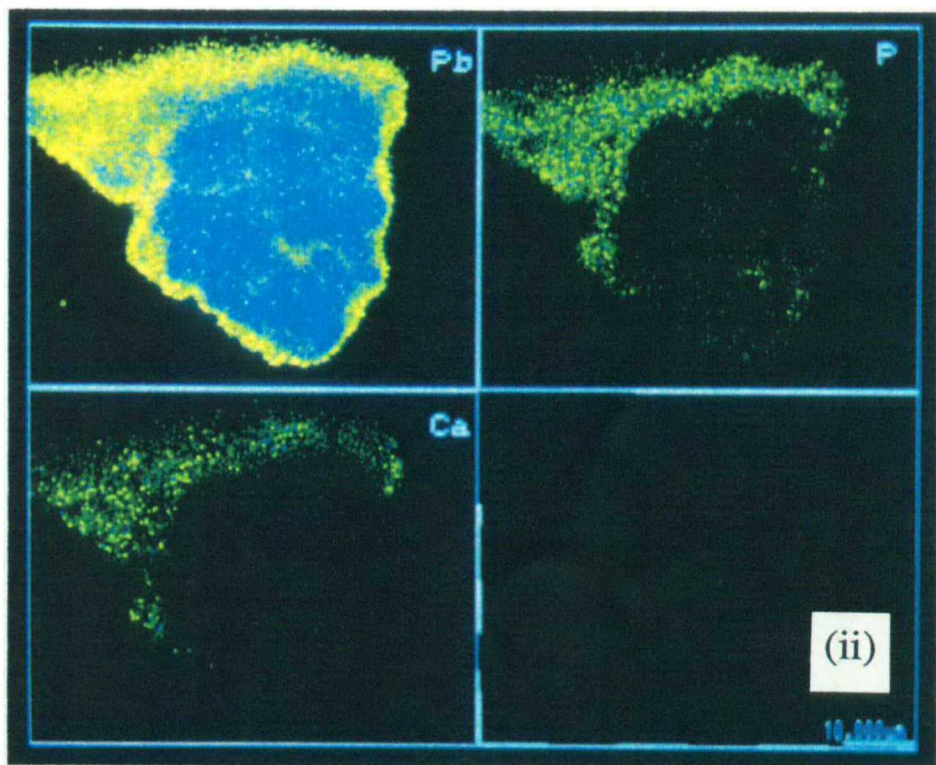
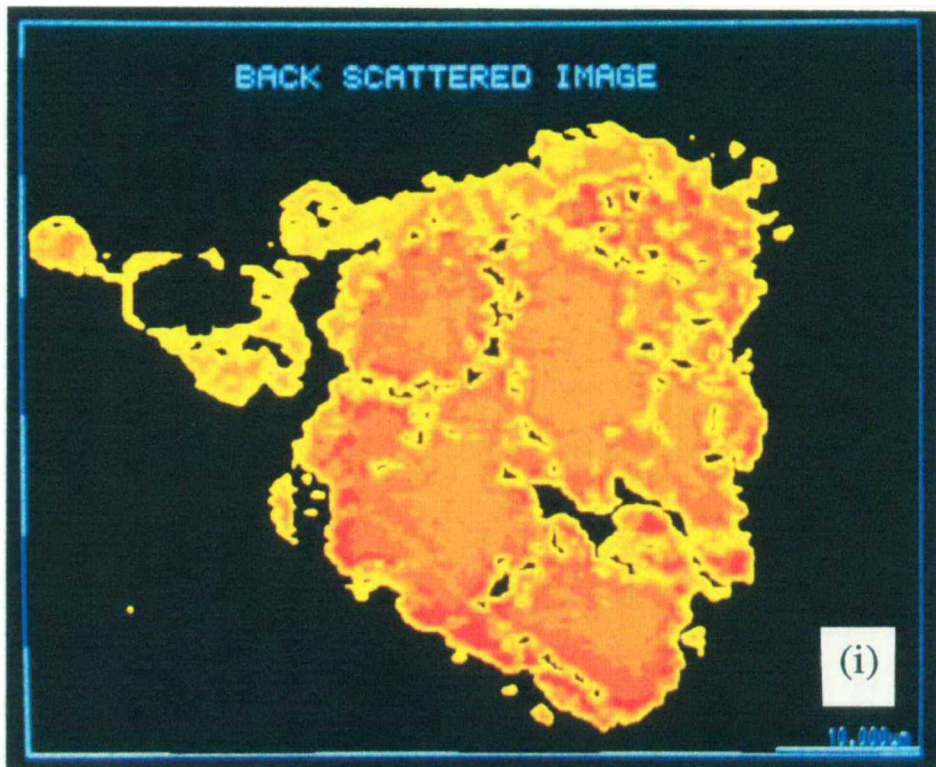
Opposite Plate

(a) SEM images of weathered galena grain. (i) Galena grain in mine-waste soil, Winstar (DVS922) showing an outer weathered zone. (ii) Both lead and sulphur are present in the inner core but sulphur is absent in the weathered zone. Quantitative analysis indicates that this weathered zone is composed of cerussite.

Following Plate

(b) SEM images of weathered paint chip. (i) Paint chip (?) in a London garden soil (83/126) showing a weathered edge. (ii) ED X-ray maps show the presence of lead throughout the grain. The weathered area contains phosphorus and lead, absent within the central core. Quantitative analysis (Table 6.4, Section 6.7.1) of this weathered edge suggests a pyromorphite composition.





6.7.2 Image Analysis

Two lead-bearing grains comprising more than one phase were analysed using the X-ray mapping technique described in Section 5.5.2(a). The resulting X-ray maps of these grains are presented in Figure 6.5 together with the back-scatter electron images.

One grain, originally galena, was from a Winster mine-waste soil (*DVS922*) and the other was from a London garden soil (*83/126*). The London soil grain is of uncertain origin but closely resembles a paint chip. The central area of this paint chip(?) contained lead but ~~was~~ was not associated with any other elements *e.g.* with phosphorus, sulphur or titanium and is therefore probably either an oxide, hydroxide or carbonate.

These images portray the alteration of lead compounds in the soil environment. Galena was observed to alter to cerussite and the paint chip(?) to pyromorphite.

6.7.3 Classification of Lead-bearing Grains

It is impractical to present here all the information collected from lead-bearing grains and analyzed using the *MIDAS* program as described in Section 5.5.2(c). These data have been archived and can be accessed via Mr. J. Watt (c/o Professor I. Thornton), Environmental Geochemistry Research, Imperial College. *MIDAS* output of tables of classification class against area for all standards and samples are given in Appendix H.

Each analysis collected information on a maximum of 3700 grains. Where lead was not present in large concentrations (*i.e.* *HF945*, *VGWH941*, *83/072*, *83/072*, *83/126*, *83/279* and float samples) the number of grains analysed was lower, down to a minimum of 235 (see Appendix H).

Histogram representations of the grain classification of *SEM-STD* and one sample, *PWF937* (shown as an example) show the fundamental differences between the pyromorphite, cerussite and galena classes (Figures 6.6(a) and (b)). Figure 6.6(c) shows anglesite (PbSO_4) erroneously classified as galena demonstrating one of the limitations of this technique (as described in Section 5.5.1(c)).

Figure 6.6

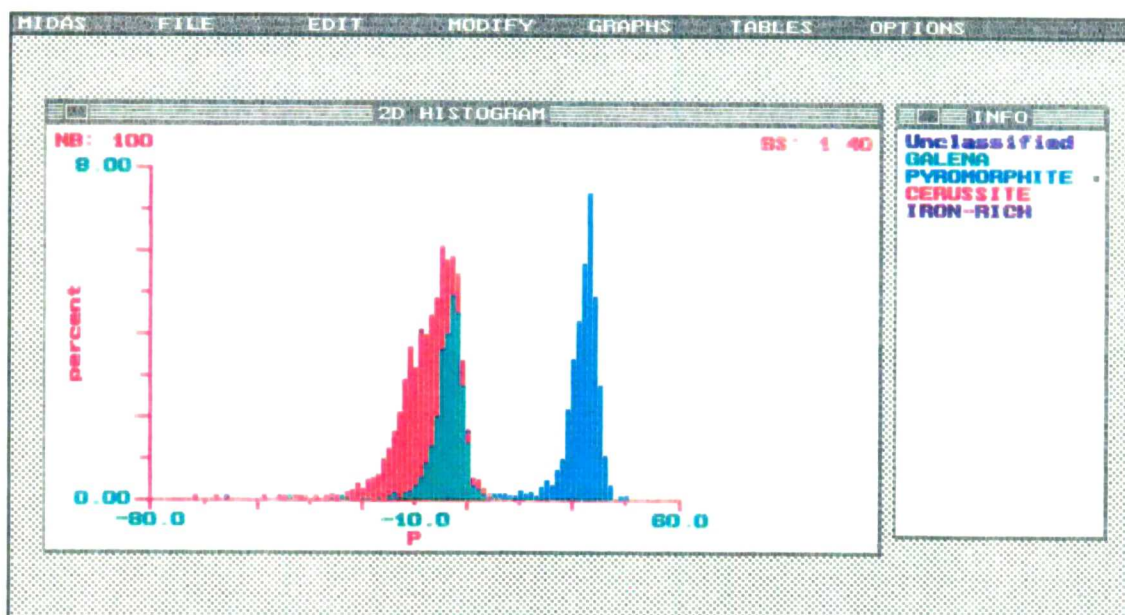
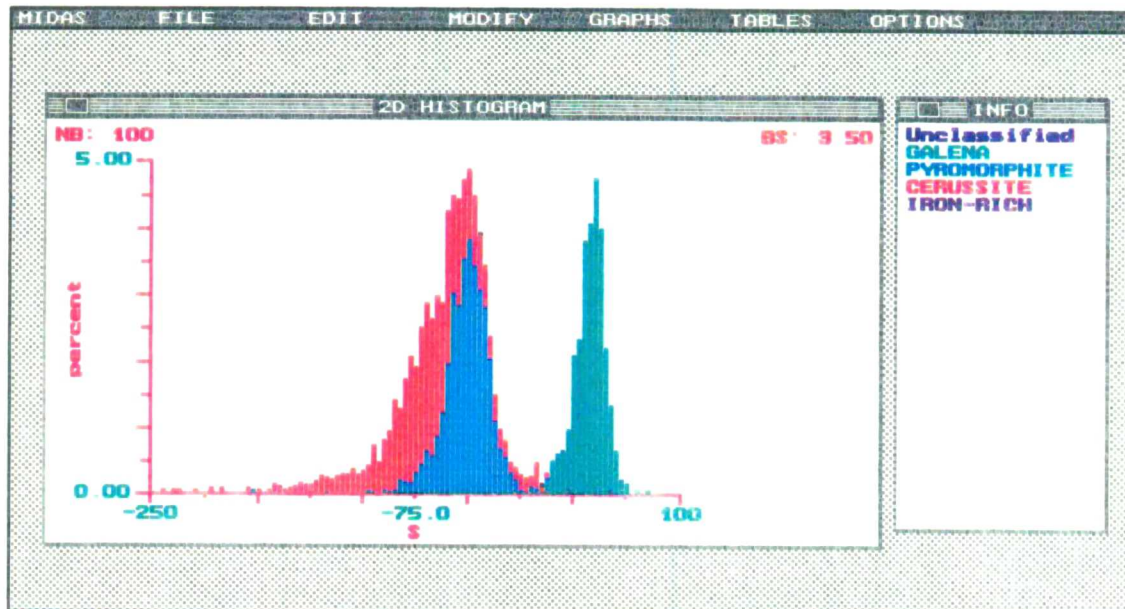
Figure 6.6: Histogram representation of the classification of lead-bearing grains

The following three plates show histograms taken directly from *MIDAS* and show the number of particles falling into each class and their relative sulphur and phosphorus concentrations.

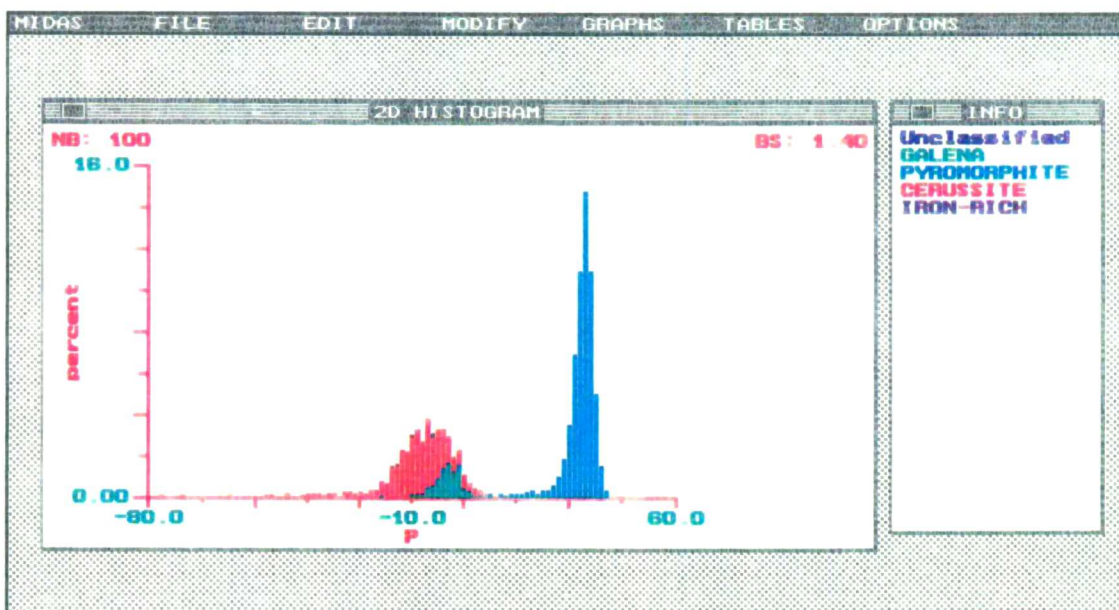
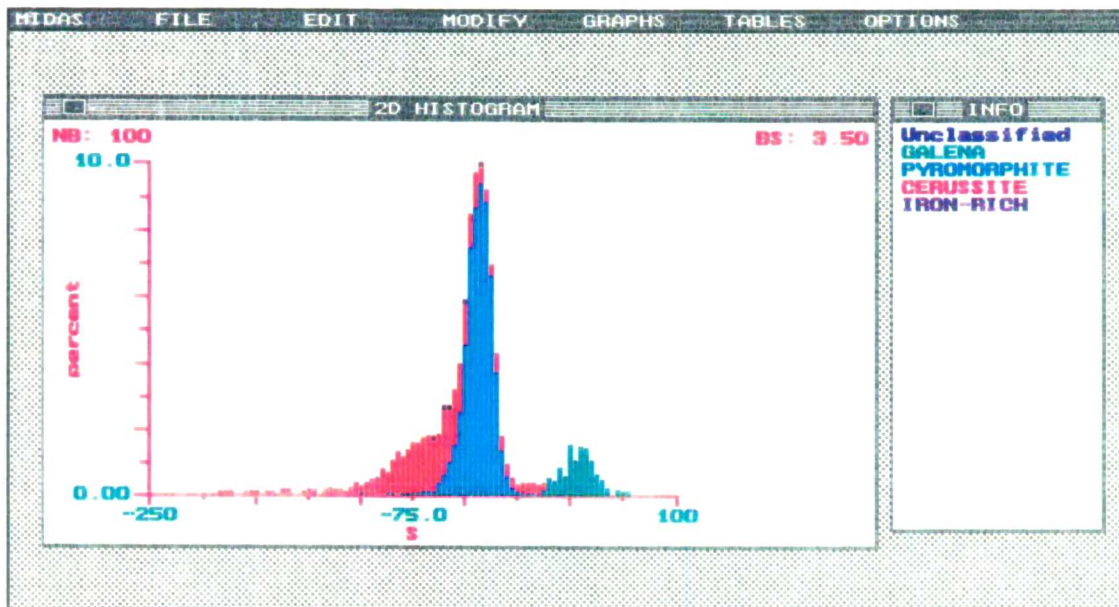
(a) Histograms of sulphur (above) and phosphorus (below) of the classification standard (*SEM-STD*) demonstrate that galena, pyromorphite and cerussite can be separated into their respective classes with negligible overlap.

(b) Classification of lead-bearing grains in the high density portion of a mine-waste soil, Winstar (*PWF937*). The sulphur histogram (above) shows the presence of small amounts of galena (high sulphur); the phosphorus histogram (below) indicates an abundance of pyromorphite (high phosphorus). The presence of small amounts of cerussite is demonstrated by the low phosphorus, low sulphur group shown in red.

(a)



(b)



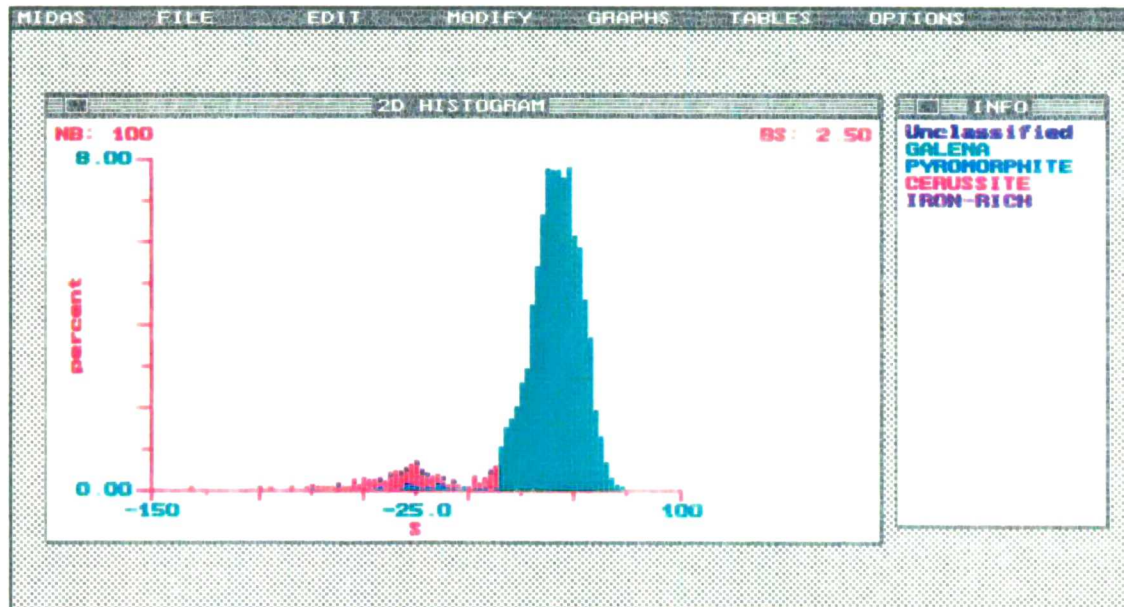


Figure 6.6(c) Sulphur histogram of smelter site sample (*SE952*) shows a wide bell shaped distribution erroneously classified as galena. XRD analysis (Section 6.9) indicated anglesite (PbSO_4) as a major component.

Galena was positively identified in all Winsters samples but grains classified as galena in other samples could be galena, anglesite or leadhillite (see Section 5.5.1(c)). For this reason, galena is expressed as "galena" in Figures 6.7 and 6.8.

Similarly, cerussite is expressed as "cerussite" as it is loosely defined as a low-sulphur, low-phosphorus and low-iron class (Section 5.5.2(c)). However, cerussite was positively identified in Winsters samples (Section 6.7.1). Examination of "cerussite" grains in mine-waste soils other than from Winsters (*TF943*, *HF945*, *CHBP953* and *CHMS960*) using the *MIDAS* window file containing 19 elements (Section 5.5.2(c); Appendix A) revealed that only lead was detectable. This class could contain grains of lead oxides/hydroxides or hydrocerussite in addition to cerussite itself. In some "cerussite" grains from London garden soils, lead was found to be associated with other elements *e.g.* titanium. This association is typical of contamination by lead-bearing paint.

It was discussed in Section 5.5.2(c) that grains of plumbogummite would fall into the pyromorphite class as both compounds contain phosphorus. However, no plumbogummite grains were identified in any samples (Section 6.7.1). Furthermore, analysis of grains in the pyromorphite class using the *MIDAS* window file indicated that aluminium, an essential constituent of plumbogummite was not present. Therefore, grains falling into the pyromorphite class are most likely to have a pyromorphite composition.

The iron-rich class describes lead-bearing grains associated with iron which could be lead adsorbed onto iron oxides (see Sections 3.2.3 and 3.4.1). No quantitative analyses of this class was performed.

For each table in Appendix H, the total area reporting to each class ("galena", pyromorphite, "cerussite", iron-rich and unclassified) is given as a percentage of the total area of lead bearing grains. If it is assumed that area is proportional to volume and that all "cerussite" is cerussite and all "galena" is galena, then area percent can be converted into a weight percent for each class. This is performed by multiplication of class percentage area by the specific gravity of the mineral represented by that class, *i.e.* galena=7.58, pyromorphite=7.04, cerussite=6.55 (Palache *et al.*, 1951) and then renormalising to 100%. For the unclassified and iron-rich classes, where density is unknown, the specific gravity is taken to be the mean of galena, pyromorphite and cerussite. These assumptions only introduce a minor error as specific gravities of the lead-bearing minerals considered are very similar.

The relative proportion by weight of each class of lead-bearing grains is summarised for all samples in Figure 6.7 and discussed below in Section 6.7.3(b).

(a) Classification scheme quality control

Analyses of the classification scheme standard, *SEM-STD*, (Appendix H) were performed in duplicate and gave mean values of 35.2 wt.% galena, 32.3 wt.% pyromorphite, 31.0 wt.% cerussite, 0.0 wt.% iron-rich and <2 wt.% unclassified. *SEM-STD* was formulated using equal masses of galena, pyromorphite and cerussite (Section 5.5.1(c)) so the correct values are 33.3 wt.% each. Thus, accuracy (deviation from correct value) is estimated at +5.7% for galena, -3.0% for pyromorphite and -6.9% for cerussite. Percentage differences between the duplicate analyses of *SEM-STD* are +/- 1.9% for galena, +/- 1.6% for pyromorphite and +/- 3.9% for cerussite. These reports of accuracy and precision are very good and suggests that the classification scheme delineates effectively between these classes (see also Figure 6.6). However, accuracy and precision calculations for the density separation standard and samples give higher errors.

The two density separation standards (*DS-STD1* and *DS-STD2*), gave average values of 40.7 wt.% galena, 23.8 wt.% pyromorphite, 35.3 wt.% cerussite and <0.5 wt.% unclassified. However, the standard was known to contain equal proportions of the three lead minerals (Section 5.4.4). The apparent overestimation of galena and cerussite (calculated to give 33.3 wt.%) is caused by a reduction in pyromorphite which is a result of the density separation technique. Although the class intervals in the *MIDAS* tables (Appendix H) are too large to show any difference in grain size, pyromorphite was observed to be friable and formed smaller grains than cerussite or pyromorphite. Thus, pyromorphite grains are likely to be less efficiently concentrated by the density separation technique than galena or cerussite grains. Evidence for this is afforded by the dominance of pyromorphite in the three low density (float) fractions analysed which gave 68.13 wt.% (*PWF937*) 58.56 wt.% (*OMS942*) and 55.34 wt.% (*88/015*) pyromorphite. All these samples are enriched in pyromorphite with respect to the high density fraction. Visual observation of SEM images suggested that pyromorphite was mostly held by aggregates with silicate minerals. Therefore, pyromorphite is preferentially retained in the low density soil fraction which tends to cause an underestimate of the amount of pyromorphite present in soils.

Precision estimates from *DS-STD* analyses are slightly worse than that of *SEM-STD*, giving $\pm 5.4\%$ for galena, $\pm 13.1\%$ for pyromorphite and $\pm 6.5\%$ for cerussite. Duplicate samples gave poor precision with averages of $\pm 41.0\%$ for galena, $\pm 29.7\%$ for pyromorphite and 11.0% for cerussite. This poor precision demonstrates the differences in managing "real" soils as opposed to artificially contaminated soils. Averages from duplicates are given in Figures 6.7 and 6.8.

The amount falling into the unclassified class was small for both standards and samples and most likely the result of unstable beam current during SEM analysis, or the presence of mixed-phase grains (*e.g.* those reported in Section 6.7.2).

(c) Classification

The following discussion on the classification of lead-bearing grains is centred on Figure 6.7 which expresses the proportion of each class as a weight percentage of total lead-bearing grains.

Pyromorphite accounts for a substantial proportion (between approximately 25 and 90 wt.%) of lead-bearing grains in all Winsters samples and also in the old industrial site soil, Derbyshire (approximately 80 wt.%). Pyromorphite is also present in significant amounts ($>5\%$) in motorway roadside soil (although this amount may be in error, see Section 6.6.3(b) and 6.7.1(c)) and London garden soils. Only trace amounts of pyromorphite ($<5\%$) were detected in Mendip mine-waste soils and the Derbyshire smelter site. Of the two Derbyshire mine-waste soils (*TF943* and *HF945*), only one (*TF943*) contained pyromorphite. The presence or absence of pyromorphite in samples according to the classification scheme is in broad agreement with the distribution described by quantitative analysis (Section 6.7.1).

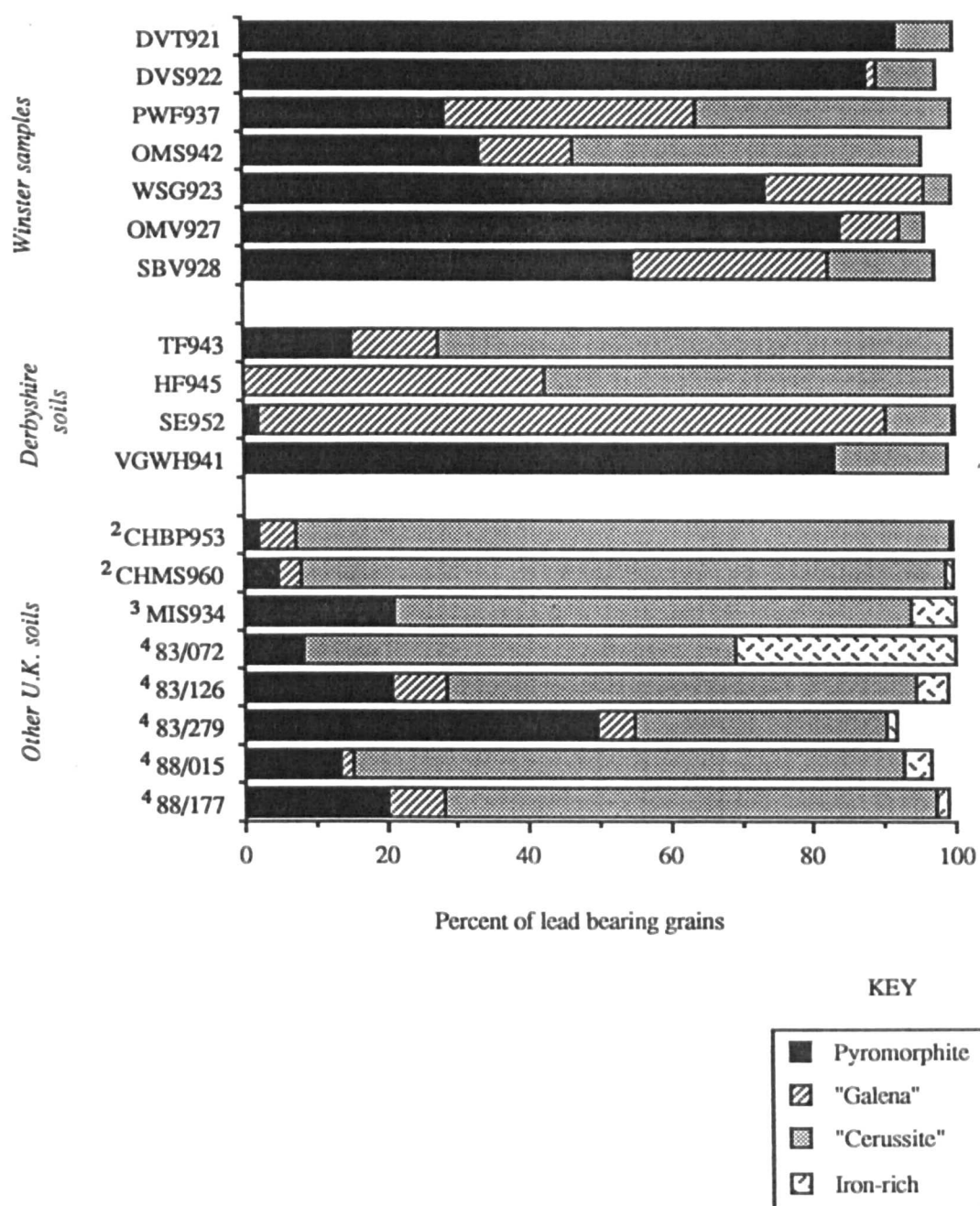


Figure 6.7 Classification of lead-bearing grains. The relative proportion by weight of each class is indicated. Unclassified grains are omitted but their proportion is indicated by non-convergence on 100%. ² Mendip soils; ³ Motorway roadside soil; ⁴ London garden soils.

Galena forms a significant proportion (5-30 wt.%) of all Winsters samples and the two Derbyshire mine-waste soils except for the topsoil and subsoil from Drummers Venture (*DVT921 and DVS922*) where it is present in very small amounts. "Galena" is also present in small amounts (approximately 5 wt.%) in Mendip mine-waste soils. This class could also include leadhillite, the lead mineral identified in Mendip soils by Mattigod *et al.* (1986; see Section 5.6.5(c)). The apparent galena in the smelter site sample (*SE952*) is in fact attributable to anglesite (see Figure 6.6) as discussed earlier in this section (Section 6.7.3). Similarly, "galena" present in soils other than those derived from mine-waste is more likely to be anglesite as this mineral has been identified in roadside and urban soils by other workers (Biggins and Harrison, 1980; Olson and Skogerboe, 1977; see Section 3.6.5(b)).

The "cerussite" class forms a substantial percentage of lead-bearing grains (>10 wt.%) dominating the solid phase of most samples. However, it must be remembered that, in non-mine soils especially, this class can represent several types of lead-bearing grains in addition to cerussite (see earlier in this Section and Section 5.5.2(c)). In the Winsters samples, cerussite does not generally dominate the solid phase; in samples *DVT921, DVS922, WSG923 and OMV927* it accounts for <10 wt.% of lead-bearing grains.

The **iron-rich** class is only of importance in the London soils with trace amounts occurring in the Mendip mine-waste soils. Of the London soils, sample *83/072* contains a relatively large amount (approximately 30 wt.%) of this class, which also has the lowest amount of pyromorphite present out of all the London garden soils.

6.8 Classification of Soil-lead

6.8.1 Calculation of Total Soil-lead Accounted for by Mineral Classes

From the percentage of lead reporting to the high density soil fraction (Section 6.6.3; Figure 6.2) and the classification of lead-bearing grains in this fraction (Section

6.7.3; Figure 6.7) it is possible to estimate the percentage of total soil-lead accounted for by the pyromorphite, galena, cerussite and iron-rich classes.

Firstly, the percentage by weight of lead-bearing grains accounted for by each class must be converted to a percentage of lead accounted for by each mineral class because

$$\begin{array}{l} \text{\% of lead held in solid phase} \\ \text{present as pyromorphite} \end{array} = \begin{array}{l} \text{Relative wt.\% of lead-bearing} \\ \text{grains present as pyromorphite} \end{array} \times \begin{array}{l} \text{Relative wt.\% of lead} \\ \text{in pyromorphite} \end{array}$$

and similarly for the galena, cerussite and iron-rich classes.

(Eq. 6.2)

This is achieved by multiplying the proportion of each class (calculated in Section 6.7.3) by the wt.% lead in the mineral represented by that class. The wt.% lead in each mineral is calculated from the empirical formula which gives: 86.6 wt.% (galena), 76.4 wt.% (pyromorphite) and 77.5 wt.% (cerussite). For unclassified and iron-rich grains, the wt.% lead is taken as the average of these three minerals which introduces only a minor error as the weight percentages of lead in the three minerals considered are very close. A further minor error is introduced by the substitution of calcium for lead in pyromorphite (see Table 6.6; Section 6.7.1) which may reduce the lead content of pyromorphite by up to 6 wt.%.

The wt.% lead pertaining to each mineral class is then multiplied by the percentage of total soil-lead reporting to the high density soil fraction (calculated in Section 6.6.3) in that sample to give the percentage of total soil-lead accounted for by the mineral classes, according to Equation 5.1 given in the introduction to the Solid Speciation Study in Chapter 5. This calculation assumes that all lead present in the high density soil fraction is held in the solid phase (see Section 6.6.2).

The proportion of total soil-lead accounted for by these mineral classes is shown for all samples in Figure 6.8 and discussed in Section 6.8.3.

6.8.2 Estimation of Error

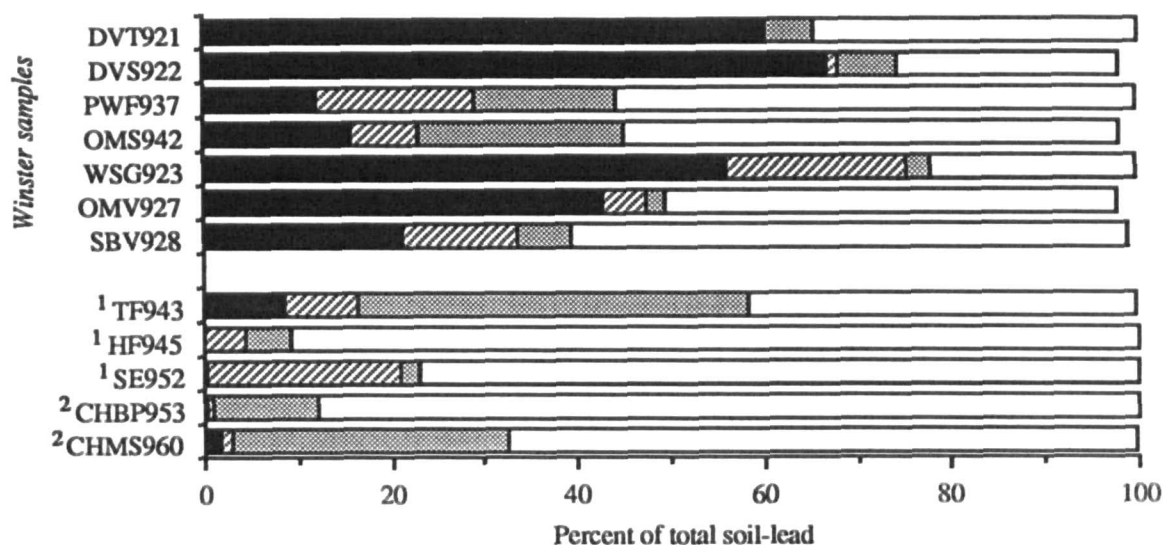
The error associated with the classification of soil-lead can be assessed from errors associated with the amount of lead in the density separates (Section 6.6.3) and the classification of lead-bearing grains (Section 6.7.3).

The average error for the amount of lead in the density separates is $\approx 20\%$, which itself is a cumulative error from the density separation procedure and ICPAES analysis. The classification of lead-bearing grains gave a duplicate sample precision of $\pm 30\%$ for pyromorphite. This value is taken to represent the error of the classification scheme, firstly because pyromorphite is the mineral of primary interest and secondly because this value is the approximate average of errors associated with galena, cerussite and pyromorphite classification. Classification of standards gave better precision but pyromorphite is calculated to be underestimated by approximately 5%.

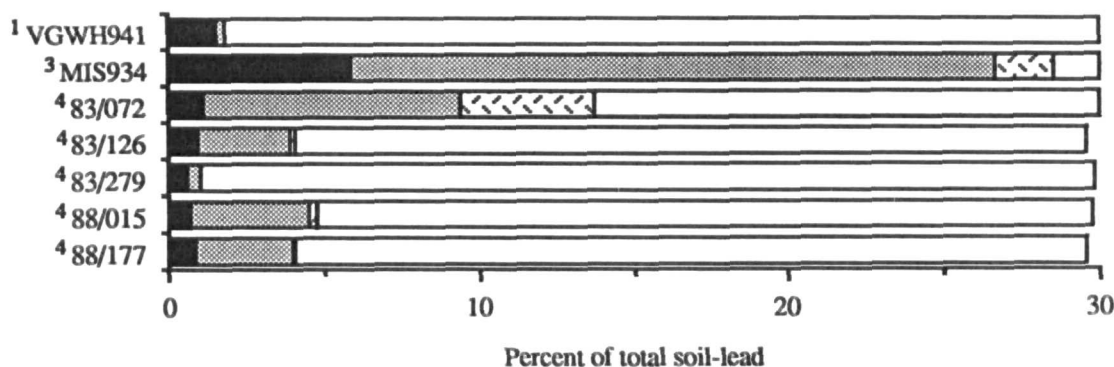
Adding the errors of lead distribution and classification of lead-bearing grains (as the calculation involves multiplication) gives an estimated error of $\pm 50\%$. The one duplicated sample (*OMS942 and OMS942D*) gave percentage differences of $\pm 44\%$ for galena, $\pm 12\%$ for pyromorphite and $\pm 43\%$ for cerussite in broad agreement with the calculated error estimate. Further errors are introduced because of the uncertainty surrounding the galena and cerussite classes and substitution of calcium for lead in pyromorphite, although these are minor errors in comparison to those from accuracy and precision.

Corroboration of the classification of soil-lead is afforded by calculation of the amount of phosphorus bound as pyromorphite. This is calculated from the wt.% ratio of phosphorus:lead in pyromorphite ($= 1:11.15$) multiplied by the amount of lead held as pyromorphite (using ΣPb). This gives the minimum amount of phosphorus that must be present in the high density fraction to form the estimated quantity of pyromorphite. In all cases the amount of phosphorus required was less than that reporting to the high density fraction (see Appendix G) indicating that sufficient quantities of phosphorus are present in this fraction. The presence of excess phosphorus in the high density fraction supports the suggestion that the reported proportion of pyromorphite is probably an underestimate although could represent a high density phosphorus (but not lead)-bearing mineral.

In summary, the classification of soil-lead is only semi-quantitative in nature, with an estimated error of $\pm 50\%$. In addition, pyromorphite is probably underestimated by this technique.



(a) Highly contaminated soils (>10,000 µg/g Pb)



(b) Moderately contaminated soils (<10,000 µg/g Pb)

KEY

	Lead held in other phases
	Solid phase - iron-rich
	Solid phase - "cerussite"
	Solid phase - "galena"
	Solid phase - pyromorphite

Figure 6.8 Classification of soil-lead. The relative proportions of total soil-lead accounted for by each class are indicated. In addition to the omission of unclassified grains, minor classes are omitted in these graphs: the iron-rich class is omitted in (a) and the galena (anglesite (?)) class in (b). The proportions of these classes (including unclassified grains) are indicated by the non-convergence on 100% in (a) and 30% in (b). Lead held in other phases includes solid material not reporting to the high density fraction, adsorbed, organic and aqueous phases. ¹ Derbyshire soils; ² Mendip soils; ³ Motorway roadside soil; ⁴ London garden soils. Note expanded scale in (b).

6.8.3 Classification

The classification of soil-lead is represented graphically in Figure 6.8. All the amounts of lead-bearing grains are lower than reported in Section 6.7.3 (Figure 6.7) because here the whole soil is considered as opposed to merely lead-bearing grains. The percentage of soil-lead accounted for by the solid phase is equivalent to the percentage of total soil-lead reporting to the high density soil fraction (Section 6.3.3) as it is this lead which is assumed to be held totally within the solid phase.

In the Winstar samples, **pyromorphite** accounts for a substantial proportion of soil-lead (up to >50% by weight). In other highly contaminated soil samples, pyromorphite does not account for a significant proportion (<5%) of soil-lead except for one Derbyshire mine-waste sample (*TF943*). In moderately contaminated soils, pyromorphite accounts for a minor amount of soil lead (<10%) even in samples *VGWH941* and *83/279* where pyromorphite forms a substantial proportion of lead-bearing grains. This is because of the small amounts of lead reporting to the high density fraction (Figure 6.2; Section 6.6.3).

Galena accounts for a significant fraction (>5%) of soil-lead in many of the Winstar mine-waste samples (*PWF937*, *OMS942*, *WSG923*, *OMV927* and *SBV928*) but is negligible in two Winstar mine-waste soils (*DVT921* and *DVS922*) where pyromorphite is dominant. "Galena" accounts for a significant proportion of soil-lead in the two Derbyshire mine-waste samples (*TF943* and *HF945*) but is negligible in the Mendip mine-waste soils (*CHBP953* and *CHMS960*) where cerussite is the dominant lead species in the solid-phase. In the smelter site sample (*SE952*), anglesite (classified as "galena") forms a considerable proportion of soil-lead. The "galena" (anglesite?) content of moderately contaminated soils was negligible (<5%).

"**Cerussite**" forms a significant but generally small proportion of soil-lead, although substantial proportions occur in some mine-waste soils. The **iron-rich** class forms a significant fraction of soil-lead only in some of the London garden soils.

6.9 XRD Analysis

Table 6.7 summarises the minerals identified in samples analysed by XRD technique as described in Section 5.5.3. XRD traces are presented in Appendix I together with residual traces after subtraction of identified minerals. The JCPDS trace of (synthetic) pyromorphite is presented with each of these resultant traces to allow comparison.

Table 6.7 Mineral identification by XRD for selected samples		
Sample	Minerals Identified	Presence of pyromorphite (Pb ₅ (PO ₄) ₃ Cl)? ¹
DVT921	Ba	Not detected
DVS922	Ba	Possible
PWF937	Ba, Cer, Gal(?)	Unlikely
OMS942	Ba, Cer	Possible
WSG923	Ba, Cer	Unlikely
OMV927	Ba, Cer, Gal(?)	Not detected
SBV928	Ba, Gal(?)	Not detected
SE952	Ang	--

Ba=Barite (BaSO₄), Cer=Cerussite (PbCO₃), Gal=Galena (PbS), Ang=Anglesite (PbSO₄), ?=not positively detected but listed by automatic identification programme

¹ Based on comparison of the 3 strongest lines from JCPDS pyromorphite (synthetic) trace with residual sample XRD trace after subtraction of major identified minerals (see Appendix I).

Minerals were identified using a search-match program based on the JCPDS mineral index file. Results were confirmed by visual identification of reflectance lines (see Appendix I). The dominant mineral in all samples was found to be barite (a gangue mineral associated with lead mineralisation) except in *SE952* where it was absent. Galena and cerussite were present in many of the Winstar samples although galena was not identified in *WSG923* or *OMS942* and cerussite was not detected in *SBV928*. However, the classification of soil-lead indicates that these minerals should have been present in detectable quantities in the high density fractions of these samples. No obvious explanation is available for the absence of these minerals except that the XRD reflections

that were detected were very weak and perhaps these minerals are bordering on the detection limit.

One of the most startling features of Table 6.7 is that pyromorphite was not positively identified in any samples despite its occurrence as a major lead-bearing phase in many of these samples (Figure 6.7; Section 6.7.3). Lead was present in substantial amounts in the high density separates and so any major lead-bearing mineral should be above the detection limit. Comparison of residual traces with the JCPDS pyromorphite trace suggests that pyromorphite may be present in some samples (see Table 6.7) but that non-detection is not caused by a shift of the pyromorphite pattern by the known calcium substitution for lead (see Section 6.7.1). The non detection of pyromorphite suggests that this compound is largely amorphous in these samples. Further evidence that pyromorphite is amorphous is afforded by the lack of any lead-bearing mineral in samples *DVT921* and *DVS922* where almost all of the lead-bearing grains consisted of pyromorphite (Figure 6.7). However, the mineral sample of pyromorphite gave a well defined trace (Appendix I) and was recognised as such by the automatic identification program.

Anglesite (PbSO_4) was the major component of lead-bearing grains in the smelter site soil (*SE952*). This was expected as pH of this soil is <6 (see Section 6.4.2). Under these conditions anglesite is theoretically predicted to be stable in the absence of phosphorus (see Figure 3.3; Section 3.6.2).

6.10 Summary

Household lead levels in Winstar have been shown to be significantly greater than those in the control village of Hartington. Older houses in the centre of Winstar contain the highest lead levels. Levels of lead on the hands of young Winstar children have been reported along with the blood lead concentrations of these children.

Pyromorphite has been shown to account for a considerable proportion of soil-lead in Winstar and is probably amorphous. Pyromorphite was not found in all highly contaminated samples, most of which are mine-waste. It has, however, also been identified

in London garden soils, motorway roadside soil and a soil from an old industrial site in Derbyshire. In these samples pyromorphite accounts for a negligible proportion of total soil-lead.

Lead compounds have been shown to alter in soils. Galena was observed to alter to cerussite in a mine-waste soil and a paint chip to pyromorphite in a London garden soil. The formation of pyromorphite in soils and its implications for the bioavailability of soil-lead to humans is discussed in the following chapter, Chapter 7.

CHAPTER 7: DISCUSSION

In this chapter the results of the Winsters Lead Study and the Solid Speciation study are discussed. The two studies are brought together in Section 7.4 where the influence of pyromorphite in on the bioavailability of soil-lead in Winsters is discussed.

7.1 Distribution of Lead in Winsters

A summary table of lead in environmental samples, handwipes and children's blood in Winsters and in environmental samples (comprising garden soil, housedust and lead loading) in Hartington is presented in Table 7.1 together with results from two similar U.K. studies.

7.1.1 Lead in Environmental Samples

From Table 7.1, it is evident that mean lead levels in all Winsters environmental samples are greatly elevated above averages reported in the U.K. National Survey (Culbard *et al.*, 1988) and the Birmingham Study (Davies *et al.*, 1990).

Mean values of lead loading, garden soil and housedust lead concentrations in Winsters have been shown to be significantly greater than those in the control village of Hartington (Section 6.2). Lead levels in Hartington are generally similar to or greater than those found in the Birmingham and National U.K. and Winsters lead levels are logically significantly greater than those in these other studies.

Table 7.1 Lead in environmental samples, handwipes and children's blood in Winster, Birmingham and a U.K. national survey									
	WINSTER (this study)		HARTINGTON (this study)		BIRMINGHAM STUDY (Davies <i>et al.</i> , 1990)		U.K. NATIONAL SURVEY (Culbard <i>et al.</i> , 1988) ¹		
	n	Geometric Mean	Range	n	Geometric Mean	Range ²	n	Geometric Mean	Range
Garden Soil (Pb µg/g)	42	7,140	2,370-23,800	5	631	197-1,660	4,126	266	13-14,100
Housedust (Pb µg/g)	45	1,560	462-6,240	5	302	143-587	4,638	561	5-36,900
Lead Loading ³ (Pb µg/m ²)	44	275	14.2-3,560	5	78.7	25.8-170		--	
Handwipes (Pb µg per pair of hands)	10	13.1	3.8-39.5		--			--	
Children's Blood	3	6.9	6.2-8.3		--			--	
(Pb µg/dl)	10	9.4	6.2-20.7		--			--	

¹ including London but excluding geochemical hotspots

² 5th and 95th percentile

³ Lead loading (µg/m²) = housedust lead concentration (µg/g) x dust loading (g/m²)

The mean concentration of lead in Winsters garden soil is greater than the national average by a factor of 27, whilst housedust is elevated by a factor of approximately 3. This extreme elevation of soil lead, to the point at which it is very much greater than that of housedust is typical of a "hotspot" situation and implies a major external source of contamination entering the home (Section 2.4.2(d)). In Winsters village, high lead concentrations ($>10,000 \mu\text{g/g}$) in garden soils are generally coincident with mineral veins and old spoil tips, mostly occurring in the older part of the village (Figs. 4.4 and 6.1(a); Table 6.2). Household lead levels are known to increase with house age (Section 2.4.2(c)) but house age could not solely account for the gross elevation of soil lead content. Thus, the primary source of elevated environmental lead levels in Winsters is geological mineralisation that has been brought to the surface by past mining activities.

7.1.2 Hand and Blood Lead

The geometric mean of lead on the hands of Winsters children is significantly greater at the 95% confidence level (Student's t-test) than the mean reported in the Birmingham study (Davies, 1989). The elevated amount of lead present on Winsters children's hands implies that the high environmental lead levels are transferred to the child by the soil-dust-hand (or soil-hand) route. Lead on the hands of children may then be inadvertently ingested by hand-to-mouth activity (Section 2.3.1).

The blood lead concentrations reported in the present study are lower than those reported in an earlier similar study by Barltrop *et al.* (1975; see Section 2.6.2)). This discrepancy reflects the decline in blood lead concentrations throughout the U.K. since the early 1970's (see Section 2.5). Comparison of children's blood lead concentrations between Winsters and Birmingham (Table 7.1) and those reported in Section 2.5.1 for urban and rural children indicate that blood lead concentrations in Winsters children may be considered elevated for a rural U.K. area but are comparable to those in urban areas. All Winsters blood lead concentrations fell below the recommended action level of $25 \mu\text{g/dl}$ (DoE and Welsh Office, 1982).

Thus, whilst significantly greater amounts of lead are present on Winsters children's hands compared to an urban situation, these elevated levels are not reflected in their blood

lead concentrations.

7.1.3 Soil, Housedust and Blood Lead Concentrations

In Section 2.5.3, quantitative models describing δ , the increment in blood lead concentration associated with an increase in soil or dust lead concentration were discussed. It is possible to calculate δ for Winsters by assuming base levels of soil, dust and blood lead concentrations for the U.K. Base dust and soil lead concentrations are assumed to be 500 and 300 $\mu\text{g/g}$ respectively (approximately that reported by Culbard *et al.*, 1988 and Davies *et al.*, 1990) and the base blood lead concentration is assumed to be 6.5 $\mu\text{g/dl}$ for children in rural areas (the approximate average of values reported by Strehlow and Barltrop, 1987; see Section 2.5.1). Winsters has G.M. dust $\approx 1,500 \mu\text{g/g}$ Pb, G.M. soil $\approx 7,000 \mu\text{g/g}$ Pb and G.M. children's blood $\approx 9.5 \mu\text{g/dl}$ (age 1-8 yr.).

These figures give values for δ of approximately 3 $\mu\text{g/dl}$ per 1000 $\mu\text{g/g}$ for dust and approximately 0.5 $\mu\text{g/dl}$ per 1000 $\mu\text{g/g}$ for soil. Reported median values of δ are 4 and 5 $\mu\text{g/dl}$ per 1000 $\mu\text{g/g}$ (see Section 2.5.1) which are slightly higher than the figure for housedust but an order of magnitude greater than the δ value for soil. The value of δ for housedust is thought to be more relevant to young children as much of their daily intake of lead is from this source (see Section 2.3).

If the mean concentration of lead in children's blood $\approx 6.9 \mu\text{g/dl}$ (age 1-3 yr.) is used to calculate δ then the value of δ for Winsters becomes even lower. However, the sample size of this group is extremely small and does not show the usual peak in blood lead concentration (see Section 6.3.2) so this group is not used in comparison with other U.K. data. In addition reported values of δ in the literature are based on a wide range of ages (see Section 2.5.3), more in keeping with the 1-8 yr. age group.

Predictions of blood lead concentrations in Winsters children (Cotter-Howells and Thornton, 1991), using models based on inner-city situations (*e.g.* Laxen *et al.*, 1987a; Davies *et al.*, 1990; Section 2.5.3), used a base blood concentration of 10 $\mu\text{g/dl}$ Pb which approximates to the average of reported values for inner-city areas. Whilst this assumption is not strictly valid as Winsters represents a rural situation, both lead loading and hand lead (indicators of children's exposure to lead; see Section 2.3.1) are elevated above that of the

Birmingham study and therefore blood lead concentrations are expected to be higher than those of an inner-city situation. However, because the assumed base blood lead concentration level is higher than the mean blood lead concentration actually found in Winsters children, all predictions using these models necessarily give higher values than those observed. For example, the multiple regression model for Edinburgh children of Laxen *et al.* (1987a) gives an expected blood lead concentration of 11.9 µg/dl and the response-curve of blood lead versus total exposure to dust and water lead (Laxen *et al.*, *op. cit.*) gives a predicted blood lead of 13.3 µg/dl for a dust lead concentration of 1,500 µg/g. The Birmingham regression model (Davies *et al.*, 1990) produces an increase in blood lead from 11.7 µg/dl (the geometric mean value for Birmingham) to 13.6 µg/dl if Winsters mean dust lead loading is inserted in the model.

7.1.4 Low Bioavailability of Soil-Lead in Winsters

The main reservoir of lead in Winsters village is soil which is highly contaminated with lead as a result of past mining activities. Soil transgresses into the home, raising the concentration of lead in housedusts. These high concentrations are transferred, in part, to the child by hand-to-mouth activity.

The value of δ (the increment in blood lead concentration associated with an increase in soil and housedust lead concentration) for housedust is lower than reported median values for the U.K. The value of δ for garden soil is extremely low, although garden soil may not represent the immediate source of lead exposure for young children. The low value of δ suggests a reduced bioavailability of soil-lead.

The contribution of the solid speciation of lead in Winsters soils (discussed in Sections 7.2.1 and 7.3) to a reduced bioavailability of soil-lead is considered in Section 7.4.

7.2 Solid Speciation of Lead in Soils

The results from the Solid Speciation Study are drawn together in this section and the origin of pyromorphite in Winster mine-waste soils deliberated. Most of the following discussion is centred around the classification of lead-bearing grains (shown in Fig. 6.7, Section 6.7.1) and of soil-lead (shown in Fig. 6.8, Section 6.8).

In all the soils studied a substantial proportion of total soil-lead is present in low density soil fraction (Section 6.6.3(b)), the majority of which is assumed to be non solid (see Section 6.6.2(a)). As noted in Section 6.6.3(b), Winster samples contain the greatest proportion of soil-lead in the solid phase (>40%), followed by other highly contaminated (>10,000 µg/g Pb) soils. Moderately contaminated soils generally contain a small percentage of soil-lead in the solid phase (<10%). Thus, whilst the composition of the solid phase of lead is important in this study, other soil phases (*e.g.* adsorbed) generally account for a greater proportion of total soil-lead. This is especially true of the moderately contaminated soils.

7.2.1 Winster Samples

Résumé

Pyromorphite accounts for a substantial proportion of total soil-lead (up to greater than 50%) and is the dominant lead mineral in most of these samples. Galena is present, accounting for a significant proportion of soil-lead (>5%) in all samples apart from two mine-waste soils which contain almost exclusively pyromorphite in the solid phase (see Section 6.7.3(b)). Cerussite generally accounts for a small amount of total soil-lead. The association of phosphorus with lead in the distribution of these elements between density separates (see Section 6.6.3; Figure 6.2) supports the observation that the solid phase of lead in these soils is dominated by pyromorphite.

SEM photographs of pyromorphite (Figure 6.3) indicate that this compound forms as discrete, homogeneous grains in mine-waste soils. The anhedral nature of these grains contrast greatly with the well developed crystal facets shown by pyromorphite from a

mineral vein (Cotter-Howells and Giddens, 1990). Pyromorphite in these soils is predominately amorphous, whereas the mineral sample from the study by (Cotter-Howells and Giddens, *op. cit.*) gave a strong X-ray diffraction pattern implying a crystalline substance (Section 6.9). Substantial amounts of calcium were present in most pyromorphite grains in the soil but extremely little was present in pyromorphite from the mineral vein (see Table 6.6, Section 6.7.1(c)). The substitution of calcium for lead is discussed below in Section 7.3.1(c).

Origin of pyromorphite in Winster soils

The origin of pyromorphite in Winster soils is not clear. Mineral veins in the area are near-surface (Section 4.2.1) and it is possible that the source of pyromorphite is the oxidised zone of these mineral veins. However, pyromorphite from mineral veins is crystalline and contains little calcium whilst that in soils is amorphous and contains substantial amounts of calcium, suggesting different modes of formation. Cerussite, also identified in Winster soils, is a well known oxidation product of galena (see Section 3.6.4) but, as with pyromorphite, it is difficult to distinguish between oxidation in the mineral vein and oxidation in the soil.

Galena, which was the major mineral mined in Winster, accounts for a relatively small proportion of soil-lead (much less than pyromorphite) but must have made up a substantial proportion of the pristine mine-waste. This suggests (although not conclusive) that galena has weathered in soils derived from mine-waste to form cerussite and pyromorphite.

Galena has been shown to alter (Fig. 6.4(a)) to cerussite in a Winster soil, which is considered an oxidising environment (see Section 4.4). Hence, this alteration represents the weathering of galena, an unstable lead compound under oxidising conditions (see Section 3.6.2). The Eh-pH diagram of Nriagu (1974; Fig. 3.4) shows that galena can oxidise directly to pyromorphite but no evidence of this reaction was observed in the present study. Cerussite is less thermodynamically stable than pyromorphite (one of the most thermodynamically stable lead compounds in soils, see Section 3.6.3; Fig. 3.4) so further reaction is possible. Thus, cerussite could represent an intermediate stage in the weathering sequence of galena to the final product of pyromorphite.

If pyromorphite is the end-product of the weathering sequence of galena in Winster

soils by virtue of its thermodynamic stability, then pyromorphite should also form as the end-product of the weathering of lead compounds in other soils, regardless of the original source of lead. The composition of the solid phase of lead in other soils from this study is discussed in the following sections. The presence or absence of pyromorphite in these soils (where sources of lead contamination other than mine-waste are present) determines whether or not pyromorphite forms in soils as a general weathering product of lead compounds and leads to a general discussion on the formation of pyromorphite in soils in Section 7.3.

7.2.2 Derbyshire Soils

(a) *Mine-waste soils*

In the Derbyshire mine-waste soil sample overlying dolomitised limestone (*TF943*; see Section 4.4.2), the solid phase of lead is dominated by cerussite (or hydrocerussite or lead oxide/hydroxide) with lesser amounts of galena and pyromorphite. The sample overlying undolomitised limestone (*HF945*; see Section 4.4.2) contains approximately equal quantities of galena and cerussite but no pyromorphite. The distribution of lead and phosphorus between density separates (Fig. 6.2; Section 6.6.3) is in broad agreement with these observations. However, the fact that some phosphorus is present in the high density fraction indicates an association with a heavy element but probably not with lead as no phosphorus-bearing lead grains are present in recognisable amounts.

Much of the Winster area overlies dolomitised limestone (see Section 4.2.1). The absence of pyromorphite in the sample overlying undolomitised limestone but presence in Winster and Derbyshire samples overlying dolomitised limestone could ^{indicate} that pyromorphite may have formed in the ore deposit by the action of dolomitic (phosphorus-rich?) waters and then incorporated into mine-waste soils. However, the presence of pyromorphite in soils overlying non-limestone geology (see Sections 7.2.2(c), 7.2.3(b) and (c)) indicates that geology is probably not a major control of pyromorphite formation in soils.

(b) Smelter site

The Stone Edge smelter site sample (SE952) contains considerable quantities of anglesite ($\approx 20\%$) with trace amounts of pyromorphite and minor amounts of "cerussite" (inverted commas indicate an uncertain composition, loosely defined as a lead-bearing compound with low-sulphur, low phosphorus and low iron (see Section 6.7.3; 5.5.2(c)). The distribution of lead and phosphorus between density separates supports these observations (see Fig. 6.2, Section 6.6.3).

Sulphates are one of the principal compounds emitted by lead smelters (Section 2.4.1). Anglesite may therefore have originally been emitted by the smelter and remained as anglesite because, in the absence of phosphorus it is thermodynamically stable (Garrels and Christ, 1965; Fig. 3.3, Section 3.6.2) at the pH of this soil ($< \text{pH } 6$; see Table 6.3, Section 6.4.2). Alternatively, anglesite could have formed in the soil from other lead compounds *e.g.* oxides or oxysulphates. However, it is clear that pyromorphite has not formed as a major weathering product of the lead smelter products.

The presence of anglesite in this sample confirms the suggestions of Elliot (1989) that the comparatively large amounts of lead in the exchangeable fraction of soils from this site was due to the presence of anglesite (see Section 3.2.3), a fairly soluble lead mineral (see Section 3.8.3; Table 3.2)

(c) Old industrial site

The solid phase in the old industrial site sample (VGWH941) accounts for a very small proportion of total soil-lead, but pyromorphite dominates this phase. The small percentages of lead and phosphorus in the high density soil fraction reflects the small proportion of soil-lead present as pyromorphite (Figure 6.2, Section 6.6.3).

Pyromorphite could represent the original source of lead in this soil (uncertain but probably paint; see Section 4.4.2) but this is unlikely as there is no major recorded use, past or present, of pyromorphite in the lead industry, except that phosphosilicates have been used in the lead paint industry (see Sections 2.1.1 and 2.2.1). It is more likely that pyromorphite has formed in this soil as a result of alteration of the original leaded paint source. SEM photographs suggest that some of the calcium-poor pyromorphite is secondary, perhaps forming in the cracks of calcium-rich pyromorphite. Calcium substitution for lead in pyromorphite is further discussed in Section 7.3.1(c).

"Cerussite" is also present in small quantities which may represent an intermediate weathering phase similar to that thought to exist in Winstar mine-waste soils or could reflect the remnants of the original source of lead *e.g.* paint.

7.2.3 Other U.K. Soils

(a) Mendip mine-waste soils

The solid lead phase in Mendip mine-waste soils is dominated by cerussite (or hydrocerussite or lead oxide/hydroxide). Negligible amounts of pyromorphite are present in *CHBP953* but small amounts appear to be present in *CHMS960* which is reflected by the substantial proportion of phosphorus present in the high density fraction of *CHMS960*. Pyromorphite was not identified by manual SEM inspection in either of these samples but may be present in small quantities.

Galena was the major mineral mined in this area and must have formed a substantial proportion of lead in the pristine mine-waste. However, the sulphur-bearing class (which could be galena, leadhillite or a mixture of both, see Section 6.7.3(c)) accounts for only a minor amount of the solid lead phase. If all this class is galena, then much of the galena must have weathered in the soil, similar to the situation in Winstar. This is in agreement with previous studies in the Mendip area (Mattigod *et al.*, 1986, Section 3.6.5). However, in this locality it is clear that galena has not been replaced by pyromorphite as the end product of the weathering sequence.

If the galena class is considered to be leadhillite, it could represent the mineral identified using XRD analysis by Mattigod *et al.* (1986) as a constituent of the solid-lead phase in soils from this area. However, this mineral only makes up a small proportion of lead in the solid phase and, as this was the only lead mineral identified by Mattigod *et al.* (*op. cit.*), it implies that the majority of solid lead is amorphous.

(b) Motorway roadside soil

The major lead-bearing solid phase in this sample is "cerussite" but considerable amounts of iron-rich and pyromorphite grains are present. The presence of the iron-rich grains is in accord with findings of sequential extraction techniques performed by several

authors (described in Section 3.2.3) who reported that this phase can be important and probably represents lead adsorbed onto, or co-precipitated with, iron oxides (see Section 3.4.1 and 3.6.1(a)). No sulphur-bearing lead grains were found in these soils, contrary to suggestions made by several authors that lead from vehicle emissions rapidly converts to lead sulphate (see Sections 2.4.1 and 3.6.5(b)).

Although pyromorphite does not dominate the solid phase of lead (and is thought to be affected by contamination (see Section 6.6.3(b) and 6.7.1(c)), it is undoubtedly present. SEM photographs (Figure 6.3, Section 6.7.1(c)) show that some pyromorphite is apparently deposited in small amounts on non lead-bearing minerals. This textural relationship is consistent with direct precipitation of pyromorphite from solution. The mode of formation of pyromorphite in roadside soils is discussed in Section 7.3.1(b).

(c) London garden soils

The solid phase forms a negligible proportion of total soil-lead in all London garden soils. This is reflected by the minor proportions of lead and phosphorus reporting to the high density soil fraction (Figure 6.2, Section 6.6.3).

The solid phase of lead is dominated by "cerussite" but considerable amounts of pyromorphite and "galena" (sulphur bearing lead grains) are present in all samples. Iron-rich lead grains are also found and in one sample, 83/072, account for a substantial proportion of the solid lead phase. Again this probably represents lead adsorbed onto or co-precipitated with iron oxides (see above and Sections 3.2.3, 3.4.1, 3.6.1(a)).

A paint chip(?) was shown to alter to pyromorphite in a London garden soil (Fig. 6.5, Section 6.7.2), providing irrefutable evidence that pyromorphite does form in soils as an alteration product of less stable lead compounds. Therefore, in the absence of any extraneous source of pyromorphite, it is likely that pyromorphite present in the London soil samples actually formed in the soil. SEM photographs show that pyromorphite generally forms incoherent, botryoidal grains in contrast to the discrete, homogeneous grains observed in Derbyshire mine-waste and old industrial site soils. This may suggest that the grains in London soils are relatively immature.

In one sample (83/279), pyromorphite dominated the solid lead-bearing phase. This could reflect a source of lead that is very unstable or soluble and weathers easily, or the composition of that particular soil influenced the kinetics of pyromorphite formation (see

Section 7.3.1).

In this study, the "galena" or, more likely, anglesite (Section 6.7.3(c)) found in London soil samples accounts for a very small (negligible) proportion of total soil-lead in agreement with the findings of Olson and Skogerboe (1975) and Biggins and Harrison (1980). These authors concluded from XRD analysis that anglesite was the most important crystalline lead-bearing mineral but in this study, other non-sulphur bearing forms of solid lead were more important than anglesite. Their non-recognition by these previous studies suggests that the majority of solid lead in soils is non-crystalline.

Summary

From the discussion above, it is clear that pyromorphite is present in soils other than those derived from lead mine-waste and has been observed to form in these non-mine-waste soils. This supports the hypothesis that the large quantities of pyromorphite found in Winster mine-waste soils have formed in the soil, although a contribution from the oxidised zone of the ore deposit cannot be ruled out.

7.3 Formation of Pyromorphite in Soils

In Chapter 3 (Sections 3.6 and 3.7), the formation of lead phosphates in soils was discussed: studies by Nriagu (1974, 1984) concluded that two lead phosphates, pyromorphite and plumbogummite were amongst the most stable lead compounds in oxidising environments and that their formation in soils was possible (Section 3.6.3). However, no conclusive observation of these compounds has been reported in the literature (Section 3.6.5).

The results from the Solid Speciation Study are now addressed in terms of the genesis of pyromorphite in soils and the identification of this mineral.

7.3.1 Genesis of Pyromorphite

Soil-lead from various origins has been shown to weather to one of the lead phosphates, pyromorphite, predicted to form in soils by Nriagu (1974, 1984). The formation of pyromorphite in soils is regarded as a weathering or alteration process in which lead enters into a more thermodynamically stable phase. However, pyromorphite does not form in all soils and plumbogummite was not identified in any of the soils in the present study.

(a) Equilibrium and kinetic considerations

The amount of pyromorphite in soils is apparently influenced by the length of time since contamination and total lead concentration. The greatest amounts of pyromorphite are found in soils where high concentrations of lead ($>10,000 \mu\text{g/g}$) have been present for a long period of time (>200 years) *e.g.* mine-waste soils. In a single sample where moderate concentrations of lead ($\approx 2,700 \mu\text{g/g}$) have been present for a long period *i.e.* VGWH941, only a small proportion of lead is present in the solid phase but this is dominated by pyromorphite. The lowest amounts of pyromorphite were found in London soils where generally moderate concentrations ($2,000$ - $6,500 \mu\text{g/g Pb}$, with one sample containing $\approx 12,500 \mu\text{g/g Pb}$) of lead have been present for 70-120 years.

One sample, the motorway roadside soil (MIS934), did not conform to the above pattern as relatively low ($\approx 600 \mu\text{g/g}$) concentrations of lead have been present in this soil only ≈ 30 years, yet comparatively large amounts of pyromorphite are present. However, it is thought that the quantitative estimate of the solid phase in this soil (and therefore the amount of pyromorphite) may be in error (see Section 6.6.3(b) and 6.7.1(c)). The formation of pyromorphite in this sample is discussed separately in Section 7.3.1(b).

The distribution of pyromorphite amongst the soils in the present study suggests that total soil-lead concentration and residence time act as two independent variables; total soil-lead concentration influencing the proportion of total soil-lead present in the solid phase and residence time increasing the percentage of the lead-bearing solid phase present as pyromorphite.

Lead compounds weather in soils by chemical reactions which tend towards equilibrium (*i.e.* minimising free energy). Whilst soils never actually reach equilibrium

(Lindsay, 1979; Section 3.7.3), lead compounds in historically contaminated soils have had a longer period of time in which to progress towards equilibrium. The dominance of pyromorphite in the solid phase of some of these historically contaminated soils suggests that equilibrium within the lead-bearing solid phase lies strongly in favour of pyromorphite, in keeping with thermodynamic predictions (Section 3.6.5). However, it would appear that it takes 10's to 100's of years for pyromorphite to form in quantities such that it accounts for a significant proportion of the lead-bearing solid phase. This is in accordance with slow kinetics of mineral formation in soils as suggested in Section 3.7.3 and implies that pyromorphite formation is unlikely to be observed on the time scale of adsorption experiments (see Sections 3.4.3 and 3.7.1). Soil factors such as grain size, amount of organic matter present *etc.* may affect kinetics of mineral formation.

Complete equilibrium in the soil involves the partitioning of lead between all soil phases (diagrammatically illustrated in Figure 3.5, Section 3.7.3). From this study, it is not possible to quantitatively or qualitatively estimate the equilibrium position between pyromorphite and non-solid lead phases *e.g.* adsorbed, organic. It is only possible to state that the proportion of total soil-lead present in the solid phase appears to be dependent on total soil-lead concentration (see above), suggesting that the solid phase acts as a reservoir for excess soil-lead that cannot be held in other soil phases *e.g.* soil solution, adsorbed, chelated because they have become saturated. Hence, pyromorphite may never account for significant proportions of total soil-lead, even with a long residence time, if total soil-lead concentration is moderate or low (*e.g.* London garden soils). More information on soil parameters would allow quantitative predictions to be made concerning the equilibrium partitioning of lead between the adsorbed, aqueous and solid lead species using computational chemical equilibrium models such as *SOILCHEM* as described in Section 3.7.2.

(b) Formation of pyromorphite in motorway roadside soil

Nriagu (1974, 1984) and Rickard and Nriagu (1978) discussed at length the formation of lead phosphates in soils from the transformation of lead-rich automobile emissions ~~at length~~ (see Section 3.7.5). However, Olson and Skogerboe (1975) and Biggins and Harrison (1980) identified lead sulphates as the major crystalline component of roadside soils. It was inferred in Section 3.7.5 that soluble lead compounds from

vehicle emissions convert rapidly to sulphates (possibly in the atmosphere) which may then weather further to pyromorphite in the soil. This reaction sequence is analogous to the suggestion that pyromorphite forms as the end product of the weathering sequence of galena (Section 7.2.1).

Pyromorphite is present in a motorway roadside soil (although quantities are uncertain) where the major source of lead is soluble vehicle emissions (see Section 7.2.3(b)). The apparent absence of pyromorphite in the studies performed by Olson and Skogerboe (1977) and Biggins and Harrison (1980) is discussed in Section 7.3.3. No sulphur-bearing grains were identified in this soil but "cerussite" and iron-rich grains are present. These lead-bearing grains may represent intermediate compounds in the weathering sequence of lead compounds emitted by vehicle emissions to pyromorphite. SEM photographs suggest that at least some pyromorphite has formed by precipitation from solution rather than *in situ* replacement of less stable lead compounds (Section 7.2.3). This observation implies that it is possible for pyromorphite to precipitate from solutions containing lead from vehicle emissions.

Hence, no evidence of a weathering sequence to pyromorphite via lead sulphates has been observed in the present study but it is possible that lead from vehicle emissions either precipitates as pyromorphite from solution or weathers to pyromorphite via cerussite (or a related compound) and/or an iron-rich phase. However, this discussion is based on only one sample which may be different from roadside soils in which sulphates have been identified (*e.g.* Olson and Skogerboe, 1977; Biggins and Harrison, 1980). Investigation of the solid speciation of lead in a comprehensive set of roadside samples would enable a more in-depth discussion on the weathering of lead from vehicle emissions in roadside soils.

(c) Composition of pyromorphite

Rickard and Nriagu (1978) and Nriagu (1984) predicted that pyromorphite formed in soils would be unlikely to be a pure end member of the pyromorphite series but would probably contain a limited amount of calcium substituting for lead (see Section 3.6.4(a)). Pyromorphite identified in soils in the present study substantiates these predictions as the majority of grains contain small amounts of calcium (up to a Pb:Ca ratio 2.2:1) although the amounts of calcium vary both between grains and within grains (see Figure 6.3,

Section 6.7.1).

Although no reason was given by the above authors for the presence of calcium in pyromorphite, an optimum substitution ratio of calcium for lead could reflect a minimum in the free energy of formation (ΔG°_f). The variation in calcium concentration is curious and could possibly reflect different conditions of formation *e.g.* fluctuations in $\{\text{Ca}^{2+}\}$ in the soil solution. However, these suggestions are speculative and detailed thermodynamic studies would have to be undertaken in order to fully explain the substitution of calcium for lead in pyromorphite.

(d) Absence of pyromorphite in certain soils

Pyromorphite does not form in all soils. None (or very little) is present in the Derbyshire mine-waste soil overlying undolomitised limestone (*HF945*), the smelter site sample (*SE952*) and the Mendip mine-waste samples (*CHBP953 and CHMS960*). The reason for the absence of pyromorphite is unclear. These soils have been contaminated with lead for approximately 200 years, the same time period within which considerable quantities of pyromorphite have formed in other soils *e.g.* Winster mine-waste soils. The pH of these soils are within the pyromorphite stability field (Nriagu, 1974; Figure 3.4) and are all considered oxidising. The ΣP content of all these soils (Table 6.3) is considerable and no lower than that of other soils where pyromorphite forms a substantial proportion of the solid phase.

Thermodynamic predictions of pyromorphite formation in soils have proved correct in many cases (see above) and so are considered reliable. In Section 3.7.6 it was concluded that lead phosphates may not form in soils, although thermodynamically predicted because either elemental activities in solution are too low for the precipitation of lead phosphates or soil kinetics prevents their formation.

It may be possible that $\{\text{HPO}_4^{2-}\}$ or $\{\text{H}_2\text{PO}_4^-\}$ in the soil solution could limit pyromorphite formation. In Section 3.7.4, the solubilities of lead phosphates were discussed and the minimum activity of phosphorus necessary to form pyromorphite constrained. The activity of an element in solution is not necessarily determined by the total concentration in the soil as it depends on many different factors *e.g.* solubility of the solid phase in equilibrium with the soil. If soil factors were such that the activity of phosphorus in the soil solution was low, below the critical amount defined by

pyromorphite solubility equilibria, then pyromorphite would not form.

If {P} were sufficiently high for pyromorphite to form, pyromorphite would not be present if the kinetics of formation are extremely slow (*i.e.* of the order of 1,000's to 10,000's of years). There is extremely little information available on factors affecting the kinetics of mineral formation, both from this study and elsewhere in the literature (see Section 3.7.3). However, it is possible that some soil factor *e.g.* grain size or organic matter content is different in the above mentioned soils to other soils in this study (where pyromorphite has formed), retarding pyromorphite formation to the point where it forms only on geological time scales.

Whilst phosphate activities and factors affecting phosphate activities in the soil solution and factors affecting the kinetics of pyromorphite formation in soils are beyond the scope of this study, these two theories provide possible explanations for the absence of pyromorphite in the above soils.

7.3.2 Non-formation of Plumbogummite

Plumbogummite has been predicted to form in soils and is slightly more thermodynamically stable than pyromorphite (Nriagu, 1974, 1984; Section 3.6.3, 3.7.5). However, this mineral is not present in any of the soils studied, even where pyromorphite is absent. There are two possible explanations for the lack of plumbogummite in soils: conditions may favour the formation of pyromorphite over plumbogummite or pyromorphite is, in fact, more thermodynamically stable with respect to plumbogummite and so forms preferentially in soils.

Soil conditions which favour pyromorphite formation over plumbogummite are high lead, low phosphorus and low aluminium concentrations in the soil solution and pH <6 or 7 (see Section 3.6.3). The soils in the present study in which pyromorphite was present cover a range of conditions but most have high pH and high ΣP (although this does not necessarily imply a high concentration in the soil solution) which would be expected to favour plumbogummite formation.

ΔG°_f of plumbogummite has been estimated using a model whereas that for pyromorphite was experimentally determined (Nriagu, 1973, 1974; Section 3.6.3). The

difference between ΔG°_f for plumbogummite and pyromorphite is small so a slight inaccuracy in the model could cause the ΔG°_f for plumbogummite to be erroneously raised to a more negative value than that of pyromorphite, thereby indicating a greater stability (see Section 3.6.3). If this was the case then pyromorphite would be expected to be more stable than plumbogummite and form under the majority of solute activities, Eh and pH conditions. This provides a plausible explanation for the complete absence of plumbogummite in these soils.

7.3.3 Identification of Pyromorphite

In Section 3.6.5(d) it was concluded from the literature that there has been no conclusive identification of lead phosphates in soils previous to this study. The analytical techniques used in these previous studies and the present study are discussed here as they are of importance to the recognition of the pyromorphite mineral.

Many solid speciation studies, including the present study have used density separations to preconcentrate lead-bearing grains from the soil (see Section 3.6.5(a) and 5.4). However, most previous studies used XRD analysis on the high density fraction to determine the solid speciation of lead-bearing grains *e.g.* Olson and Skogerboe (1977), Biggins and Harrison (1980), Mattigod *et al.* (1986) (see Sections 3.6.5(b) and (c)), whereas in this study an automated SEM/EDX technique was employed (Section 5.5.2(c)). It has been shown that pyromorphite is amorphous in Winster soils (Section 6.9 and 7.2.1) which suggests that where present in other soils, it may also be amorphous. Amorphous substances cannot be readily detected by XRD so these previous studies would not have been able to identify pyromorphite, even if it was present in substantial amounts. In contrast, the SEM/EDX technique used in this study can detect and analyse amorphous materials.

It could be argued that pyromorphite is not present in the soils analysed in these previous studies, as pyromorphite is not present in all soils. Indeed, this may be true of the study by Mattigod *et al.* (1986) who studied soils from the Mendips, a region where pyromorphite was not found in the present study. Also, Olson and Skogerboe (1977) conducted their study in the United States where soils may be very different to those

encountered in the United Kingdom and may not contain pyromorphite. However, Biggins and Harrison (1980) studied U.K. urban soils, similar to the London garden soils in this study which did contain small amounts of pyromorphite.

Furthermore, the results from this study suggest that the majority of solid lead in soils is amorphous, even where pyromorphite is absent or present in small quantities (Sections 7.2.(a) and (c)). Indeed, Olson and Skogerboe (1977) and Biggins and Harrison (1980) suggested that only 50% of the lead present in the preconcentrated fraction could be accounted for by the XRD technique. This would imply that XRD is not a suitable method of analysis for studying the solid speciation of lead in soils.

Previous studies which have used SEM/EDX methods *e.g.* Linton *et al.* (1980) (Section 3.6.5(b)) have relied on manual searching methods to locate lead-bearing grains. If pyromorphite is present in small quantities, it may not be observed. The automated approach to location of lead-bearing grains used in this study (Section 5.5.2(c)) meant that large areas of sample could be scanned, analysing many lead-bearing grains and therefore increasing the likelihood of locating pyromorphite grains (if present).

In summary, pyromorphite has not been identified in previous solid speciation studies, although it may be present, because these studies have relied on XRD techniques which are not suitable for the analysis of lead-bearing grains in soils. An automated SEM/EDX technique, such as that used in the present study, provides the best method of identifying pyromorphite. A more sophisticated classification scheme for the SEM/EDX information (see Section 5.5.2(c)) would enhance the resolution of this method enabling it to become a powerful tool in the study of the solid speciation of lead in soils.

7.4 Influence of Pyromorphite on the Bioavailability of Soil-Lead in Winster

The low value of δ for housedust and soil determined for the situation in Winster village implies a reduced bioavailability of soil-lead (Section 7.1.4).

In Section 3.8 the influence of lead minerals on the bioavailability of soil-lead was discussed. Pyromorphite was shown to have an extremely low solubility in acid and neutral environments, lower than that of other soil-lead minerals (Table 3.2, Section 3.8.3). The solubility of lead minerals in water (neutral environments) was considered to influence the bioavailability of soil-lead to plants, whilst acid solubility of lead minerals was assumed to influence bioavailability to humans.

Although the bioavailability of lead to humans depends on many factors (Section 3.8.2), the substantial amounts of pyromorphite ~~are~~ present in Winster soils (up to >50% of total soil-lead by weight; Figure 6.8, Section 6.8.3; Section 3.7.1) would contribute considerably to a reduced bioavailability of soil-lead. Hence, the solid speciation of lead in Winster soils contributes to blood lead concentrations of Winster children falling within normal U.K. ranges despite very high concentrations of lead in the soil (up to 25,000 $\mu\text{g/g}$) and evidence that these high concentrations are transferred to the child via the soil-dust-hand-mouth route.

Whilst the bioavailability of soil-lead to plants is beyond the scope of this study, the presence of substantial quantities of pyromorphite in these soils could influence the uptake of lead into plants as the low solubility of this mineral would reduce the amount of lead present in the soil solution where plants obtain most of their nutrients (Section 3.8.1).

There is much evidence in the literature to suggest that lead phosphates reduce the bioavailability of lead to both plants and humans in many different ways. For example, lead phosphate deposits in corn roots prevent the translocation of lead into aerial parts of the plant (Sections 3.8.1 and 3.8.3(a)) and precipitation of lead with a calcium phosphate inside the human body reduces the uptake of lead into the bloodstream (Section 3.8.2 and 3.8.3(b)). The formation of lead phosphates effectively immobilizes lead resulting in a low bioavailability.

Pyromorphite has been shown to form in many different types of soils although its rate of formation is slow (Section 7.3.1(a)). Therefore, it is probable that residence time reduces the bioavailability of soil-lead, although there may be a limit to the extent of pyromorphite formation (see Section 7.3.1(a)). The formation of an insoluble mineral which immobilizes a toxic element reducing its harmfulness can be seen as a corollary of the Gaia theory (Lovelock, 1982, 1989) where the Earth is a self-regulating system with the ability via physical, chemical and biological evolution to determine optimum conditions for the living biota.

However, the time factor involved suggests that 10's to 100's of years would have to pass since contamination before any reduction in bioavailability became apparent *i.e.* that pyromorphite formation occurs closer to a geological rather than a human time scale. Furthermore, if soil is not highly contaminated ($>10,000 \mu\text{g/g Pb}$) then pyromorphite may form only a very small part of total soil-lead.

CHAPTER 8: CONCLUSION

8.1 Conclusions

Lead levels in garden soil, housedust and on the hands of young children in the village of Winstar are raised above those of a typical urban situation as a result of historic lead mining practices. The mean concentration of lead in garden soils is approximately 30 times higher than a U.K. national average reflecting contamination by mine-waste. Although high soil-lead concentrations are transferred to the child via the soil-dust-hand-mouth pathway, blood lead levels are within the normal U.K. range. The calculated value of δ for housedust is lower than predicted in other studies and that for garden soil is extremely low suggesting a reduced bioavailability of soil-lead.

Pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) accounts for a substantial amount (up to over 50%) of the lead in soils from this vicinity. This compound has an extremely low acid solubility, lower than that of other common lead minerals and hence would contribute to a reduced bioavailability of soil-lead. Thus, the unexceptional blood lead concentrations found in children living in the mining village, despite evidence of an elevated intake of lead, are a result of the abundance of pyromorphite in the soil.

Pyromorphite is a stable soil-lead mineral and is believed to have formed in these mine-waste soils as the end-product of the weathering sequence of galena, in accordance with thermodynamic predictions. Pyromorphite is also considered to have formed in a number of soils from different areas of the U.K. These reflect different sources of lead contamination, including London garden soils, motorway roadside soil and soil from an old industrial site. Pyromorphite is present but accounts for only a small percentage (generally >5%) of total soil-lead. Commonly, pyromorphite forms containing up to 8 wt.% calcium substituting for lead which may represent a minimum in the free energy of formation, ΔG°_f .

The kinetics of pyromorphite formation are slow. It is thought that at equilibrium, pyromorphite dominates the solid phase but takes 10's to 100's of years to form in

substantial amounts. Also, the amount of lead held in the solid phase is dependent on total lead concentration. Therefore, substantial amounts of pyromorphite are present in soils from Winstar which are highly contaminated by historic mining activities but only small amounts are present in other U.K. soils as they are only moderately contaminated, even though lead may have been resident in the soil for some considerable time.

Pyromorphite has not been previously identified in soils. Pyromorphite was found to be amorphous in Winstar soils so cannot be identified by XRD techniques as used by many authors to study solid speciation of lead in soils. In contrast, the SEM/EDX techniques used in this study can detect and analyse amorphous materials.

However, pyromorphite was not present in some soils, even where large amounts of lead have been resident for a long period of time *e.g.* Mendip mine-waste soil. This suggests that geochemical or kinetic factors are capable of inhibiting its formation.

8.2 Recommendations for Further Work

One of the most interesting areas requiring further study is the determination of soil factors which influence pyromorphite formation. Studies on lead and phosphate activities in soil solutions from soils where pyromorphite is not present will determine if geochemical factors are capable of controlling pyromorphite formation. A study of other soil parameters *e.g.* grain size, organic matter may provide information on kinetic controls of pyromorphite formation and would also allow quantitative predictions to be made concerning the equilibrium partitioning of lead between the adsorbed, aqueous and solid lead species using computational chemical equilibrium models such as *SOILCHEM*.

In addition, a thermodynamic study of the variation in ΔG°_f of pyromorphite with calcium content would determine if there is an optimum substitution ratio of Pb:Ca. A mechanism of reaction for the weathering sequence of lead compounds to the end-product of pyromorphite would lead to a greater understanding of pyromorphite formation. This would be of special interest in roadside soils.

Laboratory experiments, simulating precipitation of pyromorphite in the soil environment would yield considerable information on the factors influencing or constraining its formation. Theoretically, a solution containing lead, phosphorus and chlorine in suitable proportions would precipitate pyromorphite. A suite of test-tube experiments involving the mixing of aqueous solutions containing lead, phosphorus and chlorine in varying concentrations would enable critical concentrations of these elements necessary for the formation of a lead phosphate precipitate. Analysis of the precipitate by SEM/EDX would determine if a pyromorphite composition was obtained and also allow a study of the morphology of the compound formed.

An extension of this experiment could be to introduce individual soil components *e.g.* clay or organic matter to determine whether these components inhibit or favour solid phase formation. Solutions could be left for periods of time from a few hours to several months to gain information on the kinetics of pyromorphite formation. This type of experiment has great potential to increase the understanding of solid phase formation in soils.

Pyromorphite would compete for phosphorus with other phosphorus minerals and phases. Therefore, the geochemistry of phosphorus in soils needs to be addressed in order to understand further the constraints of pyromorphite formation. To determine if pyromorphite could compete successfully with other phosphorus minerals for phosphorus, the relative stability of phosphorus soil minerals to pyromorphite could be investigated using a thermodynamic approach similar to that described by Lindsay (1979). The availability of phosphorus for solid phase formation could be measured in soils using chemical extraction techniques. This approach may enable geochemical constraints on the formation of pyromorphite to be identified.

In this study, pyromorphite was not observed to form from the weathering of cerussite in mine-waste soils. This may simply be because such a grain was not observed or could indicate a mode of formation other than that of *in situ* weathering in soils. Further investigation of individual lead-bearing grains in soils contaminated by mine-waste using SEM/EDX may lead to the observation of a mixed, weathering grain of cerussite. If not then an alternative mechanism for the formation of pyromorphite in mine-waste soils must be sought.

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APPENDIX A: CLASSIFICATION SCHEME FOR LEAD BEARING GRAINS

A1: Operating Conditions for the SEM-EDX

Accelerating voltage (kV)	25
Current (nA)	2
No. of grid points per line	1024
Area min. (grid points)	10
Area max. (grid points)	no limit
EDX: dwell time per feature (mS)	2000

A2: DIGISCAN/FDC Window File

eV per channel = 20

No. of x-ray windows = 19

WINDOW # 1:E1 (eV) = 1180,	E2 (eV) = 1340
WINDOW # 2:E1 (eV) = 1400,	E2 (eV) = 1560
WINDOW # 3:E1 (eV) = 1660,	E2 (eV) = 1820
WINDOW # 4:E1 (eV) = 1940,	E2 (eV) = 1820
WINDOW # 5:E1 (eV) = 1940,	E2 (eV) = 2100
WINDOW # 6:E1 (eV) = 2220,	E2 (eV) = 2380
WINDOW # 7:E1 (eV) = 2540,	E2 (eV) = 2700
WINDOW # 8:E1 (eV) = 3060,	E2 (eV) = 3220
WINDOW # 9:E1 (eV) = 3240,	E2 (eV) = 3400
WINDOW #10:E1 (eV) = 3600,	E2 (eV) = 3760
WINDOW #11:E1 (eV) = 4140,	E2 (eV) = 4300
WINDOW #12:E1 (eV) = 4420,	E2 (eV) = 4580
WINDOW #13:E1 (eV) = 4080,	E2 (eV) = 5240
WINDOW #14:E1 (eV) = 5820,	E2 (eV) = 5740
WINDOW #15:E1 (eV) = 6320,	E2 (eV) = 6480
WINDOW #16:E1 (eV) = 8080,	E2 (eV) = 8240
WINDOW #17:E1 (eV) = 8560,	E2 (eV) = 8720
WINDOW #18:E1 (eV) = 9880,	E2 (eV) = 10040
WINDOW #19:E1 (eV) = 10460,	E2 (eV) = 10620

A3: MIDAS Window File

Background corrections were made from the analysis of galena (PbS), except for lead and sulphur which were corrected using the analysis of nickel, which gives a spectrum shape similar to Pb-bearing minerals due to its high atomic number. The only significant overlap is between the Pb-M α^1 and S-K α^1 lines. Pb was analysed on the L α^1 -line as S-K α^1 corrected for Pb from the analysis of cerussite (PbCO₃).

Element	Element window	Background correction		Overlap correction	
		Window	Scaling factor	Window	Scaling factor
Mg	1	10	0.8947	0	0.0000
Al	2	10	1.3666	0	0.0000
Si	3	10	2.6323	0	0.0000
P	4	10	2.8857	0	0.0000
S	5	10	2.8320	19	4.1950
Cl	6	10	2.8257	0	0.0000
Cd	7	10	1.2487	0	0.0000
K	8	10	1.0038	0	0.0000
Ca	9	10	1.0321	0	0.0000
Ti	11	10	1.0033	0	0.0000
Ba	12	13	4.9246	0	0.0000
Mn	14	13	0.9795	0	0.0000
Fe	15	13	0.9340	0	0.0000
Zn	17	16	0.9398	0	0.0000
Pb	19	18	0.9878	0	0.0000

A4: MIDAS Classification Scheme

CLASS 1: GALENA

Pb	5.00	150.00
S	15.00	150.00
P	-100.00	10.00

CLASS 2: PYROMORPHITE

Pb	5.00	150.00
S	-350.00	15.00
P	10.00	100.00

CLASS 3: CERUSSITE

Pb	5.00	150.00
S	-350.00	15.00
P	-100.00	10.00

CLASS 4: IRON-RICH

Pb	5.00	150.00
S	-350.00	15.00
P	-100.00	10.00
Fe	20.00	100.00

APPENDIX B: WINSTER LEAD STUDY - ANALYTICAL QUALITY CONTROL

Reagent blanks, reference materials and duplicates are included in analysis to monitor the exactness of determinations. Blank determinations allow for the presence of the analyte in the reagents used; reference materials determine the accuracy (bias) of determinations and sample duplicates determine precision (reproducibility).

$$\text{Percentage deviation from accepted value} = \frac{\text{difference between obtained and accepted value}}{\text{accepted value}} \times 100\%$$

$$\text{Percentage difference between duplicate samples} = \frac{\text{difference between duplicates}}{\text{arithmetic mean of duplicates}} \times 100\%$$

Soils and Housedusts

Although analysis of samples was performed in three batches, inspection of reference material and duplicate analysis showed little variation between batches. Therefore, these analyses are pooled to give an overall estimate of analytical exactness. All reagent blanks contained lead concentrations below the detection limit of the instrument.

B1 House Soil Reference Materials				
	n	Mean (µg/g Pb)	v ¹	Percentage deviation of mean from accepted value
HRM1 (accepted value = 13.00 µg/g Pb)	12	14.9	18.6	+14.6
HRM2 (accepted value = 510 µg/g Pb)	12	486	2.19	-4.7

¹ coefficient of variation, v = standard deviation (σ)/mean (µ) x 100%

B2 Percentage difference between duplicate samples		
n	Mean	σ
16	3.22	2.83

Handwipe Samples

Analyses of blanks determines the zero level of analysis i.e. the apparent Pb concentration in the absence of any sample. The reagent blank mean value determines the zero level for standards containing no handwipes whilst the procedural blank mean value determines the zero level for standards containing handwipes. These values are used to correct standard analyses in the following table and also subsequent sample analyses in Appendix C.

It was not practical to analyse sample duplicates because of the nature of the sample. Therefore duplicate analyses of standards are used to estimate precision.

B3 Blank Determinations			
	n	Mean	Range ¹
Reagent blank	3	0.4	0.1-0.7
Procedural blank	3	1.0	0.1-1.9

¹ As only 3 determinations are made in each case, the range rather than the standard deviation is given.

B4 Analysis of Standards				
Control type	n	Pb content (µg per sample)	Percentage deviation from accepted value	Percentage difference between duplicates
Pb solution (no handwipes) ¹	2	8.4	-16.0	4.65
		8.8	-12.0	
10 µg	2	8.9	-11.0	0.00
		8.9	-11.0	
Handwipes spiked with Pb solution ²	2	17.3	-13.5	8.84
		18.9	-5.5	
20 µg	2	39.2	-21.6	11.3
		43.9	-12.2	
50µg	2	77.5	-2.5	
		84.5	+6.3	8.64
Handwipe spiked with HRM ⁷²³	2	60.3	-7.9	--
Handwipe spiked with NBS 1648 ²⁴	1			

¹ Values given after subtraction of mean Pb content reagent blank.

² Values given after subtraction of mean Pb content procedural blank.

³ House Reference Material (HRM) with an accepted value calculated to give 79.5 µg Pb in this instance (based on previous analysis).

⁴ National Bureau of Standards (NBS) reference material 1648 with certified value calculated to give 65.5 µg Pb in this instance.

Percentage deviations from accepted values are distributed with $\mu=10.86$ and $\sigma=5.04$ ($n=11$).
Percentage differences between duplicates are distributed with $\mu=6.69$ and $\sigma=3.96$ ($n=5$).

APPENDIX C: THE WINSTER LEAD STUDY - INDIVIDUAL RESULTS

The following tables list lead levels in individual household, handwipe and blood samples. Where repeat samples are present, the arithmetic mean of the two samples is given in the relevant table. Percentage differences between repeat samples are defined as for duplicate samples in Appendix B.

C1 Household lead levels in Winster and Hartington					
Household no.	Approximate age of house (yrs)	Garden Soil (Pb µg/g)	Housedust (Pb µg/g)	Dust Loading (Pb g/m ²)	Lead Loading (Pb µg/m ²)
WINSTER VILLAGE					
1	10	2,930	989	0.062	61.0
2	70	20,000	2,410	0.221	533
3	>200	14,800	5,480	0.241	1,320
4	10	8,210	1,750	0.030	53.7
5	10	2,400	963	0.156	150
6	35	2,500	1,150	0.425	449
7	10	5,070	817	0.106	87.2
8	25	8,400	468	0.112	52.5
9	>200	9,440	2,600	0.319	831
10	>100	9,160	1,240	0.089	110
11	>100	16,000	2,500	0.104	261
12	>200	8,310	1,660	0.797	1,326
13	>200	3,920	1,600	1.17	1,880
14	>300	14,300	3,980	0.082	325
15	>300	22,800	6,240	0.107	668
16	>200	10,600	3,210	0.256	820
17	>200	--	1,380	0.248	343
18	>200	23,800	1,180	0.149	175
19	>100	9,060	1,770	0.156	475
20	>300	13,100	3,160	0.476	1,500
21	>300	--	1,700	0.025	42.4
22	20	11,800	462	0.030	14.2
23	20	15,100	1,270	0.528	670
24	>100	15,800	2,310	0.347	802
25	>200	--	1,940	0.481	932
26	10	17,600	1,520	0.084	130
27	>200	22,200	4,860	0.120	583
28	>200	9,330	2,520	0.710	1,790
29	>300	8,930	1,100	0.038	41.4
30	20	3,410	2,300	0.033	76.3
31	25	3,090	1,210	0.327	395
32	10	2,370	950	0.221	210
33	10	2,970	944	0.317	299

C1 Household lead levels in Winster and Hartington					
Household no.	Approximate age of house (yrs)	Garden Soil (Pb µg/g)	Housedust (Pb µg/g)	Dust Loading (Pb g/m ²)	Lead Loading (Pb µg/m ²)
34	10	3,050	773	0.092	70.7
35	>200	6,600	1,150	0.238	274
36	>200	8,810	2,000	0.033	66.0
37	30	12,200	1,420	0.660	93.0
38	35	2,190	582	0.397	231
39	>200	14,000	1,370	0.046	62.8
40	>200	5,700	2,420 ¹	--	--
41	>200	8,810	1,730	1.03	1,760
42	>200	8,990	1,560	0.240	363
43	>200	9,770	730	0.573	418
44	>200	5,630	2,730	1.31	3,560
45	>200	2,770	1,570	0.373	584
HARTINGTON - THE CONTROL VILLAGE					
1	60	345	233	0.283	66.0
2	>200	1,660	587	0.125	73.5
3	>200	1,540	457	0.311	142
4	>200	575	279	0.608	170
5	40	197	143	0.181	25.8

¹ Hoover bag sample only - unable to calculate dust loading

C2 Repeat housedust samples taken during the same week						
Household no.	Lead Concentration (µg/g)	Percentage difference	Dust Loading (g/m ²)	Percentage difference	Lead Loading (µg/m ²)	Percentage difference
2	2,180	19.1	0.203	15.9	443	34.4
	2,640		0.238		627	
6	1,030	20.9	0.543	55.5	562	36.4
	1,270		0.307		389	
18	1,000	29.8	0.098	68.5	98.4	93.2
	1,350		0.200		270	
32	655	61.2	0.283	56.1	178	12.1
	1,250		0.159		201	

C3 Repeat garden soil samples taken in January 1988 and July 1988¹		
Household no.	Lead concentration (µg/g)	Percentage difference
2	21,840	18.2
	18,200	
4	9,650	35.0
	6,770	
19	9,000	1.21
	9,110	
30	3,560	9.19
	3,250	

¹ January 1988 sample is listed first

C4 Lead concentration in individual handwipe samples	
Age at time of sampling (years and months)	µg Pb per pair of hands ¹
1yr 0m	13.6
1yr 2m	24.4
1yr 2m	13.6
1yr 3m	6.60
1yr 4m	39.5
1yr 6m	7.60
2yr 1m	19.7
2yr 3m	14.3
2yr 5m	17.1
2yr 6m	3.80

¹ Values after subtraction of the equivalent of three procedural blanks (i.e. 3 x 1.0; see Appendix B) as three handwipes were used in sampling (Section 3.4.2) but only one in the procedural blank determination (Section 5.5.2).

C5 Lead concentration of repeated handwipe samples		
Age at time of sampling (years and months)	µg Pb per pair of hands ¹	Percentage difference
1yr 2m	12.3	19.9
	15.0	
2yr 1m	13.2	66.0
	26.2	

¹ See footnote at end of previous table

C6 Individual blood lead concentrations	
Age at time of sampling (years and months)	Blood Lead Concentration (µg/dl)
1yr 2m	6.2
2yr 3m	8.3
2yr 7m	6.2
3yr 8m	12.4
4yr 6m	20.7
4yr 9m	12.4
5yr 4m	12.4
6yr 2m	6.2
6yr 5m	10.4
7yr 6m	6.2

APPENDIX D: SOLID SPECIATION STUDY - ICPAES QUALITY CONTROL

Percentage deviations from reference materials and percentage differences between duplicates are calculated according to the definition given in Appendix B. Blank determinations for both lead and phosphorus were below the detection limit.

Lead

D1 House Soil Reference Materials (Lead)				
	n	Mean (µg/g Pb)	Range ¹	Percentage deviation of mean from accepted value
HRM1 (accepted value = 13.00 µg/g Pb)	2	17.5	14.8-20.2	+34.6
HRM2 (accepted value = 510 µg/g Pb)	2	528	512-543	+3.53

¹ As few determinations are made in each case, range rather than coefficient of variation or standard deviation is given.

D2 Percentage difference between duplicate samples		
n	Mean	Range ¹
3	5.81	0.81-13.5

¹ See footnote at end of Table D1

Phosphorus

D3 House Soil Reference Materials (Phosphorus)				
	n	Mean (µg/g P)	Range ¹	Percentage deviation of mean from accepted value
HRM1 (accepted value = 420 µg/g P)	2	399	397-400	-5.00
HRM2 (accepted value = 670 µg/g P)	2	663	655-671	-1.04

¹ See footnote at end of Table D1

D4 Percentage difference between duplicate samples		
n	Mean	Range ¹
3	2.71	0.04-4.24

¹ See footnote at end of Table D1

APPENDIX E: MASS OF DENSITY SEPARATES

$$\text{Percentage difference sink/float pair} = \frac{\text{difference between masses}}{\text{mean mass of sink/float pair}} \times 100\%$$

$$\text{Percentage deviation of final mass from initial mass} = \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \times 100\%$$

E1 Mass of Density Separates								
Sample	Total Initial Mass (g)	Mass of sinks (g)	Percentage difference sink pairs	Mass of floats (g)	Percentage difference float pairs	Mass of sample left on filter (g)	Total final mass (g)	Percentage deviation of final mass from initial mass
Quality Control								
BLK1 (1)	0.9998	0.0009	14.29	0.9852	0.19	0.0087	0.9948	-0.50
(2)	1.0000	0.0012		0.9871		0.0066	0.9883	-1.17
BLK2 (1)	1.0000	0.0010	5.26	0.9769	0.57	0.0049	0.9828	-1.72
(2)	0.9999	0.0009		0.9825		0.0050	0.9884	-1.15
DS-STD1 (1)	1.0000	0.2537	17.44	0.7034	1.96	0.0321	0.9892	-1.08
(2)	0.9998	0.2130		0.7173		0.0352	0.9655	-3.43
DS-STD2 (1)	0.9999	0.2465	10.77	0.7217	1.75	0.0351	1.0033	+0.34
(2)	0.9998	0.2213		0.7092		0.0442	0.9747	-2.51
Winster Mine-Waste Soils								
DVS921 (1)	0.9999	0.0480	4.68	0.8435	1.26	0.0376	0.9291	-7.08
(2)	0.9995	0.0503		0.8542		0.0298	0.9343	-6.52
DVT922 (1)	1.0005	0.0593	7.15	0.8147	0.58	0.0268	0.9008	-9.97
(2)	0.9998	0.0637		0.8194		0.0390	0.9221	-7.77
PWF937 (1)	0.9998	0.0552	4.26	0.8583	1.14	0.0468 ¹	0.9554	-4.44
(2)	1.0007	0.0529		0.8486		0.0271	0.9316	-6.91
OMS942 (1)	0.9973	0.0943	25.87	0.8584	1.48	0.0279	0.9806	-1.67
(2)	0.9976	0.0727		0.8712		0.0184	0.9623	-3.54
OMS942D (1)	1.0001	0.0810	8.49	0.8655	2.45	0.0145	0.9610	-3.91
(2)	1.0002	0.0744		0.8870		0.0175	0.9789	-2.13
WSG923 (1)	1.0001	0.0763	10.32	0.7658	2.21	0.0254	0.8675	-13.26
(2)	1.0001	0.0846		0.7829		0.0216	0.8891	-11.1
OMV927 (1)	1.0010	0.0427	11.39	0.8278	2.74	0.0201	0.8906	-11.0
(2)	1.0000	0.0381		0.8552		0.0189	0.9122	-8.78
SBV928 (1)	1.0005	0.0539	24.43	-	-	0.0251	-	-
(2)	1.0004	0.0689		0.7408		0.0324	0.8421	-15.8

E1 Mass of Density Separates								
Sample	Total Initial Mass (g)	Mass of sinks (g)	Percentage difference sink pairs	Mass of floats (g)	Percentage difference float pairs	Mass of sample left on filter (g)	Total final mass (g)	Percentage deviation of final mass from initial mass
<i>Derbyshire Soils</i>								
TF943 (1)	1.0004	0.0447	9.36	0.9202	0.08	0.0160	0.9839	-1.65
(2)	1.0009	0.0408		0.9209		0.0198	0.9815	-1.94
HF945 (1)	1.0020	0.0945	5.36	0.8394	1.38	0.0190	0.9339	-6.80
(2)	1.0011	0.0997		0.8279		0.0234	0.9276	-7.34
SE952 (1)	1.0004	0.0374	12.20	0.8867	2.77	0.0353	0.9594	-4.10
(2)	1.0000	0.0331		0.9116		0.0300	0.9747	-2.53
VGWH941 (1)	1.0005	0.0044	26.83	0.9617	0.38	0.0107	0.9768	-2.37
(2)	0.9998	0.0038		0.9581		0.0126	0.9745	-2.53
<i>Other U.K. Soils</i>								
CHBP953 (1)	0.9997	0.0086	60.61	0.9681	0.78	0.0148	0.9915	-0.82
(2)	1.0008	0.0046		0.9606		0.0126	0.9778	-2.30
CHMS960 (1)	1.0011	0.0262	41.47	0.9633	0.69	0.0219	1.0114	+1.03
(2)	1.0003	0.0172		0.9567		0.0198	0.9937	-0.66
M1S934 (1)	1.0002	0.0033	35.00	0.9043	3.53	0.0207	0.9283	-7.19
(2)	1.0001	0.0047		0.9368		0.0366	0.9781	-2.20
<i>London Garden Soils</i>								
83/072 (1)	1.0002	0.0060	1.68	0.9651	1.82	0.0272	0.9983	-0.19
	0.9998	0.0059		0.9477		0.0215	0.9751	-2.47
83/126 (1)	1.0007	0.0052	81.08	0.9375	1.41	0.0376	0.9803	-2.04
(2)	0.9999	0.0022		0.9244		0.0194	0.9460	-5.39
83/279 (1)	1.0019	0.0037	21.69	0.9397	2.99	0.0425 ¹	0.9867	-1.52
(2)	1.0025	0.0046		0.9682		0.0548 ¹	1.0276	+2.50
88/015 (1)	0.9990	0.0040	29.79	0.9381	1.08	0.0459 ¹	0.9880	-1.10
(2)	1.0004	0.0054		0.9280		0.0217	0.9551	-4.53
88/177 (1)	1.0024	0.0061	19.82	0.9029	2.15	0.0439 ¹	0.9529	-4.94
(2)	1.0023	0.0050		0.9407		0.0248	0.9705	-3.17

¹ It is suspected that these filters contain di-iodomethane resulting in an artificially high weight

Percentage differences between sink pairs are distributed with $\mu=20.39$ and $\sigma=18.56$ ($n=24$).

Percentage differences between float pairs are distributed with $\mu=1.54$ and $\sigma=0.93$ ($n=23$).

The moduli (i.e. $|x|$) of percentage deviation of final mass from initial mass are distributed with $\mu=4.19$ and $\sigma=3.60$ ($n=47$).

APPENDIX F: ELEMENTAL ANALYSIS OF DENSITY SEPARATES

Analytical Quality Control

Percentage deviations from accepted values and percentage differences between duplicates are calculated according to the formula given in Appendix B. Although elemental analysis of density separates was performed in two batches, there were no systematic variation between the batches so the pooled quality control data from both batches is presented here. Blank solutions contained both lead and phosphorus in concentrations below the detection limit of the instrument.

Lead

F1 House Soil Reference Materials (Lead)				
	n	Mean ($\mu\text{g/g Pb}$)	v^1	Percentage deviation of mean from accepted value
HRM1 (accepted value = 13.00 $\mu\text{g/g Pb}$)	11	18.3	18.9	+40.7
HRM2 (accepted value = 510 $\mu\text{g/g Pb}$)	10	514	2.10	+0.78

¹ See Appendix B1 for definition

F2 Percentage difference between duplicate samples		
n	Mean	σ
26	5.23	5.15

Phosphorus

F3 House Soil Reference Materials (Phosphorus)				
	n	Mean ($\mu\text{g/g P}$)	v	Percentage deviation of mean from accepted value
HRM1 (accepted value = 420 $\mu\text{g/g P}$)	11	399	5.46	-5.00
HRM2 (accepted value = 670 $\mu\text{g/g P}$)	10	644	2.11	-3.88

F4 Percentage difference between duplicate samples		
n	Mean	σ
26	6.22	5.09

Elemental Concentrations of Density Separates

It was not possible to analyse both sink fractions from all samples as in many cases there was not enough material to perform other analyses in addition to ICPAES analysis. In each case S1 [Sinks (1)] has been analysed and, if possible S2 as well. F1 [Floats (1)] from sample SBV928 was unfortunately lost so only the analysis of F2 is given. Percentage differences between sink/float pairs are calculated using a similar formula to that in Appendix E.

F5 Lead and Phosphorus Concentration of Density Separates								
Sample	Pb Sinks (µg/g)	% Pb difference sink pairs	Pb Floats (µg/g)	% Pb difference float pairs	P Sinks (µg/g)	% P differnce sink pairs	P Floats (µg/g)	% P difference sink pairs
Quality Control								
BLK1 (1)	7,130 ¹	--	327.0	5.36	4,000 ¹	--	763	13.7
(2)			345.0				875	
BLK2 (1)	2,333 ¹	--	316.0	3.51	6,400 ¹	--	772	7.48
(2)			339.0				832	
DS-STD1 (1)	391,000	2.15	27,060	13.8	15,590	9.00	1,384	13.5
(2)	399,500		31,060		17,060		1,584	
DS-STD2 (1)	589,061	31.3	32,950	1.27	17,939	2.02	2,416	11.9
(2)	429,600		33,370		17,580		2,144	
Winster Mine-waste Soils								
DVS921 (1)	207,000	--	6,220	--	24,400	--	1,013	--
(2)	--		--		--			
DVT922 (1)	141,000	--	3,169	--	16,230	--	491.2	--
(2)	--		--		--			
PWF937 (1)	180,600	6.8	15,370	0.78	12,580	1.81	1,710	2.22
(2)	168,700		15,250		12,810		1,670	
OMS942 (1)	126,400	17.93	12,140	2.52	6,510	8.82	1,231	7.88
(2)	105,600		12,450		5,960		1,332	
OMS942D (1)	133,200	9.3	13,120	3.37	6,650	7.81	1,301	9.05
(2)	121,300		13,570		6,150		1,560	
WSG923 (1)	191,400	2.4	4,973	12.9	17,210	12.7	599	5.5
(2)	186,800		4,369		15,150		663	
OMV927 (1)	151,600	--	7,335	--	12,120	--	3,630	--
(2)	--		--		--		--	
SBV928 (1)	128,800	--	--	--	20,600	--	--	--
(2)	--		13,780		--		4,125	

F5 Lead and Phosphorus Concentration of Density Separates								
Sample	Pb Sinks (µg/g)	% Pb difference sink pairs	Pb Floats (µg/g)	% Pb difference float pairs	P Sinks (µg/g)	% P differnce sink pairs	P Floats (µg/g)	% P difference sink pairs
<i>Derbyshire Soils</i>								
TF943 (1)	410,200	4.2	14,080	4.17	10,870	9.08	672	10.8
(2)	427,800		14,680		9,060		603	
HF945 (1)	13,740	5.23	15,140	20.6	263.7	1.80	1,730	2.73
(2)	13,040		12,310		259.0		1,778	
SE952 (1)	231,400	6.61	32,420	2.18	1,141	56.3	1,184	16.1
(2)	216,600		31,780		512		1,008	
VGWH941 (1)	11,320	--	2,814	6.6	1,706	--	1,857	11.8
(2)	--		2,633		--		1,650	
<i>Other U.K. Soils</i>								
CHBP953 (1)	496,100	--	31,720	3.89	1,701	--	1,416	1.26
(2)	--		32,980		--		1,434	
CHMS960 (1)	596,000	4.27	33,070	0.728	2,065	3.47	1,421	0.07
(2)	622,000		32,830		2,138		1,422	
M1S934 (1)	16,470	--	543	--	1,882	--	799	--
(2)	--		--		--		--	
<i>London Garden Soils</i>								
83/072 (1)	55,700	--	2,162	7.68	3,872	--	4,550	5.7
	--		2,002		--		4,296	
83/126 (1)	44,030	--	5,160	7.10	4,833	--	4,741	2.25
(2)	--		5,540		--		4,850	
83/279 (1)	9,790	--	3,015	3.75	3,486	--	3,380	1.07
(2)	--		2,904		--		3,790	
88/015 (1)	166,200	--	13,480	5.34	1,292	--	4,477	0.27
(2)	--		14,220		--		4,466	
88/177 (1)	60,600	--	8,630	0.93	4,625	--	2,777	4.70
(2)	--		8,550		--		2,650	

¹ combined results from the sink pair as extremely small amounts of material available

Percentage differences between sink pairs are distributed with $\mu=9.02$ and $\sigma=8.59$ ($n=10$) for Pb and with $\mu=10.2$ and $\sigma=15.7$ for P ($n=10$).

Percentage differences between float pairs are distributed with $\mu=5.60$ and $\sigma=5.02$ ($n=19$) for Pb and with $\mu=6.74$ and $\sigma=4.97$ for P ($n=19$).

APPENDIX G: DISTRIBUTION OF LEAD AND PHOSPHORUS BETWEEN DENSITY SEPARATES

$$\text{Percentage deviation of calculated total Pb from analysed total Pb} = \frac{\text{Calculated total Pb} - \text{Analysed total Pb}}{\text{Analysed total Pb}} \times 100\% \quad \text{and similarly for P.}$$

G1 Distribution of Lead and Phosphorus between Density Separates										
Sample	Amount Pb in sinks (µg)	Amount Pb in floats (µg)	Calculated total Pb (floats + sinks)	Analysed total Pb content ¹	Percentage deviation of calculated from analysed Pb	Amount P in sinks (µg)	Amount P in floats (µg)	Calculated total P (floats + sinks)	Analysed total P content ¹	Percentage deviation of calculated from analysed P
<i>Quality Control</i>										
BLK1	15.0 ²	663 ²	678 ²	836 ²	-18.90	8.4 ²	1,615 ²	1,623 ²	1,926 ²	-15.73
DS-STD1	99,197	19,529	118,700	107,700	+10.24	3,955	974	4,929	6,780	-27.30
<i>Winster Mine-Waste Soils</i>										
DVT921	9,936	5,247	15,180	17,240	-11.92	1,171	854	2,025	2,098	-3.48
DVS922	8,361	2,582	10,940	13,290	-17.64	779	400	1,179	1,500	-21.40
PWF937	9,969	13,190	23,160	25,930	-10.67	694	1,465	2,159	2,540	-15.00
OMS942	11,920	10,420	22,340	24,710	-9.57	614	1,056	1,670	1,661	+0.54
OMS942D	9,169	11,360	20,520	24,710	-16.92	538	1,126	1,664	1,667	-0.18
WSG923	14,600	4,051	18,660	23,380	-20.22	1,313	459	1,772	2,034	-12.88
OMV927	6,473	6,073	12,550	15,010	-16.39	518	3,005	3,523	3,400	+3.62
SBV928	6,942	10,210 ²	17,150	21,720	+21.03	1,110	3,056	4,166	4,788	-12.99
<i>Derbyshire Soils</i>										
TF943	18,340	12,960	31,290	27,290	+14.66	518	618	1,136	861	+31.94

G1 Distribution of Lead and Phosphorus between Density Separates										
Sample	Amount Pb in sinks (µg)	Amount Pb in floats (µg)	Calculated total Pb (floats + sinks)	Analysed total Pb content ¹	Percentage deviation of calculated from analysed Pb	Amount P in sinks (µg)	Amount P in floats (µg)	Calculated total P (floats + sinks)	Analysed total P content ¹	Percentage deviation of calculated from analysed P
TF945	1,298	12,710	14,000	11,340	+23.57	221	1,452	1,673	1,677	-0.24
SE952	8,654	28,750	37,400	31,540	+18.57	42.67	1050	1,093	885	+23.47
VGWH941	49.81	2,706	2,756	2,710	+1.54	7.5	1,786	1,794	1,710	+4.88
Other U.K. Soils										
CHBP953	4,266	30,710	34,970	33,380	+4.78	14.6	1,371	1,386	1,423	-2.63
CHMS960	15,620	31,860	47,470	34,790	+36.46	54.1	1,369	1,423	1,162	+22.47
MI934	156.7	392	548.7	603	-9.01	6.21	722.5	728.7	726	+0.37
London Garden Soils										
83/072	334.2	2,086	2,420	2,043	+18.46	23.2	4,391	4,414	3,122	+41.39
83/126	229.0	4,838	5,067	2,273	+122.9	25.1	4,445	4,470	2,474	+80.68
83/279	36.20	2,833	2,869	2,127	+34.89	12.9	2,969	2,982	2,311	+29.03
88/015	665.1	12,650	13,310	12,630	+5.41	5.2	4,200	4,205	3,923	+7.19
88/177	370.3	7,793	8,163	6,606	+23.57	28.2	3,471	3,499	2,114	+65.53

¹ from Table 6.3, corrected to represent total initial mass of density separate

² Combined analysis of sink and float pairs as very little material reporting to sinks

Moduli ($|x|$) of percentage deviations of calculated total Pb from analysed total Pb is distributed with $\mu=21.34$ and $\sigma=23.70$ ($n=22$)

Moduli of percentage deviations of calculated total P from analysed total P is distributed with $\mu=19.22$ and $\sigma=20.70$ ($n=22$)

APPENDIX H: MIDAS RESULTS

For each DIGISCAN run, two MIDAS tables of classification classes, as columns, against area (TrArea) in μm , as rows, are presented. The first table gives the number of particles of falling into each cell. In the second table the rows and columns are identical to the first but percentage of TrArea falling into each cell is tabulated. A and B following sample identification indicate duplicate analyses. The sum of the percentages TrArea reporting to each classification class are given in bold as these are used for calculations on the wt.% of lead minerals in these soils.

MIDAS CLASSIFICATION CLASSES

Class 0: Unclassified
 Class 1: Galena
 Class 2: Pyromorphite
 Class 3: Cerussite
 Class 4: Iron-rich

QUALITY CONTROL STANDARDS

SEM-STD1A

3700 features tabulated

No. of features					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS (%)
0.0 ->	18	1378	1168	1006	3570 (96.49)
1000 ->		26	25	35	86 (2.32)
2000 ->		12	6	10	28 (0.76)
3000 ->		1	5	3	9 (0.24)
4000 ->			2	2	4 (0.11)
5000 ->		1			1 (0.03)
6000 ->				1	1 (0.03)
7000 +			1		1 (0.03)
TOTALS:	18	1418	1207	1057	3700
(%)	(0.49)	(38.32)	(32.62)	(28.57)	(0.00)

3700 features tabulated

$\Sigma\text{TrArea}=516953$

Percentage ΣTrArea					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS
0.0 ->	0.95	18.99	16.69	15.40	52.03
1000 ->		6.78	6.58	9.41	22.78
2000 ->		5.18	2.63	4.28	12.09
3000 ->		0.70	3.36	1.87	5.92
4000 ->			1.66	1.67	3.33
5000 ->		1.09			1.09
6000 ->				1.35	1.35
7000 +			1.40		1.40
TOTALS:	0.95	32.74	32.33	33.98	100.00

SEM-STD1B

3700 features tabulated

No. of features					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS (%)
0.0 ->	29	1416	1096	1138	3679 (99.43)
2000 ->		3	8	2	13 (0.35)
4000 ->		1	1	2	4 (0.11)
6000 ->		1	1	1	3 (0.08)
8000 ->					0 (0.00)
10000 ->					0 (0.00)
12000 +		1			1 (0.03)
TOTALS:	29	1422	1106	1143	3700
(%)	(0.78)	(38.43)	(29.89)	(30.89)	(0.00)

3700 features tabulated

ΣTrArea=412686

Percentage ΣTrArea					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS
0.0 ->	2.15	25.75	23.60	26.24	77.74
2000 ->		1.60	5.02	1.86	8.48
4000 ->		1.09	1.37	2.74	5.20
6000 ->		1.83	1.82	1.85	5.50
8000 ->					0.00
10000 ->					0.00
12000 +		3.08			3.08
TOTALS:	2.15	33.34	31.82	32.69	100.00

STD1A

3700 features tabulated

No. of features					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS (%)
0.0 ->	8	789	1318	1360	3475 (93.92)
1000 ->	2	50	34	48	134 (3.62)
2000 ->		20	13	16	49 (1.32)
3000 ->		11	2	14	27 (0.73)
4000 ->		5	3	3	11 (0.30)
5000 ->		1		1	2 (0.05)
6000 ->		1			1 (0.03)
7000 ->					0 (0.00)
8000 +		1			1 (0.03)
TOTALS:	10	878	1370	1442	3700
(%)	(0.27)	(23.73)	(37.03)	(38.97)	(0.00)

3700 features tabulated

ΣTrArea=840957

Percentage ΣTrArea					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS
0.0 ->	0.01	16.38	13.11	14.10	43.59
1000 ->	0.31	8.82	5.40	8.27	22.81
2000 ->		5.79	3.75	4.19	13.73
3000 ->		4.34	0.81	5.82	10.98
4000 ->		2.66	1.58	1.56	5.80
5000 ->		0.64		0.60	1.25
6000 ->		0.81			0.81
7000 ->					0.00
8000 +		1.05			1.05
TOTALS:	0.32	40.49	24.65	34.54	100.00

STD1B

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	11	957	1279	1382		3629	(98.08)	
2000 ->		22	10	23		55	(1.49)	
4000 ->		3	1	5		9	(0.24)	
6000 ->		1		4		5	(0.14)	
8000 ->				1		1	(0.03)	
10000 ->						0	(0.00)	
12000 +		1				1	(0.03)	
TOTALS:	11	984	1290	1415	0	3700		
(%)	(0.30)	(26.59)	(34.86)	(38.24)	(0.00)			

3700 features tabulated

ΣTrArea=902868

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.02	27.91	18.13	25.74		71.80		
2000 ->		7.43	2.76	6.67		16.87		
4000 ->		1.49	0.47	2.90		4.86		
6000 ->		0.80		3.25		4.04		
8000 ->				0.95		0.95		
10000 ->						0.00		
12000 +		1.48				1.48		
TOTALS:	0.02	39.12	21.36	39.51	0.00	100.00		

STD2A

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	5	1184	1153	1179		3521	(95.16)	
2000 ->		46	37	67		150	(4.05)	
4000 ->		11		10		21	(0.57)	
6000 ->		2	1	3		6	(0.16)	
8000 ->						0	(0.00)	
10000 +				2		2	(0.05)	
TOTALS:	5	1243	1191	1261	0	3700		
(%)	(0.14)	(33.59)	(32.19)	(34.08)	(0.00)			

3700 features tabulated

ΣTrArea=1838884

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.33	27.07	17.48	24.48		69.36		
2000 ->		6.68	5.08	10.15		21.91		
4000 ->		2.86		2.44		5.30		
6000 ->		0.71	0.36	1.17		2.24		
8000 ->						0.00		
10000 +				1.19		1.19		
TOTALS:	0.33	37.32	22.91	39.43	0.00	100.00		

STD2B

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	1	1147	1120	1013		3281	(88.68)	
1000 ->	4	81	85	102		272	(7.35)	
2000 ->		23	18	46		87	(2.35)	
3000 ->		13	8	13		34	(0.92)	
4000 ->		2		6		8	(0.22)	
5000 ->		3		8		11	(0.30)	
6000 ->		1		3		4	(0.11)	
7000 ->				2		2	(0.05)	
8000 +			1			1	(0.03)	
TOTALS:	5	1270	1232	1193	0	3700		
(%)	(0.14)	(34.32)	(33.30)	(32.24)	(0.00)			

3700 features tabulated

ΣTrArea=1557196

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.00	18.83	14.11	12.76		45.69		
1000 ->	0.33	7.62	7.27	9.19		24.41		
2000 ->		3.38	2.72	6.99		13.10		
3000 ->		2.85	1.77	2.89		7.51		
4000 ->		0.55		1.75		2.31		
5000 ->		1.05		2.80		3.85		
6000 ->		0.40		1.26		1.66		
7000 ->				0.91		0.91		
8000 +			0.56			0.56		
TOTALS:	0.33	34.69	26.43	38.55	0.00	100.00		

ANALYSIS OF SINKS

Winster mine-waste soils

DVT921

3088 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	4	8	2813	128		2953	(95.63)	
500 ->			70	5		75	(2.43)	
1000 ->			21	1		22	(0.71)	
1500 ->			17	1		18	(0.58)	
2000 ->			12			12	(0.39)	
2500 ->			3	3		6	(0.19)	
3000 ->						0	(0.00)	
3500 +			2			2	(0.06)	
TOTALS:	4	8	2938	138	0	3088		
(%)	(0.13)	(0.26)	(95.14)	(4.47)	(0.00)			

3088 features tabulated

ΣTrArea=237948

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.01	0.15	29.29	2.22		31.67		
500 ->			20.99	1.33		22.32		
1000 ->			10.94	0.55		11.49		
1500 ->			12.39	0.76		13.15		
2000 ->			11.31			11.31		
2500 ->			3.44	3.54		6.97		
3000 ->						0.00		
3500 +			3.08			3.08		
TOTALS:	0.01	0.15	91.45	8.40	0.00	100.00		

DVS922A

3700 features tabulated

No. of features					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS (%)
0.0 ->	180	102	2934	220	3436 (92.86)
2000 ->	8		160	9	177 (4.78)
4000 ->	2		44	6	52 (1.41)
6000 ->			17		17 (0.46)
8000 ->			7	2	9 (0.24)
10000 ->			3	1	4 (0.11)
12000 ->			1		1 (0.03)
14000 +			4		4 (0.11)
TOTALS:	190	102	3170	238	3700
(%)	(5.14)	(2.76)	(85.68)	(6.43)	(0.00)

3700 features tabulated

ΣTrArea=1745498

Percentage ΣTrArea					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS
0.0 ->	1.17	0.79	34.16	3.09	39.20
2000 ->	1.30		25.67	1.64	28.61
4000 ->	0.54		12.02	1.70	14.27
6000 ->			6.81		6.81
8000 ->			3.49	1.04	4.52
10000 ->			1.84	0.58	2.42
12000 ->			0.73		0.73
14000 +			3.44		3.44
TOTALS:	3.00	0.79	88.15	8.06	100.00

DVS922B

3700 features tabulated

No. of features					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS (%)
0.0 ->	208	45	3094	240	3587 (96.95)
2000 ->			69	5	74 (2.00)
4000 ->	1	1	23		25 (0.68)
6000 ->			7		7 (0.19)
8000 ->					0 (0.00)
10000 ->			3	2	5 (0.14)
12000 ->					0 (0.00)
14000 +			1	1	2 (0.05)
TOTALS:	209	46	3197	248	3700
(%)	(5.65)	(1.24)	(86.41)	(6.70)	(0.00)

3700 features tabulated

ΣTrArea=771011

Percentage ΣTrArea					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					TOTALS
0.0 ->	0.97	0.91	36.46	3.31	41.65
2000 ->			24.31	1.96	26.28
4000 ->	0.68	0.61	14.17		15.45
6000 ->			6.00		6.00
8000 ->					0.00
10000 ->			3.96	2.83	6.79
12000 ->					0.00
14000 +			1.89	1.95	3.84
TOTALS:	1.65	1.52	86.78	10.05	100.00

PWF937A

3700 features tabulated

No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)
TrArea:						
0.0 ->	5	453	1886	1224		3568 (96.43)
500 ->		47	9	26		82 (2.22)
1000 ->	2	11	3	6		22 (0.59)
1500 ->		8		4		12 (0.32)
2000 ->		4		2		6 (0.16)
2500 ->		1		1		2 (0.05)
3000 ->		4		1		5 (0.14)
3500 ->						0 (0.00)
4000 ->		1				1 (0.03)
4500 +		2				2 (0.05)
TOTALS:	7	531	1898	1264	0	3700
(%)	(0.19)	(14.35)	(51.30)	(34.16)	(0.00)	

3700 features tabulated

ΣTrArea=356307

Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS
TrArea:						
0.0 ->	0.02	13.82	22.38	20.96		57.18
500 ->		9.43	1.60	4.96		15.99
1000 ->	0.60	3.77	1.17	2.06		7.59
1500 ->		3.84		1.98		5.81
2000 ->		2.48		1.28		3.76
2500 ->		0.72		0.73		1.45
3000 ->		3.59		0.85		4.44
3500 ->						0.00
4000 ->		1.24				1.24
4500 +		2.54				2.54
TOTALS:	0.62	41.42	25.15	32.82	0.00	100.00

PWF937B

3697 features tabulated

No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)
TrArea:						
0.0 ->		323	2129	1097	7	3556 (96.19)
2000 ->	1	24	29	51		105 (2.84)
4000 ->		9	4	11		24 (0.65)
6000 ->		2	1	5		8 (0.22)
8000 ->		2		1		3 (0.08)
10000 +				1		1 (0.03)
TOTALS:	1	360	2163	1166	7	3697
(%)	(0.03)	(9.74)	(58.51)	(31.54)	(0.19)	

3697 features tabulated

ΣTrArea=1146240

Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS
TrArea:						
0.0 ->		11.92	21.87	21.99	0.02	55.80
2000 ->	0.32	6.02	7.28	12.52		26.14
4000 ->		3.83	1.53	4.73		10.10
6000 ->		1.10	0.66	3.06		4.82
8000 ->		1.56		0.70		2.26
10000 +				0.88		0.88
TOTALS:	0.32	24.43	31.35	43.88	0.02	100.00

OMS942A

3700 features tabulated

No. of features					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					
0.0 ->	127	224	1040	2243	6
5000 ->		5	7	33	
10000 ->		2	3	6	
15000 ->		2		1	
20000 +				1	
TOTALS:	127	233	1050	2284	6
(%)	(3.43)	(6.30)	(28.38)	(61.73)	(0.16)

 Σ TrArea=1534494

Percentage Σ TrArea					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					
0.0 ->	0.37	9.46	15.38	41.38	0.01
5000 ->		2.33	2.84	14.80	
10000 ->		1.49	2.15	4.68	
15000 ->		2.43		1.23	
20000 +				1.44	
TOTALS:	0.37	15.71	20.38	63.53	0.01

OMS942B

3700 features tabulated

No. of features					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					
0.0 ->	360	187	1558	1490	10
5000 ->		14	21	41	
10000 ->			6	8	
15000 ->		1	2	1	
20000 +				1	
TOTALS:	360	202	1587	1541	10
(%)	(9.73)	(5.46)	(42.89)	(41.65)	(0.27)

 Σ TrArea=2283690

Percentage Σ TrArea					
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +
TrArea:					
0.0 ->	1.61	6.59	24.62	33.28	0.12
5000 ->		3.96	5.87	12.67	
10000 ->			3.07	4.10	
15000 ->		0.79	1.45	0.87	
20000 +				1.00	
TOTALS:	1.61	11.34	35.02	51.91	0.12

OMS942DA

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	456	217	1376	1570	5	3624	(97.95)	
1000 ->		3	19	33		55	(1.49)	
2000 ->		1	4	10		15	(0.41)	
3000 ->			2	2		4	(0.11)	
4000 ->						0	(0.00)	
5000 +				2		2	(0.05)	
TOTALS:	456	221	1401	1617	5	3700		
(%)	(12.32)	(5.97)	(37.86)	(43.70)	(0.14)			

3700 features tabulated

ΣTrArea=325720

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	2.71	5.89	20.91	27.63	0.11	57.24		
1000 ->		1.28	8.71	14.63		24.62		
2000 ->		0.84	2.80	6.97		10.61		
3000 ->			2.16	2.17		4.32		
4000 ->						0.00		
5000 +				3.20		3.20		
TOTALS:	2.71	8.01	34.58	54.59	0.11	100.00		

OMS942DB

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	778	196	1376	1254	4	3608	(97.51)	
500 ->		9	15	39		63	(1.70)	
1000 ->		1		6		7	(0.19)	
1500 ->		5	6	5		16	(0.43)	
2000 +			6			6	(0.16)	
TOTALS:	778	211	1403	1304	4	3700		
(%)	(21.03)	(5.70)	(37.92)	(35.24)	(0.11)			

3700 features tabulated

ΣTrArea=196912

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	2.83	6.85	19.46	24.36	0.01	53.50		
500 ->		3.14	4.83	13.69		21.65		
1000 ->		0.56		3.59		4.14		
1500 ->		4.27	5.61	3.87		13.75		
2000 +			6.96			6.96		
TOTALS:	2.83	14.81	36.85	45.51	0.01	100.00		

WSG923

3137 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	16	630	2321	120		3087	(98.41)	
500 ->		14	20	1		35	(1.12)	
1000 ->		7	1			8	(0.26)	
1500 ->		2				2	(0.06)	
2000 ->			1			1	(0.03)	
2500 +		3	1			4	(0.13)	
TOTALS:	16	656	2344	121	0	3137		
(%)	(0.51)	(20.91)	(74.72)	(3.86)	(0.00)			

3137 features tabulated

ΣTrArea=126309

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.48	16.74	39.24	4.09		60.54		
500 ->		7.05	10.83	0.51		18.38		
1000 ->		6.79	1.14			7.92		
1500 ->		2.79				2.79		
2000 ->			1.85			1.85		
2500 +		6.23	2.28			8.51		
TOTALS:	0.48	39.59	55.34	4.59	0.00	100.00		

OMS927

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	200	236	3150	30		3616	(97.73)	
5000 ->	2	10	55	2		69	(1.86)	
10000 ->			8	2		10	(0.27)	
15000 ->			4			4	(0.11)	
20000 +			1			1	(0.03)	
TOTALS:	202	246	3218	34	0	3700		
(%)	(5.46)	(6.65)	(86.97)	(0.92)	(0.00)			

3700 features tabulated

ΣTrArea=1928026

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	3.53	4.31	56.80	1.97		66.62		
5000 ->	0.66	3.42	18.34	0.61		23.03		
10000 ->			4.44	1.25		5.69		
15000 ->			3.38			3.38		
20000 +			1.28			1.28		
TOTALS:	4.19	7.74	84.24	3.83	0.00	100.00		

SBV928

1996 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	190	379	1112	281	2	1964	(98.40)	
5000 ->		8	15	1		24	(1.20)	
10000 ->		1	2	1		4	(0.20)	
15000 ->		1		2		3	(0.15)	
20000 ->						0	(0.00)	
25000 ->						0	(0.00)	
30000 +			1			1	(0.05)	
TOTALS:	190	389	1130	285	2	1996		
(%)	(9.52)	(19.49)	(56.61)	(14.28)	(0.10)			

1996 features tabulated

ΣTrArea=893852

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	2.67	15.50	37.78	9.76	0.00	65.71		
5000 ->		6.93	11.17	0.86		18.96		
10000 ->		1.49	2.67	1.37		5.53		
15000 ->		1.90		4.21		6.10		
20000 ->						0.00		
25000 ->						0.00		
30000 +			3.70			3.70		
TOTALS:	2.67	25.81	55.33	16.19	0.00	100.00		

Derbyshire Soils

TF943A

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	27	307	1285	1719		3338	(90.22)	
500 ->		29	24	188		241	(6.51)	
1000 ->		4	11	60		75	(2.03)	
1500 ->		1	2	23		26	(0.70)	
2000 ->		1		8		9	(0.24)	
2500 ->		2		1		3	(0.08)	
3000 ->			1	4		5	(0.14)	
3500 ->				1		1	(0.03)	
4000 +				2		2	(0.05)	
TOTALS:	27	344	1323	2006	0	3700		
(%)	(0.73)	(9.30)	(35.76)	(54.22)	(0.00)			

3700 features tabulated

ΣTrArea=624140

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.40	5.66	9.75	25.95		41.77		
500 ->		3.18	2.50	21.65		27.32		
1000 ->		0.78	2.15	11.59		14.52		
1500 ->		0.28	0.54	6.30		7.12		
2000 ->		0.38		2.85		3.23		
2500 ->		0.88		0.42		1.30		
3000 ->			0.54	2.18		2.72		
3500 ->				0.62		0.62		
4000 +				1.40		1.40		
TOTALS:	0.40	11.16	15.47	72.96	0.00	100.00		

TF943B

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	10	227	644	2332	1	3214	(86.86)	
100 ->		44	44	231		319	(8.62)	
200 ->	3	11	8	78		100	(2.70)	
300 ->		1	3	29		33	(0.89)	
400 ->				13		13	(0.35)	
500 ->			3	9		12	(0.32)	
600 ->				2		2	(0.05)	
700 ->			1	3		4	(0.11)	
800 ->				1		1	(0.03)	
900 +				2		2	(0.05)	
TOTALS:	13	283	703	2700	1	3700		
(%)	(0.35)	(7.65)	(19.00)	(72.97)	(0.03)			

3700 features tabulated

ΣTrArea=177630

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.03	4.74	7.24	31.39	0.00	43.41		
100 ->		3.54	3.46	18.72		25.71		
200 ->	0.44	1.43	1.15	10.54		13.56		
300 ->		0.22	0.59	5.62		6.43		
400 ->				3.29		3.29		
500 ->			0.92	2.74		3.66		
600 ->				0.75		0.75		
700 ->			0.43	1.26		1.70		
800 ->				0.46		0.46		
900 +				1.04		1.04		
TOTALS:	0.46	9.92	13.80	75.81	0.00	100.00		

HF945

656 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	9	123		441		573	(87.35)	
1000 ->	1	12		34		47	(7.16)	
2000 ->		5		10		15	(2.29)	
3000 ->		4		5		9	(1.37)	
4000 ->		4		4		8	(1.22)	
5000 ->		1		1		2	(0.30)	
6000 +		2				2	(0.30)	
TOTALS:	10	151	0	495	0	656		
(%)	(1.52)	(23.02)	(0.00)	(75.46)	(0.00)			

656 features tabulated

ΣTrArea=280312

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.04	10.05		19.88		29.97		
1000 ->	0.37	6.36		17.01		23.75		
2000 ->		4.59		8.87		13.47		
3000 ->		4.95		6.26		11.21		
4000 ->		6.16		6.58		12.74		
5000 ->		2.05		2.06		4.12		
6000 +		4.75				4.75		
TOTALS:	0.42	38.91	0.00	60.67	0.00	100.00		

SE952A

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	2	3267	44	242	14	3569	(96.46)	
50.0 ->		76		9		85	(2.30)	
100 ->		17	2	6		25	(0.68)	
150 ->		11		2		13	(0.35)	
200 ->		3	2			5	(0.14)	
250 ->		2				2	(0.05)	
300 ->						0	(0.00)	
350 ->						0	(0.00)	
400 ->						0	(0.00)	
450 +				1		1	(0.03)	
TOTALS:	2	3376	48	260	14	3700		
(%)	(0.05)	(91.24)	(1.30)	(7.03)	(0.38)			

3700 features tabulated

ΣTrArea=30869

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.01	51.96	0.71	3.73	0.30	56.70		
50.0 ->		17.47		2.13		19.60		
100 ->		6.61	0.75	2.41		9.77		
150 ->		6.04		0.99		7.03		
200 ->		2.10	1.49			3.59		
250 ->		1.84				1.84		
300 ->						0.00		
350 ->						0.00		
400 ->						0.00		
450 +				1.47		1.47		
TOTALS:	0.01	86.02	2.95	10.73	0.30	100.00		

SE952B

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	1	3360	16	212	11	3600	(97.30)	
100 ->		57		14		71	(1.92)	
200 ->		17	1	2		20	(0.54)	
300 ->		4	1	1		6	(0.16)	
400 ->		1		1		2	(0.05)	
500 +		1				1	(0.03)	
TOTALS:	1	3440	18	230	11	3700		
(%)	(0.03)	(92.97)	(0.49)	(6.22)	(0.30)			

3700 features tabulated

ΣTrArea=63430

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.01	65.68	0.24	5.43	0.09	71.45		
100 ->		12.39		3.30		15.69		
200 ->		6.42	0.35	0.80		7.57		
300 ->		2.03	0.56	0.51		3.10		
400 ->		0.69		0.65		1.34		
500 +		0.85				0.85		
TOTALS:	0.01	88.06	1.15	10.69	0.09	100.00		

VGWH941

594 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)		
TrArea:								
0.0 ->	56	1	443	59		559 (94.11)		
500 ->			19	6		25 (4.21)		
1000 ->			6	2		8 (1.35)		
1500 ->			1			1 (0.17)		
2000 +			1			1 (0.17)		
TOTALS:	56	1	470	67	0	594		
(%)	(9.43)	(0.17)	(79.12)	(11.28)	(0.00)			

594 features tabulated

ΣTrArea=61531

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	1.01	0.33	41.19	7.03		49.56		
500 ->			22.61	6.17		28.78		
1000 ->			11.20	3.68		14.89		
1500 ->			2.73			2.73		
2000 +			4.04			4.04		
TOTALS:	1.01	0.33	81.78	16.88	0.00	100.00		

Other U.K. Soils

CHBP953

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)		
TrArea:								
0.0 ->	36	64	92	3268	49	3509 (94.84)		
500 ->		7	4	143		154 (4.16)		
1000 ->		2		26		28 (0.76)		
1500 ->				8		8 (0.22)		
2000 +				1		1 (0.03)		
TOTALS:	36	73	96	3446	49	3700		
(%)	(0.97)	(1.97)	(2.59)	(93.14)	(1.32)			

3700 features tabulated

ΣTrArea=388024

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.37	2.63	1.06	55.02	0.22	59.30		
500 ->		1.31	0.76	25.95		28.01		
1000 ->		0.63		7.91		8.54		
1500 ->				3.60		3.60		
2000 +				0.54		0.54		
TOTALS:	0.37	4.57	1.81	93.03	0.22	100.00		

CHBP960

3700 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	4	31	134	3410	30	3609	(97.54)	
500 ->		3		41	3	47	(1.27)	
1000 ->		1	1	13		15	(0.41)	
1500 ->				8		8	(0.22)	
2000 ->			1	8		9	(0.24)	
2500 ->				5		5	(0.14)	
3000 ->				3		3	(0.08)	
3500 ->				1		1	(0.03)	
4000 ->			1			1	(0.03)	
4500 +				2		2	(0.05)	
TOTALS:	4	35	137	3491	33	3700		
(%)	(0.11)	(0.95)	(3.70)	(94.35)	(0.89)			

3700 features tabulated

ΣTrArea=234017

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.18	1.25	1.08	42.48	0.12	45.11		
500 ->		0.90		12.98	0.87	14.75		
1000 ->		0.57	0.61	6.96		8.14		
1500 ->				5.88		5.88		
2000 ->			1.03	7.53		8.56		
2500 ->				5.92		5.92		
3000 ->				4.13		4.13		
3500 ->				1.65		1.65		
4000 ->			1.90			1.90		
4500 +				3.96		3.96		
TOTALS:	0.18	2.72	4.62	91.49	0.99	100.00		

M1S934

292 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->			71	159	52	282	(96.58)	
500 ->				2		2	(0.68)	
1000 ->				5		5	(1.71)	
1500 ->						0	(0.00)	
2000 ->						0	(0.00)	
2500 ->				2		2	(0.68)	
3000 +			1			1	(0.34)	
TOTALS:	0	0	72	168	52	292		
(%)	(0.00)	(0.00)	(24.66)	(57.53)	(17.81)			

292 features tabulated

ΣTrArea=27646

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->			8.59	27.09	5.92	41.60		
500 ->				5.45		5.45		
1000 ->				21.71		21.71		
1500 ->						0.00		
2000 ->						0.00		
2500 ->				19.88		19.88		
3000 +			11.36			11.36		
TOTALS:	0.00	0.00	19.95	74.13	5.92	100.00		

London Garden Soils

83/072

2225 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	14		223	1365	561	2163	(97.21)	
50.0 ->			1	17	6	24	(1.08)	
100 ->			3	10	3	16	(0.72)	
150 ->				4	5	9	(0.40)	
200 ->			1	3	1	5	(0.22)	
250 ->						0	(0.00)	
300 ->				2		2	(0.09)	
350 ->				2	1	3	(0.13)	
400 ->					2	2	(0.09)	
450 +				1		1	(0.04)	
TOTALS:	14	0	228	1404	579	2225		
(%)	(0.63)	(0.00)	(10.25)	(63.10)	(26.02)			

2225 features tabulated

ΣTrArea=18435

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS		
TrArea:								
0.0 ->	0.16		4.37	32.23	11.85	48.61		
50.0 ->			0.45	6.15	2.68	9.28		
100 ->			1.97	6.72	2.13	10.81		
150 ->				3.68	4.89	8.58		
200 ->			1.15	3.38	1.23	5.77		
250 ->						0.00		
300 ->				3.59		3.59		
350 ->				4.03	2.00	6.03		
400 ->					4.69	4.69		
450 +				2.64		2.64		
TOTALS:	0.16	0.00	7.94	62.44	29.46	100.00		

83/126

1539 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS	(%)	
TrArea:								
0.0 ->	10	45	450	937	41	1483	(96.36)	
100 ->			5	20	1	26	(1.69)	
200 ->	1		4	8		13	(0.84)	
300 ->			1	4		5	(0.32)	
400 ->		1	1	1		3	(0.19)	
500 ->		1		1		2	(0.13)	
600 ->		1		3		4	(0.26)	
700 ->				1		1	(0.06)	
800 +				1	1	2	(0.13)	
TOTALS:	11	48	461	976	43	1539		
(%)	(0.71)	(3.12)	(29.95)	(63.42)	(2.79)			

(cont. overleaf)

1539 features tabulated

Σ TrArea=31009

Percentage Σ TrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS
TrArea:						
0.0 ->	0.14	1.38	11.93	33.79	1.05	48.30
100 ->			2.43	9.18	0.45	12.05
200 ->	0.78		3.00	5.77		9.55
300 ->			1.11	4.52		5.64
400 ->		1.51	1.57	1.51		4.60
500 ->		1.74		1.70		3.45
600 ->		2.20		6.25		8.46
700 ->				2.32		2.32
800 +				2.83	2.82	5.65
TOTALS:	0.92	6.84	20.04	67.87	4.33	100.00

83/279

692 features tabulated

No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)
TrArea:						
0.0 ->	82	45	281	214	9	631 (91.18)
100 ->	1	1	16	7	2	27 (3.90)
200 ->		2	6	6		14 (2.02)
300 ->			5	4		9 (1.30)
400 ->			3	1		4 (0.58)
500 ->	2			2		4 (0.58)
600 ->						0 (0.00)
700 ->			1			1 (0.14)
800 ->						0 (0.00)
900 +			1	1		2 (0.29)
TOTALS:	85	48	313	235	11	692
(%)	(12.28)	(6.94)	(45.23)	(33.96)	(1.59)	

692 features tabulated

Σ TrArea=23518

Percentage Σ TrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS
TrArea:						
0.0 ->	2.89	1.97	14.64	10.22	0.21	29.93
100 ->	0.75	0.78	8.16	4.06	1.07	14.82
200 ->		1.98	6.12	6.15		14.25
300 ->			7.04	6.16		13.21
400 ->			5.36	1.86		7.22
500 ->	4.51			4.52		9.03
600 ->						0.00
700 ->			3.28			3.28
800 ->						0.00
900 +			4.06	4.20		8.27
TOTALS:	8.16	4.73	48.66	37.17	1.28	100.00

88/015

3700 features tabulated

No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)
TrArea:						
0.0 ->	25	30	394	2852	312	3613 (97.65)
200 ->	2	2	13	44	2	63 (1.70)
400 ->	1			11	1	13 (0.35)
600 ->			1	3		4 (0.11)
800 ->			1	3		4 (0.11)
1000 ->						0 (0.00)
1200 ->				2		2 (0.05)
1400 ->						0 (0.00)
1600 +	1					1 (0.03)
TOTALS:	29	32	409	2915	315	3700
(%)	(0.78)	(0.86)	(11.05)	(78.78)	(8.51)	

3700 features tabulated

ΣTrArea=93909

Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS
TrArea:						
0.0 ->	0.24	0.88	6.48	52.42	2.55	62.57
200 ->	0.62	0.67	4.38	12.91	0.61	19.18
400 ->	0.46			5.74	0.49	6.70
600 ->			0.81	2.35		3.16
800 ->			1.00	2.84		3.84
1000 ->						0.00
1200 ->				2.76		2.76
1400 ->						0.00
1600 +	1.79					1.79
TOTALS:	3.11	1.55	12.68	79.01	3.65	100.00

88/177

3700 features tabulated

No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)
TrArea:						
0.0 ->	89	50	427	2883	232	3681 (99.49)
200 ->		1	5	10		16 (0.43)
400 ->			2			2 (0.05)
600 ->						0 (0.00)
800 ->						0 (0.00)
1000 +		1				1 (0.03)
TOTALS:	89	52	434	2893	232	3700
(%)	(2.41)	(1.41)	(11.73)	(78.19)	(6.27)	

3700 features tabulated

ΣTrArea=41788

Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +	TOTALS
TrArea:						
0.0 ->	0.85	3.55	13.86	63.85	1.82	83.94
200 ->		0.53	3.20	7.25		10.98
400 ->			2.27			2.27
600 ->						0.00
800 ->						0.00
1000 +		2.81				2.81
TOTALS:	0.85	6.89	19.34	71.10	1.82	100.00

ANALYSIS OF FLOATS

PWF937F

235 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +		TOTALS (%)	
TrArea:								
0.0 ->		1	154	71		226	(96.17)	
200 ->			3	2		5	(2.13)	
400 ->		1				1	(0.43)	
600 ->			1			1	(0.43)	
800 ->				1		1	(0.43)	
1000 +			1			1	(0.43)	
TOTALS:		2	159	74	0	235		
(%)	(0.00)	(0.85)	(67.66)	(31.49)	(0.00)			

235 features tabulated

ΣTrArea=9159

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +		TOTALS	
TrArea:								
0.0 ->		0.07	36.38	11.49		47.94		
200 ->			11.01	4.59		15.61		
400 ->		6.24				6.24		
600 ->			7.35			7.35		
800 ->				10.41		10.41		
1000 +			12.46			12.46		
TOTALS:	0.00	6.31	67.20	26.49	0.00	100.00		

OMS942F

260 features tabulated

		No. of features						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +		TOTALS (%)	
TrArea:								
0.0 ->	13	8	97	105		223	(85.77)	
100 ->			11	12		23	(8.85)	
200 ->			1	3		4	(1.54)	
300 ->			4	2		6	(2.31)	
400 ->						0	(0.00)	
500 ->			1			1	(0.38)	
600 ->			2			2	(0.77)	
700 +			1			1	(0.38)	
TOTALS:	13	8	117	122	0	260		
(%)	(5.00)	(3.08)	(45.00)	(46.92)	(0.00)			

260 features tabulated

ΣTrArea=15524

		Percentage ΣTrArea						
Class:	0.00->	1.00->	2.00->	3.00->	4.00 +		TOTALS	
TrArea:								
0.0 ->	1.52	1.99	20.46	19.43		43.40		
100 ->			9.52	10.63		20.15		
200 ->			1.33	4.87		6.19		
300 ->			9.12	4.52		13.64		
400 ->						0.00		
500 ->			3.75			3.75		
600 ->			8.29			8.29		
700 +			4.57			4.57		
TOTALS:	1.52	1.99	57.04	39.45	0.00	100.00		

88/015F

395 features tabulated

No. of features					
Group:	1.00->	2.00->	3.00->	4.00 +	TOTALS (%)
TrArea:					
0.0 ->	61	81	210	5	357 (90.38)
50.0 ->	3	2	11	1	17 (4.30)
100 ->	3	1	6		10 (2.53)
150 ->	1	1	1		3 (0.76)
200 ->					0 (0.00)
250 ->	1		1	1	3 (0.76)
300 ->		1	1		2 (0.51)
350 ->					0 (0.00)
400 ->			1		1 (0.25)
450 +	1		1		2 (0.51)
TOTALS:	70	86	232	7	395
(%)	(17.72)	(21.77)	(58.73)	(1.77)	

395 features tabulated

Σ TrArea=9232

Percentage Σ TrArea					
Group:	1.00->	2.00->	3.00->	4.00 +	TOTALS
TrArea:					
0.0 ->	7.76	7.94	21.34	0.28	37.31
50.0 ->	2.18	1.20	8.16	0.88	12.41
100 ->	4.01	1.36	8.30		13.67
150 ->	1.90	2.09	1.79		5.79
200 ->					0.00
250 ->	2.79		3.13	2.91	8.83
300 ->		3.45	3.42		6.87
350 ->					0.00
400 ->			4.67		4.67
450 +	5.36		5.09		10.45
TOTALS:	23.99	16.04	55.90	4.07	100.00

APPENDIX I: XRD TRACES

The ensuing black and white traces represent raw XRD data for the heavy density fraction following samples:

SO1 (mineral sample of pyromorphite)

DVT921

DVS922

PWF937

OMS942

WSG923

OMV927

SBV928

SE952

Reflectance lines on these traces are identified as follows:

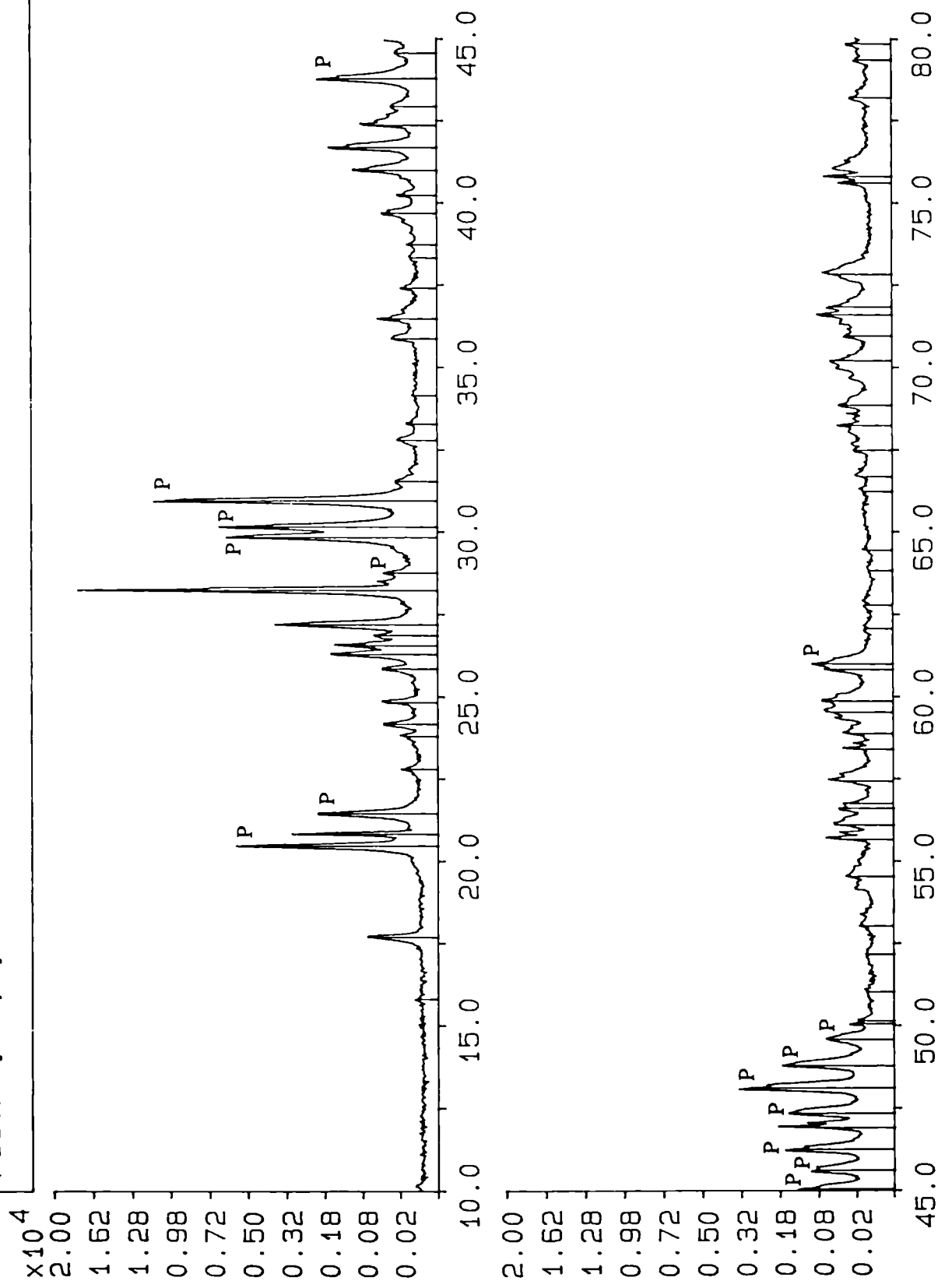
P = pyromorphite

B = barite

C = cerussite

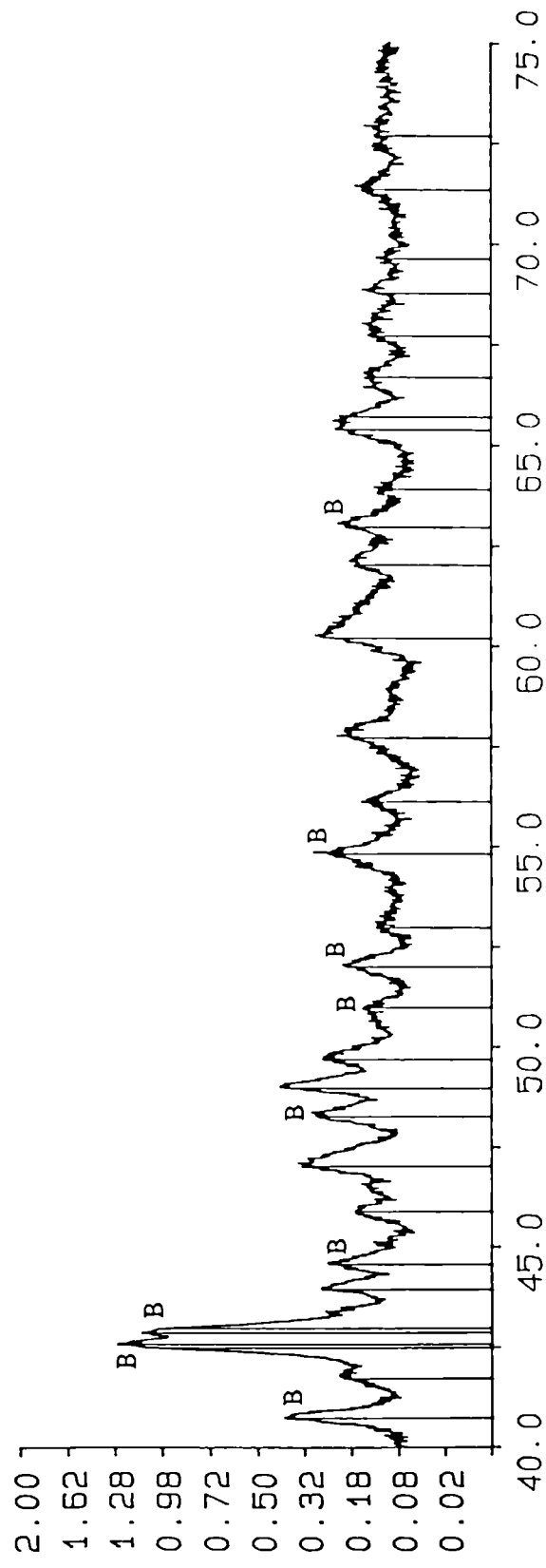
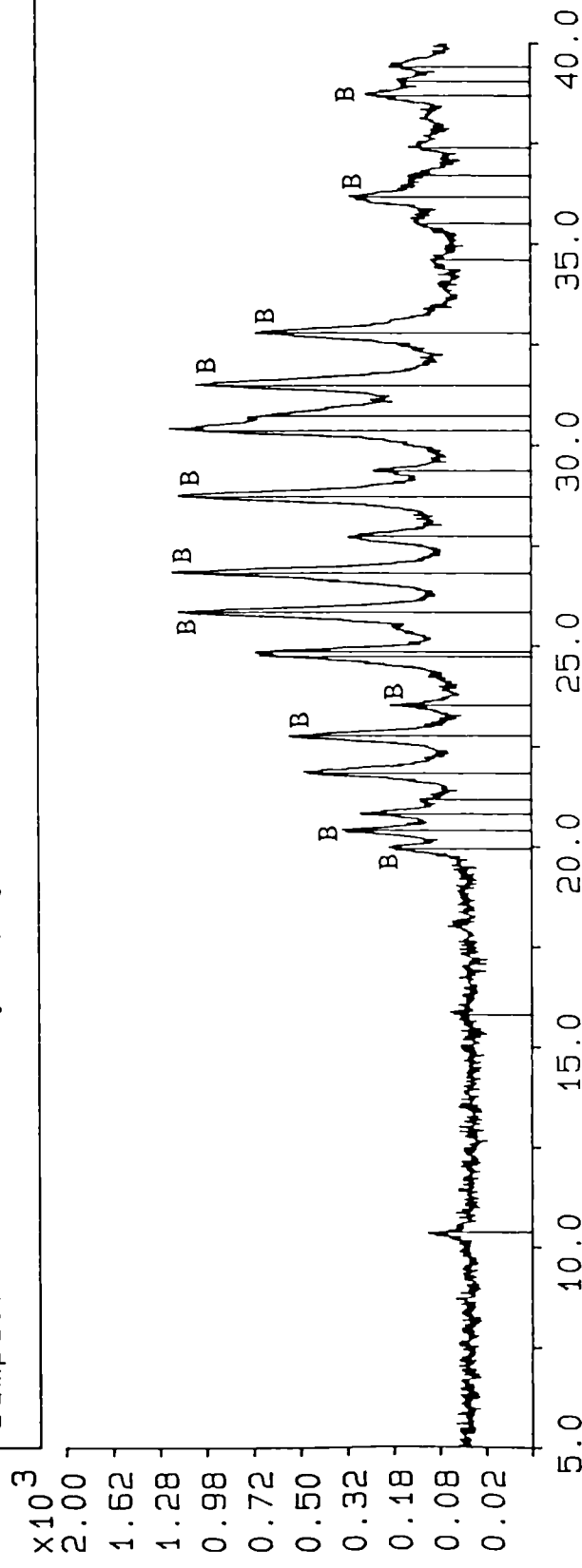
A = anglesite

Colour traces are shown for all the above samples with the exception of SO1 and SE952. These are the residual traces after identified minerals have been subtracted. The JCPDS (synthetic) pyromorphite trace is also shown for comparison.



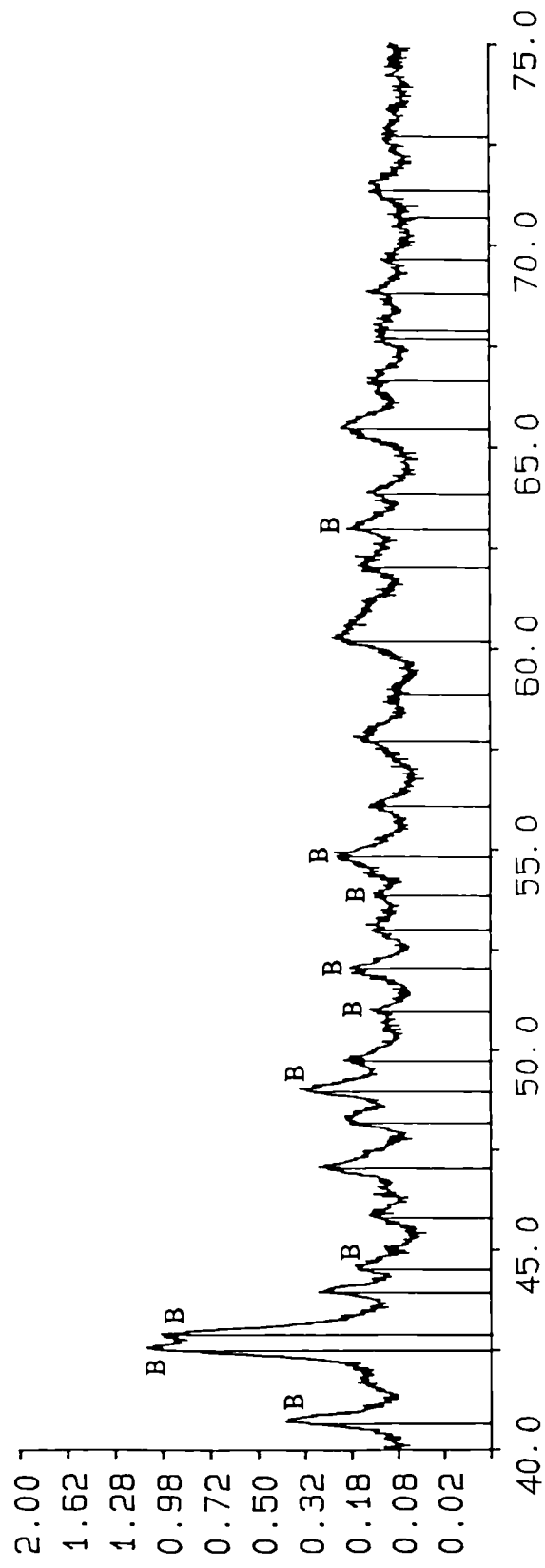
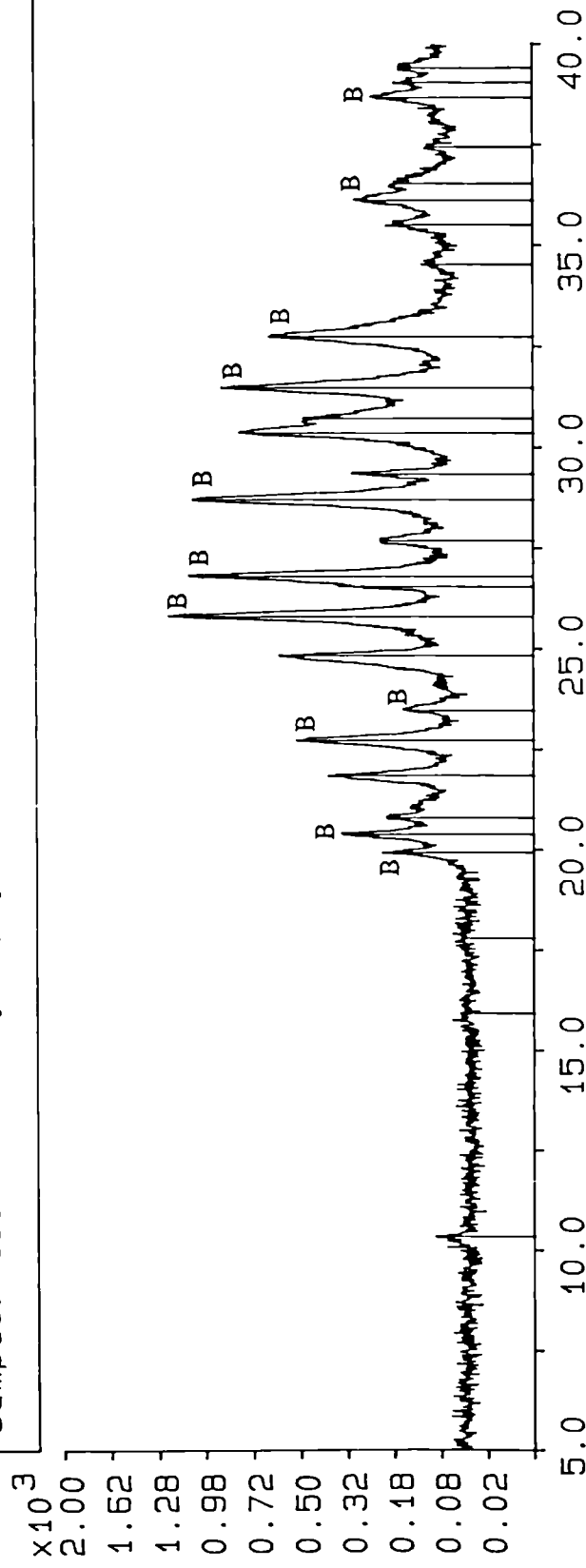
Sample: 921 File: [300, 2] JH921.RD

08-JUL-91 18:10



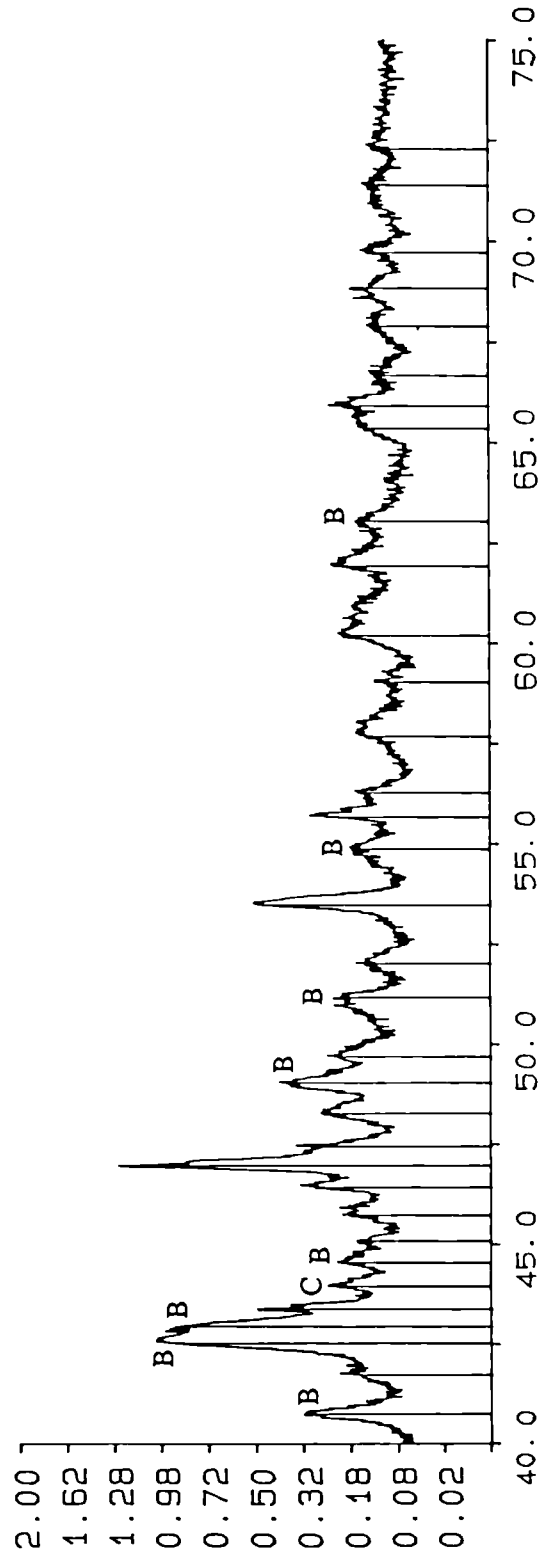
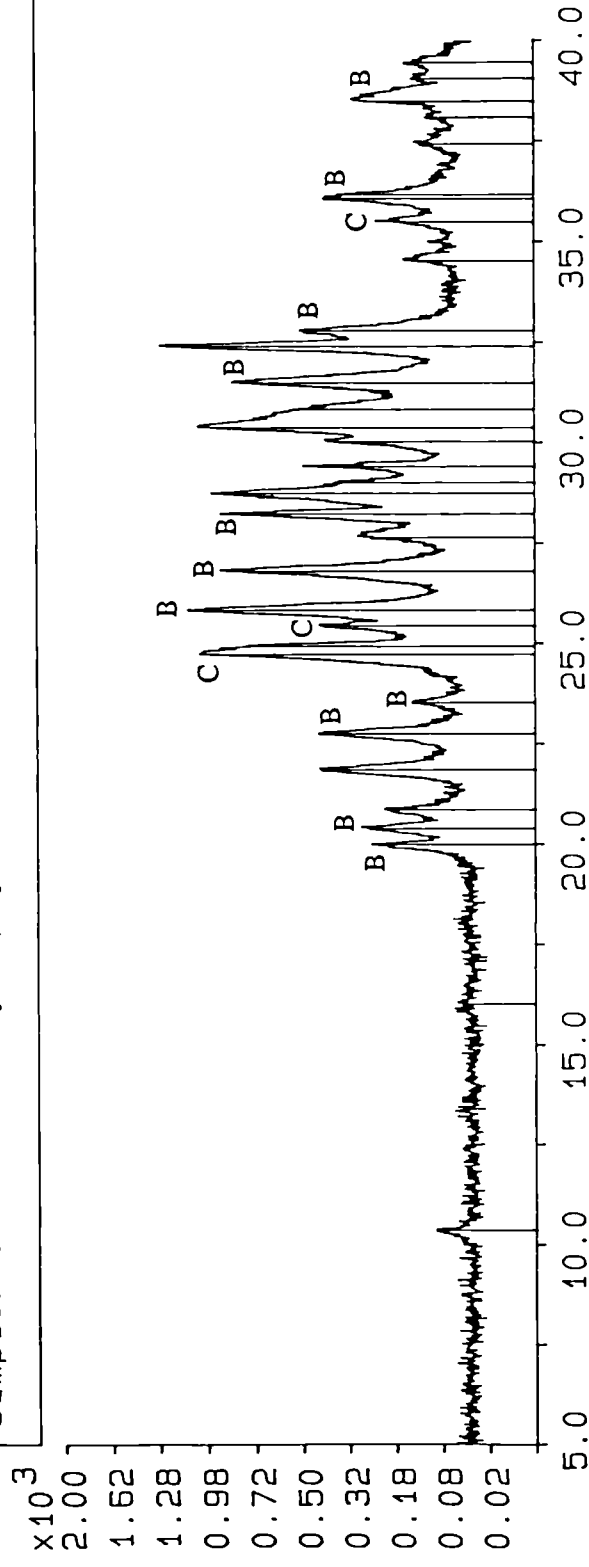
Sample: 922 File: [300, 2] JH922.RD

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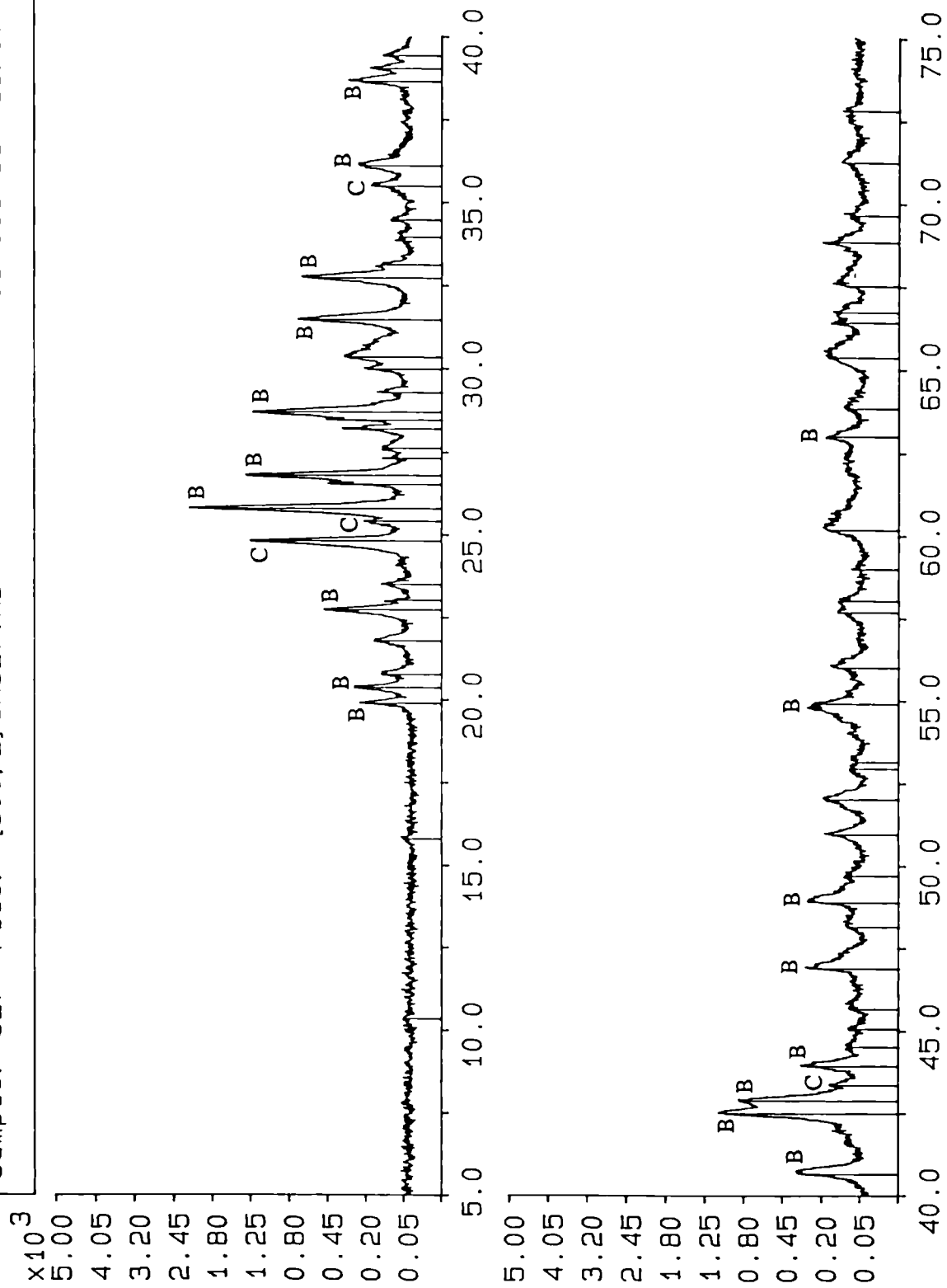
Sample: 923 File: [300,2] JH923.RD

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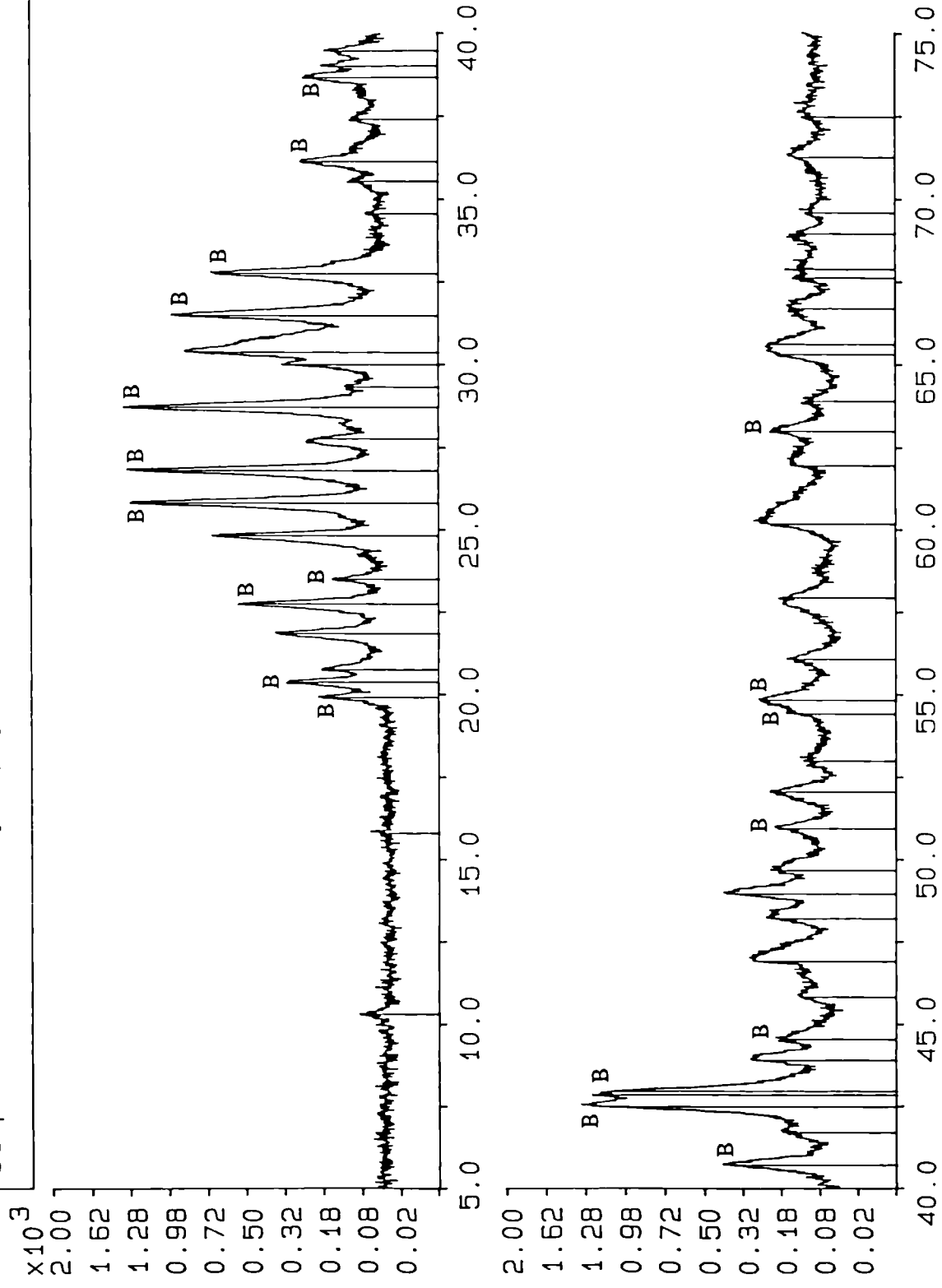
Sample: 927 File: [300, 2] JH927.RD

08-JUL-91 18: 07

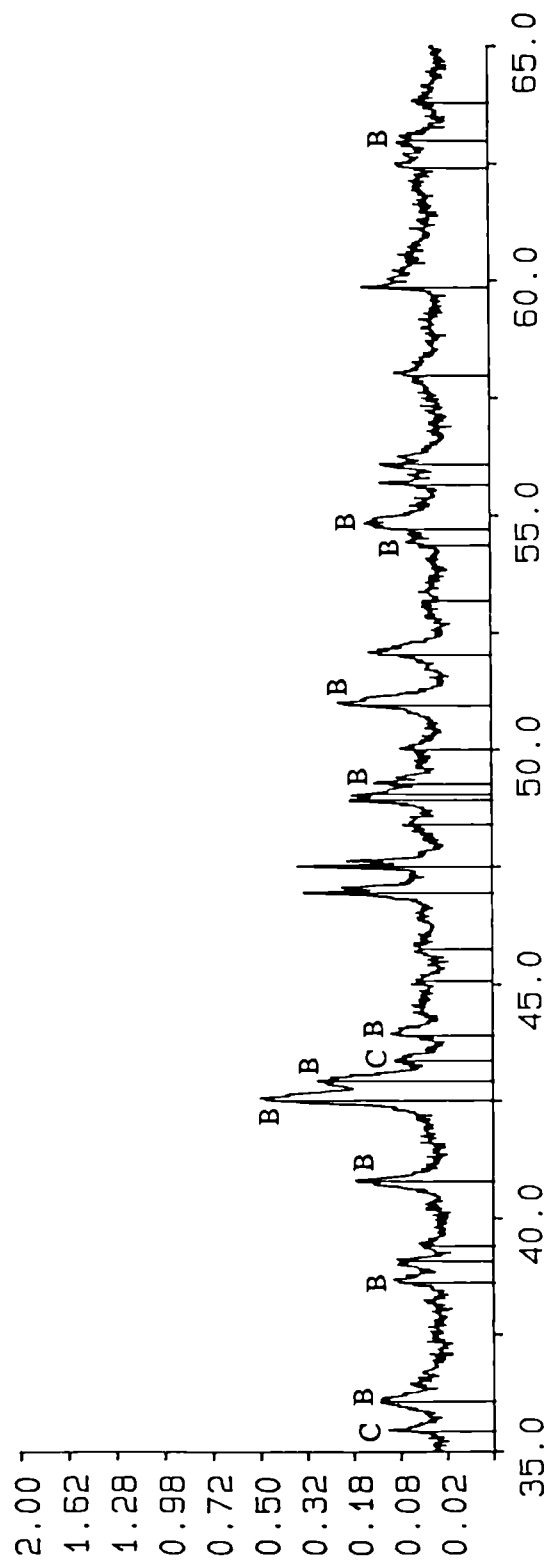
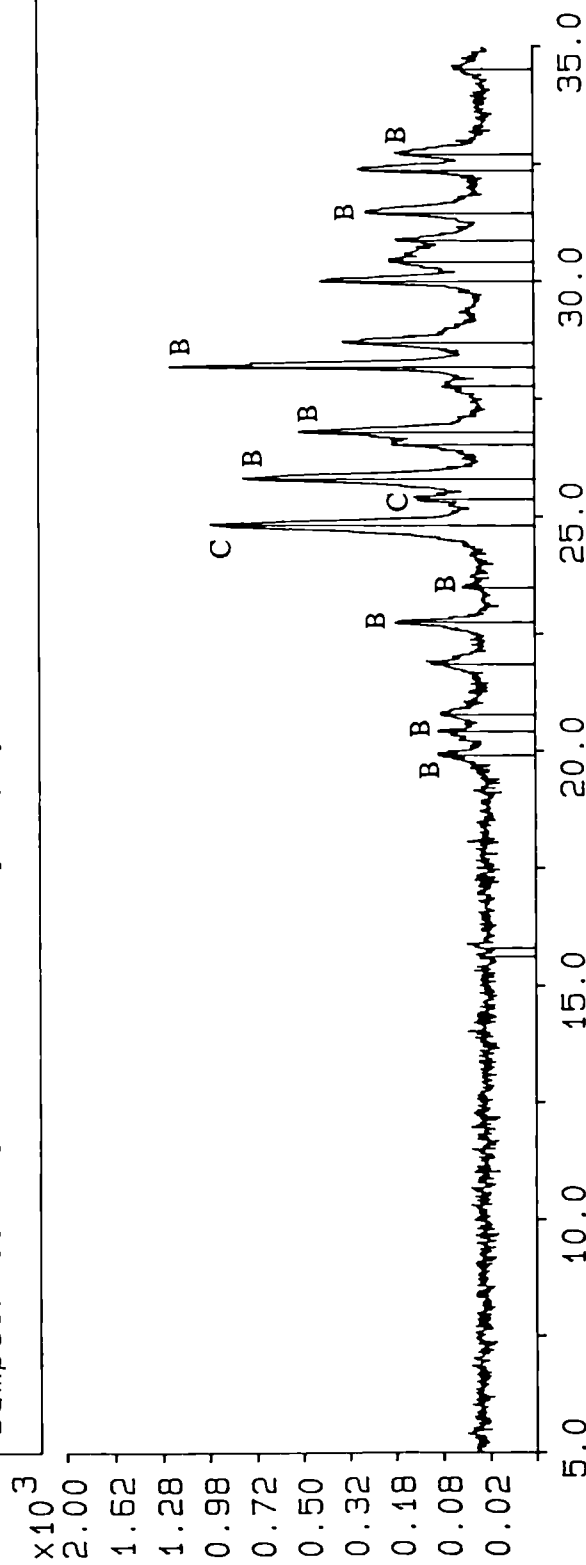


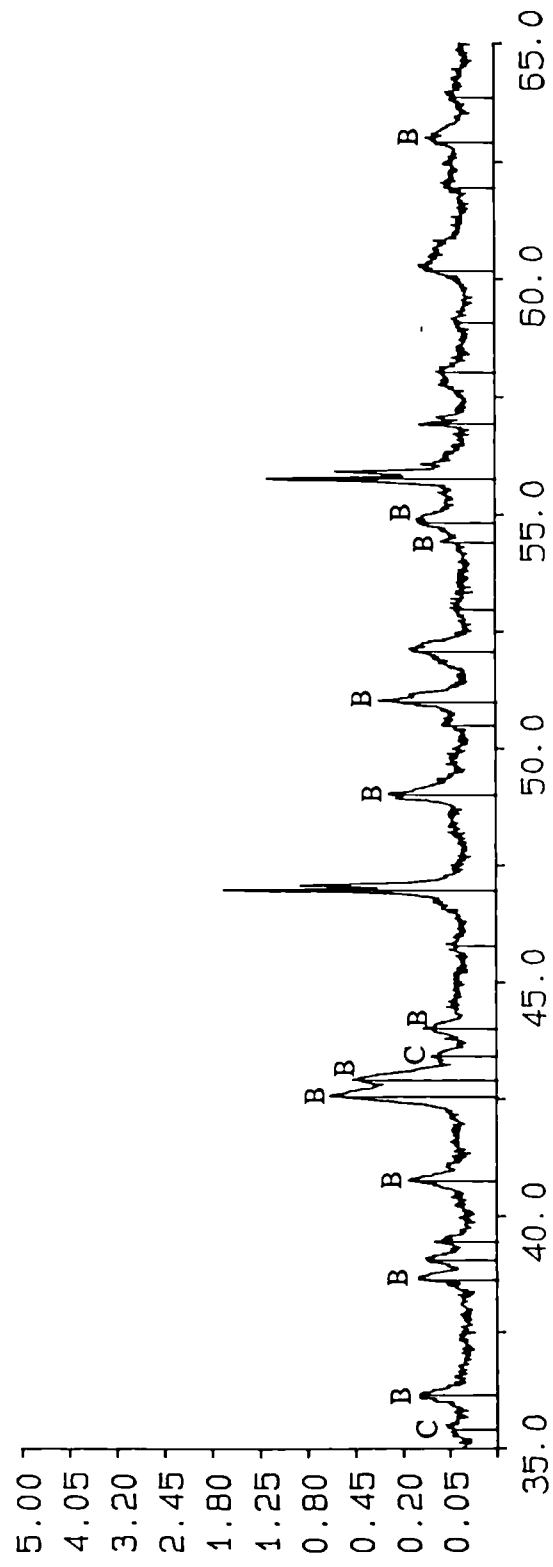
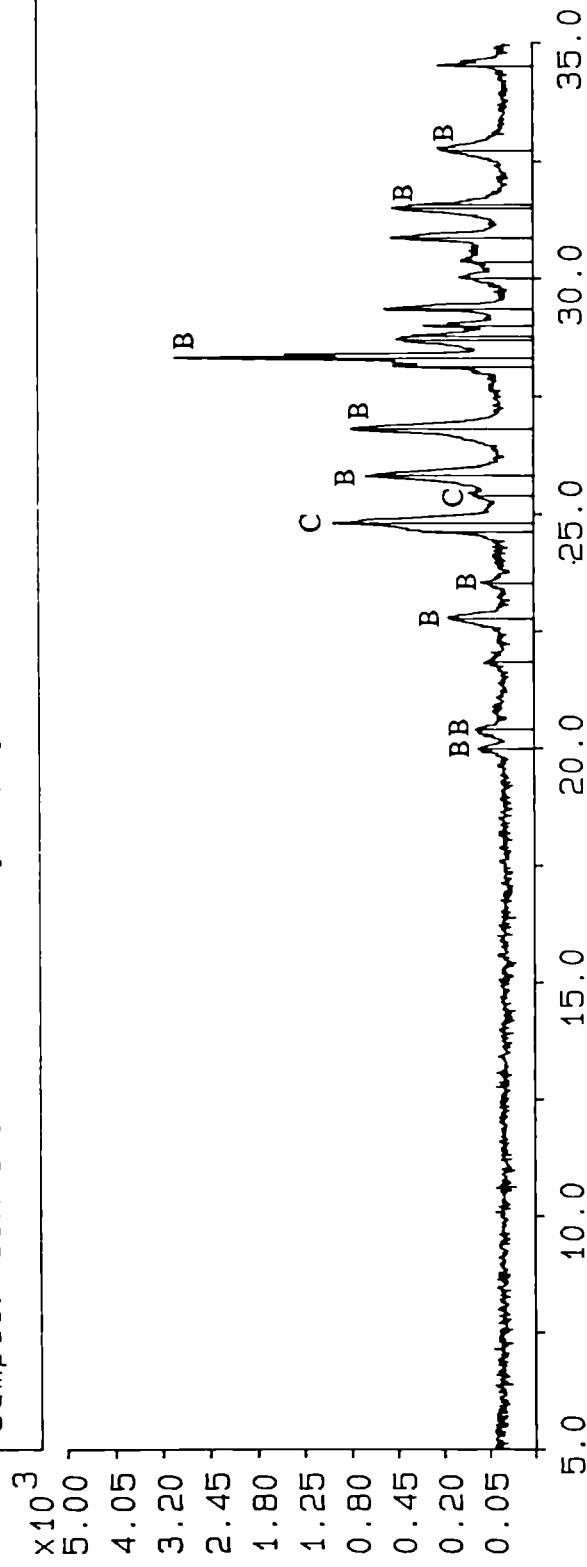
Sample: 928 File: [300,2] JH928.RD

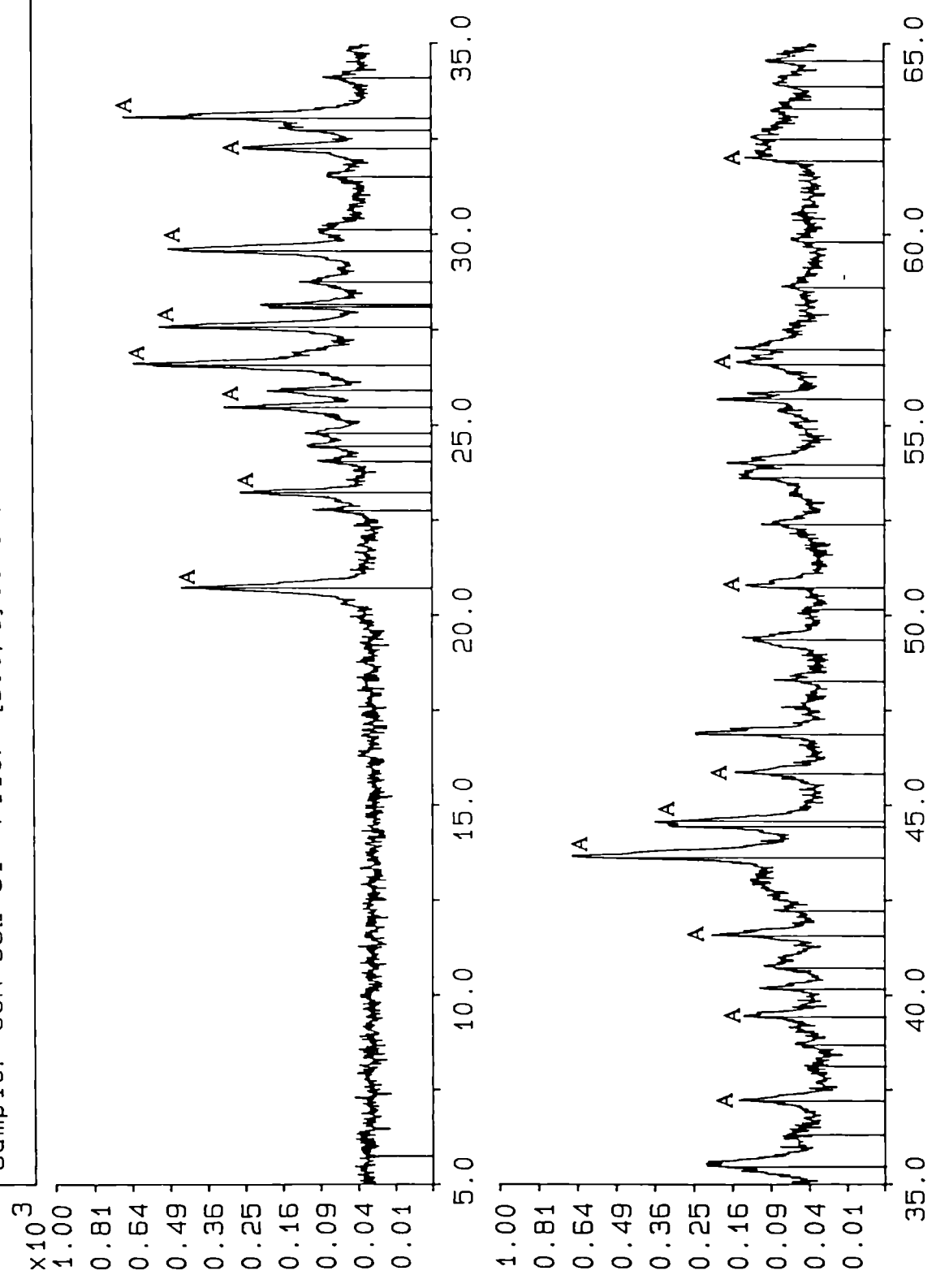
08-JUL-91 18:06



Sample: JCH 937 S1 File: [300, 1] JCH937.RD 08-JUL-91 18: 15







APPENDIX J: LIST OF BULK SOIL SAMPLES

The following list of bulk soil samples used in the Solid Speciation Study is intended to be used as a reference throughout the thesis.

Winster mine-waste soils

DVT921 - Drummers Venture topsoil
DVS922 - Drummers Venture subsoil
PWF937 - Painters Way Farm
OMS942 - Site of Orchard Mine (in centre of Winster village)
WSG923 - Stream sediment from ore Washing Site
OMV927 - Winster vegetable garden soil
SBV928 - Winster vegetable garden soil

Derbyshire Soils

TF943 - Tideslow Farm (mine-waste soil)
HF945 - Hollow Farm (mine-waste soil)
SE952 - Stone Edge smelter site
VGWH941 - Via Gellia old industrial site.

Other U.K. Soils

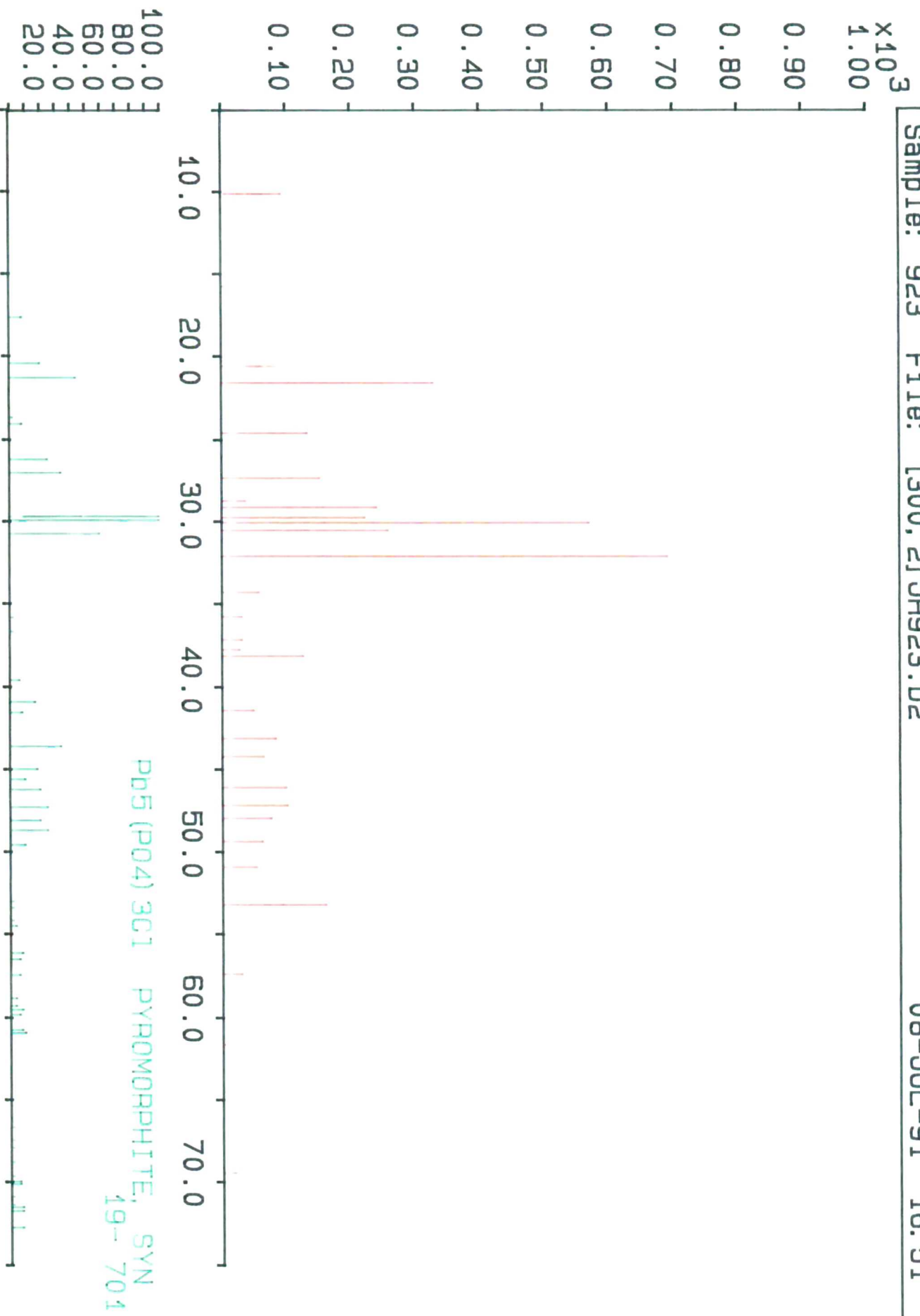
CHBP953 - Charterhouse ore washing site (now soil), Mendips
CHMS960 - Charterhouse mine-waste soil, Mendips
M1S934 - Motorway (M1) roadside soil

London Garden Soils

Hammersmith and Fulham - 83/072
83/126
83/279
Westminster - 88/015
88/177

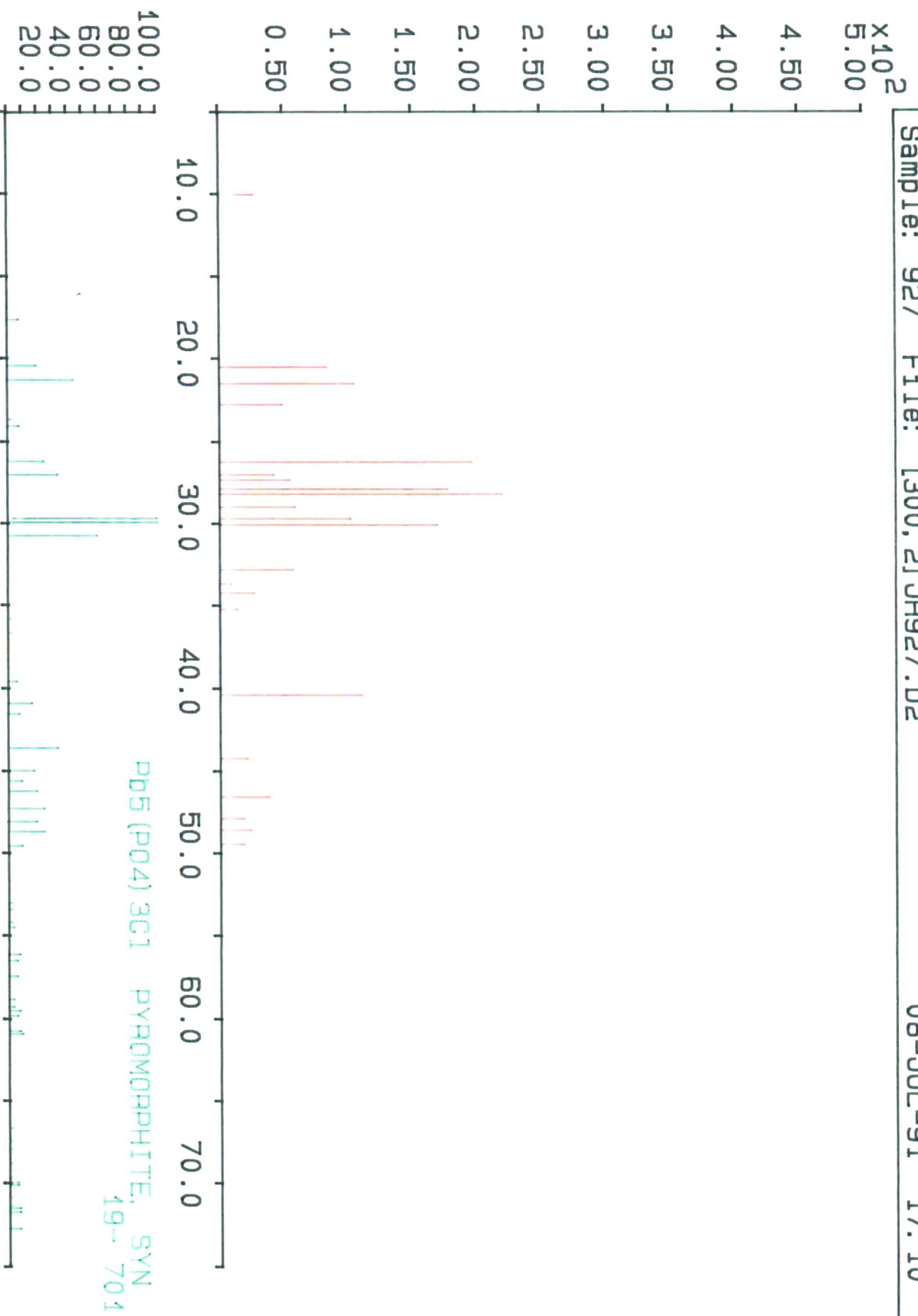
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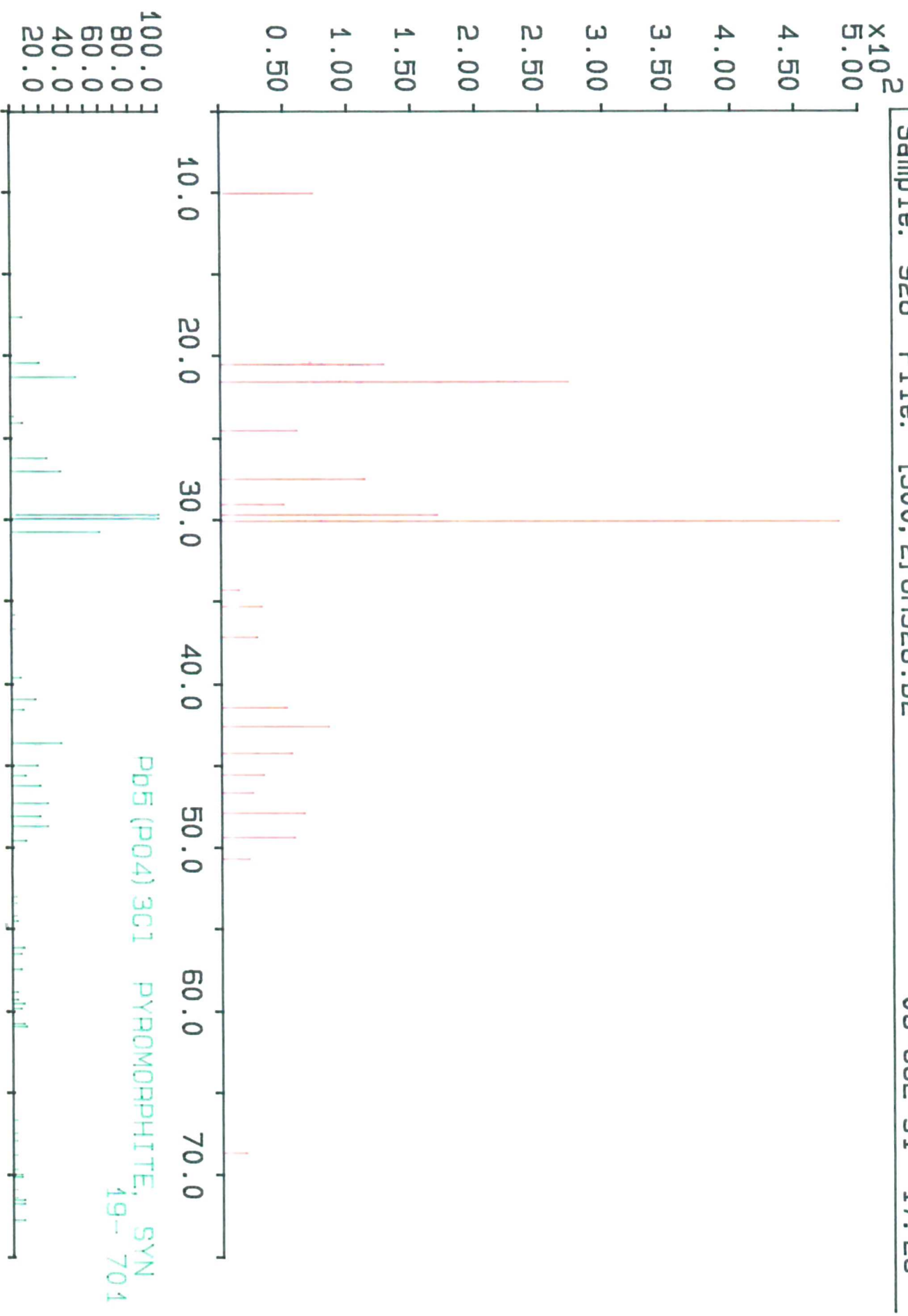
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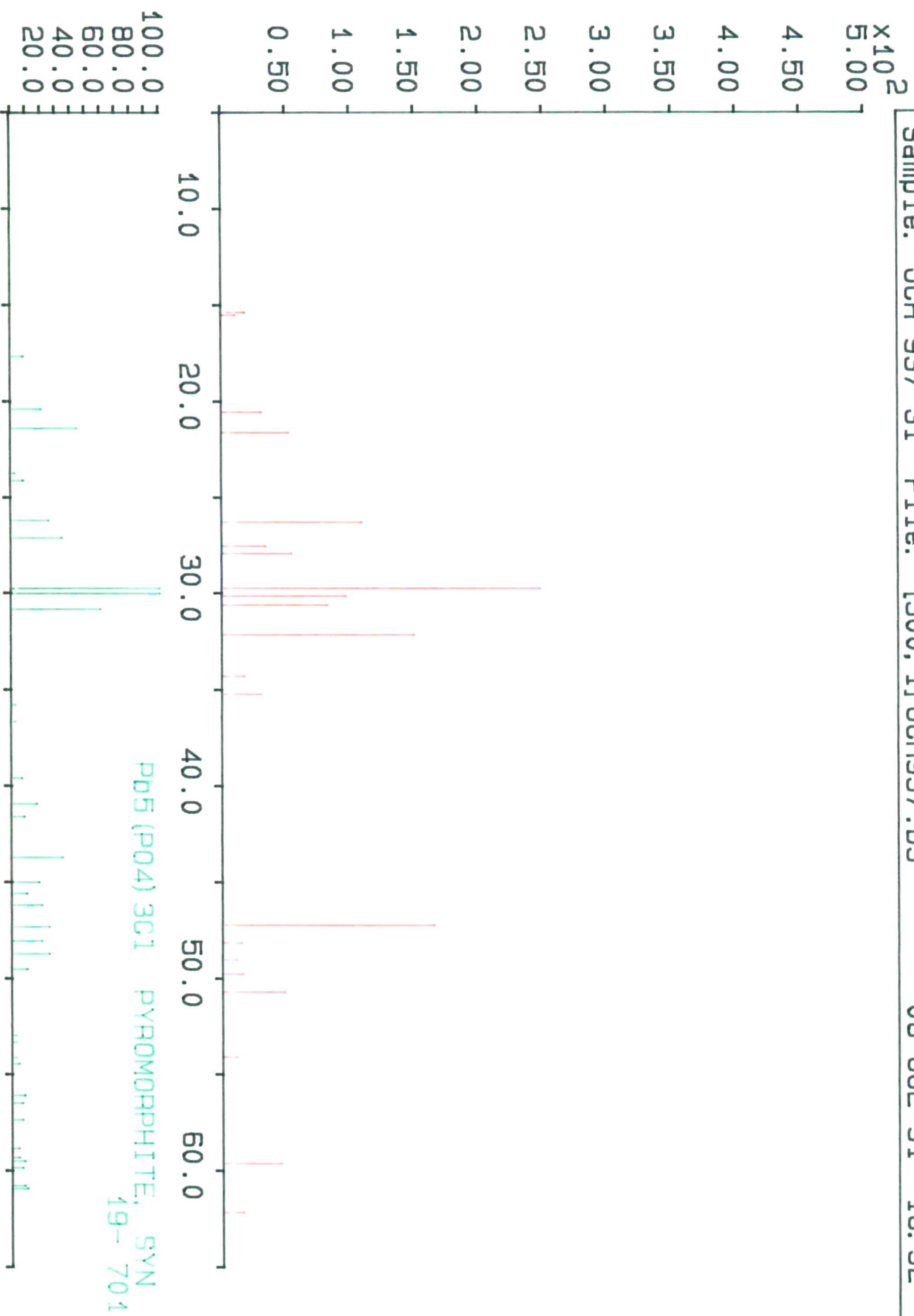
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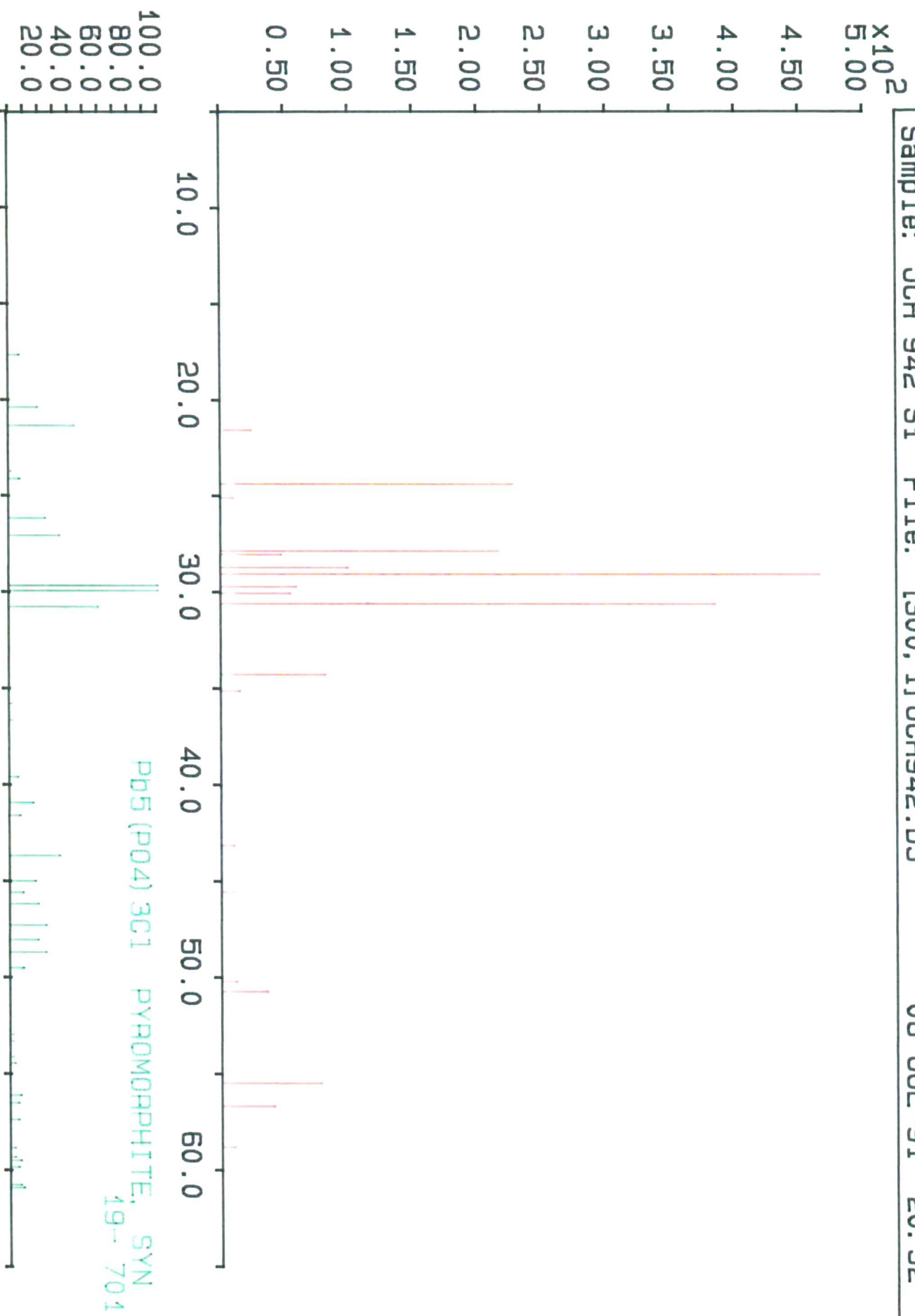
Sample: JCH 937 S1 File: [300,1] JCH937.D3

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Sample: JCH 942 S1 File: [300, 1] JCH942.D3

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.PUBLICATIONS

PYROMORPHITE: A SECONDARY LEAD MINERAL

J. Cotter-Howells and R. Giddens

Abstract: Pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$] is an oxidised weathering product of galena found at localities in the Derbyshire Peak District. It is an important soil lead mineral, possibly controlling the levels of lead in natural waters. Its formation may be limited by the availability of phosphorus.

Pyromorphite has the chemical formula $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$. It is a secondary lead mineral formed by weathering of the common lead ore, galena (PbS) under oxidising conditions.

The following micrographs are of a pyromorphite specimen collected from Tideslow Rake [GR SK145782] in the Derbyshire Peak District by Dr. N. Butcher approximately 5m below ground surface. Similar specimens have been found in the Winsters area approximately 20kms south-east of Tideslow Rake. Both specimens were associated with basaltic horizons. The pictures were obtained using a scanning electron microscope at a magnification of 500-10,000x at Imperial College.

Plates 1 and 2 show well formed fans of hexagonal prisms, reflecting the crystal structure of pyromorphite (Plate 3). The splayed nature of the fans is typical of in-situ weathering of ore deposits. Plate 4 is an example of interlocking crystals. X-ray spectra show that the sample contains lead, phosphorus and chlorine.

Pyromorphite has an apatite structure similar to that of bone material, hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Neuman and Neuman 1953). A limited amount of lead can substitute for calcium in bone material. Similarly, a small amount of calcium can substitute for lead in pyromorphite.

Pyromorphite has been found in the oxidised zone of lead ore deposits at many localities (Palanche 1951; Read 1971). Grains of pyromorphite have been found in lead-mine waste soils from Winsters by the author (unpublished results) but it is unclear whether these formed in the soil from galena or were incorporated into the soil in their present form.

A thermodynamic study (using experimental and predicted data) of pyromorphites and other lead minerals by Nriagu (1973; 1974) concluded that chloropyromorphite (previous reports refer to chloropyromorphite as simply pyromorphite) is the most stable lead mineral under the geochemical conditions occurring in the surface environment i.e. $E_h = +0.2$ to $+0.8$, $\text{pH} = 4$ to 11 . It has an extremely low solubility [$K_{sp} = 10^{-84.1} \pm 0.1$ (Nriagu 1973)] and may be important in maintaining a low concentration of lead in natural waters (Wedepohl et al 1969; Nriagu 1974).

The formation of pyromorphite can be limited by the availability of either chlorine or phosphorus. Chlorine is widely distributed in the surface environment and only small amounts of chlorine are required to form pyromorphite. Phosphorus however, is a major constituent of pyromorphite but occurs only as a trace element in most

soils. Therefore, the availability of phosphorus is likely to be a limiting factor in the formation of pyromorphite, especially in the case of an oxidised lead deposit where lead is abundant. If phosphorus is not available, galena will weather to anglesite (PbSO_4) or cerussite (PbCO_3) depending on the pH (Garrels and Christ 1965).

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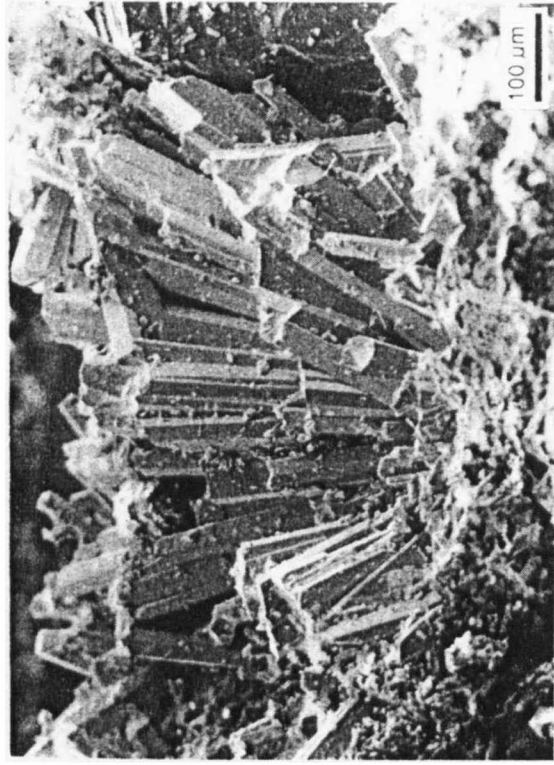


Plate 1.

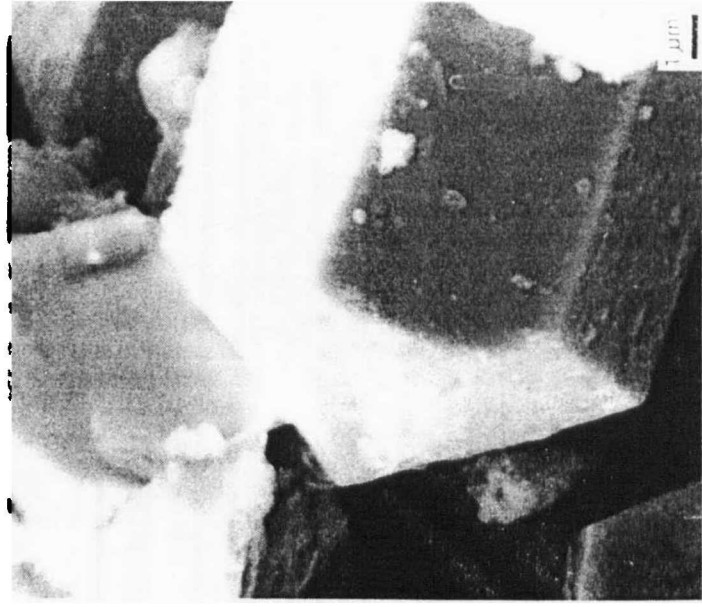


Plate 2.

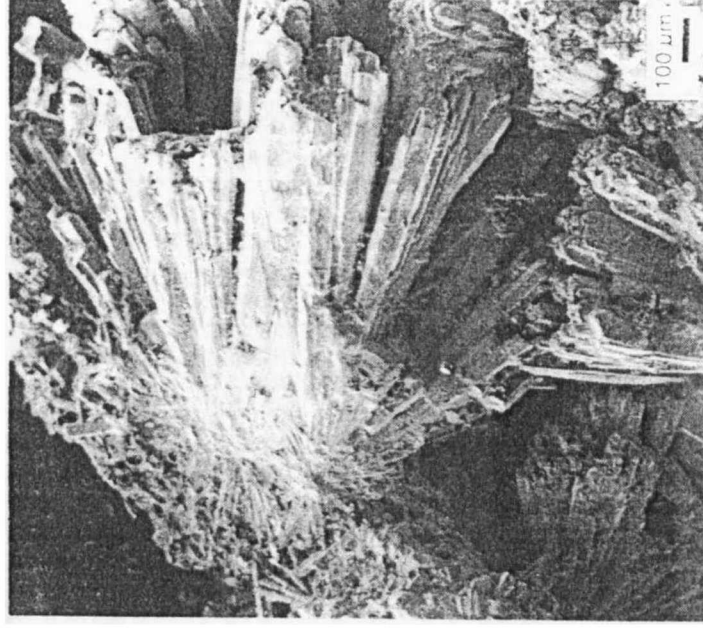


Plate 3.

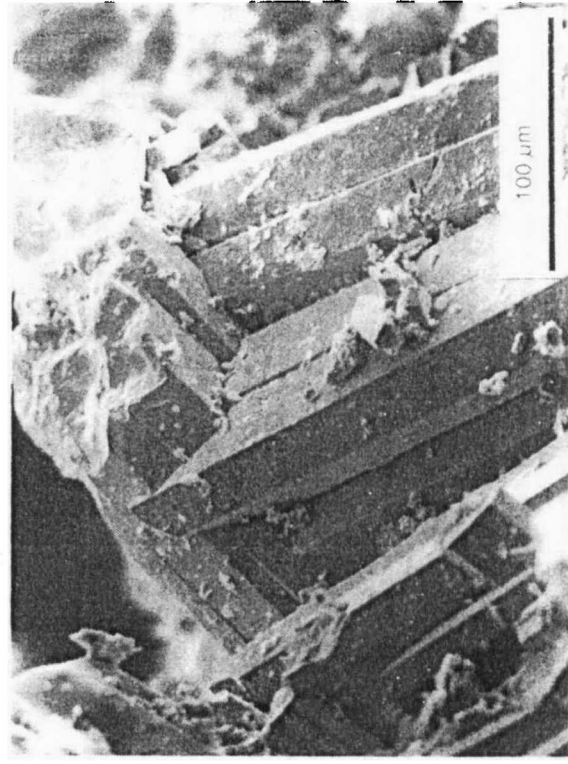


Plate 4.

Plates 1 to 4: Micrographs of pyromorphite crystals showing form, habit and hexagonal symmetry.

Sources and pathways of environmental lead to children in a Derbyshire mining village

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Abstract

Garden soil and housedust samples, from households in a Derbyshire village closely associated with historic lead mining, have highly elevated lead levels. Handwipe samples from children also have relatively high lead concentrations suggesting that elevated levels of lead are transferred to the child by the soil-dust-hand-mouth pathway. However, this is not reflected in their blood lead concentrations which are within normal UK ranges and less than predicted by some lead exposure models. SEM analysis of soil grains has revealed that many are composed of pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$], a stable soil-lead mineral. This mineral is formed from the weathering of galena [PbS] but it is not clear to what extent weathering has occurred in the soil. Pyromorphite has an extremely low solubility which may contribute to a low human bioavailability of lead in these soils, resulting in the lower than expected blood lead concentrations.

Introduction

There has been much concern recently, that intellectual development in young children may be impaired by long term environmental exposure to lead (MRC, 1985; MRC, 1988). Publications concerning this exposure consider garden soil and housedust as important sources of lead: for example, Yankel *et al.* (1977), Duggan (1983), Duggan and Inskip (1985). Young children inadvertently ingest dust by hand to mouth activity and sucking objects (Harvey *et al.*, 1985) and may even eat soil or dust, the habit known as pica. Two British studies have considered the relative importance of different pathways of lead to young children; one by the Royal Commission (1983) in their review of lead in the environment and the other by Davies *et al.* (1990) based on surveys undertaken in Birmingham. Both conclude that housedust accounts for approximately half of a young child's total daily lead exposure.

Elevated levels of lead have been found in Derbyshire stream sediments and soils (Colbourn and Thornton, 1978; Webb *et al.*, 1978) where there is a long history of mining. Village communities in Derbyshire closely associated with past mining activities contain raised lead concentrations in soil and housedust samples (Bartrop *et al.*, 1975; Culbard *et al.*, 1988). An investigation of lead exposure in the local population was conducted by Bartrop *et al.* (1974, 1975). Mean blood lead concentrations of $25.0 \mu\text{g dL}^{-1}$ were reported for children living in these villages, although no adverse health effects were apparent.

Blood lead levels have been falling at approximately 4% per annum since the early 1970s (DoE 1990), coinciding with the reduction of lead content in petrol, paint and food. During the same period, analytical instrumentation has greatly improved the accuracy of blood

lead determinations. This paper examines the sources and pathways of environmental lead to children in Winstar, one of the Derbyshire mining villages.

Winstar Village

Winstar village (GR SK241604) is situated in Derbyshire, Central England. It is underlain by mineralised limestone and three lead veins run directly through the village at shallow depth (Figure 1). Lead mining in the Winstar area dates back to the Roman occupation of Britain and culminated in an intensive lead mining phase involving mechanisation during the eighteenth century. The lead mining industry collapsed at the end of the eighteenth century and no mining has taken place in the immediate vicinity of Winstar since this time.

Present day Winstar village can be divided into two parts (Figure 1). The central part of the village comprises eighteenth century housing built during the heyday of mining whilst newer housing, mostly post-Second World War, has been built on the eastern periphery of the village. The older houses form an irregular array almost completely enclosing a central hillock of mine spoil which forms the gardens of many of the surrounding houses. Very little evidence of past mining activities is present in the orderly rows of the newer houses, although two houses have mine shafts in their gardens.

Method

Sampling

Soil and dust samples were collected in January 1988, handwipe samples in May 1988 and venous blood samples in September 1989. Forty-five households were sampled at random within Winstar. Samples of housedust, garden soil and if applicable, vegetable garden soil were collected

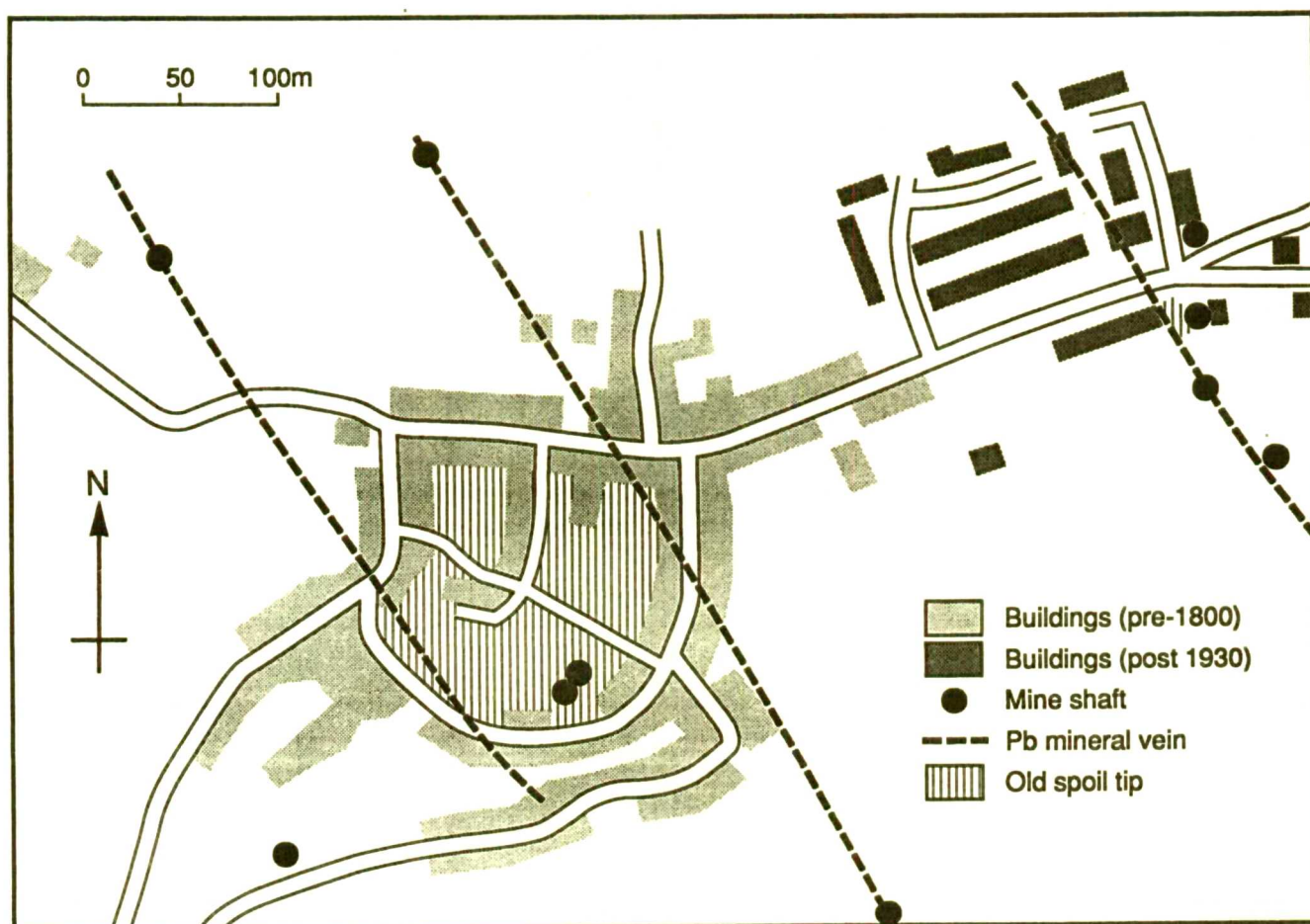


Figure 1 Sketch of Winstar village showing housing and mining features.

Table 1 Lead in environmental samples, handwipes and children's blood in Winstar (this study), Birmingham and a UK national survey.

	Winstar (present study)			Birmingham study (Davies et al., 1990)			UK national survey (Culbard et al., 1988) ¹		
	n	GM	Range	n	GM	Range ²	n	GM	Range
Garden soil (Pb $\mu\text{g g}^{-1}$)	42	7,140	2,400–22,800	86	313	92–1,160	4,126	266	13–14,100
Vegetable soil (Pb $\mu\text{g g}^{-1}$)	11	9,580	2,235–22,160		N/A		193	270	24–2,560
Housedust (Pb $\mu\text{g g}^{-1}$)	45	1,560	462–6,240	94	424	138–2,093	4,638	561	5–36,900
Lead loading (Pb $\mu\text{g m}^{-2}$)	44	275	14.2–3,560	93	60	4–486		N/A	
Handwipes ($\mu\text{g Pb}$ per pair of hands)	10	13.1	3.8–39.5	704	5.7	1.9–15.1		N/A	
Children's blood (Pb $\mu\text{g dL}^{-1}$)									
1–3 year-olds	3	6.9	6.2–8.3	97	11.7	6–24		N/A	
1–8 year-olds	10	9.4	6.2–20.7		N/A			N/A	

¹ including London but excluding geochemical hotspots.

² 5th and 95th percentiles.

N/A – not analysed.

GM – geometric mean.

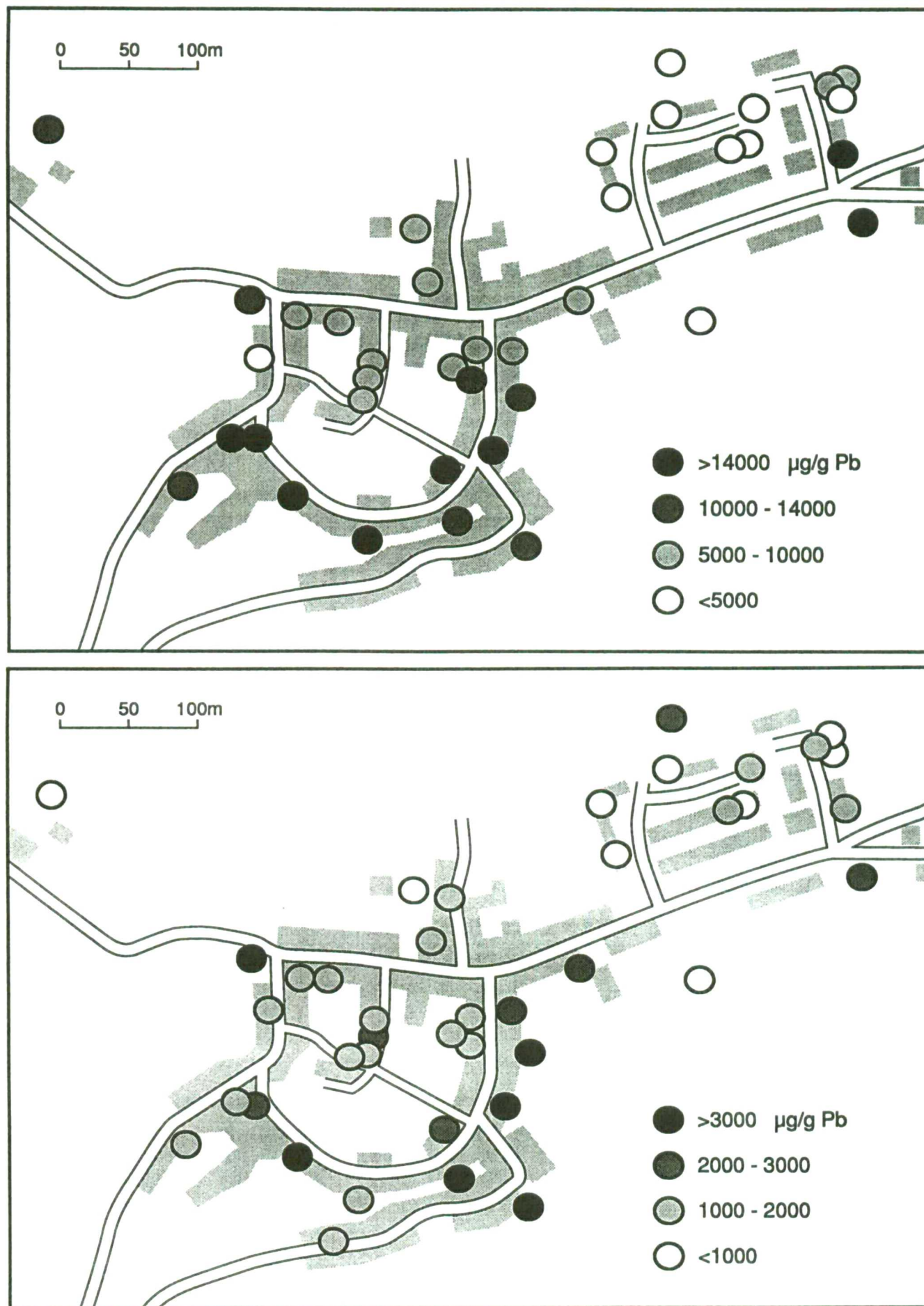
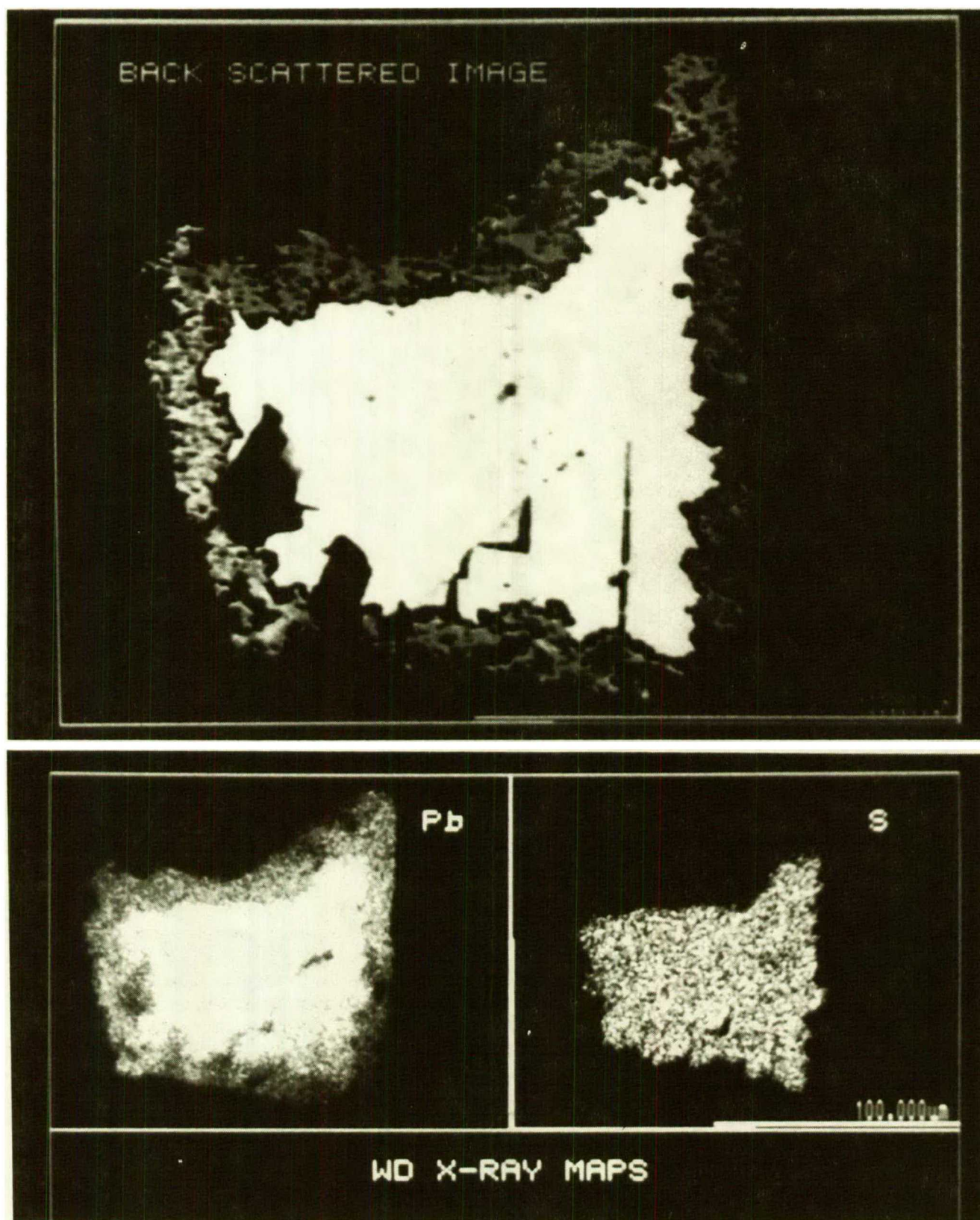


Figure 2(a) Distribution of lead in garden soil, Winsters. (b) Distribution of lead in housedust, Winsters.



Figures 3(a) and (b) SEM analysis of grain of galena showing outer weathered zone. Both lead and sulphur are present in the inner core but sulphur is absent in the weathered zone. Quantitative analysis indicates that this weathered zone is composed of cerussite (lead carbonate).

from each household. Four square metres of each householder's living room carpet was vacuumed and the dust collected in a filter thimble inserted into the vacuum nozzle (Watt *et al.*, 1983). This method allowed dust loading and hence dust lead loading (the amount of lead

per square metre) to be calculated. Soil samples comprised 25 (0–5 cm) depth subsamples of exposed earth. To evaluate sample variability, four duplicate housedust samples were taken during the same week and four duplicate soil samples 5 months later.

Table 2 House age and lead concentration in Winstar.

	<i>n</i>	GM (Pb $\mu\text{g g}^{-1}$)	Range
Houses <60 years old			
Housedust	16	925	462–2,290
Garden soil	16	4,300	2,400–17,600
Houses >60 years old			
Housedust	29	2,080	1,000–6,240
Garden soil	26	9,720	3,920–22,800

GM – geometric mean.

The quantity of lead present on the hands of young (1–2.5 yr old) Winstar children attending playgroup was determined using the handwipe technique of Davies and Watt (1986). The sampler's hands were first washed and wiped, then each child's pair of hands were wiped with a total of three wet-wipes which were placed in a self-sealing plastic bag and retained for analysis. Repeat samples were taken from two children on different days to evaluate variability.

Venous blood samples were taken from children aged 1–8 yr by a local practitioner and analysed at the Trace Element Unit, Southampton General Hospital.

Analysis

Dusts were passed through a mm sieve to remove carpet fibres whilst soils were disaggregated, sieved to <2 mm and ground to a powder in a "Tema" mill. Soils and dusts were digested in 4:1 concentrated nitric-perchloric acid and taken to dryness over 24 hours (1 hour 50°C, 3 hours 150°C, 18 hours 180°C). Samples were then leached in 5M HCl and made up to final volume with de-ionized water (DIW). (Thompson and Walsh, 1989.)

Handwipes were digested in warm concentrated HNO₃ and taken to dryness by boiling at 80°C. The residues were leached in HCl and made up to volume with DIW. (Davies and Watt, 1986.)

Solutions from soil and dusts were analysed using an ARL 34000 inductively coupled plasma atomic emission spectrometer; lead in handwipe samples was determined by a Perkin-Elmer 5000 flame atomic absorption spectrophotometer.

Throughout the analysis a rigorous data quality control procedure was adhered to. Each batch contained 10% duplicate pairs, 5% house reference materials and 5% reagent blanks. Analytical error was within $\pm 10\%$ for soils and dusts, and $\pm 20\%$ for handwipes.

SEM analysis

X-ray maps were compiled for individual Pb-rich grains in polished block samples of soil from the Winstar area using a JEOL 733 scanning electron microscope (SEM). X-ray mapping involves the collection of X-rays as the electron beam scans across a field of view. These X-rays are analysed by energy dispersive (EDX) or wavelength dispersive (WDX) systems. Multi-element analysis is

achieved by EDX but this system cannot differentiate between lead and sulphur, essential for the analysis of galena (PbS). Galena grains were therefore analysed using single element analysis by WDX which can differentiate between lead and sulphur. X-ray mapping has two major limitations: (i) light elements e.g. carbon, oxygen and hydrogen cannot be analysed and (ii) the maps yield qualitative information only.

Results

A summary of lead levels found in Winstar soil and dust samples and on the hands of young children is presented in Table 1 together with comparative data from two similar UK studies. Geometric means are reported as the data shows a typical positively skewed distribution.

Soils and Dusts

The mean concentration of lead in housedust is 1,560 $\mu\text{g g}^{-1}$ and that in garden soil is 4.5 times greater at 7,140 $\mu\text{g g}^{-1}$. Mean lead loading in dusts from the village was found to be 275 $\mu\text{g m}^{-2}$. A soil-trodden carpet at one farm contained 19,400 $\mu\text{g Pb m}^{-2}$ but this is an exceptional case and not included in the mean. All the garden soils exceeded 2,000 $\mu\text{g g}^{-1}$ Pb and 50% of the housedusts contained more than 1,000 $\mu\text{g g}^{-1}$ Pb with 33% of the housedusts exceeding 2,000 $\mu\text{g g}^{-1}$ Pb.

Duplicate samples indicate a sample variability maximum of 35% in garden soil, 60% in dust lead concentration and 50% in dust lead loading. These figures are similar to those reported by Laxen *et al.* (1988) and reflect the considerable temporal and spatial variation in household dust lead concentration and lead loading. Soil variability is thought to be a product of the sampling strategy coupled with heterogeneity associated with extremely high lead levels. However, the mean household lead levels found in this study are in broad agreement with those from two other studies on the Derbyshire mining villages (Bartrop *et al.*, 1975 and Culbard *et al.*, 1988), demonstrating that a representative sample can be taken in a study of this kind.

Figures 2(a) and (b) show the spatial distribution of household lead concentrations in Winstar. Houses in the centre of the village, which are all pre 1800, generally contain greater quantities of lead in both housedust and garden soil than the newer houses to the east of the village centre. This is clearly shown in Table 2 where the geometric mean of lead concentrations in older households is double that of newer households.

Hand and blood Lead

The geometric mean of lead on the hands of Winstar children aged 1–2.5 yr is 13.1 $\mu\text{g Pb}$ per pair of hands, significantly greater at the 95% confidence level than the mean of 5.7 $\mu\text{g Pb}$ previously reported in Birmingham (Davies, 1989). Two duplicate samples gave variabilities of 21% and 66%. This is in good agreement with the average geometric coefficient of variation (Kirkwood, 1979) of 34% from hand lead values (with the exception of one outlier of 406.1 $\mu\text{g Pb}$) reported by Davies and Watt (1986).

Blood sampling in Winstar was limited because of the

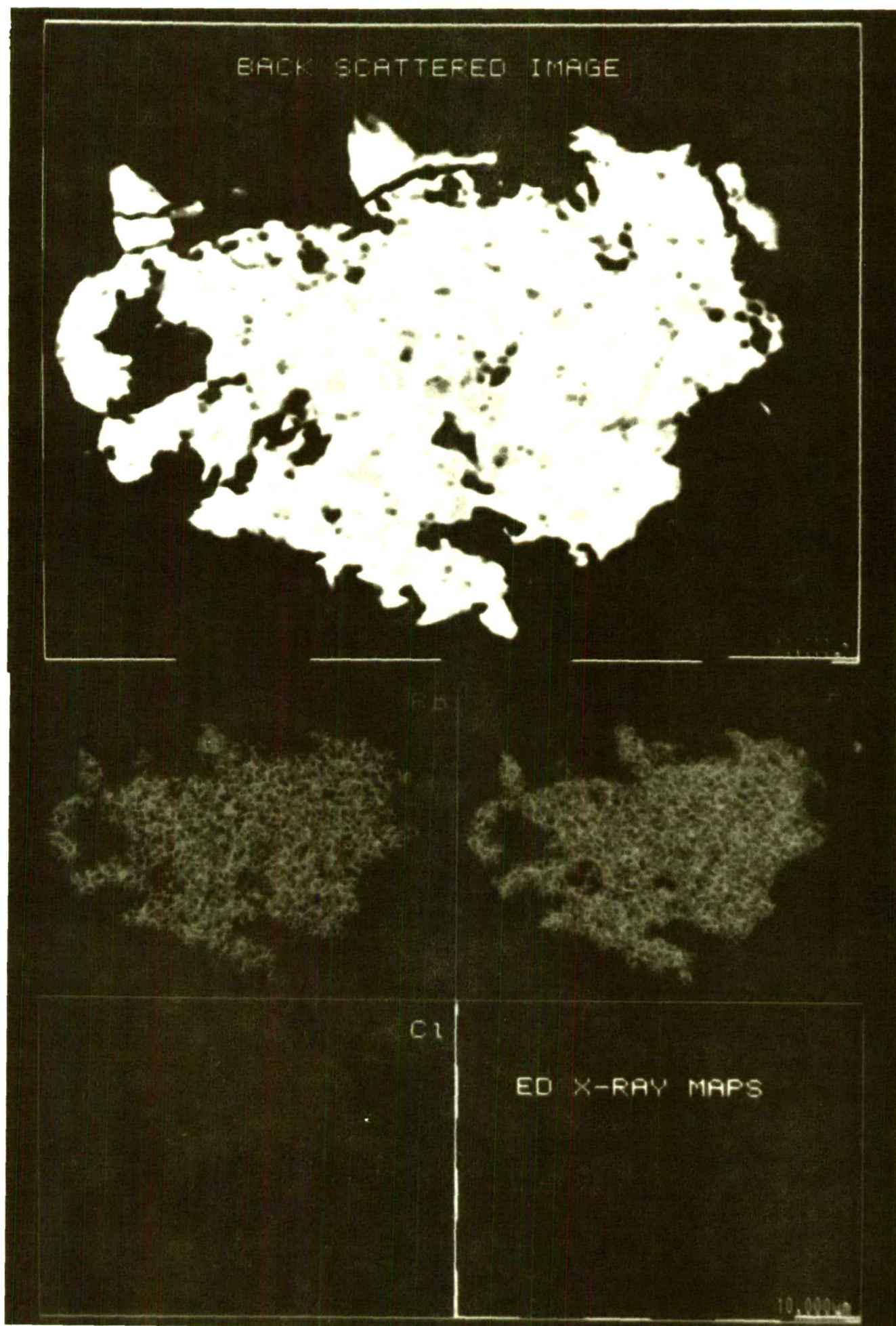
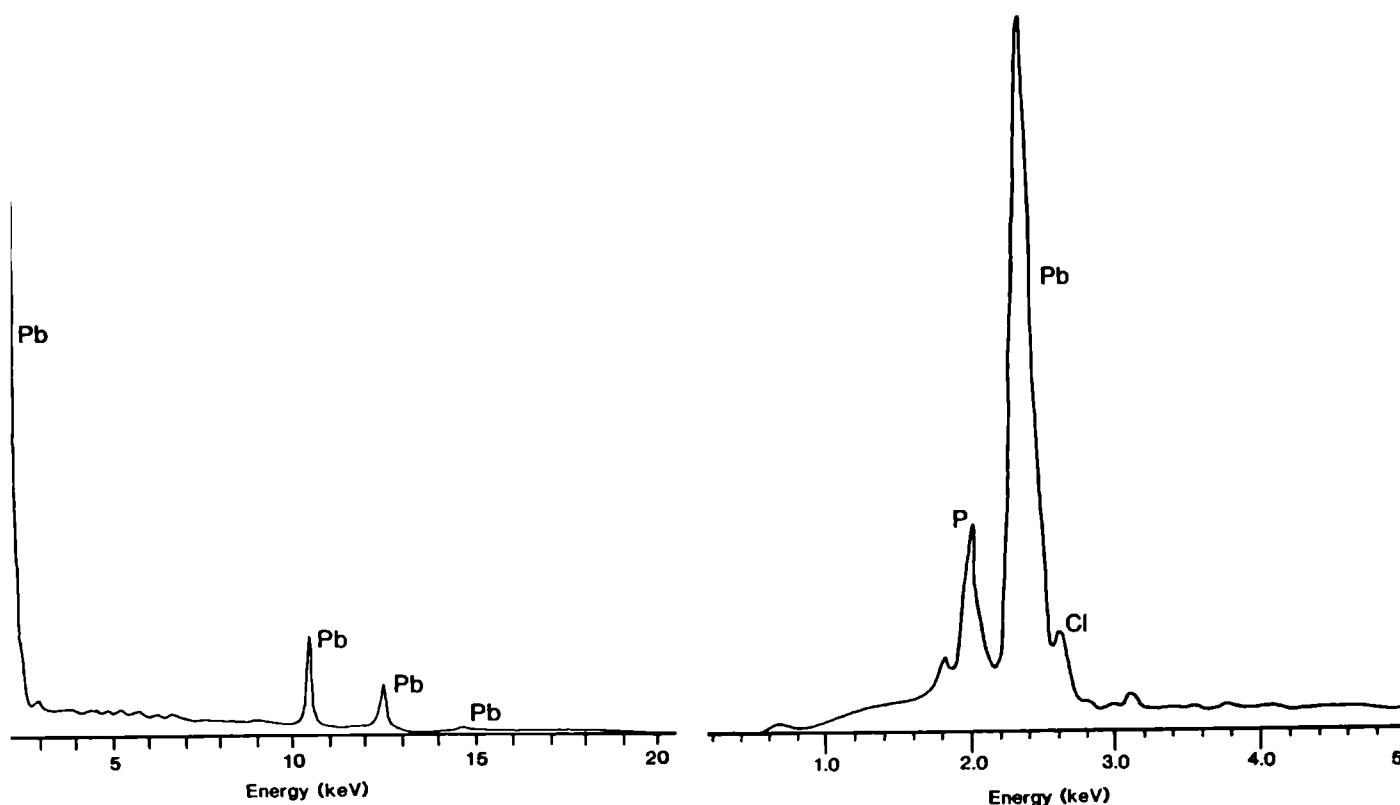


Figure 4(a) and (b) SEM analysis of grain of pyromorphite $[Pb_5(PO_4)_3Cl]$ showing the presence of lead and phosphorus with minor amounts of chlorine.



Figures 5(a) and (b) SEM qualitative energy dispersive spectrum shows a chlorine peak on the expanded scale.

small population size, prohibiting any rigorous statistical analysis. The overall geometric mean of lead in children's blood (1–8 yr) is $9.4 \mu\text{g dL}^{-1}$ and $6.9 \mu\text{g dL}^{-1}$ for those aged 1–3 yr. Typically, children's blood lead reaches a maximum at 2 years (Duggan, 1983; RCEP, 1983). Our apparently anomalous result is probably caused by the extremely small sample size ($n = 3$).

Discussion

From Table 1, it is evident that mean lead levels in all Winsters environmental samples are greatly elevated above averages reported in the UK National Survey (Culbard *et al.*, 1988) and the Birmingham Study (Davies *et al.*, 1990). The mean concentration in garden soil is greater than the national average by a factor of 27. This extreme elevation of soil lead, to the point at which it is very much greater than that of housedust has been found in other historic mining areas (Davies *et al.*, 1985; Thornton, 1988; and Moffat, 1989) and implies a strong external source of contamination entering the home. In Winsters village, high lead concentrations ($>10,000 \mu\text{g g}^{-1}$) in garden soils are generally coincident with mineral veins and old spoil tips, mostly occurring in the older part of the village (Figures 1 and 2(a), Table 2). Household lead levels are known to increase with house age (Thornton *et al.*, 1985; Davies and Thornton, 1987) but this effect could not solely account for the gross elevation of soil lead content. Thus, the primary source of elevated environmental lead levels in Winsters is geological mineralisation that has been brought to the surface by past mining activities.

The elevated amount of lead present on Winsters children's hands implies that the high environmental lead levels are transferred to the child by the soil-dust-hand (or soil-hand) route. The dust may then be inadvertently ingested by hand-to-mouth activity (Harvey *et al.*, 1985). However, the relatively large amounts of lead on children's hands are not reflected in the children's blood lead levels ($\text{GM} = 9.4 \mu\text{g dL}^{-1}$), which are within the normal UK range. Recent analyses of children's blood lead have produced geometric means of $11.7 \mu\text{g dL}^{-1}$ (age 1–3 yr) for Birmingham (Davies *et al.*, 1990), $10.7 \mu\text{g dL}^{-1}$ (age 6–9 yr) for Edinburgh (Laxen *et al.*, 1987), and $7.3 \mu\text{g dL}^{-1}$ (age 6–7 yr) for children attending schools situated on heavily trafficked roads (DoE, 1990). Strehlow and Barltrop (1988) examined children's blood lead levels in urban and rural areas over a period of three years. Geometric means of 7.4 to $8.3 \mu\text{g dL}^{-1}$ were reported for London and 6.4 to $6.8 \mu\text{g dL}^{-1}$ for Suffolk (age 5–7 yr) and were found to be significantly different for each year. Thus, Winsters children's blood lead concentrations may be considered elevated for a rural UK area but are similar or only slightly elevated compared to urban areas and all values fall below the recommended action level of $25 \mu\text{g dL}^{-1}$ (DoE and Welsh Office, 1982).

Several authors have predicted a rise in blood lead levels associated with an increase in dust and soil lead concentrations: for example, a literature review by Duggan and Inskip (1985) suggests that, on average, blood lead levels increase by $5 \mu\text{g dL}^{-1}$ for a $1,000 \mu\text{g g}^{-1}$ rise in dust or soil lead concentration. If a national dust lead concentration average of $500 \mu\text{g g}^{-1}$ and a blood lead level

average of $10.0 \mu\text{g dL}^{-1}$ in children are assumed, then the expected blood lead level in Winsters children would be $15.0 \mu\text{g dL}^{-1}$ based on lead concentrations in housedust ($\text{GM } 1,500 \mu\text{g g}^{-1}$). A response-curve of blood lead versus total exposure to dust and water lead for Edinburgh children (Laxen *et al.*, 1987) gives a predicted blood lead of $13.3 \mu\text{g dL}^{-1}$ for a lead concentration in dust of $1,500 \mu\text{g g}^{-1}$. The Birmingham regression model (Davies *et al.*, 1990) produces an increase in blood lead from $11.7 \mu\text{g dL}^{-1}$ (the geometric mean value for Birmingham) to $13.6 \mu\text{g dL}^{-1}$ if Winsters mean dust lead loading is inserted in the model.

The blood lead levels reported in this study are appreciably lower than predicted values. The above models are based on the urban/inner-city environment where the major sources of lead are fossil fuel residues and paint, whilst the primary source of lead in Winsters is of geological origin. Thus, chemical forms of lead present in mine-waste soils will be different to those present in urban soils and dusts, reflecting these contrasting sources. The bioavailability of lead has been shown to be influenced by chemical speciation (Barltrop and Meek, 1975; Chamberlain *et al.*, 1978) and may contribute to the discrepancy between predicted and actual blood lead levels in this study.

SEM X-ray maps show galena weathering directly to cerussite (PbCO_3) in the soil environment (Figure 3), consistent with the pH (6.6–8.2) of these soils (Garrels and Christ, 1965). Many lead-rich grains were composed of pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) (Figures 4 and 5), which is a stable soil-lead mineral (Nriagu, 1974). The mode of formation of this mineral is not clear. It may have formed in the mineral vein and then been incorporated into the soil or formed within the soil as a result of further weathering of galena.

Pyromorphite is only very slightly soluble ($K_{\text{sp}} = 10^{-84.4}$) (Nriagu, 1973), less so than galena ($K_{\text{sp}} = 10^{-27.5}$) (Smith and Martell, 1976). It could contribute to a low bioavailability of lead in these soils, below that of urban soils where more soluble forms of lead are present (e.g. lead chloride and bromide). A low soil-lead bioavailability would reduce the uptake of lead into the child so that despite increased lead intake via the soil-dust-hand-mouth route, blood lead concentrations could remain within normal UK ranges.

Conclusion

Past lead mining activities have caused the gross elevation of lead concentrations in garden soils and the contamination of housedusts in the Derbyshire village of Winsters. There is evidence to suggest that the high levels of lead are transferred in part to the child via the soil-dust-hand-mouth pathway. However, blood lead concentrations of children living in the village are within normal UK ranges. The solid phases of Winsters soils contain appreciable amounts of pyromorphite, a stable soil-lead mineral. The extremely low solubility of this mineral may contribute to a low human bioavailability of soil-lead, resulting in the 'normal' blood lead concentrations found in young Winsters children.

Acknowledgements

The authors gratefully acknowledge Dr H.T. Delves of the Trace Element Unit, Southampton General Hospital for blood analysis; Dr James G.P. for taking blood samples and the people of Winsters village for letting us into their homes. The work has been funded by NERC and DoE and one of us (J.C.H.) would like to acknowledge a NERC studentship. Thanks are also due to Dr Dave Johnson and John Maskall for their helpful comments and discussions during the preparation of this manuscript.

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