

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

# POLLUTION OF SOILS BY LEAD AND ITS UPTAKE AND PATHWAYS IN THE ECOSYSTEM.

by

IAN WYNNE EASTWOOD BA(Hons) PGCE

A thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Sponsoring Establishment : Department of Recreation and Environmental Studies, Sheffield City Polytechnic.

Collaborating Establishment : Department of Environmental Health and Housing, North East Derbyshire District Council.

July 1987.

ABSTRACT.

POLLUTION OF SOILS BY LEAD AND ITS UPTAKE AND PATHWAYS IN THE ECOSYSTEM.

by Ian Wynne Eastwood BA(Hons) PGCE

The thesis reviews literature relating to lead in the environment with particular reference to the distribution and pathways of lead in the soil and plant ecosystem. Methods of conducting large area soil surveys and assessing the distribution of lead and other heavy metals including cadmium, copper and zinc are also examined. A survey was conducted over a 370 $km^2$ area of North East Derbyshire, England. Maps showing the distribution of the metals reveal anomalously high concentrations related in many instances to past industrial activity.

A simple reliable and rapid acid digestion procedure was developed and the procedure evaluated through an interlaboratory survey involving 22 laboratories. This demonstrated that analysts should seek to improve analytical performance through achieving better interlaboratory correlation rather than intralaboratory precision. A stratified random sampling protocol was developed and evaluated which allowed an estimate of precision to be placed on the results of the trace metal soil survey.

An assessment was carried out of the contribution that lead from aerially deposited dust and soil sources makes to the distribution of lead in potato plants. A micro sampling cup technique was developed which permitted (for the first time as far as can be ascertained) the analysis of lead in discrete sections of solid plant tissue from single plants grown under field conditions. This overcomes the problems of sensitivity which normally requires that samples are bulked or dosed with lead salts. Results are presented for the distribution of lead in potato plants grown in several field locations and in soils containing varying concentrations of lead. The major source of lead in the plants via the soil with aerial sources having a negligible effect on tissue distribution. Comparisons are made between results obtained by conventional flame atomic absorption spectrometry and the microsampling cup procedure.

CONTENTS

ACKNOWLEDGEMENTS.

I would particularly like to thank the following people for their assistance during the work:

Mr D G Hunt and Mr N Tranmer (North East Derbyshire District Council, Department of Environmental Health and Housing) and Councillor C Fox for their financial support, loan of British Standard Dust Deposit Guages and interest in the North East Derbyshire heavy metal soil survey; Mr A Reeson and Mr D Skinner and for the hours of work by the Community Service Agency Teams of Clay Cross and Eckington during the long months of soil sample collection; Dr D Turner (Associated Octel Company, Ellesmere Port, Cheshire) for his interest and the donation of a micro balance; Mr A F Barnes (Cookson Group plc [formerly Lead Industries Group], London) for his interest and very welcome financial support to the extent of £500; Mr C R Robin (Electronic Development Co., Guildford, Surrey) for the manufacture of nickel microsampling cups and cup trays; the landowners who gave permission to have access to their land during the study, including Mr Pelly (Wentworth Estates, Wentworth, South Yorkshire), Mr Weldon (Hood Hill Farm, Nr. Chapeltown, South Yorkshire) and Mr Hall (Rowter Farm, Castleton, Derbyshire); Dr C W McLeod (Department of Chemistry, Sheffield City Polytechnic) for providing plant and soil certified reference materials; all the laboratory technical staff who over the years have given valuable assistance when required, Mr A P Newman, Mr S Douglas, Mr K Woodhouse, Mr S Devine and for cartographic advice Miss V Hitchen and Mrs J Butt.

My present supervisors, Mike Wild and Phil Newell (Department of Recreation and Environmental Studies, Sheffield City Polytechnic), Dr David Mowthorpe (Department of Chemistry, Sheffield City Polytechnic) and my former supervisor Prof. Ken Jackson (Department of Chemistry, University of Saskatchewan, Canada - formerly Sheffield City Polytechnic) for their encouragement, advice, perseverance, understanding, considerable expertise and guidance throughout this work; Dr M S Cresser for acting as my external examiner.

My Mother and Father for their unwavering support over the years and to Dawn my Wife for her special support.

CHAPTER 1. INTRODUCTION.

CHAPTER 2. DETERMINATION OF LEAD IN SOIL USING A LARGE BATCH DIGESTION PROCEDURE

CHAPTER 3. DEVELOPMENT OF A SAMPLING PROTOCOL FOR LARGE AREA SOIL SURVEYS OF TRACE METAL CONTAMINATION.

CHAPTER 4. THE DISTRIBUTION OF LEAD AND OTHER HEAVY METALS IN THE SOILS OF NORTH EAST DERBYSHIRE, ENGLAND.

CHAPTER 5. DETERMINATION OF LEAD IN PLANT MATERIAL BY ATOMIC ABSORPTION SPECTROMETRY.

CHAPTER 6. AN ASSESSMENT OF THE CONTRIBUTION OF SOIL AND AERIALLY DEPOSITED LEAD TO THE DISTRIBUTION OF LEAD IN POTATO PLANTS.

List of Tables.

List of Figures

List of plates.

# CHAPTER 1. INTRODUCTION.

## 1.1. Lead in the environment.

The last 20 years have seen a growth in public interest in the condition of the environment and in particular aspects of its pollution. Whilst there are many potential environmental pollutants, perhaps no other pollutant has stirred up quite as much emotion in the population as the heavy metal lead. For centuries it has been recognised that lead is a poison. Frank poisoning, rare today, has historically been associated with human exposure to lead in food and drink, for example in ancient Rome [1], and also through occupational exposure. Today occupational exposure is rare with legislation for the work place to protect the employee [2]. Public concern has recently centred on the levels of lead in the body which result from general environmental exposure at concentrations below which clinical signs and symptoms appear. These fears have been fuelled to some extent by the debate over the contribution which alkyl lead, added to petrol, may have on concentrations of lead in air and soil, and subsequently the levels of lead in food.

This concern has resulted in the undertaking of a large volume of research into the occurrence and mobility of lead in the environment. Several reviews have been published which summarise much of the published work produced during this period [3,4,5,6,7,8,9,10].

In 1974 the Fourth Report of the Royal Commission on Environmental Pollution ([11]) recognised the public concern and declared an intention to review the question of lead pollution in the environment. Since 1974 successive governments have reduced the levels of lead additives in petrol and paint. In 1978 the Department of Health and Social Security set up a working party chaired by Professor Lawther to 'review the overall effects on health of environmental lead from all sources and, in particular, its effects on the health and development of children and to assess the contribution lead in petrol makes to the body burden.'

Lawther's Working Party reported in 1980 ([12]) concluding that "in the vast majority, airborne lead, including the lead from petrol, is usually a minor contributor to the body burden" and that "normally food is the major source" but there is "no evidence that this is substantially enhanced by contamination by airborne lead". The Lawther Report made several recommendations including: reduction of all aerial emissions (including lead in petrol), particularly in areas of continuous or prolonged exposure where the levels should not exceed 2 $\mu g/m^3$; reduction of lead in tap water where problematic; controls on the lead content of paints; and measures to reduce exposure to lead in food, cosmetics and toys. The Working Party did not come to any definite conclusions on the effects of low lead levels on performance, behaviour or intelligence of children. It did recommend that where a child was found to have a blood lead level greater than 35 $\mu g/dl$ the source of lead should be identified and steps taken to remove the child from the exposure.

The Working Party Report has been criticised by the Conservation Society ([13]) and by the Campaign for Lead-Free Air (CLEAR) ([14]) on the basis that the Working Party understated the effects on health of low level lead concentrations, the influence of lead in petrol, the airborne source/food pathway and also failed to produce effective measures for reducing levels of lead in the environment. Two further reports have been published which comprehensively review the subject, both the U.S. National Academy of Sciences ([15]) and the Australian Academy of Sciences ([16]), support the recommendation to reduce the exposure of the general public, in particular children, to lead. Whilst the recommendations of these reports are not necessarily applicable to the United Kingdom the findings in 1983 of the Ninth Report of the Royal Commission on Environmental Pollution ([17]) are of importance.

The Ninth Report, chaired by Professor Southwood, also called for all possible steps to be taken to remove lead from the environment including the removal of lead from petrol, the development of alternatives to lead shot used for fishing and a reduction in the level of lead in paints. The Report not only recommended the removal of lead from petrol in the United Kingdom, but also called for a reduction of lead in petrol in other countries. This was to reduce the amount of lead in imported food and to reduce the concentrations of lead in transfrontier aerial movements. The Ninth Report noted that the "present average blood lead concentration of the U. K. population is approximately one quarter of the level at which features of frank lead poisoning occasionally occur (around 60 μg/dl)". No other toxin is so widely distributed in human and animal populations to the extent that it is

universally present at levels greater than "one tenth of that at which clinical signs and symptoms occur". For most people in the U. K. the Ninth Report again identified "food and drink as the major pathway for lead uptake", but stressed that "there is considerable uncertainty as to the relative contributions of the several sources of lead to this pathway". It went on to recommend that "there should be continuing effort to gain a better understanding of the various pathways and mechanisms by which food is contaminated with lead", and "that priority should be given to research to assess the relative contribution that different sources and pathways can make to lead in dust". The Government [18] responded to the Ninth Report by taking several positive steps to remove lead from the environment. In particular it set up a programme for the removal of lead from petrol, which has resulted in the current availability of lead free petrol in 211 service stations in Britain [19]. The policy was reaffirmed in the recent 1987 Budget [19] when Mr Nigel Lawson, the Chancellor of the Exchequer, announced the introduction of a differential duty allowing lead free petrol, which costs more to refine, to be made available at the same retail price of leaded petrol.

It was in the light of this research climate that the project described in this thesis was initiated in 1981. Literature relating to the work presented in this thesis is discussed in the following sections 1.2. to 1.6. The research programme and its aims are outlined in section 1.7.

## 1.2. Sources of lead.

There are two broad classifications of sources of lead in the environment, natural and anthropogenic sources (resulting from human activities). Natural sources owe their origin to native lead (Pb, from the latin plumbum). It occurs in insoluble forms primarily as sulphides (galena PbS), but can also be present as oxides (anglesite $PbSO_4$ and crocoite $PbCrO_4$), or as carbonate (cerussite $PbCO_3$), and it is in these forms that it is normally extracted from the earth by mining activity. The lead content of granitic rocks is mainly controlled by their potassium feldspar content since lead is of a similar ionic size to that of potassium. The mean lead content of some 1220 granitic rocks has been calculated at 23 mg/kg. Metamorphic rocks typically have a lower lead concentration than granitic rocks, the average of 3846 gneisses and schists being 17 mg/kg. Sedimentary rocks are generally of a lower concentration than granite with the mean lead content of 924 sands and sandstones around 10 mg/kg, of 363 clays and shales 23.3 mg/kg, and of 779 black shales 23.8 mg/kg [20]. Mineral veins, containing ore materials have considerably higher concentrations than other parent rocks.

The lead is released to the earth's surface by natural weathering of rocks, by igneous activity, by the radioactive decay of radon gas (in the form of the isotope 210Pb), windblown dusts, fires and by vegetation. Nriagu [21] has estimated a worldwide annual emission of lead to air of 24.5 thousand tonnes from natural sources compared with 449 thousand tonnes from anthropogenic sources.

It is difficult to quantify the natural concentrations of lead in the environment since man has been mining and processing lead for thousands of years. The early Egyptians were glazing pottery with lead as far back as 7000-5000 BC, with the earliest known specimen of metallic lead predating 3800 BC [22]. Well known in biblical times, it is even mentioned in the book of Exodus, with the process of cupellation alluded to in the book of Jeremiah. Lead was not commercially useful until Roman times where it was being produced as a waste by-product of the silver mining industry in Europe [23]. Table 1 illustrates the growth in the consumption and anthropogenic emissions of lead on a worldwide basis as estimated by Nriagu [21].

Table 1. Historical worldwide consumption and anthropogenic emissions of lead to the air.

| Time span. (years) | Lead consumption. (thousand tonnes) | Anthropogenic lead emissions. (thousand tonnes) |
|---|---|---|
| Pre -1850 | 55,000 | 2,420 |
| 1850-1900 | 25,000 | 1,100 |
| 1901-1910 | 10,700 | 471 |
| 1911-1920 | 11,200 | 493 |
| 1921-1930 | 14.200 | 1,120 |
| 1931-1940 | 14,600 | 1,639 |
| 1941-1950 | 14,900 | 1,672 |
| 1951-1960 | 24,000 | 2,694 |
| 1961-1970 | 33,000 | 3,704 |
| 1971-1980 | 38,000 | 4,265 |
| TOTAL | 241,000 | 19,578 |

Source: Nriagu [21]

In an attempt to quantify the natural concentrations of lead in the environment estimates have been made using isolated locations, away from pollution, such as the polar ice caps and oceans. The reliability of some estimates is questionable since measurements made before the 1970's may be higher than they should be as a

result of contamination during sampling and analysis [24]. Chronological studies of the change in concentration of lead with increased depth in peat [25] and pack ice [26] illustrate how lead levels have risen over the earth's surface particularly since the Industrial Revolution [27]. Table 2. shows the recent concentrations of lead in various environmental media that have been calculated and compared with estimates for natural environments.

Table 2. Concentration of lead in the U.S. today and estimated natural concentrations.

| Environmental medium. | Present day concentration. | Estimated natural concentration. | Ratio of concentrations |
|---|---|---|---|
| AIR. | | | |
| Rural/remote | 0.1-100 ng/m$^3$ | 0.01-0.1 ng/m$^3$ | 10-1,000 |
| Inhabited | 0.1-10 µg/m$^3$ | 0.1-1.0 ng/m$^3$ | 100-10,000 |
| SOIL. | | | |
| Rural/remote | 5-50 µg/g | 5-25 µg/g | 1-2 |
| Inhabited | 10-5,000 µg/g | 5-25 µg/g | 2-200 |
| WATER. | | | |
| Fresh | 0.005-10 µg/l | 0.005-10 µg/l | 1 |
| Marine | 0.005-0.015 µg/l | 0.001 µg/l | 10 |
| FOOD. | 0.01-10 µg/g | 0.0001-0.1 µg/g | 100 |

Source: National Research Council [15]

It is apparent from Table 2 that anthropogenic emissions have raised the levels of lead in most instances above what might be considered a natural background level. The anthropogenic lead is released into the environment by non-ferrous metal mining, iron and steel production, waste incineration, petrol combustion, smelting and refining of the lead ore, and other ores in which lead may be present. It is also released during the production, utilisation,

recycling and disposal of lead materials and the burning of coal. Many studies have been performed to monitor the effect that lead, as an anti-knock compound in petrol, has upon soils and plants along highways [28,29,30,31,32,33,34,35,36,37,38,39,40,41,42] in locations including Australia [43], Venezuela [44] and Hong Kong [45]. Other studies have looked at sources close to the human interface, including those around smelting complexes [46,47,48,49,50,51,52,53,54,55,56], old mine workings and spoil heaps [57,58,59,60,61,62,63,64,65,66,67] and industrial sources in general [35,68,69,70].

In the U.K. 293 thousand tonnes of lead were processed in 1982, approximately 60 per cent owing its origin to recycling of the metal. A breakdown of its use is shown in Table 3. Much of the lead used in a metallic form is recoverable, and in some cases up to 90% of the metallic product can be recovered by recycling. That which cannot be recovered together with much of the compound lead eventually reaches the environment by normal biogeochemical pathways until trapped in a relatively permanent environmental sink such as soil or ocean sediments. It is through these pathways that lead has become so widely dispersed that no part of the earth's surface or any form of life remains uncontaminated by anthropogenic lead.

The products of these anthropogenic sources are recently observed phenomena when compared with the long history of natural contamination. Their potential health effects as low level contaminants have been the subject of much scrutiny and debate [14,15,16,63]. The pathway that lead takes through foodchains,

ultimately based on soil and plants, is closely monitored in order to determine the contribution to the total body burden of lead. Davies [71] discusses urban sources of pollution in relation to the levels of lead in London garden soils and their suitability for growing vegetables for human consumption. His findings showed that a substantial proportion of root and leafy vegetables grown in London gardens and allotments probably exceeded the 1 mg/kg (wet weight) limit for lead in food [72]. Other studies in urban areas and domestic gardens reinforce these findings [49,73,74,75,76,77,78].

Table 3. Consumption of lead in the U.K., 1982.

| Form of lead. | Product use. | Consumption. (thousand tonnes) | (Percentage) |
|---|---|---|---|
| METALLIC FORM. | Sheet and pipe. | 54 | 19.1 |
| | Battery castings and grids. | 44 | 15.6 |
| | Cable sheathing. | 21 | 7.4 |
| | Solder. | 9 | 3.2 |
| | Shot. | 5.5 | 1.9 |
| | Other in metallic form. | 30 | 10.6 |
| COMPOUND FORM. | *Anti-knock compounds. | 54 | 19.1 |
| | Battery oxides. | 45 | 15.9 |
| | Paint. | 1.5 | 0.5 |
| | Other in compound form. | 19 | 6.7 |
| | TOTAL: | 283 | 100 |

*Approximately 80% of manufactured anti-knock compound is exported.

Source: 9th Royal Commission Report [17]

Whilst there are many sources of lead in the environment this review will confine itself to studies closely related to aspects of lead in soil, which is the major sink for lead, and lead in plants

(particularly food stuffs) as these constitute the major routes by which man is exposed to lead.

## 1.3. Lead in the soil ecosystem.

Lead exists naturally at 'background' levels in all soils, originating from the weathering and decomposition of the parent rock material, igneous, metamorphic or sedimentary in origin [8]. The concentrations are approximately equal to the average concentrations of the earth's lithosphere [79]. The world-wide average lead concentration of 4,970 soils has been calculated at 29.2 mg/kg with a range of <1-888 mg/kg [20]. Harrison and Laxen-Duncan [79], suggest typical concentrations for natural soils at between 10 mg/kg and 200 mg/kg., with polluted or mineralised soils between 100 mg/kg and 10,000 mg/kg.

Anthropogenic lead is made available to the soil by a variety of environmental processes [4,8,79,80], primarily by the atmospheric deposition of vehicular particulate lead, smelter emissions and remobilisation by wind of contaminated dusts. Many workers have established that the highest concentrations of lead in soil profiles generally occur at the surface horizons [42,81,82,83] owing to enrichment from the atmosphere and by biological processes.

Lead may exist in the soil in a variety of chemical forms [79,84] which govern the type of analysis which can be performed on the soil. When tightly bound in complex molecules lead is very difficult to extract from soil, consequently very strong chemical

reagents may be required in order to determine the total lead content of the soil. Such species of lead may not be readily available to plants for uptake [71,84,85,86] and therefore it is often important to know the extractable or available lead content of the soil, if plant uptake of lead is being investigated [87].

### 1.3.1. Available lead.

Little is known about the mobility and availability of lead in soils, but it has been observed that lead is lost from soils only very slowly by leaching. Therefore a soil is likely to remain polluted for a long period of time [75]. It tends to accumulate in the topsoil and litter horizons [43,85], held with other plant available nutrients in the soil-clay-humus complex [8,61,79,88], although lead itself is not an essential nutrient [8]. Plant availability to lead is dependent on a number of factors [57,61,71,79,85,89,90,91,92], including soil texture [55,84,85,92,93], cation exchange capacity [79,85], organic matter [79,88,94], and in particular pH [79,85,89,90,92]. The latter factor is important as it has been noted that raising of pH by the application of lime or phosphate reduces the availability of lead to plants [85], therefore pH can be an important factor in experimental design. It also affects the extractability of lead from samples [84], and its value should be stated where possible to permit comparative interpretations of results. Crump and Barlow [93], discuss factors governing availability and the problems associated with its assessment. Extracting available lead is problematic, not least since the use of extractants is generally

not underpinned by any significant theoretical framework, though it has been of use in agronomy and environmental research [95].

The extraction of available lead has been achieved through the use of a variety of extractants and the efficiencies of various methods have been investigated [90,91,96,97,98]. Khan [84] identified four groups of lead compounds and suggested techniques suitable for extraction of each type. The first group includes ionic and molecular forms of the metal, removable from samples by water [67]. Readily exchangeable metal ions from inorganic clay or organic material can be removed by ion exchange with ammonium acetate or other neutral salts [79,85,92,95]. More firmly bound ions in exchange complexes can be displaced using dilute acetic acid [38,85,91,95,98,99], or other dilute acids, such as hydrochloric acid [43]. Predictions of total lead have been made using the acetic acid/acetate method by Nicklow, et al. [75]. Organically complexed lead has been extracted by ethylene diamine tetra-acetic acid (EDTA) [61,73,98,100] or other chelating agents by liquid/liquid extraction. The use of some of these reagents and techniques by various authors is discussed below and is summarised in Appendix 1.a.

Acetic acid extracts.

Acetic acid is widely used as an extractant of available lead [84], as it is said to stimulate plant uptake and gives a guide to plant availability [101]. The general procedure is to extract an air dried sample with 0.5M acetic acid [35,46,47,98,102] for a given period of time, usually overnight, filtering the residue and

evaporating to dryness over a steam bath, before uptake in a suitable analytical medium. The H+ ions in the acid displace bound ions from the exchange complexes in the soil, but as it acts below normal pH ranges, must be considered to only give an estimate of available lead [64]. Neuhauser and Hartenstein [91] and Clayton and Tiller [93] record the relative efficiency of this extraction method for various soils. Nicklow, et al. [75] describes its use in Morgan Solution (100 g of sodium acetate, 50 ml water and 30 ml glacial acetic acid at pH 4.8), modified with EDTA, to predict total soil lead.

Acetate extracts.

Although the amount of lead that can be extracted by neutral ammonium acetate is generally quite small [64] it has been used by several investigators [33,67,85,103,104,105,106], particularly in early studies. Samples are usually shaken with 0.5M acetate solution overnight. The residue may then be leached for a further period prior to analysis. Petrov, et al. [92] describe tests involving preconcentration by liquid/liquid extraction, and claim to improve detection limits up to 10 times by this method, although contaminated samples can give erroneous results.

Liquid/liquid extraction.

Organic complexing agents, such as the clay-humus complex, are largely found at the surface layers of the soil, with the effect that lead is tightly bound by the processes of absorption and chelation. This is presumed to represent much of the pool of plant

available nutrients in the soil [61,84]. Extraction of the metals as diethyl dithiocarbomates (DDC) chelates is becoming popular [107], and a variety of reagents are available for this purpose, usually referred to by their acronyms (Table 4.)

Table 4. Some reagents used in liquid/liquid extraction.

| | |
|---|---|
| APDC | Ammonium pyrrolidine dithiocarbamate |
| ATDC | Ammonium tetramethyl dithiocarbamate |
| NDDC | N-diethyl dithiocarbamate |
| NaDDC | Sodium diethyl dithiocarbamate |
| PBHA | N-phynyl benzohydroxamic acid |
| 1-PBC | 1-pyrrolidine dithiocarbamate |
| HMA | Hexamethylene ammonium |
| HMDC | Hexamethylene dithiocarbamate |
| DEDTC | Sodium diethyl dithiocarbamate |
| Dithizone | Diphenyl carbazone |

Source: Various references.

The chosen reagent is normally introduced to the lead sample solution into the aqueous phase as NaDDC, or the organic phase as ATDC or APDC, and substitution of the metal occurs to form METAL.DDC. This phase is then quantitatively extracted into an organic solvent [108]. Chloroform is usually acknowledged as the best solvent although Pedersen, et al. [108] note that it may cause loss of elements during electrothermal atomisation procedures. However, Patke and Agarawal [109] compare it favourably with carbon tetrachloride, methyl iosbutyl ketone (MIBK) and other isoamyl alcohols in its use with PBHA at pH 9.5, and mask any interferences with ascorbic acid. Aznarez, et al. [110] achieve 99% recovery with 1-PDC/chloroform at pH 4. Xylene is also used as a solvent because it is halogen free, lighter than water and nearly insoluble in water, and this results in good separation characteristics [105]. Other solvents used include MIBK and n-butyl acetate [92].

Advantages of this type of extraction procedure include: increased stability of METAL.DDCs in acid aqueous solutions; increased specificity of extraction [107]; the elimination of undesirable matrix effects; improvement of atomic absorption detection sensitivities since the elements of interest are in an aqueous free solvent [111].

EDTA extraction.

Ethylene diamine tetra-acetic acid is very widely used as an extractant of plant available lead [95,98,108,112], particularly for soils rich in organic matter [84]. The soil lead is extracted as EDTA chelates, but as the organic complex sites are largely in the surface layers, more EDTA extractable lead will be extracted here than from lower layers. Davies and Roberts [51] have tested its utility in predicting lead contents of soil and vegetation, and Edmonds, et al. [113] present a detailed extraction procedure. Clayton and Tiller [98] evaluated the efficiency of EDTA in relation to other extractants and concluded that EDTA can extract a definite component of soil metal corresponding to that capable of being absorbed by plants. Pribil [114] supports its suitability as an extractant for plant available lead.

Other techniques.

The use of dilute hydrochloric acid has been demonstrated by Gulson et al. [43] and by Harrison and Laxen-Duncan [115]. Neuhauser and Hartenstein [91] add a note of caution to the use of extractants to predict plant available lead, stating that the availability of

heavy metals depends on numerous and unpredictable factors, and until such factors are resolved, a standard extraction procedure should be used by all investigators to provide a basis for comparisons of published data. They recommend 1) a minimum extraction period and 2) a ratio volume of 0.1N HCl to weight of soil needed to achieve maximum extraction. Their views are supported by a series of comparisons on the efficiency of reagents described above.

1.3.2. Total lead.

The determination of total lead in soil usually requires the use of strong reagents in order to dissociate all the lead held within the molecular structures of the soil. In unpolluted soils, where lead is present as background levels, this is mainly within the silicate lattices [79]. Appendix 1.a. summarises some of the many digestion and extraction procedures used to determine the total lead in soil. The general procedure follows a pattern where the soil is digested in an acid, or mixture of acid and then evaporated to dryness to facilitate the oxidative destruction of organic matter present in the sample. This is then followed by leaching of the residue and filtration with a dilute acid to provide samples for analysis. Alternatively the sample may be ashed in a crucible, using a variety of temperatures and ashing aids. The latter techniques are mainly used for the digestion of vegetation samples (for examples of their use in soils see [33,60,62,109,115,116,117,118]).

Many comparative studies have been undertaken to test the efficiency of reagents and techniques [17,58,104,109,115,117,119,

[120,121]), and it is probable that not all the reported agents have the same oxidising power. Harrison and Laxen-Duncan [115], Karamanos, et al. [100] and Veneman, et al. [120] claim efficiencies of between 93% and 98% for various concentrations of $HNO_3$, whilst Veneman, et al. [120] have also achieved 98% extraction with an $HNO_3$:$HClO_4$ acid mixture. Harrison and Laxen-Duncan [115] tested several acid combinations and state that the best results are achieved with an HF:$HNO_3$ mixture. Heinrichs [122] discusses the advantages of using $HNO_3$:HCl, whereas Scott and Thomas [117] compare a modified HF:$HClO_4$ procedure with a $HNO_3$:$H_2SO_4$:$HClO_4$ wet ashing technique and finds the latter to be safer and quicker if used with small samples at low temperatures.

For samples with a high organic matter content (usually determined by loss on ignition), the use of perchloric acid is recommended for complete oxidation [79,117,123], although prior digestion with $HNO_3$ is recommended [119], due to the risk of explosion. For samples which contain strongly absorbing substances such as plasticisers, Markunas, et al. [124] described a modification of the $HNO_3$:$HClO_4$ digestion to prevent interference during analysis by atomic absorption spectroscopy. Stoeppler, et al. [125] favoured the use of a pressure digestion unit, with up to twelve sample positions for use with $HNO_3$. In all instances, the use of ultrapure reagents is stressed [62,123,126] to avoid unnecessary contamination, which is an important factor discussed in a later section. Techniques have been described by Garcia-Miragaya, et al.[44], Miller and McFee [70] and Harrison and Laxen-Duncan [79], which describe the sequential extraction of the lead in various components of soil.

In conclusion, most lead in heavily polluted soils can be extracted with concentrated $HNO_3$, or other $HNO_3$:ACID mixtures, except where the soil has a high degree of organic matter, when a perchloric:nitric acid mixture may be used with caution. Safety aspects can be an important element in the choice of reagent to be used, for example HF will require far more care than $HNO_3$ with only a comparatively small percentage gain in recovery efficiency. Likewise lengthy procedures requiring complex mixtures and digestion stages may be too costly in time and effort for little benefit over a simple $HNO_3$ digestion procedure. This is particularly the case when large numbers of routine samples must be analysed [95].

### 1.3.3. Soil sample preparation.

Whatever the analysis to be carried out on a soil, the sample must undergo some preparation prior to its introduction to reagents to be used in the preferred analytical technique. Sample collection will be discussed in the next section, but as Severson, et al. [127] point out, different techniques of preparing soil samples have an effect on the values obtained from subsequent chemical determinations. They suggest a standardisation procedure for regulatory guidelines, allowing accurate and precise analysis by single laboratories and between laboratories. Although aggregate size is not considered by some to be of great importance, Veneman, et al. [120] and Severson, et al. [127] performed a series of tests with DTPA (pH 7.3), using samples of varying mesh sizes, some prepared with a mechanical mortar and pestles used by the U. S. Geological Survey. He concluded that a more homogenised sample

simulated the plant-soil relationship, but in general sieving to mesh size 10, <2 mm, was sufficient for most types of analysis. Ure [112] suggests that for total lead analysis the sample should be further ground to <150 μm by agate ball mill free from contamination. Further milling using agate mortar and pestles, tungsten carbide or stainless steel ball mills is also recommended by other authors [63,73,108].

On collection, soil samples should be transported in polythene bags [71], and then dried [61]. In a survey of 71 investigators analysing soils, 24 stated that they air dried their soils, whereas 17 oven dried their samples to constant weight over a range of temperatures between 30-110°C. However, Harrison and Laxen-Duncan [115] point out that oven drying tended to increase moisture absorption, therefore air drying is recommended were possible. The Agricultural Development and Advisory Service (ADAS) [128] recommends drying in a current of air not exceeding 30°C, 'until the soil feels quite dry'. Bartlet and James [129] have reported that dried, pulverised, sieved soil samples are prepared and stored for laboratory research, but this can lead to problems when the samples are remoistened. The results of tests recommend that soil should be kept moist and aerobic during storage, in order to facilitate restoration to the metastable state on addition of water, of particular importance in the analysis of plant available lead. Stones, fibrous material and plant roots are removed from the soil sample as far as possible [128] prior to grinding. Sample handling is discussed in detail by Hamilton [130].

1.3.4. Soil sampling and surveying.

Any soil sample is only one of many which could be taken to represent a chosen site. Sampling bias can lead to distortion of the data, and the conclusions drawn may not be representative or justifiable due to incomplete consideration of this and many other environmental factors such as climate, weather and cultural practices, all of which have a bearing on the results obtained [83]. Therefore, the reasons for site selection should always be expressed, and the methods of choosing the sampling sites stated [119,123], using statistically based methods if at all possible so that results obtained by apparently random sampling are not overstated [36]. From the literature surveyed in this report it is apparent that many investigators fail to report their sampling techniques in any detail, whilst others mention representative sampling of some sort, but do not elaborate on their methodology. (Appendix 1.b. summarises some of the techniques used by various authors to sample soils.)

Amongst the representative sampling techniques used, transects and point samples within a reference grid proved to be popular and were used efficiently. Soil depth is an important factor and many investigators used soil pits and profiles, stating the depths at which their samples were taken. Others used steel augers and divided the profile up into samples for subsequent analysis. Once collected samples must be stored in suitable containers, normally plastic bags, which must be clean and capable of preventing cross contamination between samples.

Rother, et al. [131] describe a method of soil sampling developed at the Rothampstead Experimental Station, which aims to reduce variations caused by plants, using steel tubes to take 10 cores at 150 mm depth. Glenn [34] tested the weight variability of volumetric soil test samples taken with the standard 4.25 $cm^3$ Urbana Laboratories Soil Scoop, finding that errors arise due to differences in soil moisture content, degree of pulverisation and organic matter content; gravimetric analysis, although slower, is recommended. Andresen, et al. [132] established a permanent network of forest sites which could be sampled regularly with time, and assist future studies of the forest soils.

The formation of baseline data in order that future changes may be monitored has been carried out by Wilkins [133] for pasture in West Pembrokeshire, Parry, et al. [35] in Merseyside as a component of local planning policy, Davies and Roberts [62] near Halkyn Mountain, Clywd, Davies and Paveley [134] in Wales and by the Joint Unit for Research on the Urban Environment (JURUE) in the London borough of Greenwich [135] and Walsall [136]. The presentation of baseline data for regional geochemical studies of this nature is normally achieved by the use of computer mapping. This is discussed by Davies and Roberts [137] with special reference to the synographic mapping system SYMAP and SYMVU, which allows isoline or contour maps to be produced with irregular outlines generated on the basis of values observed. They are particularly useful in presenting the skewed data that is found in distributional studies of heavy metals [62,116]. Many further examples of the use of computer graphics in environmental studies of this nature are presented by Teicholz and Berry [138].

The quantity of soil required depends on the size of the sample area under investigation and limitations of sample preparation in the laboratory. ADAS [139] describes a series of routine methods, using a 'W' configuration, which are normally used to sample small field size areas (normally less than 4 ha). Studies covering regional areas [35,62,133,135,136] have used sampling frequencies of only 1 or 2 soil samples per kilometer square area, which are said to be representative of the sample area, using stratified or random selections of sample locations. Authors have tended to neglect the importance of sampling, particularly in regional studies of this nature, and this is discussed in more detail in Chapter 3.

## 1.4. Lead in the plant ecosystem.

The soil is made up of 84 of the known elements, although their proportions vary enormously, with eight elements accounting for 98% of the weight of silicate rocks [71]. The availability of an element in the soil is dependent upon its stability at the soil formation stage, and other soil properties such as organic content [8]. The soil is a major supplier of nutrients, as well as contaminants, to the plants and animals supported by it [84], but lead is neither a macro nor a micro nutrient to plants [6], with no beneficial role in metabolism [71]. Therefore its mechanism of entry into plants is one of considerable interest and some of the studies that have been performed in this area are discussed in section 1.6.

Studies of lead in the plant ecosystem tend to fall into three categories. Firstly there are those concerned with the use of plants to monitor levels of lead in the ecosystem from specific and nonspecific pollution sources [10,41,140]. Secondly, there are the investigations into the uptake and entry of lead into plants via roots or leaf surfaces [46,62,76,90,104,141,142,143,144,145,146,147,148,149,150,151,152,153,154], though most of these have involved the use of greenhouse or pot experiments which may not duplicate movements which occur in the field environment. Generally the studies in this second category have concluded that although the activities of the root soil interface are probably not metabolically linked [71], lead is taken up from polluted soils at this site [8,85]. Thirdly there are the investigations into subsequent transport mechanisms within plants, which suggest that this interface acts as a barrier to foliar uptake [89,155,156]. Khan [64] discusses the results obtained from various investigations made into the relationship of lead in soils and plants, and also discusses pathways of lead from plants.

The need to study vegetation is becoming increasingly important, in the light of recent research in urban areas which has indicated that the lead content of domestically grown vegetables may exceed the current lead in food regulation level of 1 μg/g [71]. Potential hazards caused by their consumption resulted in a decrease in the World Health Organisation [73] recommended daily intake level of 5 μg/kg body weight. As Davies [73] says, there is a dearth of information concerning the role of home grown vegetables in the economy of the community, and as concern over the health effects of lead heightens, more monitoring studies of urban

garden vegetables will add to those already produced [37,71,73,74,76,78]. This is also the case in areas where the background level of lead is naturally high, or elevated by metallic ore mining [63,157,158].

1.4.1. Plant sampling and surveying.

A wide variety of plant samples has been used by authors, Appendix 1.c. lists some of the vegetation types used, but shallow root vegetables and agricultural crops tend to predominate because the major site of plant exposure to lead is at the root interface, or top 0 - 20 cm of a soil profile [84]. Davies [61,73] acknowledges the suitability of fast growing crops such as radish for use in plant-soil studies, though their significance in terms of lead in the diet is comparatively negligible. Other authors favour grasses and leafy vegetables when monitoring foliar uptake to gain maximum contamination of the upper parts of the plant [10]. The use of vegetation in monitoring surveys is reviewed by Lepp [7], Martin and Coughtrey [9] and Manning and Feder [10] in some detail. Surveys fall into the following categories, those concerned with roadside studies, smelter and other point source studies and those studies near general industrial sources such as in urban areas with diffuse or undefined pollution sources.

As with soil sampling the plant samples analysed must be representative of the original specimen and be collected and handled with care to avoid unnecessary contamination. Often samples from several different plants are bulked together prior to analysis. This has the effect of concentrating the amount of lead

in the sample but results in a loss of information on variations occurring between and within individual specimens. Where possible, stainless steel tools should be used, such as trowels and scissors [159], both inside the laboratory and outside. Dead or senescent material is usually removed and discarded since this is more difficult to clean. Ratcliffe and Beeby [38] have demonstrated that dead tissue may accumulate more lead from automotive exhaust fumes than living material. These variations may be further increased as a result of genetic variations within species causing differential metal tolerance between plant specimens. This is discussed in some detail by Martin and Coughtrey [9] and Lepp [6]. Harris, et al. [160] have identified variations in metal uptake within different plant cultivars, particularly between maincrop and early potatoes. These differences were thought to reflect physiological variations rather than changes in edaphic and climatic conditions.

### 1.4.2. Plant sample preparation.

Once in the laboratory many investigators wash samples in water prior to drying and digestion [37,47,49,57,59,61,64,65,67,73,74,76,77,78,105,106,148,131,161] to remove surface contaminants, but there is general agreement that washing leaf samples with water may only remove about half of the deposited surface lead [33]. It is possible that many early studies, and some recent studies, reporting lead concentrations in plants, may in reality be reporting an internal plant tissue concentration plus up to 50% of the concentration of the surface contamination. This makes comparison of data between studies reporting a lead concentration

for a particular vegetation type difficult, particularly if the washing procedure has not been accurately reported. It could be argued that washing of vegetables with water only simulates the way in which food is prepared for domestic consumption. The lead concentration obtained by this procedure would be a true reflection of the potential exposure to man. ADAS [128] recommends that plants contaminated with soil should be washed under running tap water or in a weak solution of non-ionic detergent, rinsed in distilled water and dried with a cloth or paper tissue. Roots can be washed under running tap water and dried with a cloth. The physical act of drying with a cloth should be done with caution since sharp contaminated particles may be ground into the delicate plant tissue surface.

Saiki and Maeda [162] have investigated the removal of external deposits from plant samples using water, detergent and HCl. Whilst HCl was most effective, detergent was marginally better than washing with water only. Care should be taken when using HCl to avoid leaching if used on leaves with a poorly developed cuticle. Sonneveld and van Dijk [163] came to similar conclusions preferring a combination of detergent and HCl washing procedures. Other authors have considered the effect of washing plant tissues [28,50,164]. Washing techniques are compared by Ratcliffe and Beeby [38] and the types of techniques range from washing in double distilled water [146], through the use of mild detergents [49,64,65], chloroform [143], acids and water [155] to chloroform and ultrasonic cleaning [60]. Martin and Coughtrey [9], Arvik and Zimdahl [155] and Harris [165] discuss the surface characteristics of vegetation and in particular the protection offered to foliage

by wax surfaces at the stomata, which may prevent the movement of soluble lead salts into the plant from airborne sources. However, Godzik, et al. [50] suggest that the protection from a waxy cuticle is insignificant.

Once the sample has been suitably treated, it is usually oven dried to constant weight, over a range of temperatures and times. ADAS [128] recommend a number of drying temperatures for different vegetation types. For potatoes they recommend oven drying at 60°C for 24 hours followed by 18 hours at 102 ± 2°C. Preer, et al. [77] give an exellent account of all aspects of preparation of vegetable material.

Once washed and dried, samples are normally milled to a fine homogeneous powder before digestion of the organic material. Samples are milled in a variety of hammer [128] and grinding mills [159]. For general routine analysis samples must pass a 1 mm mesh sieve, though they must be finer for slurry suspension methods [159]. Removal of organic materials is achieved by wet and dry ashing techniques and a summary of the techniques used is given in Appendix 1.d. Ashing is a well established technique for destroying organic matter before trace metal determinations [166,167,168].

Dry ashing is the most commonly used sample treatment [159]. It normally involves pre-drying the samples in an oven at 100 - 200°C, followed by thorough heating in a muffle furnace. The temperature is gradually increased or 'ramped', so that the sample is first charred smoothly before it is ashed at a temperature which will not

volatilise the elements of interest [167,169]. Holak [167] describes a temperature programmable furnace which performs the heating cycle automatically. The temperature range used is between 430°C and 560°C, with uptake of the residue in mineral acids such as $HNO_3$ and HCl. Occasionally, $H_2SO_4$:$H_2O$ is introduced to the sample as an ashing aid [169,170] allowing slightly higher temperatures to be used. Organic material is removed when a carbon free ash is obtained, and reliability is not affected by the position in the furnace within normal temperature ranges [77]. The primary factor is said to be the ratio of volume of sample weight to volume of sample solution, which should not exceed >0.3 g sample : 5 ml sample solution [77]. Feinburg and Ducauze [166] suggest that mineralisation is a limiting step in the monitoring of ecological samples, but dry ashing seems best suited to eliminate the problem, and a direct method of calcination at 750°C is described. Other criticisms are that the method is time consuming [99,159], prone to non-negligible volatilisation losses [99,102] and requires complex correction procedures [171]. However, Satzger, et al. [169] argue that the method is safe and suffers less contamination of reagents.

Wet ashing usually involves $HNO_3$:$H_2SO_4$ and $HNO_3$:$H_2SO_4$:$HClO_4$ mixtures in a crucible arrangement, offering a less common but rapid oxidation procedure, with fewer losses through volatilisation [159], but it is acknowledged that the technique is prone to reagent contamination [102,159] and the chemicals may be hazardous if not used with due caution [103,172].

Wet and dry ashing techniques were compared by Preer, et al. [77] and good agreement was achieved with standard reference materials. Harrison and Laxen-Duncan [115] also tested the efficiency of dry ashing. Thornburg [172] assesses some of the pitfalls, advantages and precautions that should be taken during ashing techniques.

Acid digestion bombs are not widely used and data is scarce on possible losses during the decomposition process. Van Eenbergen and Bruninx [173] have tested the Parr acid digestion bomb using radioactive nuclides on Standard Reference Materials (SRMs) (orchard leaves) treated with $HNO_3$:$HClO_4$ and found virtually no losses occurred, but some elements tended to precipitate under unfavourable conditions. The acid is also recommended by Heinrichs [122] for plants, along with HF:$HClO_4$, whilst the latter mixture is also recommended for soils. A sublimation method for the determination of lead in plants is described by Shamisporor and Wahdat [171], where the organic materials and lead are oxidised in an oxygen atmosphere at elevated temperatures. The lead oxide is reduced to elemental lead at the high temperatures, sublimes and condenses. The lead is then dissolved in $HNO_3$. The method compares favourably with other procedures.

The introduction of solid samples to analytical flame techniques has been used for many biological [174] and environmental [169] samples since Delves [175] introduced his microsampling cup for the analysis of blood lead in 1970 and discussed the limitations of the tantalumboat assembly for biological sampling, due to the formation of oxides in the flame, shortening its effective lifetime. The advantages of the microsampling cup system are that vaporisation in

the flame permits fewer interferences than in furnaces [174], and avoids time-consuming dry ashing cycles. However, the weighing of the microsample is slow and error prone and Jackson, et al. [169] describe a technique for the introduction of an homogenised sample in a water suspension, followed by drying prior to insertion into the flame. This presents a uniform sample to the flame, which can be easily replicated, and is quick and simple to use over an extended detection range of 0.072 µg - 60 µg/g Pb. Any non-specific absorption is simply time resolved from the lead atomic absorption signal. Stoeppler and Backhaus [176] also describe the preparation of a sample solution for solid sampling. Nichols, et al. [177] state that qualitative advances to solid sampling could be achieved if biological samples >5 mg could be run without pretreatment and need to char. In a modified closed sample constant temperature crucible, up to 8 mg of SRM orchard leaves can be analysed without ashing, and up to 30 - 50 mg with conservative charring at 377°C (610K). Regulation of interference from smoke particles is achieved by maintaining the temperature above 727°C (2000K).

## 1.5. Analysis of soil and plant materials.

Once the soil or plant sample has been prepared, a determination of the lead content is made. The choice of analytical technique is often made on the basis of availability of equipment and budget constraints [73,178], rather than fidelity and sensitivity of technique. Baker and Chesnin [119] present seven criteria by which the acceptability of analytical method and total acceptable error can be judged. They are;

i) sensitivity required,

ii) accuracy of method,

iii) presence of interference,

iv) time required per sample,

v) number of technical skilled laboratory personnel required,

vi) required use of standard reference materials,

vii) cost per sample.

Normally the final choice is a series of compromises dependent on local circumstances [178]. The utility and popularity of some methods for soil lead and plant lead analysis will now be discussed. A summary of some techniques used by various authors is given in Appendix 1.e.

### 1.5.1. Analytical techniques.

Flame atomic spectroscopy has continued to be the most popular technique, with flameless techniques increasing in popularity. Spectrophotometric and colorimetric methods have declined in popularity after their wide spread use in the 1960's and early 1970's. Several more expensive techniques are now available, including differential pulse anodic stripping voltammetry and X-ray fluorescence, but they tend to be beyond the scope of the small laboratory. They are more often used by national laboratories and monitoring organisations. A brief description of the various methods will be made, presenting criteria by which to choose a method suited to individual needs. Some of the reported detection limits for analysis of lead using different analytical techniques are given in Table 5.

Table 5. Detection limits for lead reported for various analytical techniques.

| ANALYTICAL METHOD. | DETECTION LIMIT. | CRITERIA. |
|---|---|---|
| Colorimetry-Dithizone. | 20 $\mu g/dm^3$ | 10 ml aliquot of sample solution. |
| X-Ray spectroscopy. | 0.2 $\mu g/cm^2$ | Surface of an air filter by thin film technique. |
| Anodic Stripping Voltammetry. | 0.01 $\mu g/dm^3$ | Hanging drop mercury electrode |
| Flame AAS. | 10 $\mu g/dm^3$<br>30 $\mu g/dm^3$ | Double beam, 217nm.<br>Single beam, 283.3nm. |
| Flameless AAS. | 0.02 $\mu g/dm^3$ | 100µl aliquot |

Source: Bryce-Smith [123], Harrison and Laxen-Duncan [79].

a. Flame Atomic Absorption Spectrometry (AAS).

This is acknowledged to be a dependable and adaptable method of analysis because of its low cost, ease of use and rapid results [79]. The principles are well established [99], and investigators need to have little knowledge of the fundamental techniques involved, only that they show that all reasonable steps have been taken to achieve good precision and reproducibility, and that within the optimum procedures validated for its use, the technique has limitations which must be taken into consideration when working near the limits of detection.

Two resonance lines are favoured for flame atomisation of lead; 217nm and 283.3nm. Some instruments work more efficiently at one wavelength than others [168] and manufacturer's literature should be consulted to determine the characteristics of specific pieces of

apparatus. Atomic absorption spectroscopy requires that an element be completely dissociated from its chemical bonds, and any phenomena which affect the formation of free atoms in the flame will affect the degree of absorption or emission. Interferences, as these phenomena are known [84], are usually of four main types; chemical (due to the formation of stable compounds), ionisation, spectral (normally with lead at 217nm) and matrix (when different amounts of sample and solution reach the flame per unit time). Ebdon [179] and Marr and Cresser [178] discuss some of the errors and methods of correction of interferences, which must be achieved if meaningful results are to be obtained from sample analysis [51,77,101,103,108,109,110,111,113,116,119,122,123,124,125,180,181,182,183,184].

Many suggestions have been put forward for the alleviation of matrices and interference problems in flame AAS. Background correction facilities are usually available on most instruments but Hannaker and Hughes [111] say this is only partially effective in minimising non-specific molecular absorption signals. Chelation extraction is said to eliminate matrix effects [111,119,185], with organic solvents enhancing the absorbance of metallic elements in the flame [168].

Lau, et al. [101] describe a method of atom-trapping to be used in conjunction with conventional AAS, with a silica tube mounting and appropriate connections to cold water and air. Atom species and their precursers present in the flame can be trapped on the cold surface of the tube, later being released quickly into the flame. Since the analyte is concentrated in the flame, rather than

externally by solvent extraction, time is saved and there is less risk of contamination. Pre-coating graphite tubes with a suitable material also allows interferences to be avoided during flameless AAS [161]. Jackson, et al. [174] describe the use of a microsampling cup sample introduction system, developed by Delves [175] for blood lead analysis, for the analysis of biological samples. This method was further developed by Jackson, et al. [153] and applied to the analysis of lead in slurried solid samples of vegetation. The method is simple, reagent free, accurate, faster than competitive methods and has adequate precision. It is preferred to conventional flame AAS either when higher sensitivity is required or when the sample size is small and has the potential to be useful where the uptake of lead is to be investigated, as different parts of the plant could be individually analysed for lead.

When samples contain a low concentration of analyte in large concentrations of varying matrix constituents it is often difficult to prepare useful standard solutions. To overcome this it is possible to add small amounts of conventional standard solution in increasing amounts to aliquots of each sample, so that a calibration curve can be drawn, aiming for linearity within the concentration range [79]. Hannaker and Hughes [111], Baker and Chesnin [119] and Bryce-Smith [123] advise the use of standard additions technique to eliminate matrix effects, though Sturgeon, et al. [182] do not favour the procedure suggesting that it has an inherent risk of imprecision. Woodis, et al. [186] present statistical techniques to study for 'ruggedness' when small variations in procedural operations are introduced, such as

synergistic effects of matrix ions in the flame. Whatever comparisons and quality controls are carried out, standards and unknown samples must be of a similar matrix [51,111].

b. Flameless Atomic Absorption Spectroscopy (AAS).

The use of this technique is becoming more popular due to the developments that have occurred in recent years [119], and is said to be up to 10 times more sensitive than conventional flame AAS [168]. However, the need has not been eliminated for chemical pretreatment of samples because components in the matrix are not entirely removed in the drying/ashing cycles [123], so some form of acid decomposition [182] or chelation extraction [37,79,92,110,125] is recommended.

There are a variety of electrothermal atomisers used in conjunction with AAS, such as the carbon rod [64], but the graphite furnace is most widely used and will be discussed here.

c. Graphite Furnace Electrothermal Atomisation.

Although solid sampling is a possibility [177], because the porous graphite filters out interferences as the analyte and matrix enters into the light path, some sample predigestion and solubilisation are usually undertaken [122,182]. However, matrix effects and interferences still present problems and are widely discussed in the literature [187].

Ediger [188] describes chemical manipulations in the furnace, aiming to decrease the volatility of the analyte during charring whilst increasing the volatility of the matrix, to promote removal before atomisation. Andersson [189] discusses the coating of the graphite tube with lanthanum carbide to eliminate sulphur interferences from organic samples [110,190]. Heinrichs [122] discusses chlorine interferences when HCl is used as a solvent [85,110,191], and the use of matrix modification using organic acids such as 4% $NH_4NO_3$ is advised by Manning and Slavin [191], along with molybdenum coating of tubes, offering detection limits of 0.02 mg Pb. Reagan and Warren [180] suggest the introduction of 1% ascorbic acid into lead solutions, assisting efficient formation of the atomic vapour, and Sturgeon, et al. [182] stress the need to remove all perchloric acid from a sample, prior to analysis, if it has been used for predigestion. They also describe the use of the L'vov platform which allows precise and accurate determination of trace elements; the analyte vapour experiences greater effective temperatures with a greater degree of dissociation, reducing background absorption. A deuterium lamp is recommended for background correction in flameless AAS [77,111,123].

d. Colorimetry-dithizone Procedures.

This technique is used mainly for trace element determinations by formation of colour complexes. However, thorium, cadmium and lead dithizonates are not easily differentiated by the colorimeter, and although refinements cover a range of pH's it is less widely used for lead [168]. The technique is mainly used when no instrumentation is available, but it is only of modest sensitivity,

it has high risk of interference, is time consuming, and considerable experience is needed to achieve reliable results [79].

e. Emission Spectroscopy.

This technique was first introduced in 1932 and although it has fallen from use as a major technique [168], it is widely used for selected elements after preconcentration [119]. Ebdon [179] discusses the various emission spectroscopic techniques available.

f. Inductively Coupled Plasma (ICP)-Atomic Emission Spectrometry.

This technique has been developed to such an extent that analysis has now become routine [168,192]. Sample preparation is relatively straightforward and matrix problems are more readily resolved [51]. Samples are usually presented as liquids and provided the acid background is common for the sample and matches the standards a single calibration curve can be used. It has excellent detection limits, is quite free from interferences and has a more reproducible excitation source than flame techniques. However it is costly to run, consuming argon at 5-20 l/minute, and requires heavy capital investment [179]. Schramel [193] discusses the use of ICP spectroscopy for trace element analysis in bio-medical and environmental samples.

g. Activation Analysis.

New applications are emerging for this method in the determination of heavy metals in samples for their evaluation of eco-toxic

effects, but it requires skill and technical support [115], and although sensitive [126], is not particularly suitable for lead determinations due to the short lifetimes of the Pb-isotopes.

h. Mass Spectrometry.

This is usually used when high precision is more important than speed or cost and Ure, et al. [193] have used it to good effect in the determination of trace element content in Scottish soils. Calibration and correction for interferences are described along with sample preparation. Barnes, et al. [194] used the technique to certify the lead concentration in several biological standard reference materials.

i. X-ray Fluorescence (X-RF) Spectroscopy.

This was first used during the 1960s and it is now considered a useful tool for the direct, non-destructive, measurement of elements in materials [50,168]. It is well established for the analysis of plant materials, employing a variety of sample preparations such as loose dry packed powder, aqueous solutions, or compressed pellets. Each of these preparations has an inherent disadvantage and a new sample holder, a modification of the traditional X-RF polythene cup is described by Dietz and Tackett [170] and tested to determine accuracy and optimal precision.

j. Polarography.

This involves the isolation of lead by electrodeposition of the metal from a solution of decomposed biological material [167,168], and is used by Barnes, et al. [29] as a check routine.

k. Differential Pulse Anodic Stripping Voltammetry (ASV).

This is a reliable method, advocated for small laboratories [125], although chemical pretreatment causes problems and recommendations are made to alleviate them. The technique is based on the preconcentration of metals present in a solution by electrodeposition on a suitable electrode at a fixed, sufficiently negative potential. Current peaks are observed and recorded during anodic potential scan if metals have been deposited allowing quantitaive or qualitative measurement [169]. Typical electrolytes are 0.6 M HCl and 0.2 M ascorbate. The electrodes are either hanging drop mercury electrodes [113,195] or glassy carbon electrodes. It has better detection limits than conventional AAS [195], although there are difficulties in achieving complete digestion, but overall it constitutes an inexpensive and elegant physically independent reference method [126]. It does allow the simultaneous detection of more than one metal [113,169], and the freedom from matrix effects as a standard additions technique is always used.

1.5.2. Errors and Contamination.

The ultimate source of error in any analysis arises at the point of sampling and depends upon how representative the sample is of the material from which it is taken. After sampling errors however, sampling pre-treatment, operator errors and instrumental errors all have some impact upon the final result obtained for the sample [176,179]. The more steps there are in the sample handling the greater the chance there is of errors occurring.

After sampling error, contamination errors are of prime concern and may explain discrepancies which occur in results obtained for duplicate analysis of a sample within a laboratory [196]. Thiers, in 1957, is reported to have said, "unless the complete history of any sample is known with any certainty, the analyst is well advised not to spend his time in analysing it" [99,108,118,169,196]. The utmost care is needed in all stages of an analytical procedure, for contamination is always understood to be the increase in the measured amount or concentration of a component resulting from its introduction to sources other than the sample [126]. Contamination risk is inherent at all stages of treatment; from laboratory equipment [79,197], sampling and sample preparation (particularly grinding), and reagents and filtering materials [123,126,176,179, 195]. The use of ultrapure reagents is stressed [77], and most investigators now use these quality reagents. Moody and Lindstrom [197] consider the sample container to be one of the largest sources of contamination, and good cleaning procedures are essential. Moody and Lindstrom [197], Aznarez, et al. [110], Baker and Chesnin [119], Satzger, et al. [169] and Stoeppler, et

al. ([125,195]) all recommend acid washing and cleaning regimes (5% $HNO_3$ or 5% $H_2SO_4$ for 24 hours followed by distilled water), as prerequisites for good detection limits.

The list of potential operator errors that can occur is exhaustive ([178,179]). A frequent source of error is the use of incorrect standard solutions, and it should be remembered that standards below 10 ppm should be freshly prepared daily. Many errors can also be attributed to incorrect dilution of samples. Instrumental errors are not common in AAS techniques since it is a ratio method and they cancel each other out ([179]). Errors caused by interferences have been discussed under the previous section.

Considerable advances have been made in the past few years in the sampling and analysis of samples, but when considering past data it is not always possible to identify errors and distinguish the effects of changes in methods of measurement from actual changes in lead concentration ([17]). Settle and Patterson ([198]) have estimated that many if not all of the reported analyses of lead in plants, animals, sediments, and waters are incorrect, perhaps by 3 orders of magnitude.

### 1.5.3. Standard reference materials (SRMs) and quality control.

Sturgeon, et al. ([182]) suggest that of the myriad of trace determinations carried out on sediments each year, little is known about the accuracy of the data, largely because of the lack of use of sufficient numbers of well characterised and representative SRMs. SRMs are essential in establishing the accuracy of a

procedure and the resulting data, and they should be of a composition which closely resembles the sample under investigation [193]. Stoeppler, et al. [195] echo these sentiments and demonstrates the need for long term storage of carefully selected samples in specimen banks, to provide homogeneous, well characterised materials for the continuous improvement and checking of analytical methods.

Generally results may all agree within a very small range, ie. they are precise, but the question remains, do they reflect what is actually there ie. accuracy? The accuracy and precision of results needs to be assessed if any confidence is to be placed in the results [119,125], a point to which few investigators seem to give due consideration particularly in environmental rather than procedural investigations.

Stoeppler, et. al. [125,195] recommend three control checks:

i) use of appropriate SRMs with certified elements to be determined, if they exist. For the analysis of whole solid environmental samples it is virtually impossible to obtain a standard since for certification the sample must be homogenised, often by grinding;

ii) simultaneous application of independent analytical procedures to the sample material [182];

iii) inter-laboratory comparisons which can detect particular sources of remaining errors, if performed by experts [200].

Appendix 1.f. summarizes some of the quality control techniques used by various authors, although some do mention a form of quality control but the vast majority do not.

## 1.6. Soil - plant - air relationships to lead.

The contribution that soil and air make to the concentration of lead in plants, and subsequently, food is uncertain. The Ninth Royal Commision Report [17] recommended that there should be a continuing effort to understand the various pathways and mechanisms by which food is contaminated. The Lawther Report [12] had earlier come to similar conclusions stating that "part of the lead content of some foods comes from the air through direct contamination and from translocation from soil into vegetables and grasses. The contribution that this makes to the body burden needs further investigation." Much research has been carried out on the effects of lead and other heavy metals, from various sources, on plants and has been reviewed by Zimdahl, et al. [5,6,80], Lepp [6], Haque and Subramanian [8], Antonovics, et al. [201], Holl and Hampp [202], Hepple [3].

The interface between the soil-air-plant is highly complex since all three elements are in a constant state of flux, due to the constantly changing environment around the plant. The detailed study of the interrelationships has largely been confined to laboratory based studies under controlled environmental conditions. There are two reasons for researchers adopting these controlled laboratory approaches;

a) due to the complexity of environmental factors controlled laboratory experiments are desirable so that factors influencing uptake can be identified.

b) the use of high concentration aqueous lead salts in laboratory based studies improves analytical sensitivity and reproducibility.

These studies tend to have been of a physiological nature and have been attempts to understand the mechanisms by which lead may be absorbed by plants from synthetic soil and air media but these do not necessarily mimic the natural response to conditions in the field environment [5,8,203]. However, they are of use if combined with parallel field studies.

### 1.6.1. Movement of lead in soil to plants.

Sources of lead in soil have been discussed earlier, however the most severely contaminated soils in Britain are in mineralised areas which have been mined. Thornton [204] estimates that some 4,000 $km^2$ of Britain is contaminated, with lead concentration in soil over 150 µg/g. In Derbyshire alone the contaminated soils extend to some 250 $km^2$ of agricultural land [205], with values over 1,000 µg/g Pb in surface soils within 500 m of old lead workings, spoil heaps and smelter sites. Zinc and cadmium are normally present in these areas resulting in an enhancement of plant toxicity effects. There is some evidence to suggest that the toxic effects of several metals may be interlinked [206,207,208,209,210,211], additive [212], or even synergistic [213].

The uptake of lead by plants is affected by almost every environmental factor [214]. The following is a list of factors, which have been modified from work by Chaney [215], which affect movement of lead from the soil to plants.

1. Amount of lead in soil.
2. The metal(s) present.
3. The soil pH.
4. The soil organic matter content.
5. The phosphate content of the soil and its availability.
6. The cation exchange capacity of the soil.
7. Reversion of lead to unavailable forms.
8. The plant under investigation, species, variety, plant part.
9. Characteristics of the metal (s).
10. Presence or absence of competing ions.
11. Rooting depth of the plant and soil metal distribution.
12. Plant age and seasonal effects
13. Soil moisture, aeration and temperature.

It has been suggested that factors 1 to 8 are more concerned with toxicity and that all are of importance in the accumulation of metals by plants [215]. Berrow and Burridge [216] have discussed the processes involved in soil plant relationships. The main processes involved are direct absorption across the root epidermis, absorption via an organic or mineral-organic carrier complex, or exchange mediated by chemical processes. Almost all uptake is usually considered to be mediated by soil solution, with direct exchange being limited, except in the case of a few metallic mineral nutrients. Organic complexing, chemical exchange and

solution of metals are the major processes occuring in soil and the metal ion or complex may diffuse through soil solution to the root surface or be carried by mass flow, induced by the transpiration stream through plants. The release of organic compounds eg. polyphenols, by the plant may be important [217] together with the action of rhizosphere micro-organisms. Uptake from soil does not occur to the same extent in all roots and is dependent on many factors which vary between specific sections of root [218]. Roots may also have effects on metal diffusion rates, eg. the pH of the soil in the immediate root environment may differ from surrounding soil [219].

The exact mechanisms involved in plant uptake of lead from soil and plant tolerance are not fully understood, though it is thought to be of a similar nature to copper [201]. Thurman [220] concludes that "At present, no precise answer to the question of mechanisms of tolerance can be advanced; indeed, in the case of certain elements (eg lead), very little relevant information is available." The mechanism of absorption of lead (Pb2+) by roots is passive [5]. Initial entry into the root free space is passive, this being gained by bulk flow of soil water. For subsequent entry into the symplasm, dissolved metals must enter the cells of the root cortex; the endodermis presenting an effective barrier to free inward diffusion of ions within the root [221]. This was established again using plant parts dosed with hydroponic solutions of lead (Pb2+) not necessarily in the form in which it will occur in the natural environment.

Berrow and Burridge [216] proposed that mobilised trace elements occurred in the following principal forms within soils:

ionic, molecular or colloidal forms in solution;
readily exchangable ions in inorganic or organic fractions;
exchange-active materials;
more firmly bound ions in exchange complexes;
chelated ions, organic or organo-mineral complexes;
incorporated in precipitated sesquioxides and insoluble salts;
fixed in crystal lattices of secondary minerals.

They are obviously in a very different form to a simple lead (PB2+) solution and will have quite different affinities to plants. It is of interest to assess the fraction of an individual metal in soil that is actually taken up by plants but apart from some work by Tyler [222] with Anemone nemorosa L., the data for field conditions is limited. Andersson [223] concluded that lead was generally unavailable for plant uptake, though it has to be said again that work on plant uptake is based on laboratory experiments using solution culture experiments [223,224,225,226,227]. However Jarvis, et al. [226,227] use a flowing culture rather than standing solutions.

Generally soil lead is considered to be low in availabilty to plants. Once available, movement and translocation of lead from roots is limited and impeded by several biochemical and/or physical processes involving lead binding, inactivation and/or precipitation [6]. Hammett [228] conducted much of the early work and demonstrated that lead was localised in the cell walls and nuclei

of absorbing roots. Tandler and Solari [229] found that lead was bound to orthophosphate ions within the nucleolus of onion root tips fixed in a lead solution. Other studies have shown lead to be fixed in the cytoplasm of cells associated with electron-dense precipitates localised in membranous inclusions, vesicles of organelles. Malone, et al. [230] have shown that the roots of corn plants exposed to lead in a hydroponic solution accumulated surface lead precipitates and lead crystals in the cell walls. They suggested that dictosome vesicles were responsible for active extrusion of apparently soluble lead from root cells. In corn, an encased deposit of lead was observed to migrate towards the outside of the cell where the membrane surrounding the deposit then fused with the plasmalemma. The material surrounding the deposit then fused with the cell wall outside the plasmalemma. These kinds of deposits were observed in stems on leaves, supporting the view that once translocated, lead could be extruded from cells throughout the plant.

Plants have been found to vary in their ability to take up lead from contaminated soils under greenhouse conditions [231]. Studies of uptake by whole plants tend to give results which reflect the influence of processes occurring in the soil which have regulated the rate of access of a particular metal to sites of absorption [203]. The main factors identified as influencing whole plant uptake are soil pH [232] and the presence and levels of other ionic species. Considerable inter- [227] or intra- [145] specific differences may exist with respect to metal uptake, though the reasons for these are uncertain, probably resulting from genetic variability [9]. Harris [142] has used a washing procedure to

establish potential relationships between soil derived and deposited lead in the shoots of winter wheat plants over a period of time using field trials. Despite high total soil lead levels shoot lead concentrations were comparatively low. In early growth stages atmospheric deposition and soil uptake were thought to contribute equally to the overall shoot lead concentrations, but at maturity translocation from the root may account for 70 - 80% of the total lead present, even though uptake was low.

### 1.6.2. Movement and distribution of lead in plants.

The concentration of lead and other heavy metals within particular plant parts varies with seasons [233,234,235,236]. Some of these changes are due to pluvial or leaching losses. The 'mechanisms of trace metal movement within plants are little understood' [6]. Many workers have noted accumulations of lead in the root systems. Hughes, et al. [203] suggest the reasons for this are two fold. Firstly the natural constituents of the root possess a high affinity for heavy metal ions, and this coupled with a failure to penetrate the endodermal barrier could cause lead to accumulate in the root free space. Secondly, even if the metals can penetrate into living cytoplasm, mechanisms of immobilisation and detoxification have been demonstrated [230]. Studies of the localisation of lead impacted on root surfaces show that it remains at the site without movement. When roots are treated with lead salts, very little lead is translocated to edible fruits [87,140,141,214]. Many studies (eg.[140,237,238,239]), show the lead content of fruits, vegetables and grain to be less than in other vegetative plant parts. Harris, et al. [160] investigating stem

tubers (potatoes) showed relatively low metal uptake, though high levels of lead were found in the roots of main crop varieties. Varietal differences were evident for all metals determined except cadmium and chromium. In the haulms of the early cultivars studied, foliar lead was found to be greater than the haulm lead concentration.

Once absorbed by the roots metals move to the rest of the plant body via the xylem. Hughes, et al. [203] point out that whilst ascent of the xylem conduits seems straightforward, the whole process as related to metals is very poorly understood. Indeed arguably the most important transfer, that relating to initial xylem entry within the stele, is so difficult to study that little is known of its operation even for major macronutrient ions.

Tiffin [240,241] shows that it is within the xylem that most metals become chelated. The identity of the organic agents involved in these reactions is uncertain, though unspecified polycarboxylic polyamino acids may act as sole chelators for copper and nickel [240,241], and oxalic acid has been shown to be important in chromium transport [242]. Lead and cadmium have not been studied in any detail.

Major internal and plant specific factors which regulate metal ascent of the xylem could be marked seasonal changes in organic content of the xylem sap [243], and the considerable interspecific differences in the organic constituents of this transport fluid [244]. This possibly explains wide variations in mobility, and

redistribution of metals observed between different species and cultivars.

Interactions may also occur between the fabric of the xylem and metals. The equilibria between metals and organic ligands in the xylem sap are in a dynamic state. This will reflect changes in the composition of the xylem sap during its ascent of the transport conduits. Lepp [245] using tree ring records produced evidence suggesting that in perennial plants permanent fixation of metals may occur in the walls of these conduits, and regulation of this fixation is complex [246].

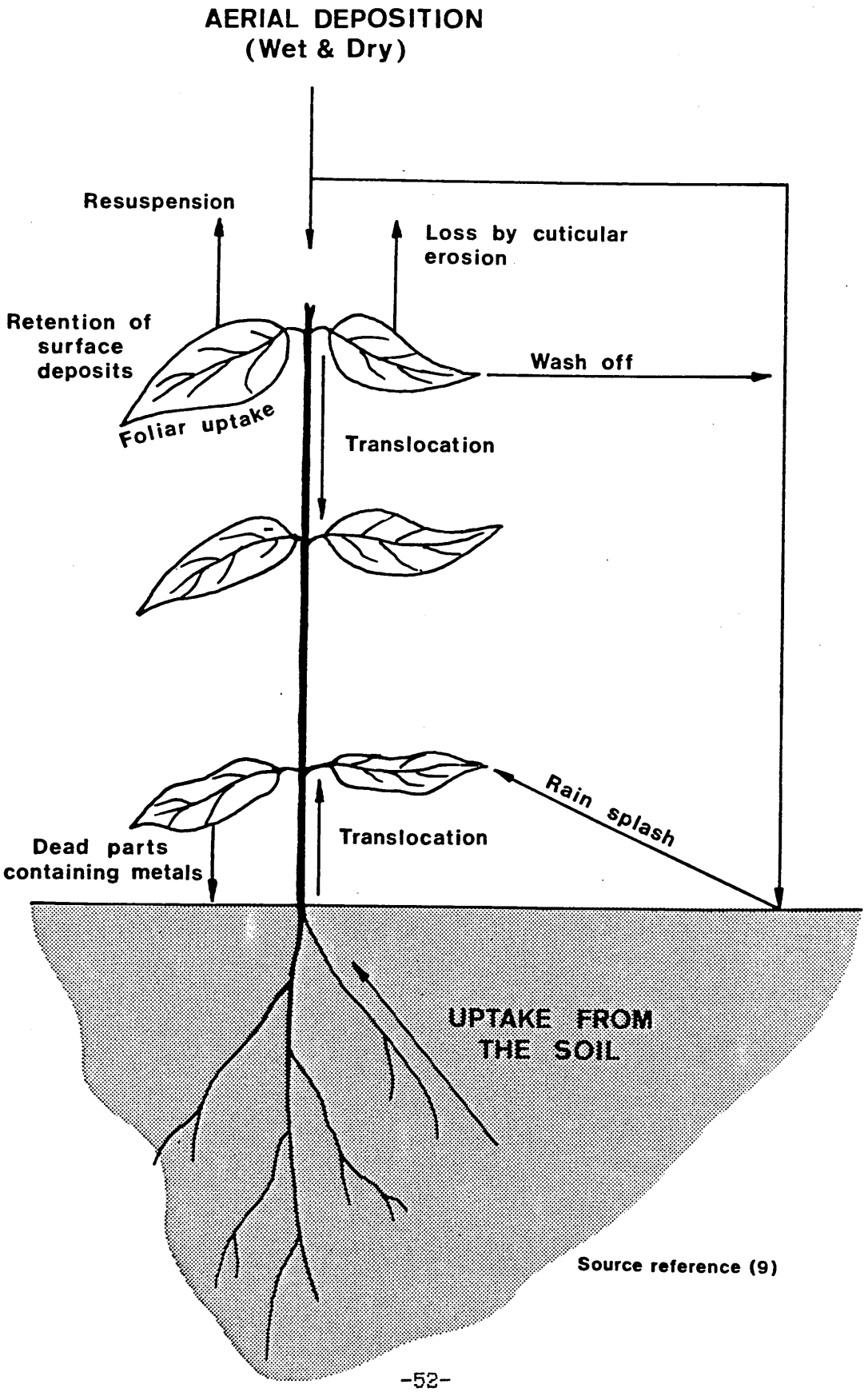
In summary, rates of soilborne lead access to aerial plant parts are governed by 'available' soil lead concentrations, interactions with constituents of both the root system and the xylem, by rates of immobilization/abstraction along the major transport pathways, and the environmental factors which regulate the flow of xylem sap.

### 1.6.3. Movement of lead to aerial plant parts.

The potential sources and routes of lead to the aerial parts of plants are summarised in Figure 1. Factors which affect lead uptake of this nature are;

1. Chemical composition of adherent particles,
2. Rate of deposition.
3. Leaf type (shape, surface texture, area, colour, etc.).
4. Leaf condition/damage.
5. Stage of growth in season.

Figure 1. Summary of the sources and routes of lead to the aerial parts of plants.



6. Wash off.

7. Rain splash.

8. Local meteorology.

Problems exist in distinguishing between lead burden derived from soil uptake and that from aerial deposition, though attempts have been made to overcome this problem [87,156,247,248,249,250]. Ter Haar [249] considered perennial ryegrss and radishes grown in normal and filtered air. It was found that about half of the lead content of the grass and virtually all of that in the radishes was obtained from soil via the roots. Rigorous washing of the vegetation samples may remove large portions of deposited material, but foliar uptake into the plant and even translocation from the site of uptake can take place [251].

Evidence of foliar uptake of lead from particulates deposited on leaf surfaces is conflicting. Zimdahal, et al. [4,5], found that foliar uptake was likely to be minimal, even though experiments using the lead isotope (Pb210) cited by them suggest otherwise. It is concluded that the greatest danger is to livestock grazing pastures in which the foliage is contaminated by surface foliar deposits of lead. The chemical and physical form of the metal on the leaf surface are of great importance. Generally uptake occurs when solutions are applied to leaf surfaces, whilst minimal uptake occurs when the metal is in particulate form. Acid rain, causing solubility of the lead in particles and then facilitating foliar uptake, should not be discounted. Lindberg, et al. [252] have shown that interactions between acid rain, intercepted fog or dew and dry-deposited material may result in dissolved metal

concentrations higher than those found in rain alone. However, it has been reported that even at low pH and high concentrations of lead there is minimal passage of lead through isolated cuticles.

Dollard ([156]) using radioactive tracer Pb210 examined the foliar uptake and redistribution of lead in radish (Raphanus sativus L.), carrots (Daucus carota L.) and dwarf french beans (Phaseolus vulgaris L.) grown under glasshouse conditions for periods of 8-12 weeks. In radish a small amount of the lead applied to the leaf surfaces was transported to the swollen storage organ (0.05-0.28%). The movement was through intact and damaged cuticles, with enhanced effect for damaged cuticles. Carrot plants absorbed and transported a fraction (0.43%) of the applied activity and by the end of the study this had reached the leaf petiole. Less than 0.01% of the applied activity reached the tap root. No movement of lead into the pod or seed tissue was detected. It was estimated that for radish foliar absorption of lead and transport to the root could account for about 35% of the internal burden of the root storage tissues. For carrots this pathway contributed about 3%, highlighting the differences that occur between species.

Once particulates are in a soluble form the degree of surface uptake may be highly dependent on the residence time of the solution on the leaf surface. In the natural environment many factors govern the retention time of solutions upon leaves. Carlson, et al. ([253]) have found experimentally that re-entrainment by windspeeds of up to 6.7 m/s had no effect on removal of lead chloride particles (1-3 μm diameter) from soybean leaves, but that simulated rainfall removed up to 95% of topically applied lead.

Washing procedures vary considerably in the literature. To assess the metal burdens before and after washing, Little [231,254], cut elm leaves (Ulmus procera Salisbury) into two halves along the main vein. Even most vigorous washing techniques are unlikely to remove all surface particles because fine particles show greater adhesion to surfaces [255], and some particles may become embedded in the cuticle [256]. The surface texture of the leaf not only affects entrapment of particles but also washing procedure, with rough, hairy and sticky leaves being difficult to wash. Many authors have described studies of washed and unwashed leaves [162,257,258,259,260] and this has been discussed previously. Direct analysis of lead particulates on plants and attempts to look at uptake in leaf needles of Virginia pine (Pinus virginiana), using a scanning electron microscopy and X-ray microprobe analysis by Elias and Croxdale [257] were unsuccessful due to sensitivity limits of the instruments and low concentration of surface lead.

Hughes, et al. [203] have reported on the uptake of heavy metals from surface deposits. The mechanisms of uptake require that particles are made soluble, so releasing the metals, which when dissolved will gain ready access to the free space of the peripheral aerial tissues. In the free space of the leaf several alternative processes can govern the fate of the absorbed metal. They suggest that binding within the apoplast may occur, with subsequent loss at leaf abscission. Metals may penetrate the leaf symplast and either interact with metabolic processes of detoxification, as can occur for root cells [230]. Losses may also occur due to leaching. Finally metals may enter the sieve elements and move some distance from sites of entry via the phloem transport

system. This latter step involves crossing a membrane to enter the sieve element [261], but once inside the sieve element movement will occur with the bulk flow of organic assimilates. The presence of high levels of phosphate in the phloem sap may be viewed as a potential interference in transport of lead [202]. Translocation of labelled lead [262] has been shown to occur following solution applications, and several heavy metals have been identified as natural constituents of phloem sap [263].

Metals deposited on bark or stem surfaces also have the potential to enter the plant. Movement of Pb210 through tree bark has been demonstrated [264]. The lack of endodermis, giving the potential existence of a surface to xylem-element lumen continuum via the free space, renders the operation of this pathway a distinct possibility [203].

## 1.7. The research programme.

### 1.7.1. Justification for research approach.

It can be seen from the preceding discussions that a vast body of literature already exists in areas related to this study. This is in part due to the multidisciplinary nature of environmental investigations. From the literature review presented above it is apparent that more information is required on the baseline levels of heavy metals in the environment and Parry, et al. [35] have demonstrated that it can be of value in local planning policy development.

However, the sampling of large areas to ascertain distributional patterns of heavy metal is poorly understood, with many authors [35,62,135,136] taking little account of the effect of obtaining only a small number of samples to represent a large area. For example, Bradley [265] surveyed an area of 100 $km^2$ in Dyfed, Wales, taking a total of 121 samples at 1-km intervals using National Grid intersection as sampling locations. He makes no reference to the efficiency of the sampling methods, but is at pains to record the efficiencies of the analytical extraction. The question of how representative the result is of the study area is not considered, and this is a common fault among similar studies.

This report will give details of the development of an appropriate sampling protocol and its application in the production of baseline distributional data for lead and other heavy metals in soils.

The pathways and contribution that lead, from highly contaminated soils and other sources, makes to the distribution of lead in food plants is uncertain and further research has been recommended in this area [17]. Many of the studies which have been carried out relating to this area are based on laboratory or green house studies of plants dosed with high concentrations of lead salts, which may not react in the same manner as plants grown in the field environment and therefore cannot be compared. Haque and Subramanian [8] recognise this and suggest future work should investigate the field environment rather than just the laboratory. Analytical sensitivity has been a major limiting factor forcing workers to dose plants with salts of abnormally high lead concentrations.

This report will investigate the development of a solid sampling technique, which enables lead to be analysed in discrete solid vegetation samples taken from various plant parts. This leads to a description of the distribution of lead resulting from soil and aerial sources, as seen in plant tissues of a single specimen. This data will be supported by results obtained using conventional flame AAS.

The development of a sampling protocol for large area heavy metal distribution studies is of particular interest, as are the results of this survey, the largest trace metal soil survey conducted in England. This, together with the analysis of lead in individual plant specimens represents a significant development in our knowledge of lead in the ecosystem.

### 1.7.2. Practical limitations and methodologies.

Many of the practical limitations and possible methodologies have been discussed above. Perhaps the biggest limitations on the proposed studies are time and money since monitoring and field studies require many hours of sampling, sample preparation and analysis. The micro sampling technique developed is not sufficiently sensitive to permit the investigation of lead distributions within plants at the cellular level but it does permit the analysis of lead in discrete plant parts from a single plant. This overcomes the problems of loss of information due to bulking samples from different specimens and contamination errors due to grinding. Where appropriate such limitations are discussed in more detail in the following chapters.

1.7.3. Summary of aims.

The main aims of the work presented in this thesis are;

1. to determine the distribution of lead and other heavy metals in the soils of the regional area of North East Derbyshire,

and

2. to investigate the pathways of lead in the ecosystem and the contibution that lead from soil and airborne dust makes to the distribution of lead in plants, with specific reference to potato plants grown in semi-controlled ecosystems.

In order to achieve these aims it is proposed to develop;

a. a rapid and accurate analytical procedure for the analysis of lead in large numbers of soil samples,

b. a scientifically based soil sampling protocol applicable to the study of the background distribution of lead and other heavy metals over large regional areas,

and

c. an analytical procedure for the determination of lead in whole solid samples of vegetation by solid sampling microsampling cup introduction.

The execution and evaluation of this work is presented in the following chapters.

# CHAPTER 2. DETERMINATION OF LEAD IN SOIL USING A LARGE BATCH DIGESTION PROCEDURE

## 2.1. Introduction.

The need to monitor the total concentrations of lead in the soil environment in order to produce background data on regional contamination has been discussed previously. Regional studies of soil contamination require the processing of many soil samples and, at a minimum, duplicate analytical determinations. It is therefore essential that a sufficiently sensitive, accurate, rapid, simple, and cost effective procedure be adopted.

Many digestion procedures have been used by authors (see 1.3.2.) and Harrison and Laxen-Duncan [79,115] favoured the use of HF:$HNO_3$ mixtures, giving excellent recoveries of total lead. Clayton and Tiller [98] and Balraadjsing [266] also favour the use of $HNO_3$ to determine the total lead in soil. Jackson and Newman [267] have shown that digestion procedures can lead to incomplete extraction of lead and increased risk of sample contamination [268] when compared with its direct determination in undigested soil by electrothermal atomisation atomic absorption spectrometry (ETA-AAS). However when using highly toxic HF to obtain a better recovery extreme care must be taken in its handling and use, and specialist laboratory ware (PTFE vessels and lined fume cupboard) is essential. In the main this prohibits its use by undergraduate students, and graduate students are often discouraged from using it except where absolutely necessary [95]. The additional care involved in using HF will slow down the preparation of samples and increase costs, with only a small increase in recovery rate over

reagents such as $HNO_3$. Hot $HNO_3$ disrupts the silicate matrices and requires only ordinary laboratory glassware and an ordinary fume cupboard.

For these reasons Davies [95], favours the use of an *aqua regia* (15 $cm^3$ $HNO_3$ + 5 $cm^3$ HCl) digestion procedure. Soil (5 g of <2 mm fraction) is weighed into a conical glass beaker and the organic matter is removed by warming with 20 volume hydrogen peroxide. After volume reduction by evaporation the *aqua regia* is added and the mouth of the beaker is sealed with thin plastic film. The beaker is set to warm at 110°C for 60 minutes. After further evaporation and filtering the final volume is 25 $cm^3$ in 0.1M $HNO_3$. This procedure has been used in a large area soil survey of Wales, in which the soils are divided into batches of 50 samples for analysis, and then a further 10 samples chosen at random to be run for duplicate analysis. An 'in house' standard sample is used for quality control together with externally certified samples. Using this procedure one sample batch takes 3 days to process from first weighing to the determination of 8 elements by flame AAS, with a precision generally equal to 10%. This is typical of procedures adopted by authors.

In this chapter a procedure has been developed which allows the analysis of total lead in 48 samples (including 'in house' standards and analytical blanks) in under 1½ days from first weighing to determination, by one operator. Additional elements take approximately 1 hour per element, per batch, providing that mass dilutions are not required on the digested samples. It represents a great improvement in safety, processing time and cost

reduction. It is also demonstrated by validation through an interlaboratory survey that there is no appreciable loss of precision or accuracy when compared with procedures used by other workers. The results of the interlaboratory survey are presented here and have been published in the journal 'Environmental Pollution' in 1984 (see list of publications, no. 5).

## 2.2. Experimental.

### 2.2.1. Equipment.

Sampling: - Stainless steel trowel, plastic bags, labels,

Sample preparation:

- porcelain mortar and pestles,
- nylon 2 mm sieve,
- ball mill (porcelain pots and balls)
  (Model 11B, Pascal Engineering Co. Ltd., U.K.,
- silver sand,
- pyrex test tubes (200 x 24 mm diameter)
  graduated to 50 ml,
- rectangular aluminium blocks (229 x 102 x 102 mm)
  drilled out to 60 mm to hold 8 test tubes.
- stands for aluminum blocks,
- gas burner unit with six bunsen ports,
- 'Zippette' auto pipette,
- 50 ml volumetric flasks for standard solutions,
- Varian Model 1275 atomic absorption spectrophotometer.

2.2.2. Reagents.

- Distilled water,
- 5% $H_2SO_4$ (Reagent grade),
- Concentrated $HNO_3$ (Reagent grade),
- 1 + 1 $HNO_3$ (Reagent grade),
- 20 Volume $H_2O_2$ (Reagent grade).
- Pb standard solution (B.D.H.).

2.2.3. Procedures.

The following general procedures were used in the optimisation of the digestion method. Where they vary this is stated in sections 2.3.1. - 2.3.4.

2.2.3.1. Collection and preparation of soil samples.

Three top soil samples were collected using a stainless steel trowel at a depth of between 0 - 10 cm from three sample locations.

SOIL α. This was obtained from a grassed field site in well managed freely drained park land at Wentworth, South Yorkshire (Grid Ref. 396980). The soil was a well developed friable sandy loam soil with good crumb structure and the organic content was estimated, by loss on ignition, to vary from 13 to 25%. No stones or parent material were present.

SOIL β. This sample was collected from a well grazed but imperfectly drained grass field 50 m north east of the site of soil

ɣ (Grid Ref. 137835). The soil was well developed, but had a poor crumb structure and a plastic texture. The organic content varied between 13 and 25% and no parent material was present.

SOIL ɣ. Collected from the top of a fine gravel, poorly drained spoil heap near the site of an old Derbyshire lead mine (unworked for over 100 years) (Grid Ref. 137835). The soil was coarse and sandy, had a poor structure and a high organic content (25 to 30%). The high organic level may have reflected additional losses during ignition due to the presence of $CaCO_3$ and $MgCO_3$. Limestone gravel was present as a residual parent material and consequently the soil was of a high calcareous mineral content.

Approximately one kilogramme of samples α, β & ɣ was collected from each of the locations and returned to the laboratory in labelled clean plastic bags. During sampling the collection of large stones, vegetation and other foreign material was avoided. Each soil was oven-dried at 100°C for 48 hours. Samples were ground by hand, using acid washed porcelain mortars and pestles until able to pass a 2 mm sieve. Further grinding to less than 250μm. was achieved using a porcelain ball mill. Grinding was carried out for at least 4 hours, though harder samples took longer. Balls and pots were subsequently cleaned by dry grinding with clean dry silver sand for 2 hours, followed by thorough rinsing with distilled water. Ground samples were then stored for analysis in fresh clean plastic bags. At all times during handling of the soil samples every precaution was taken to reduce the risk of cross contamination, including the use of extractor fans over the work surface.

2.2.3.2. Determination of total lead in soil.

The principles of the digestion procedure were as follows during the optimisation of the digestion technique. 1 g of each of the finely ground soil samples were weighed into pyrex test tubes and a volume of the acid (either concentrated $HNO_3$ or 1 + 1 $HNO_3$) added. The test tubes were placed in the aluminium blocks, and heated to about 100°C for a period of time. The digestion block assembly is illustrated in Figure 2 and Plate 1. After digestion the tube and contents were cooled and if desirable $H_2O_2$ was added to remove any residual organic material. Distilled water was then added up to the pre-calibrated 50 ml mark on each tube. The top of the tubes were sealed with a thin plastic film, shaken and the diluted digests allowed to settle overnight, ready for analysis the following day. The supernatant was nebulised into an air acetylene flame of a flame atomic absorption spectrometer. Lead was determined at 283.3 nm and aqueous calibration standards used.

2.3. Optimisation of digestion technique.

The aim was to produce a routine bulk digestion technique, using a sufficiently strong acid to obtain a 'total' lead concentration, which did not require the same degree of safety precautions as methods using HF. The addition of other reagents during the digestion described by other workers [95,98,115,120,121,] such as $H_2O_2$ or HCl was also undesirable, since they would represent additional steps costly in time and potentially a source of contamination. It was also desirable to remove the need to filter

Figure 2. The aluminium digestion block.

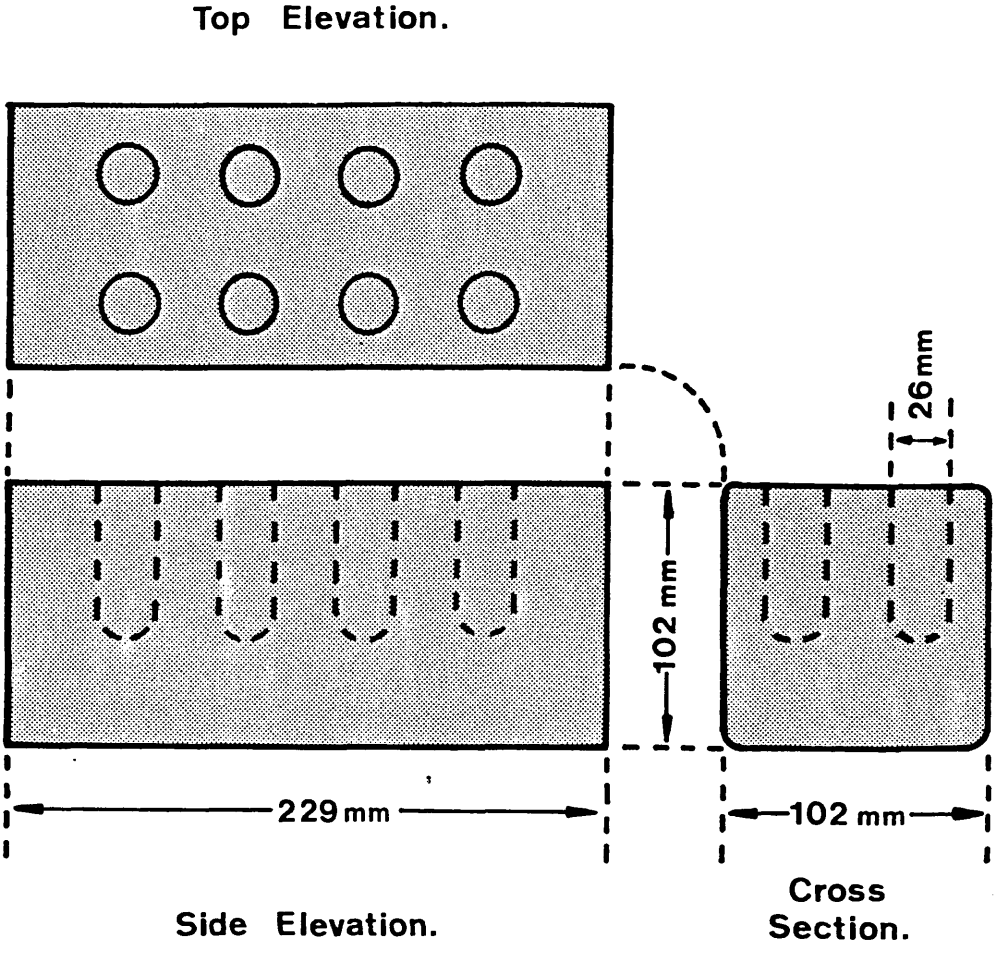
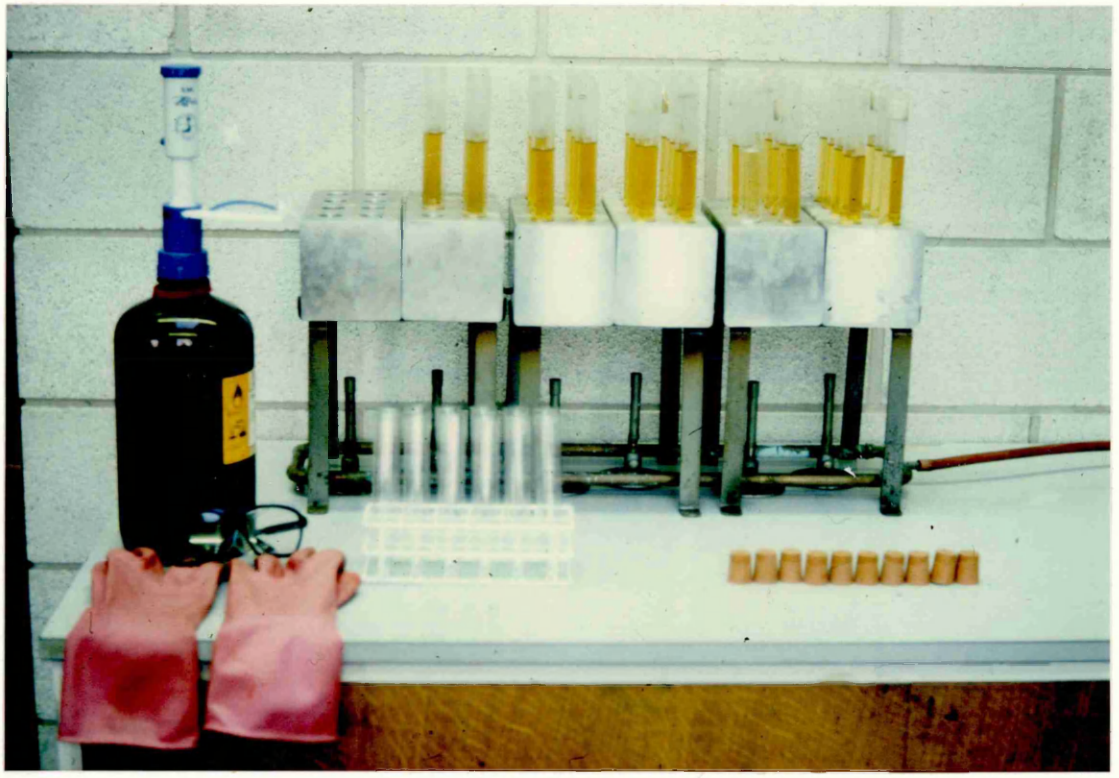


PLATE I.



The aluminium block digestion system.

samples since this is a time consuming process and can be a source of contamination.

To overcome the problems of filtering samples, tall narrow pyrex test tubes were used, of suitable size to hold 50 ml of digest. Once the soil sample was digested, the digests were shaken in the tubes and it was found that if left to settle overnight any residual material sedimented to the bottom of the tube. There was no evidence of the supernatant concentration stratifying down the digestion tube.

Work space was an important consideration since a bulk digestion procedure was required. A series of aluminium heating blocks was manufactured, each drilled to take 8 of the digestion tubes. Six blocks were arranged side by side and in this way 48 digestion tubes could be handled in an area 23 cm deep x 63 cm wide, suitable for the average fume cupboard (see Plate 1). The blocks were mounted on stands above six gas burners and the temperature was moderated by raising and trimming the flame. The use of tall tubes had an additional benefit since most of the digestion tube (140 mm) protruded from the aluminium block and was cooled by the draft from the fume cupboard, causing the acid to reflux steadily on the tube walls.

### 2.3.1. Concentrated nitric acid vs. 1 + 1 nitric acid.

The procedure described in 2.2.3.1. was carried out on the three soil samples $\alpha$, $\beta$ and $\gamma$. A 20 ml volume of acid, recommended by several authors [95,96,115], was used to ensure complete wetting

and maximum dispersion of the soil to be digested through the acid. The acid was added at 5 ml intervals to aid initial mixing in the tube. Replicates of the soils α, β and γ were digested in concentrated $HNO_3$ and 1 + 1 $HNO_3$, for 2 hours. No other reagents were added to the digests.

The results are presented in Table 6. It is apparent from the table that for all the soil samples, 1 + 1 $HNO_3$ consistently extracted lead more efficiently than concentrated $HNO_3$. A 't' test performed on the data (Table 7.) confirmed the significant difference between the two acid mixtures. However the precision (coefficient of variance) was poorer for 1 + 1 $HNO_3$ than concentrated $HNO_3$. Since a safe routine method for the determination of 'total' lead in soil was being sought, the procedure using 1 + 1 $HNO_3$ was adopted despite marginally poorer precision.

### 2.3.2. Effect of digestion time on digestion efficiency.

The digestion period varies considerably in the literature according to the procedure being followed, and the optimum digestion period for every soil will depend upon its constituents. Various authors have described different digestion periods, Harrison and Laxen-Duncan [115] use a $HNO_3$ digestion at 70 - 90°C for a 2 hour period; Clayton and Tiller [98] use a $HNO_3$ digestion boiled on a water bath for 1 hour, while Davies [95] uses a $HNO_3$:HCl digestion warmed at 110°C for 1 hour.

Table. 6. Concentrated nitric acid vs. 1 + 1 nitric acid. (µg/g Pb in soil.).

| Soil. | Acid. | n. | Mean. (µg/g) | Std. Dev. | C.V. (%) | Max. (µg/g) | Min. (µg/g) | Range. (µg/g) |
|---|---|---|---|---|---|---|---|---|
| γ | X | 23 | 3133 | 39.0 | 1.25 | 3194 | 3016 | 178 |
| γ | Y | 40 | 3534 | 55.4 | 1.57 | 3704 | 3429 | 275 |
| β | X | 11 | 548 | 10.7 | 1.96 | 568 | 530 | 38 |
| β | Y | 11 | 624 | 22.1 | 3.54 | 662 | 593 | 69 |
| α | X | 21 | 72 | 11.3 | 15.60 | 103 | 63 | 40 |
| α | Y | 21 | 100 | 18.9 | 18.90 | 175 | 82 | 93 |

Where: X = concentrated nitric acid.
Y = 1 + 1 nitric acid.

n = number of sample observations.

S = Sample Standard Deviation (Std. Dev.) defined by:

$$S = \sqrt{\frac{\Sigma x^2 - (\Sigma x)^2/n}{n - 1}}$$

C.V. = Coefficient of Variation defined by:

$$C.V. = \frac{\text{Std. Dev.}}{\text{Mean.}} \times 100$$

Table. 7. Results of 't' tests of data in table 6.

| Soil. | 't' test. | Region of acceptance of hypothesis (H). | 't' | Result. |
|---|---|---|---|---|
| γ | X ($\mu_1$) vs. Y ($\mu_2$) | 1.671 (t61,95) | -33.50 | Reject $H_o$ |
| β | X ($\mu_1$) vs. Y ($\mu_2$) | 1.725 (t20,95) | -10.27 | Reject $H_o$ |
| α | X ($\mu_1$) vs. Y ($\mu_2$) | 1.684 (t44,95) | - 6.10 | Reject $H_o$ |

For all the above cases assume:

1) $H_o = \mu_1 = \mu_2$ ie. the means of the two methods are equal, there is no significant difference between the two methods of digestion.
   $H_1 = \mu_1 < \mu_2$ ie. The mean of one method is lower than the mean of the other method.

   Where: $\mu_1$ = X (concentrated nitric acid.)

   $\mu_2$ = Y (1 + 1 nitric acid.)

2) 't' = the test statistic, where 't' is defined by;

$$'t' = \frac{(\text{Mean}_1 - \text{Mean}_2)}{\sqrt{S_1^2/n_1 + S_2^2/n_2}}$$

   and is distributed $n_1 + n_2 - 2$ degrees of freedom.

3) 95% significance level has been adopted.

4) $H_o$ is rejected if the t value is outside the range for a one tailed test of t (tn-2,95%). If this is found then $H_1$ is to be accepted.

To investigate the optimum period of digestion soil sample ɣ was chosen at random and digested for varying time periods, 45, 70, 95, 120, 170, 230, 290, 350 minutes, within the same digestion batch using 1 + 1 $HNO_3$. The results are presented in Table 8. and it can be seen that for this sample, although a higher result is obtained for samples digested within a 45 minute period the overall precision was poorer when compared to samples digested for 2 hours. There was apparently little improvement in precision after the 2 hour period.

2.3.3. Effect of addition of hydrogen peroxide.

The addition of 20 volume $H_2O_2$ is sometimes used to remove organic matter prior to digestion [95]. This is a time consuming procedure and may be unnecessary. When 1 ml of 20 volume $H_2O_2$ was added to the cooled digests (Table 8. digests B 1 - 4), which were subsequently warmed, there was no improvement in recovery or precision. This suggests that the organic material had already been removed during digestion.

2.3.4. Summary of optimised digestion technique.

The technique preferred on the basis of these results can be summarised as follows;

1 g of finely ground soil sample was weighed into pyrex test tubes and 20 ml of 1 + 1 $HNO_3$ was added slowly by 5 ml additions using a 'Zippette'. The test tubes were placed in the aluminium blocks and heated for 2 hours at about 100°C. After digestion the tubes and

Table. 8. Effect of digestion time (A) and addition of hydrogen peroxide (B) on 1 + 1 nitric acid digestion efficiency (µg/g Pb in soil.).

| | Time. (mins) | Acid Vol. (ml) | n. | Mean. (µg/g) | Std. Dev. | C.V. (%) | Max. (µg/g) | Min. (µg/g) | Range. (µg/g) |
|---|---|---|---|---|---|---|---|---|---|
| A1. | 45 | 20 | 5 | 3624 | 48.7 | 1.34 | 3704 | 3582 | 122 |
| A2. | 70 | 20 | 5 | 3586 | 35.8 | 0.99 | 3638 | 3537 | 101 |
| A3. | 95 | 20 | 5 | 3531 | 21.1 | 0.60 | 3561 | 3505 | 56 |
| A4. | 120 | 20 | 5 | 3499 | 16.4 | 0.47 | 3520 | 3478 | 42 |
| B1. | 170 | *+20 | 5 | 3484 | 16.5 | 0.47 | 3512 | 3471 | 41 |
| B2. | 230 | *+20 | 5 | 3522 | 44.5 | 1.26 | 3596 | 3481 | 115 |
| B3. | 290 | *+20 | 5 | 3534 | 23.5 | 0.66 | 3561 | 3502 | 59 |
| B4. | 350 | *+20 | 5 | 3489 | 44.7 | 1.28 | 3547 | 3429 | 118 |

* = 1 ml additions of 20 volume hydrogen peroxide.

contents were cooled, and this may be accelerated using a refrigerated water bath. Distilled water was added up to the precalibrated 50 ml mark on each tube. The top of the tubes were covered in a thin plastic film, shaken and the diluted digests allowed to settle overnight, ready for analysis the following day. The supernatant is nebulised directly from the tube into an air acetylene flame of a flame atomic absorption spectrometer. Lead was determined at 283.3 nm using aqueous standards.

### 2.3.5. Precision testing.

The precision of the procedure described above was assessed by replicate analysis of an existing laboratory soil sample. Some 147 replicate digestions of the same soil sample, plus blanks, were carried out over three batches of 52 digestion tubes. The mean result for the soil sample was 50.0 μg/g Pb (Std. Dev. = 0.16) giving a precision (coefficient of variance) of 0.32%, with good batch to batch reproducibility. Using the procedure it was evident that good intralaboratory precision was being achieved.

## 2.4. Evaluation of digestion technique by interlaboratory survey.

If the results of different surveys of soil lead pollution are to be comparable, it is obviously important that analysts use methods that give similar lead recoveries and as already demonstrated the variety of methods used are very diverse. Whilst analysts can check their intralaboratory precision using the procedure described above, interlaboratory precision is more difficult to evaluate. A measure of the accuracy being achieved using a particular procedure

can be gained by either the analysis of certified reference materials or by participation in interlaboratory surveys. Few interlaboratory surveys have been published. Yamagata [269], has reported an interlaboratory C.V. of around 10% for lead, copper and zinc in soil. Davis and Carlton-Smith [270], recently reported an interlaboratory correlation for several metals as the average maximum deviation (MPD%) from the true value. A soil relatively low in contamination (24 μg/g Pb) had an unacceptably high MPD of ± 27%. A more contaminated soil, (90 μg/g Pb), had an improved correlation with an MPD of ± 14%. Similar results have been indicated in other interlaboratory surveys [271,272,273,274]. In order to evaluate the accuracy and comparative precision of the procedure described above an interlaboratory survey has been carried out, and is described below.

### 2.4.1. Preparation and collection of survey samples.

A further three top soil samples were collected using a stainless steel trowel at a depth of between 0 - 10 cm from three sample locations.

SOIL A. This was obtained from a grassed field site in well managed freely drained park land near Wentworth, South Yorkshire (Grid Ref. 396980). The soil was a well developed friable sandy loam soil with good crumb structure and between 13 and 25% organic material (estimated by loss on ignition). No stones or parent material were present.

SOIL B. Collected from the top of a fine gravel, poorly drained spoil heap near the site of an old Derbyshire lead mine (unworked for over 100 years)(Grid Ref. 137835). The soil was coarse and sandy, had a poor structure and a high organic content (25 to 30%). The high organic level may have reflected additional losses during ignition due to the presence of $CaCO_3$ and $MgCO_3$. Limestone gravel was present as a residual parent material and consequently the soil was of a high calcareous mineral content.

SOIL C. This sample was collected from a well grazed but imperfectly drained grass field 50 m north east of the site of soil B (Grid Ref. 137835). The soil was well developed, but had a poor crumb structure and a plastic texture. The organic content was between 13 and 25% and no parent material was present.

Approximately five kilogrammes of soil samples A, B & C were collected from near each of the locations previously described for soil samples $\alpha$, $\gamma$ and $\beta$, and returned to the laboratory in labelled clean plastic bags. During sampling the collection of large stones, vegetation and other foreign material was avoided. Each soil was oven-dried at 100°C for 48 hours. Samples were ground by hand, using acid washed porcelain mortars and pestles until able to pass a 2 mm sieve. Further grinding to less than 250$\mu$m. was achieved using a porcelain ball mill. Samples were ground twice, each time for the normal 4 hour period. Great care was taken to ensure the homogeneity of all three soil samples, since the study was to investigate inter- and intra- laboratory precision and not sample imprecision. Balls and pots were subsequently cleaned by dry grinding with clean dry silver sand for 2 hours, followed by

thorough rinsing with distilled water. Ground samples were then stored for analysis in clean large plastic containers ready for use in the survey. At all times during sample handling every precaution was taken to reduce the risk of cross contamination, including the use of extractor fans over the work surface and disposable spatulas.

2.4.2. Survey procedure.

Fifty laboratories were invited to participate in the survey. However, of these only 24 agreed to take part. The participating laboratories were considered to be of a very high standard including; 8 University/Polytechnic research laboratories involved with environmental monitoring; 4 Ministry of Agriculture Fisheries and Food laboratories; 3 Forensic Science Laboratories; 3 water industry laboratories and several other national laboratories.

Three days prior to mailing the samples to participants the soil samples were carefully sub-sampled and sealed into acid washed polypropylene containers. The containers were packed in plastic bags and placed in padded envelopes for posting. All samples were posted to participants on the same day and they all received by post seven soil samples each of approximately 5 g. The seven samples were made up of five replicate samples of soil A, and one each of soils B and C. The samples were merely labelled with a number 1 - 7. No background information about the samples was given to the participants. The inclusion of replicates permitted an assessment of the intralaboratory precision at 'normal' levels of lead in soil without the analyst's knowledge, reducing the

possible risk of 'unintentional' bias during analysis. Participants were requested to report only one 'total' lead concentration (in mg/kg) for each soil sample. A brief questionnaire was supplied with the samples requesting the participants to indicate the condition of the samples received through the post, outline the analytical procedure used, and provide an indication of how experienced they were at soil lead analysis.

In order to confirm the stability of the mailed samples, a package of identical samples was retained in the laboratory at room temperature for two weeks, to simulate a maximum potential postal delay. The results of lead analysis after this period were the same as those when the soil was packaged, within the precision limits of our laboratory. This confirmed that the soil samples had remained stable for this period.

2.4.3. Results.

Of the 24 laboratories agreeing to take part, 22 supplied results and not one of them reported receiving damaged samples.

All the results supplied by participants are listed in Table 9. A key has been included which categorises the experimental procedure used by each analyst. It can be seen that two analysts (laboratories 3 and 22) reported results by more than one procedure. Figure 3 (a) shows the mean of each laboratory's five results on Soil A., which are plotted to illustrate the deviation from the mean of all results reported. The overall precision is

Table 9. Results from all laboratories (Pb mg/kg soil).

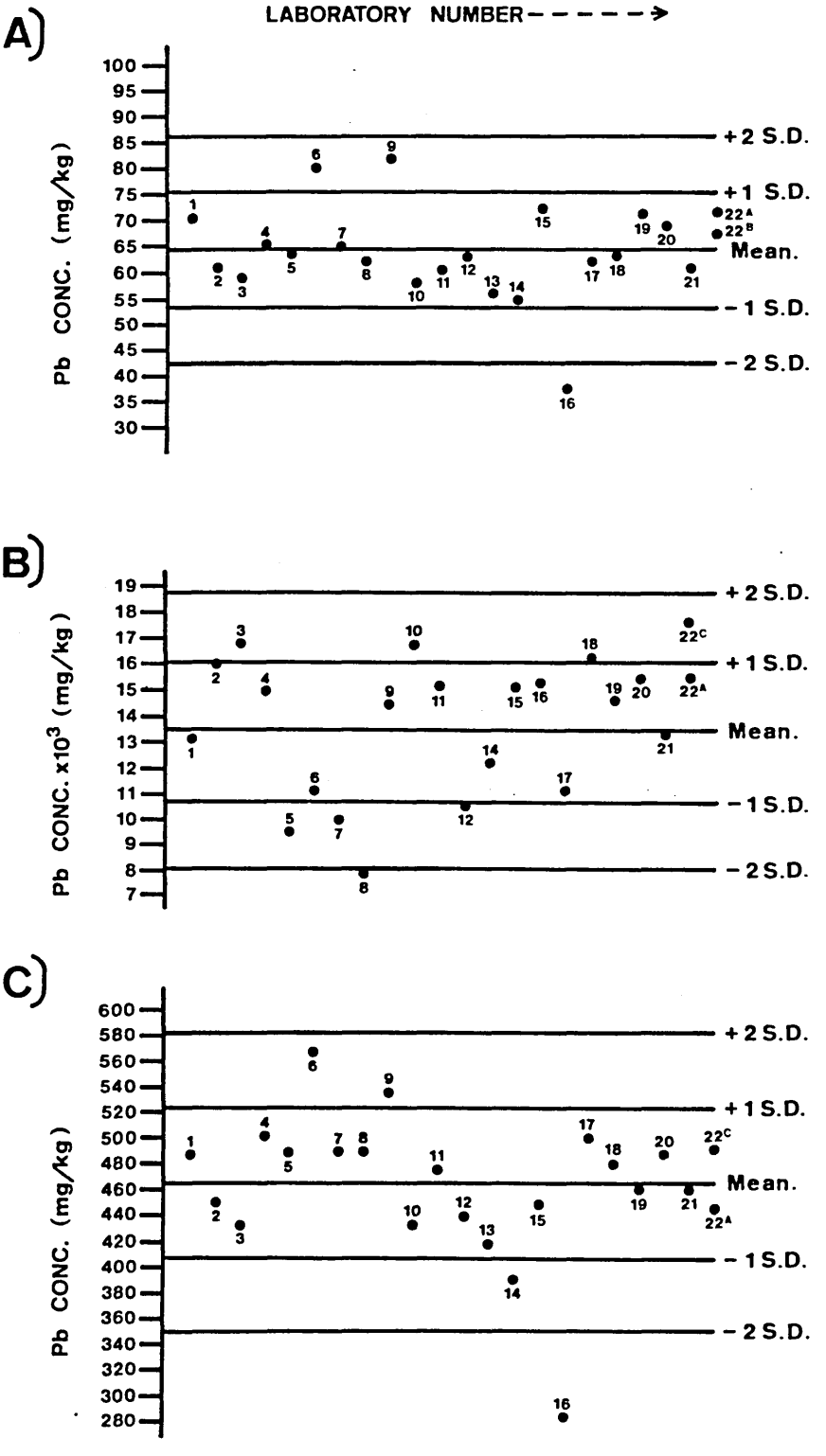
| Laboratory number. | Sample number. | | | | | | | Analytical procedure. (see key). |
|---|---|---|---|---|---|---|---|---|
| | SOIL (A) | | | | | SOIL (B). | SOIL (C). | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| 1 | 69,6 | 70,9 | 67,4 | 70,0 | 72,5 | 13134 | 486,5 | A |
| 2 | 63 | 58 | 56 | 62 | 64 | 16000 | 450 | A |
| 3a | 57 | 62 | 60 | 60 | 58 | 16900 | 433 | C |
| 3b | - | - | - | - | - | 16100 | - | A |
| 4 | 65,0 | 65,0 | 65,0 | 65,0 | 65,0 | 15000 | 500 | E |
| 5 | 63,6 | 63,8 | 63,8 | 64,0 | 65,0 | 9460 | 486 | A |
| 6 | 80 | 95 | 95 | 93 | 93 | 11100 | 567 | E |
| 7 | 66,7 | 64,4 | 67,9 | 67,9 | 57,7 | 9950 | 490 | A |
| 8 | 61 | 63 | 64 | 61 | 63 | 7750 | 490 | E |
| 9 | 83 | 81 | 82 | 83 | 81 | 14500 | 535 | F |
| 10 | 60,0 | 56,7 | 56,7 | 56,7 | 63,3 | 16665,0 | 433,3 | A |
| 11 | 60,0 | 60,0 | 61,0 | 61,0 | 60,0 | 15100,0 | 475,0 | A |
| 12 | 37 | 65 | 62 | 63 | 65 | 10500 | 440 | E |
| 13 | 54 | - | 57 | - | 58 | - | 418 | D |
| 14 | 55 | 59 | 48 | 59 | 55 | 12200 | 390 | A |
| 15 | 72 | 77 | 71 | 68 | 72 | 15130 | 448 | G |
| 16 | 40,9 | 36,0 | 36,3 | 37,8 | 36,6 | 15210 | 281,8 | B |
| 17 | 63,5 | 62,0 | 62,5 | 62,0 | 62,8 | 11067 | 500 | E |
| 18 | 64,0 | 63,5 | 63,5 | 64,0 | 63,5 | 16200 | 480 | D |
| 19 | 72 | 70 | 70 | 73 | 71 | 14600 | 460 | F |
| 20 | 66,5 | 68,7 | 70,6 | 70,1 | 70,5 | 15374 | 487,9 | A |
| 21 | 59 | 59 | 58 | 58 | 70 | 13330 | 460 | D |
| 22a | 76 | 72 | 70 | 69 | 73 | 15400 | 490 | A |
| 22b | 68 | 67 | 66 | 67 | 69 | - | - | C |
| 22c | - | - | - | - | - | 17500 | 448 | G |

KEY:

A = Nitric acid digestion and flame AAS.
B = Nitric acid cold leaching (30s) and flame AAS.
C = Nitric acid digestion and ETA-AAS.
D = Nitric/hydrochloric acid digestion and flame AAS.
E = Nitric/perchloric acid digestion and flame AAS.
F = Dry ashing (450-550°C) prior to acid digestion and flame AAS.
G = X-ray fluorescence spectrometry.

(N.B.- Laboratory No. 20 shows our laboratory results.)

Figure 3. The deviation of each laboratory about the overall mean for: a) samples 1 - 5 (Soil A); b) Soil B; c) Soil C.



indicated by lines showing ± 1 and ± 2 standard deviations (SD) from the mean. This has been done for Soil B and C in Figures 3 (b) and 3 (c) respectively.

Statistical treatment of the data was only carried out on the results obtained by laboratories using atomic absorption spectrometry. It was expected that X-ray fluorescence spectrometry might give systematically higher results than atomic absorption procedure. Extreme outliers (more than two SD from the overall mean) were rejected from statistical treatment, and only the first set of AAS data results from laboratories 3 and 22 were included (3a and 22a respectively). All rejected data points are listed in Table 10. Table 11 lists the mean and relative standard deviation (RSD) of all results reported for each sample after the rejection of outliers. Table 12 gives the intralaboratory precision calculated from the results recorded for samples 1 - 5 (Soil A). In Tables 9 & 12 the results submitted by our own laboratory have been highlighted for comparison with the other laboratories which expressed a desire to remain anonymous.

The survey design permitted an analysis of variance on the results of Soil A since replicate results were available (samples 1 - 5). This statistical treatment was performed in a similar way to that described by Jackson ([275]). The calculation was made for all laboratories (except outliers) using AAS, and additionally laboratories were categorised according to experience (ie. more or less than 10 samples routinely analysed per week) and also by digestion/extraction solution used (ie. nitric acid versus others). The data relating to these analyses are given in Table 13, where

Table 10. Data values excluded from statistical treatment.

| Laboratory number. | Samples rejected. |
|---|---|
| 3b | 6. |
| 6 | 2,3,4,5. |
| 8 | 6. |
| 12 | 1. |
| 13 | All samples. |
| 15 | All samples. |
| 16 | 1,2,3,4,5,7. |
| 22b | All samples. |
| 22c | All samples. |

Table 11. Mean and relative standard deviation for all results (excluding outliers).

| Sample number. | Number of laboratories. | Mean (mg/kg). | SD (mg/kg). | RSD (%) |
|---|---|---|---|---|
| 1 | 18 | 65.8 | 7.70 | 11.7 |
| 2 | 18 | 64.7 | 6.03 | 9.3 |
| 3 | 18 | 63.8 | 7.31 | 11.5 |
| 4 | 18 | 64.9 | 6.41 | 9.9 |
| 5 | 18 | 65.6 | 6.43 | 9.8 |
| 6 | 18 | 13773.2 | 2383.06 | 17.3 |
| 7 | 18 | 476.5 | 39.03 | 8.2 |

Table 12. Intralaboratory precision for Soil A. (Samples 1-5)[a].

| Laboratory number. | Mean (mg/kg). | SD (mg/kg). | RSD (%) |
|---|---|---|---|
| 1 | 70.1 | 1.87 | 2.7 |
| 2 | 60.6 | 3.43 | 5.7 |
| 3 | 59.4 | 1.95 | 3.3 |
| 4 | 65.0 | 0.00 | 0.0 |
| 5 | 64.2 | 0.82 | 1.3 |
| 7 | 64.9 | 4.28 | 6.6 |
| 8 | 62.4 | 1.34 | 2.1 |
| 9 | 82.0 | 1.00 | 1.2 |
| 10 | 58.7 | 2.95 | 5.0 |
| 11 | 60.4 | 0.55 | 0.9 |
| 12 | 63.7 | 1.50 | 2.3 |
| 14 | 55.2 | 4.49 | 8.1 |
| 17 | 62.6 | 0.63 | 1.0 |
| 18 | 63.7 | 0.27 | 0.4 |
| 19 | 71.2 | 1.30 | 1.8 |
| **20** | **69.3** | **1.73** | **2.5** |
| 21 | 60.8 | 5.17 | 8.5 |
| 22 | 72.0 | 2.74 | 3.8 |
| 15[b] | 72.0 | 3.20 | 4.4 |

[a] n = 5, except Laboratory No. 12 (n = 4).

[b] Results obtained by X-ray fluorescence spectrometry.

(N.B.- **Bold type** indicates our laboratory results.)

Table 13. Analysis of variance for results from samples 1 - 5 (Soil A).

| Category | Number of Laboratories | n | Mean (mg/kg) | Variance[a] | | RSD(%)[a] | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $\sigma^2$ inter | $\sigma^2$ Intra | Inter | Intra | Overall[b] |
| V | 17 | 85 | 64,85 | 40,01 | 6,439 | 9,7 | 3,9 | 10,3 |
| W | 10 | 50 | 65,83 | 53,23 | 5,309 | 11,1 | 3,5 | 11,2 |
| X | 7 | 35 | 63,45 | 23,20 | 8,053 | 7,6 | 4,5 | 8,4 |
| Y | 10 | 50 | 63,66 | 32,24 | 7,650 | 8,9 | 4,3 | 9,6 |
| Z | 9 | 40 | 66,33 | 52,87 | 4,708 | 10,9 | 3,3 | 10,9 |

[a] Inter and intra refer to interlaboratory and intralaboratory, respectively.

[b] Calculated from all (n) results.

Where: n = Total number of results reported.

V = All laboratories.

W = Laboratories who analyse <10 samples per week.
X = Laboratories who analyse >10 samples per week.

Y = Laboratories using nitric acid methods.
Z = Laboratories using other digestion methods

the final column (the overall RSD) was calculated separately using all reported results (after rejecting outliers). Any effects of analytical experience and procedure on the mean results and overall RSDs, separated into the above categories, for samples 6 and 7, are presented in Table 14.

2.4.4. Discussions.

The survey did not permit a true evaluation of accuracy of all laboratories due to the absence of certified concentrations for the samples. However, when the samples were analysed in our own laboratory a sample of the Certified Reference Material N.I.E.S. Pond Sediment (Certificate Value = 105 ± 6 µg/g Pb)[276] was also analysed for lead and good agreement was found, with a concentration of 103.7 ug/g Pb being obtained.

Comparison of the results from individual laboratories with the overall mean for each sample is of use. Figure 3 demonstrates this and some bias according to analytical procedure can be observed.

a) Of the two analysts ashing the soils (laboratories 9 and 19), number 9 obtained high results on six of the seven samples. This may be expected since samples were ashed prior to weighing, and oxidation of organic material would cause the residue to be enriched with lead. In the case of laboratory 19, samples were weighed out prior to ashing, and the method apparently gives compatable results to those of the other laboratories.

Table 14. The effect of analytical experience and procedure on a) sample 6 (Soil B), b) sample 7 (Soil C).

| Category. | Number of laboratories. | Mean (mg/kg). | SD (mg/kg). | RSD (%) |
|---|---|---|---|---|
| a) V | 19 | 13773.2 | 2383.1 | 17.3 |
| a) W | 12 | 13280.0 | 2218.9 | 16.7 |
| a) X | 7 | 14618.4 | 2586.6 | 17.7 |
| a) Y | 11 | 14056.3 | 2558.8 | 18.2 |
| a) Z | 8 | 13383.9 | 2224.9 | 16.6 |
| b) V | 19 | 476.5 | 39.03 | 8.2 |
| b) W | 12 | 486.9 | 43.57 | 8.9 |
| b) X | 7 | 458.6 | 22.29 | 4.9 |
| b) Y | 10 | 459.4 | 33.07 | 7.2 |
| b) Z | 9 | 495.5 | 37.72 | 7.6 |

Where: V = All laboratories.

W = Laboratories who analyse <10 samples per week.
X = Laboratories who analyse >10 samples per week.

Y = Laboratories using nitric acid methods.
Z = Laboratories using other digestion methods

b) X-ray fluorescence used by laboratories 15 and 22 gave results with a high bias, with the exception of Soil C. It would be expected that this procedure would give a better indication of 'total' lead, since most acid digestion methods leave a small proportion of lead bound in the silicate matrix. These differences in recovery of lead using X-ray fluorescence and acid digestion AAS will vary according to the soil matrix.

c) The cold acid procedure used by laboratory 16 consistently yielded low results with the exception of Soil B. This was expected when compared with more destructive procedures. The result for Soil B may well have been normal as a result of the lead being less tightly bound in that sample.

Overall precision for soil samples 1 - 5 and 7 is similar (Table 11.) However, the precision for sample 6 was much poorer at 17.3%. It is possible that this is due to extrapolation and/or dilution errors arising from the high concentration of lead in the sample 6.

It is apparent from Table 15 that the digestion procedure, described previously and used by our laboratory (No.20) gave good agreement with the overall results from all other laboratories.

The intralaboratory precision for Soil A is generally good (Table 12.), in most cases well within 5%, with our laboratory (No.20) achieving 2.5% using the digestion technique described earlier. This is confirmed in the analysis of variance results in Table 13. The last three columns of this Table show that the overall

Table 15. Comparison between the results for Laboratory 20 and the mean results for all other Laboratories, for Soils A, B and C.

| Soil sample. | Laboratory 20 (mg/kg). | All Laboratories. Mean (mg/kg). |
|---|---|---|
| Soil A. | 69.3 * | 64.85 * |
| Soil B. | 15374.0 | 13773.2 |
| Soil C. | 487.9 | 476.5 |

* = mean of samples 1 - 5.

precision is only slightly better than the interlaboratory precision. Consequently, it is apparent that the major contribution to the overall RSD is interlaboratory imprecision, with intralaboratory imprecision having comparatively little effect.

Tables 13 and 14 can be used to examine whether variation in analysts' experience has any significant effect on results, by comparing laboratories analysing <10 samples per week with those analysing >10 samples per week. The mean results are similar between the two sets of laboratories suggesting that little bias occurs due to the inexperience of the analyst. There is no indication of the inexperienced analysts producing poorer precision, since neither interlaboratory nor intralaboratory variances differ significantly ($F_{0.95}$) between the two groups. When nitric acid digestion results are compared with results obtained by laboratories using other digestion procedures, there is no indication of bias (Tables 13 - 14). Also, there is no evidence of significantly different precision (Table 13). However, it is likely that some acid mixtures (eg. nitric/perchloric) would extract more lead from soil than nitric acid alone. Had more laboratories using these methods participated in the survey then it is probable that this would have been seen.

## 2.5. Conclusions.

The results of the survey clearly demonstrate that analysts should seek to improve analytical performance through better interlaboratory correlation rather than merely concentrating on intralaboratory precision.

Although some of the laboratories had an appreciable bias with respect to the overall mean results, correlation between most laboratories using acid digestion and AAS is quite reasonable. It was apparent that nitric, nitric/hydrochloric and nitric/perchloric acids were equally effective in digesting the soils used in the survey. This may not be the case for all soil types, however, and in order to compare results reported by different laboratories, methodology should be standardised and interlaboratory correlation monitored as part of a routine quality control.

It is clear from the results of the interlaboratory survey that the digestion procedure developed above gives good agreement with techniques used by other laboratories. It has the additional benefit of allowing the processing and analysis of large batches of soil samples and is consequently of value in the application for which it was designed, that is large area soil contamination surveys.

Finally, the soils used in the survey have been analysed by different laboratories and consequently can be used as an in-house standard reference material. This is essential for quality control

of batch reproducibility during the work reported in the following chapters of this thesis.

This work was published in the journal 'Environmental Pollution' in 1984 (See list of publications, no. 5). The paper received a good response with over 120 requests for reprints from all over the world, indicating an interest in the need for standard procedures and quality control.

# CHAPTER 3. DEVELOPMENT OF A SAMPLING PROTOCOL FOR LARGE AREA SOIL SURVEYS OF TRACE METAL CONTAMINATION.

## 3.1. Introduction.

The sampling of the environment for trace metals is a difficult objective [277], particularly if a representative sample is to be obtained [276,279]. The larger the size of the study area the greater the problems of producing a suitable sample. This is particularly the case in large area regional geochemical surveys.

The Institute for Geological Sciences [280] has for many years been involved in a programme of regional geochemical mapping which has aimed to provide information for the following specific purposes:

a) Mineral exploration - identifying the occurrence of metalliferous minerals of potential economic significance.

b) Pollution studies - to provide reliable information on the natural and anthropogenically raised levels of elements (including heavy metals) to enable a realistic assessment of contamination.

c) Agriculture and medical geography - providing data which can be used in epidemiological studies of degenerative diseases of man, animals and crops.

d) Geological mapping - producing lithological, compositional and structural variations not easily detected by visual mapping procedures.

e) Studies of geochemical aspects of crustal development and ore-forming processes - allowing the development of quantitative models for use in metals exploration.

Plant and Moore[281] identify three principal sampling media which can be used for geochemical studies of this nature namely; rocks, soils and stream sediments. Rocks are unsuitable for regional surveys since,

1) few rock types provide regular outcrops;
2) the occurrence of areas of deep weathering;
and 3) problems arise from obtaining samples from potentially mineralised faults and structures.

Soil sampling is also considered unsuitable by them because of,

1) the variation in soil types nationally;
2) limited soil cover in upland areas;
3) wide variations in pH and Eh in soils which critically affects solubility and concentrations of metals;
and 4) problems of ensuring consistant sampling of specific soil horizons by non-expert sampling teams.

Plant [282] suggests that rock and soil samples produce information of limited areal significance and that large numbers of samples must be collected, prepared and analysed to represent even relatively small areas and this is both slow and costly. For these reasons the Institute of Geological Sciences has favoured the use of stream sediments. The sediment samples represent an

approximation to the composition of the products of weathering of rocks up stream of the sample location and therefore reflect the average concentration of a stream catchment basin. Samples have been taken using wet screening to collect a fraction of sediments smaller than 150 μm, grab sampling the top few centimeters of a sediment and panning to produce a heavy mineral concentrate. The latter samples represent a density of one sample per 2 $km^2$ based on second and third order sediment samples collected immediately above stream confluences.

This general procedure has been used to good effect in nationwide geochemical studies [283,284,285,286,287]. Plant [280] accepts that trace element maps produced in this way are not always applicable to agricultural or human investigations which would ideally be based on the systematic analysis of soil, vegetation or dust, rather than stream sediments. There are few surveys available which provide systematic data on either 'total' or 'available' trace elements in soils, primarily due to the costs and time required.

The production of background data relating to soil contamination has been undertaken by several investigators. However, because of costs and limitations of time the sampling protocols which have been used are questionable in terms of their suitability for obtaining a representative sample of the study area.

Parry, et al. [35] describe the use of a trace metal soil survey as a component of strategic and local planning policy development, for a 650 $km^2$ area of Merseyside in which soil samples were analysed

for available lead, zinc, copper and cadmium. Despite studying available metals no reference is made to the potential influence that variations in pH and Eh may have had upon the results obtained. The sampling strategy adopted merely involved collecting a soil sample (0-5 cm depth) from each of the four land-use categories (parkland, gardens and allotments, agricultural grassland, agricultural arable land) within a 2 km grid square (4 $km^2$ area). No attempt was made to stratify the sample to reflect the proportion of land in each category. These four samples were then combined to form the 'representative' sample for the 4 $km^2$ area and then subsequently analysed. This is typical of the kind of approach taken by authors investigating trace metal contamination of soil by regional surveys.

The Joint Unit for Research on the Urban Environment (JURUE) has described two surveys of a similar nature. Using a predictive sampling approach ([135]), grid areas were classified into 5 groups ranging from high to low 'urban intensity' on the basis of road network patterns and then field surveys carried out in twenty of each of the groups. The data from this was then used to plot a predicted level of pollution for grid squares over an area 900 $km^2$. This 'predictive' approach may be unsuitable for some industrial areas with very discrete local 'hotspots' of soil contamination. This has been illustrated by Kenyon [310] who observed very poor sampling precision in urban/industrial areas. Alternatively, 'significance of soil contamination' in the study area has been employed ([136]), in which grid squares were grouped into three types A, B and C. Type 'A' included samples at a density of 7 sites per $km^2$, 'B' - 4 sites and 'C' - 2 sites, where 'A' represented an area

expected to be highly contaminated, and/or where redevelopment of the land was likely in the near future.

Other workers have chosen a simpler approach. Bradley [265] studying a 100 $km^2$ area of Dyfed, Wales, used the National Grid intersections to generate 121 sample locations (sampling density 1.21 per $km^2$). Similarly Davies [95], sampled a regular 1 x 1 km grid in the Halkyn Mountain area of North Wales to produce a regional map of metal contamination of soils. None of the above workers adequately considered the implications in terms of the accuracy and precision of collecting samples using the strategy that they had adopted. For this reason it is impossible to compare the patterns revealed by different studies, and more consideration is needed of the process of obtaining a representative sample for regional trace metal soil surveys.

Many reports have illustrated how difficult it can be to obtain a representative sample from soil, because the high spatial variability of soil properties leads to inevitable sampling error. This is particularly true of random sampling which can lead to large errors unless a large number of samples are collected and pooled. Aljibury and Evans [288] found that to obtain an average soil moisture content to within ± 10%, over 30 random samples needed to be collected from an 18 acre section of land. Other workers have found similar difficulties with random sampling [289,290,291]. Hammond, et al. [292] demonstrated that a multistage random sampling technique was preferable to simple random sampling, providing that the analyte was distributed in a fairly uniform manner. Poor precision was obtained by Khan and

Nortcliff [293] with a systematic unaligned sampling scheme used to study the spatial variability of extractable Fe, Mn, Cu and Zn. When 49 samples were collected within an area of 1 ha, the relative standard deviation (RSD) varied from 14% (Copper) to 65% (Iron). Robinson and Lloyd [294], writing one of the earliest papers on soil sampling in 1915 described sampling using a grid pattern. In order to obtain a reasonably small error (±13.4% for phosphate) very intensive sampling was required with some 25 samples taken from a 200 x 400 yard area. It was suggested that laboratory errors were negligible compared with sampling errors and this has been echoed many times since. In general, however, systematic sampling should lead to smaller errors than simple random sampling [295]. This has been illustrated by Berry [296] and Webster [297], who have obtained improvements up to 10-fold in precision. The most successful systematic approach was probably that of McBratney and Webster [298] who showed how the special dependencies of soil can be taken into account. The semivariogram for the analyte was used to calculate the variance in the neighbourhood of each sampling point. The global variance was then obtained by pooling the calculated variances.

A random sampling technique which might provide an acceptable sampling precision involves the subdivision of heterogeneous soil populations into less heterogeneous strata; i.e., stratified random sampling [299]. Cline [300] suggested the use of stratified random sampling in soil sampling, but no data were presented. Using some of the above principles this chapter demonstrates how stratified random sampling can be applied readily to trace metal soil surveys giving greater precision than simple random sampling.

## 3.2. Experimental.

### 3.2.1. Equipment and reagents.

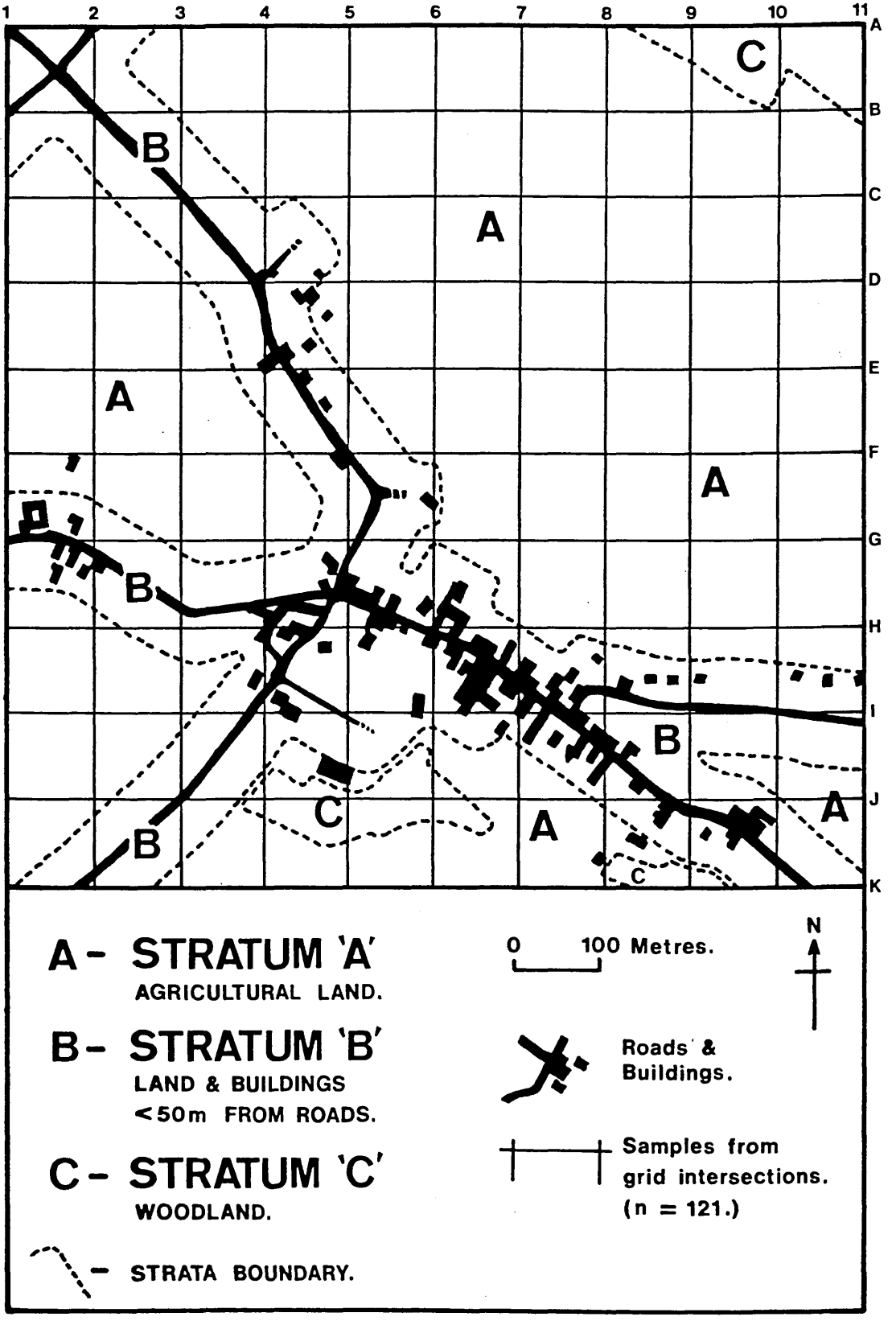
The equipment and reagents used are identical to those described under section 2.2.1./2.2.2.

### 3.2.2. Soil survey area and sampling.

In order to statistically evaluate the precision which would be obtained if an area were sampled randomly, an intensive survey of the distribution of trace metals in soil, over an area of land, is required. This information was supplied by dividing a km-square into 100 m squares (each of 1 ha) by means of a grid and collecting a soil sample at each grid intersection. This generated a total of 121 samples, an overall sampling density of 1.21 samples/ha$^{-2}$. The grid is shown in Figure 4 (Ordnance Survey Grid reference SK 3898). The major human impacts in the area arise from the village of Wentworth, South Yorkshire, England (population 595), roads which cross the area and the use of the surrounding farmland. The land surrounding the village is mainly open field primarily used for mixed farming, with the exception of the three areas of woodland (stratum C in Figure 4.). The local soil is Stagnogley, of the Brown Earth group, a deep clayey soil with impeded drainage overlying carboniferous shale, sandstone and drift material in which natural background metal concentrations are normally small.

The trace metals under investigation were lead and copper, total rather than available. The significance of available

Figure 4. Map of km-square illustrating 121 grid sample locations together with sampling strata.



concentrations is questionable as these may be considerably more variable over a small distance, due to local changes in pH and other micro environmental factors eg. slope, drainage, climate, etc. It was expected that the distribution of total lead would vary considerably due to localised pollution arising from motor vehicle emissions near the roads and in the village. The roads, although quiet by urban standards, are a commuter route and at times during the summer the village attracts many visitors. It was expected that the copper concentrations would be more evenly distributed, with possible introductions arising from applications of sewage sludge and from pig manure (copper compounds often being included in the diet.).

All soil samples were collected at grid intersections. At each grid intersection, 5 equal amounts of soil (approximately 100 ml each) were collected from within a 10 m radius. The five points chosen were equally spaced from each other and from the grid intersection. This allowed a degree of flexibility in choice of the exact location since soil near walls and buildings, on footpaths, roads or recently disturbed ground, should be avoided in studying general background concentrations of metals. Where a grid intersection fell in the centre of a road the sample was obtained from within 5 m of either side of the road. Each sample was collected, using a stainless steel trowel, at a depth of 5 cm below the root zone. Stones and other foreign matter were avoided. Between samples the trowel was cleaned with a clean paper tissue and the 5 samples were pooled and placed in a labelled, clean, polyethylene bag. All samples were collected within a seven day period.

### 3.2.3. Soil sample preparation and the determination of lead and copper.

Once returned to the laboratory all evident stones, vegetation and animal matter were removed from the samples. The samples were then oven dried at 105°C for 24 hours and subsequently ground by hand using a porcelain mortar and pestle, to pass a 2mm nylon sieve. Each sample was further ground by a ball mill for at least 4 hours. The prepared samples were then digested and analysed for lead using the procedure described in Chapter 2 (2.3.4.). Copper was determined at 324.8 nm using the same digest by direct nebulisation from the digestion tube. All samples were analysed in duplicate and results reported as a mean of the two concentrations.

## 3.3. Distribution of lead and copper.

A complete list of results for lead and copper is presented in Tables 16 and 17 respectively, and a statistical summary is presented in Table 18. The distributions were only slightly skewed indicating that sampling errors were mostly random. The large deviation about the average concentration values (x) is shown as the standard deviation (s) and the RSD. In order to examine the apparent inhomogeneity and hence determine if the area could be stratified, maps were generated using the SYMAP routine, a SYnagraphic MAPping programme ([301]). For ease of interpretation 3-dimensional projections were also produced using the 3-Dimensional plotting routine available through the Statistical Analysis System (SAS)([302]). The isarithmic maps for lead and copper are shown in figures 5 and 6 respectively with the roads included as reference points. Figures 7 and 8 display the lead and

Table. 16. Results of total lead in soils for all 121 sample locations in the km-square study (mg/kg Pb).

| V.C. | HORIZONTAL COORDINATES. | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| A | 230,2 | 100,0 | 53,0 | 65,5 | 60,5 | 51,0 | 48,5 | 63,5 | 277,0 | 308,0 | 249,5 |
| B | 71,5 | 366,8 | 106,5 | 49,5 | 74,0 | 57,5 | 86,0 | 47,0 | 51,2 | 51,0 | 135,5 |
| C | 59,5 | 64,2 | 340,8 | 72,0 | 75,5 | 71,0 | 69,5 | 81,0 | 111,2 | 56,0 | 53,5 |
| D | 70,5 | 86,5 | 88,2 | 115,5 | 92,0 | 67,0 | 61,0 | 75,0 | 73,0 | 29,5 | 38,0 |
| E | 73,5 | 87,3 | 76,5 | 344,6 | 97,5 | 47,0 | 82,5 | 63,0 | 71,5 | 49,5 | 42,8 |
| F | 55,0 | 82,5 | 114,5 | 64,5 | 200,6 | 96,0 | 201,0 | 126,0 | 54,5 | 49,0 | 72,5 |
| G | 275,6 | 117,0 | 73,5 | 65,0 | 159,0 | 87,0 | 73,2 | 85,0 | 110,0 | 116,5 | 122,5 |
| H | 71,5 | 63,5 | 36,0 | 130,5 | 749,0 | 523,0 | 76,0 | 123,0 | 98,8 | 93,8 | 72,5 |
| I | 24,5 | 35,5 | 30,5 | 148,0 | 123,0 | 924,0 | 942,0 | 333,5 | 184,2 | 209,0 | 194,5 |
| J | 72,0 | 53,0 | 70,5 | 170,5 | 88,0 | 147,5 | 107,0 | 198,5 | 233,2 | 265,0 | 119,0 |
| K | 47,0 | 26,5 | 29,5 | 40,0 | 22,0 | 46,0 | 24,5 | 113,0 | 133,0 | 154,5 | 132,5 |

V. C. = Vertical coordinates.

All concentrations reported as a mean of duplicate analysis.

Table. 17. Results of total copper in soils for all 121 sample locations in the km-square study (mg/kg Cu).

| V.C. | HORIZONTAL COORDINATES. | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| A | 52,2 | 53,2 | 25,5 | 26,6 | 23,9 | 21,2 | 23,4 | 25,8 | 64,8 | 69,3 | 50,5 |
| B | 31,5 | 52,0 | 39,2 | 24,4 | 24,0 | 21,7 | 26,3 | 24,3 | 19,0 | 20,0 | 33,0 |
| C | 20,9 | 24,3 | 49,1 | 33,2 | 28,9 | 25,9 | 22,2 | 24,7 | 26,1 | 20,4 | 23,5 |
| D | 22,5 | 35,1 | 35,6 | 42,5 | 30,1 | 26,6 | 26,1 | 23,0 | 26,3 | 15,0 | 23,0 |
| E | 27,9 | 59,8 | 27,0 | 90,0 | 32,0 | 20,6 | 30,6 | 21,8 | 20,1 | 19,4 | 20,8 |
| F | 21,6 | 28,3 | 27,6 | 30,2 | 47,7 | 32,6 | 68,3 | 36,7 | 25,6 | 20,2 | 25,7 |
| G | 75,0 | 40,1 | 29,2 | 24,0 | 51,6 | 34,1 | 29,4 | 30,0 | 34,2 | 29,4 | 35,4 |
| H | 26,0 | 19,4 | 24,1 | 87,8 | 38,2 | 57,9 | 33,0 | 39,6 | 33,7 | 37,0 | 27,7 |
| I | 29,8 | 26,0 | 28,0 | 39,4 | 34,2 | 39,6 | 68,4 | 78,2 | 47,2 | 61,0 | 41,9 |
| J | 34,3 | 26,6 | 27,4 | 33,6 | 31,2 | 45,1 | 41,8 | 69,0 | 47,4 | 75,7 | 49,5 |
| K | 23,6 | 22,2 | 17,0 | 22,9 | 15,0 | 19,0 | 23,6 | 24,4 | 35,8 | 42,4 | 40,9 |

V. C. = Vertical coordinates.

All concentrations reported as a mean of duplicate analysis.

Table. 18. Statistical summary of total lead and copper concentrations for km-square study (all 121 samples).

| Element | n | x mg/kg | range mg/kg | s mg/kg | RSD % |
|---|---|---|---|---|---|
| Lead | 121 | 127 | 22 - 942 | 146 | 115 |
| Copper | 121 | 35 | 15 - 90 | 16 | 46 |

Where; x = mean concentration values.

s = standard deviation.

Table. 19. Statistical summary of lead (a) and Copper (b) concentrations for stratum A, B and C.

| Element. | Stratum | n | x mg/kg | range. mg/kg | s mg/kg | RSD. % |
|---|---|---|---|---|---|---|
| a) Lead | A | 82 | 71 | 22-201 | 28 | 40 |
| | B | 31 | 259 | 36-942 | 232 | 90 |
| | C | 8 | 189 | 88-308 | 79 | 42 |
| b) Copper | A | 82 | 28 | 15-68 | 9 | 33 |
| | B | 31 | 50 | 22-90 | 18 | 35 |
| | C | 8 | 45 | 31-69 | 15 | 33 |

Where; x = mean concentration values.

s = standard deviation.

Figure 5. Lead concentrations in the km-square study area. (contour intervals are 50, 100, 200, 400, 600 and 800 mg/kg).

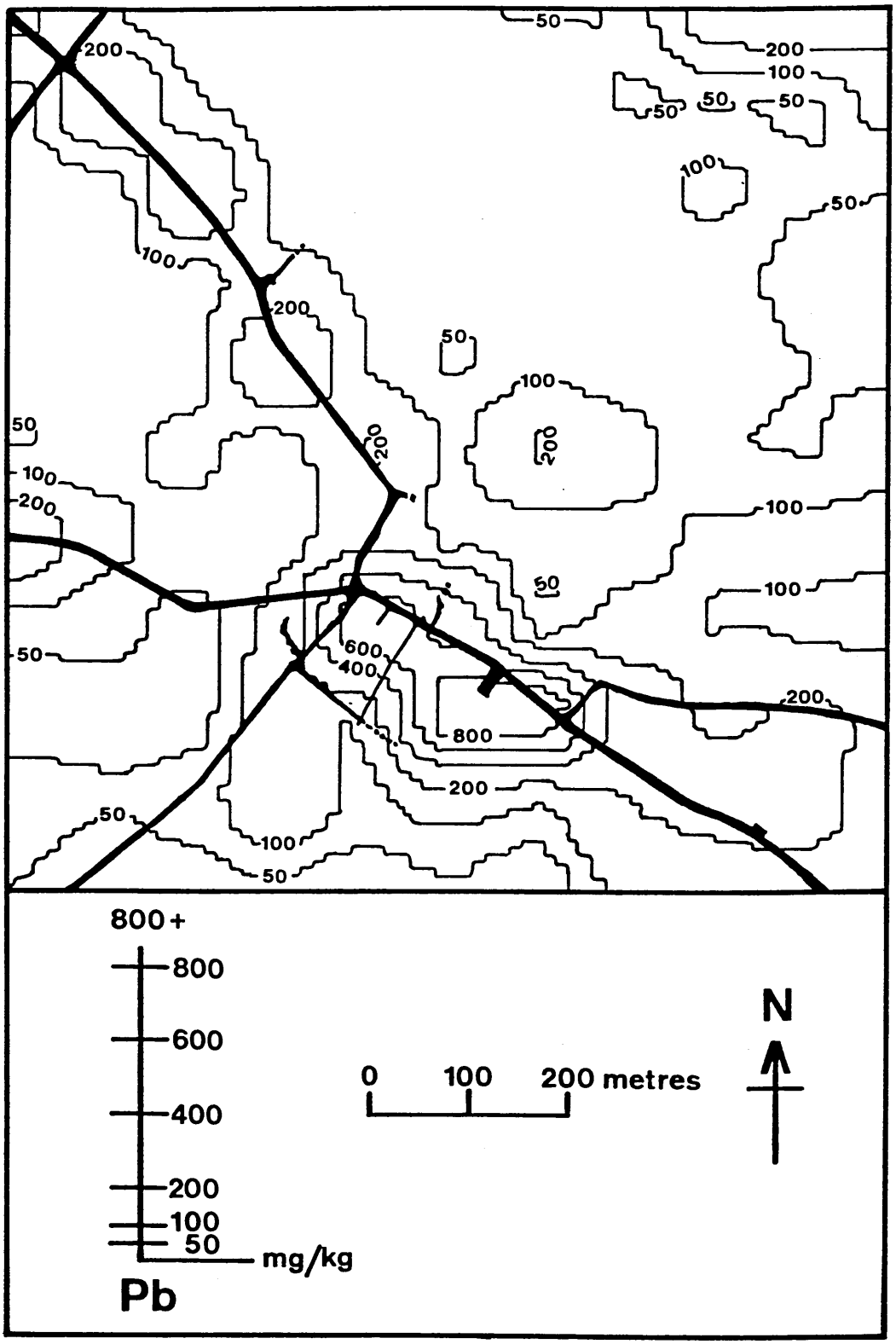


Figure 6. Copper concentrations in the km-square study area. (contour intervals are 20, 30, 40, 50, 60, and 80 mg/kg).

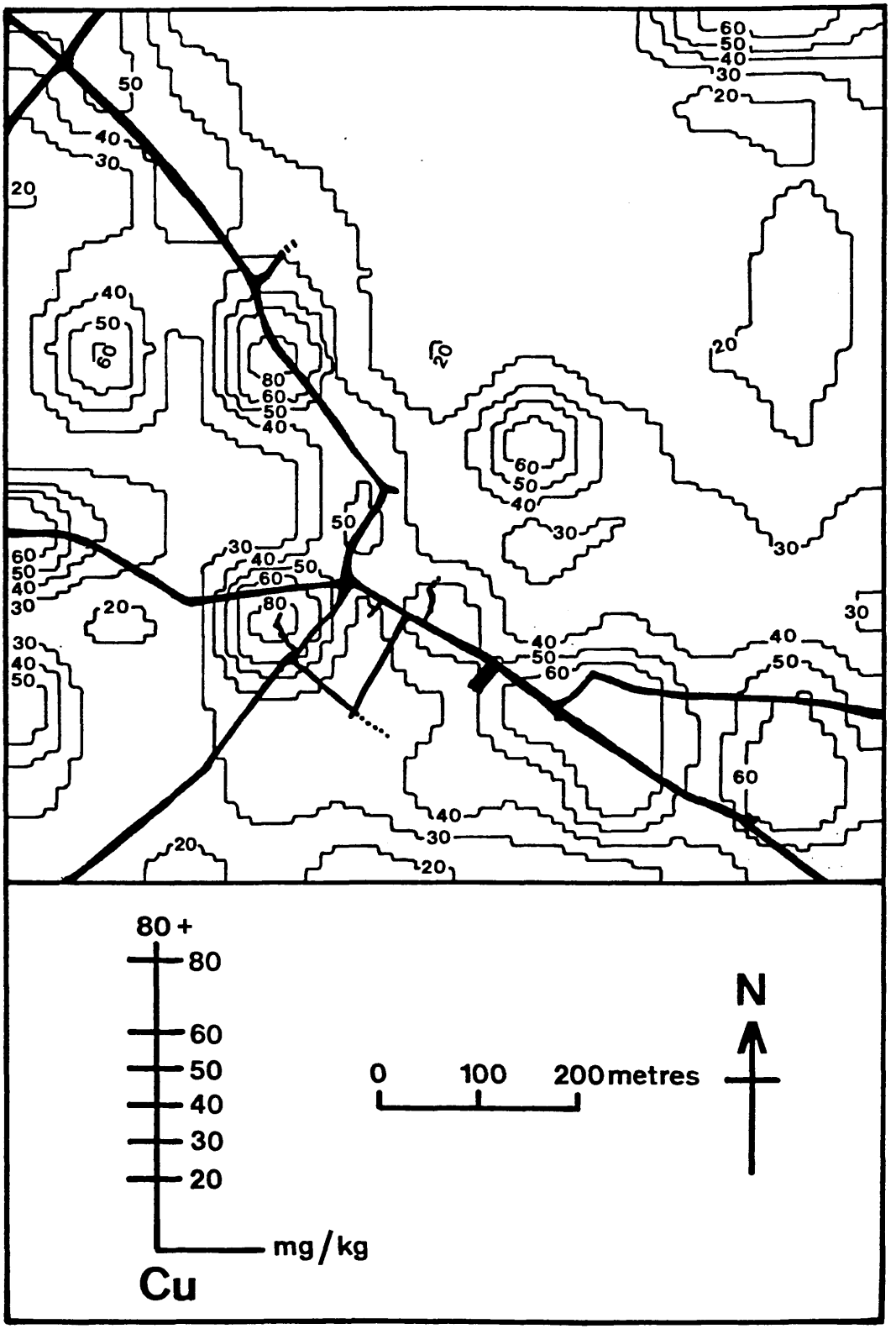


Figure 7. 3-Dimensional projection of lead distribution.

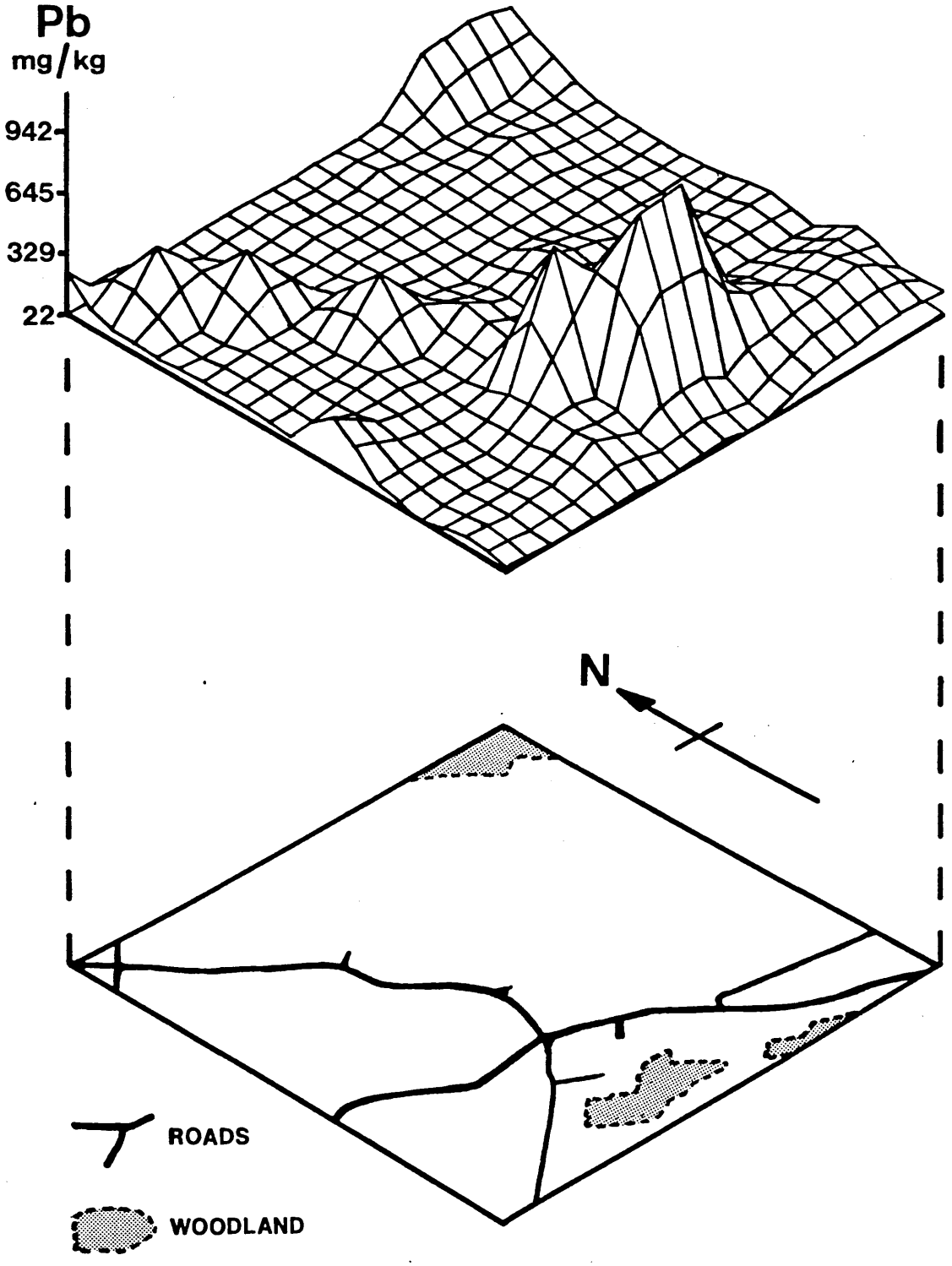
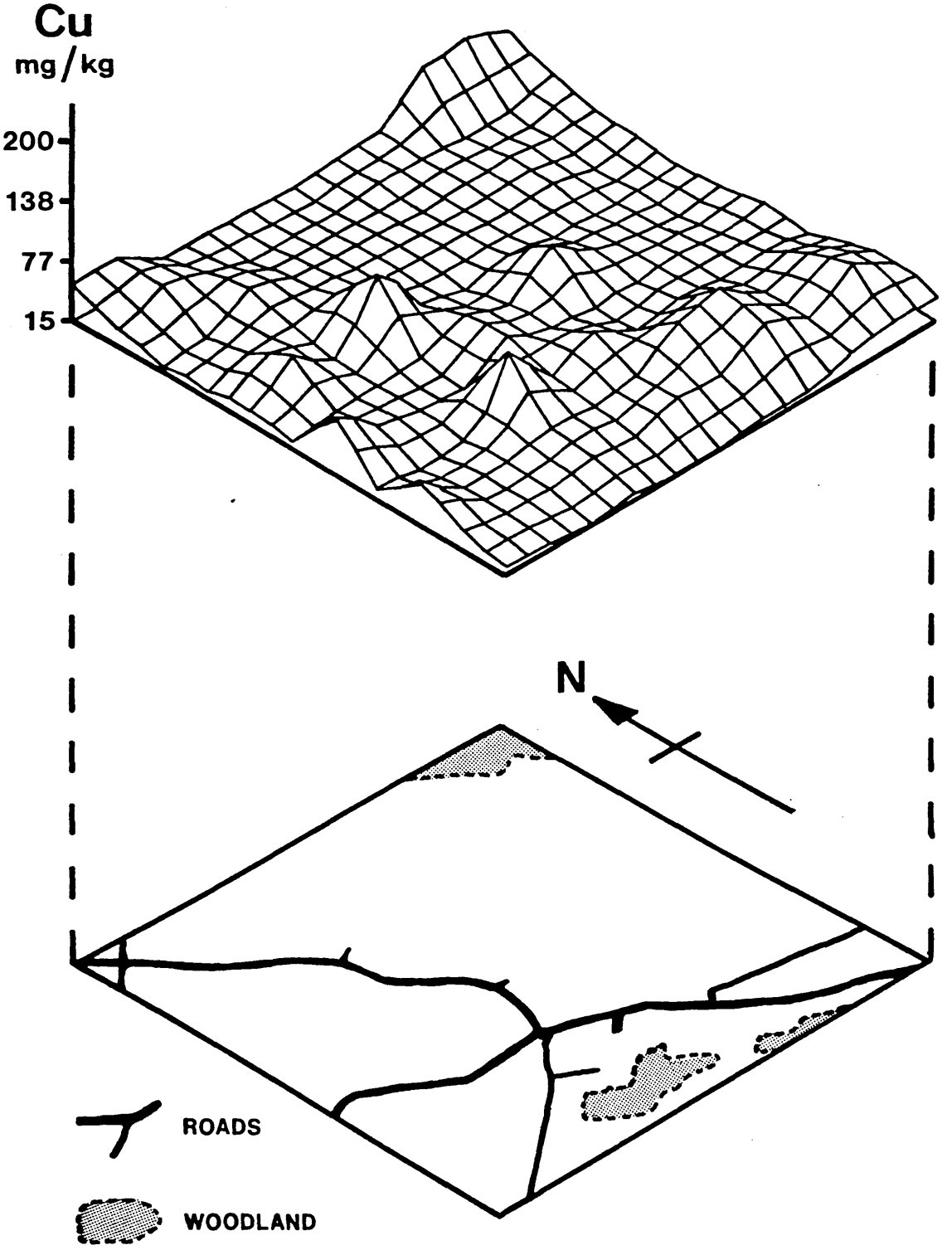


Figure 8. 3-Dimensional projection of copper distribution.



copper concentration respectively, generated three-dimensionally to illustrate graphically how certain areas have been elevated (the high peaks on the maps) above what may be considered to be the background levels for the area. This is a useful tool, particularly in communicating with individuals who have difficulty in interpreting 'contour' type maps.

From the maps it can clearly be seen that both lead and copper have been elevated above the normal background for the area. Several reports (eg.[303,304,305]) have demonstrated that lead concentrations are higher near roads (30-50 m), and this is apparent from Figure 5. It can be seen from Figure 7 that there is a clear association between the village and increased soil lead concentrations (>800 mg/kg), probably due to multiple sources over many years such as motor vehicle emissions, the burning of coal and burning of domestic refuse. There is also a high lead concentration (>200 mg/kg) in the north east woodland, which may be due to the entrapment of airborne particles (containing heavy metals) by foliage and subsequent cycling of the contaminated leaves in the humus complex. There is no explanation provided by the landscape for the elevated concentration (>200 mg/kg) 200-300 m north of the village. However, the area is of mixed farmland and it is possible that at some time in the past metal contaminated sewage sludge may have been applied to the land. The distribution of copper (Figures 6 and 7.) indicates generally lower concentrations than that found for lead. However there is still some association between the higher concentrations (around 50 mg/kg) and the roads, village and woodlands. This probably again results from domestic pollution, vehicular emissions and sewage sludge applications.

The implications for health of total lead and copper concentrations of these levels are negligible for the local population. The Inter-Departmental Committee on the Redevelopment of Contaminated Land (ICRCL) [306] suggests a trigger concentration (i.e. the concentration below which a site could be regarded as uncontaminated) of 500 mg/kg for soil lead in domestic gardens, allotments and parks, and 1000 mg/kg for playing fields and open spaces. The vast majority of the land does not exceed these trigger concentrations at which remedial action would have to take place if the area were to be developed in any way. However, for lead, certain areas around the village may exceed the trigger value but not to any great extent compared with urban areas. It should be remembered that the trigger concentrations are determined on single spot samples and not on composite samples used in this study. However, it is logical to suggest that for a composite sample to exceed the trigger concentration at least one of the 5 pooled samples must have grossly exceeded the trigger value or several of the pooled samples have marginally exceeded the trigger value. ICRCL trigger concentrations exist for available copper (50 mg/kg) but not for total copper. It is possible that some of the high total copper concentration observed in this study may exceed the available copper trigger concentration.

## 3.4. The development of a sampling protocol.

The purpose of undertaking this study was to evaluate the sampling errors which would be involved in reporting one average metal concentration for an area of study of 1 $km^2$, similar to the area used by Davies [95] and Bradley [265], but a smaller area than that

used by Parry, et al. [35]. The known lead and copper concentrations of the 121 grid sample were used to estimate, for an actual study area, the precision which would be obtained for both random and stratified sampling procedures. For both these procedures the statistical analysis was evaluated using a computer programme written by Prof. K. W. Jackson [307]. The statistical principles are explained below.

3.4.1. Simple random sampling.

If n samples, randomly collected from a total population N, are pooled to produce a composite sample, the expected variance (V) of the composite concentration value would be given by;

Equation (1). $$V = \frac{\sigma^2}{n}\left(\frac{N - n}{N - 1}\right)$$

where $\sigma$ is the standard deviation of the population N. If it is assumed that N (the maximum number of samples that it is possible to collect from the study area) is very large, then equation 1 simplifies to;

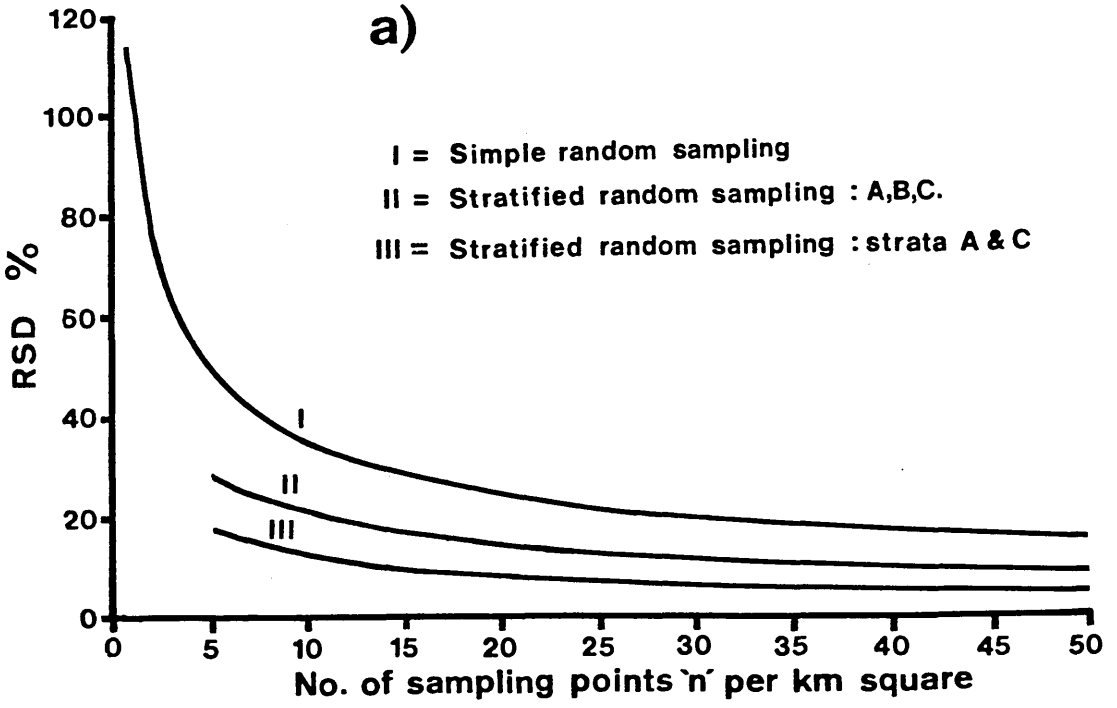
Equation (2). $$V = \frac{\sigma^2}{n}$$

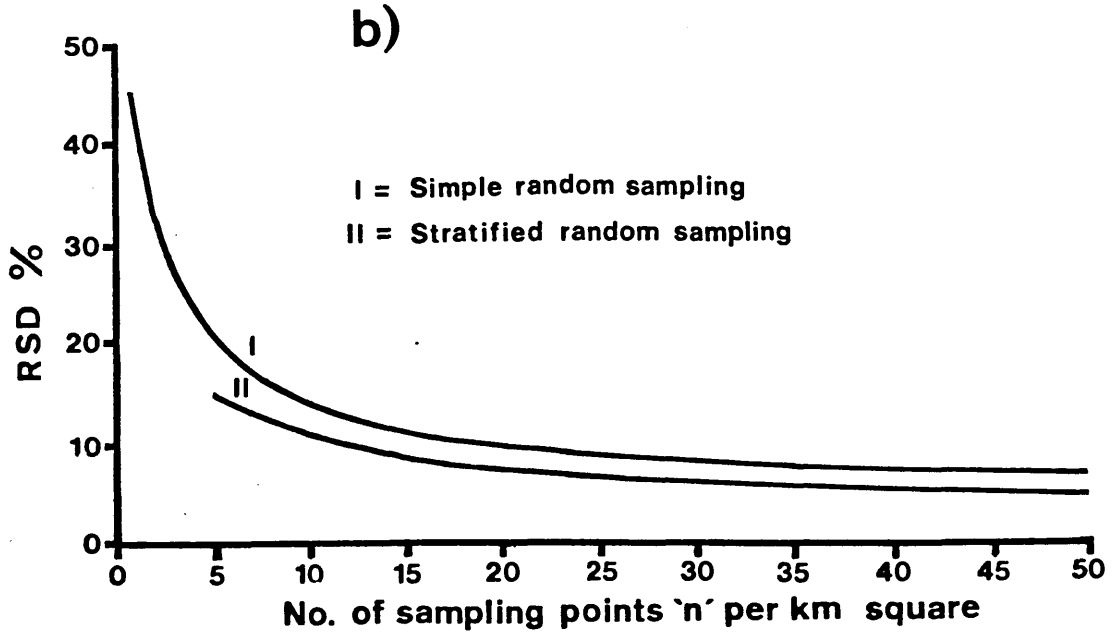
So that equation (2). could be applied it was assumed that $\sigma$ was the same as the measured standard deviation of the 121 concentration values ( i.e. s in Table 18 where lead = 146 mg/kg and copper = 16 mg/kg). The equation thus predicts the dependence of overall variance (sampling plus analysis) on the number of samples (n) collected. Using this equation it was possible to

generate the curves (I) in figures 9a and 9b for lead and copper respectively. It can be seen that precision improves rapidly as more and more points are sampled. However the improvement in precision is small once more than 30 points have been sampled. When the number of sample points is increased from 30 to 50 the improvement in RSD is only 5% (i.e. from 21% - 16%). In the field this would demand a considerable amount of work in order to achieve little improvement. In any case the volume of sample required would be too large to process. The assumption that 's' could be used instead of '$\sigma$' in applying equation (2) was verified by means of a computerized simulation of random sampling in the field. The computer programme randomly selected 'n' points from the 121 measured concentrations and averaged them to provide a theoretical composite sample concentration $c_1$. This process was repeated 20 times by the computer giving concentrations $c_1$, $c_2$,.....,$c_{20}$. The RSD of these 20 concentration values obtained in this was identical to that predicted by the statistical curve, when the process was repeated for values of n from 1 to 5. Hence it was valid to use 's' in equation (2). It also illustrates that it was reasonable to treat the data as though sampling had been random rather than on a regular grid.

It is apparent from both the statistical treatment and the computerised simulation, that simple random sampling will lead to very poor sampling precision unless a large number of samples is collected and pooled. These findings agree with those of other workers [288,289,290,291], but cast a shadow over the reliability of some trace metal soil surveys where only 1 sample (RSD

Figure 9. Overall precision for monitoring (a) lead and (b) copper in soil when 121 grid location are randomly sampled.



potentially around 115% for the km-square used in this study) has been used by other authors to represent an area the size of 1 $km^2$.

### 3.4.2. Stratified random sampling.

On the basis of the concentrations of copper and lead observed and an awareness of the potential impact of different forms of land use it was possible to stratify the study area into smaller units (strata) with predictably different average lead and copper concentrations. The strata are indicated on Figure 4. The largest stratum (A) consists of agricultural farmland away from roads, the village and any woodland. There were no obvious physical characteristics within the area which could justify its further stratification. Stratum (B) comprises all areas within 50 metres of roads and included the village and dwellings. The 50 m demarcation line was chosen to conform with the Commission of the European Communities recommendation (308) that airborne lead should not be monitored within 50 m of any road if background concentrations are to be monitored. This suggests that higher localised concentrations of heavy metal particulates would be found within this stratum. The smallest stratum was stratum (C) which included three small areas of woodland in which concentrations of lead and copper were generally elevated. Table 19 shows the average concentrations (x) found in the number of samples (n) collected from each stratum. It can be clearly seen that the average concentration of lead in each stratum is considerably different, a justification for the method of stratification which on a large scale survey must be based solely on land use and ecological observations. For copper, strata B and C have similar

average concentrations, but A is considerably lower. Examination of the RSD about each average concentration for the strata shows that in all cases it is smaller than found for unstratified data (Table 18).

The principle of stratified random sampling is to pool the variances within each of the identified strata. It has already been shown that the precision within each stratum is better than the overall precision, consequently the pooled within-strata variance should be smaller than the unstratified variance given by equation (2). As a result there should be a marked improvement in the sampling precision observed.

For 'i' strata, equation (1) is modified to;

Equation (3) $$V = \frac{1}{N^2} \sum \frac{N_i^2 \ \sigma_i^2}{n_i}$$

where $N_i$ is the maximum number of samples in the stratum, and $\sigma_i$ is the population standard deviation (309).

If the precision within each stratum had been equal, then the number of samples should be proportional to the area of the stratum. However, the strata have different precisions (Table 19). Consequently, the number of samples, $n_i$, which should be collected from each stratum is given by;

Equation (4) $$n_i = n \ \frac{N_i \ \sigma_i}{\Sigma N_i \ \sigma_i}$$

and equations (3) and (4) can combine to give;

Equation (5) $$V = \frac{(\Sigma N_i \sigma_i)^2}{N^2 n}$$

In order to apply equation (5) to the samples collected from each stratum, it was assumed that $\sigma_i$ was approximately the same as $s_i$ (s for 'i' strata are given in Tables 19a and b). Values for N and $N_i$ were also required. The maximum numbers of samples which could possibly be collected from the three strata are in proportion to the areas of the strata. The areas for strata A, B and C are in the ratio $N_A:N_B:N_C$ = 82:31:8 and this is given by the value for n in Tables 19a and b. (i.e. the number of samples in each stratum). So that equation (5) could be solved any 'large' values of $N_i$ could be used, provided they were in the ratio 82:31:8. The chosen values for $N_A:N_B:N_C$ were 82000, 31000 and 8000 respectively, with N equal to 121000. Substitution of these figures into equation (5) allows the curves (II) in Figures 9a and b, after converting V to RSD.

It can be seen by referring to Figures 9a and b that a marked improvement is obtained by stratified random sampling over simple random sampling. When n = 10, the predicted precision for lead is improved from 36% to 21% RSD, and for copper the improvement is from 15% to 11% RSD. Equation (4) predicts the relative proportions of $n_A:n_B:n_C$ to be 0.228:0.709:0.062, roughly 2:7:1 if n = 10, therefore 2 samples should be sampled from stratum A, 7 from stratum B and 1 from stratum C. It would not be feasible to collect fewer than around five stratified samples, consequently the curves in Figure 9a and b are not extrapolated under a value of n = 5.

Many trace metal soil surveys conducted to provide baseline data seek to establish the background concentrations of metals in the environment. In such instances it would be reasonable to preclude sampling in areas of potentially localised pollution, i.e. within 50 m of roads, near houses, walls or disturbed ground. This could be simulated using the data by eliminating stratum B. Applying equation (5) to the remaining strata (A and C) for lead produced the curve (III) in Figure 9a. It can be seen that there is a further improvement in sampling precision when potentially polluted sites are ignored, with n = 10 having an RSD of 13%. When n = 5 the RSD is about 18% which is an increase in imprecision over n = 10 of 5-6%; however this would require 50% less field work and in terms of savings on time and survey costs could represent an acceptable level of imprecision. Certainly it represents a considerable improvement over the sampling imprecision that may be common in previously published studies. For copper the concentrations are much less affected by roads and the village, so subsequent elimination of stratum B produced a curve which predicted only a marginal improvement over the curve (II) in Figure 9b. It is apparent that there is very little to be gained by not sampling in stratum B in the case of copper.

The overall precision, evaluated above, includes both sampling and analytical precision. Equation (6) shows that variances are additive;

Equation (6) $s_D^2 = s_S^2 + s_A^2$

where $s_O$, $s_S$ and $s_A$ are the overall, sampling and analytical standard deviation (or RSD) respectively. If 10 stratified random samples were collected to make one composite sample, then for lead $s_O$ = 21% (from Figure 9a.) and it can be assumed from previous work that $s_A$ = 3%. In Chapter 2.4. $s_A$ was demonstrated to be 0.32% for a single soil sample, and during the interlaboratory study (Chapter 2.4.3.) $s_A$ was found to be 2.5% using the block digestion procedure. Using equation (6) $s_S$ can be calculated as 20.8%. For copper the corresponding values are $s_O$ = 11% (from Figure 9b.), $s_A$ = 3% and $s_S$ can be calculated at 10.6%. Elimination of stratum B for lead when n = 10 produces values of $s_O$ = 13%, $s_A$ = 3% and hence $s_S$ = 12.6%. It can be seen that in all these cases $s_O$ is only slightly larger than $s_S$ demonstrating clearly that sampling accounts for almost all of the overall imprecision, with the impact of analytical imprecision being only slight.

## 3.5. Conclusions.

The data show clearly that major errors are bound to occur during random soil sampling for background concentrations of heavy metals. However, sampling precision can be greatly improved by stratifying the area and restricting the sampling to areas away from apparent pollution sources such as roads. Lead is often the least homogeneously distributed trace metal primarily due to the influence of motor vehicle emissions, discrete mineral workings and industrial sites. Consequently lead surveys would benefit considerably from the stratified sampling approach.

In order to establish the true pattern of spatial variation that might exist it was essential that the reconnaissance survey described above was carried out. Only then was it possible to identify the strata and their boundaries that exist in a real field situation. The survey can serve as a model for stratifying similar areas for further field studies. Clearly if the area to be studied were not of a similar make up to the model, with little distinction between woodland and farmland, then the best way to identify the boundaries between strata would be to carry out further reconnaissance surveys. This would be costly in time and effort. It could be overcome to a large extent by experienced personnel carrying out a phase 1 assessment using large scale Ordnance Survey maps and aerial photographs to identify land use and ecological strata and their boundaries and by rejecting in the field obviously contaminated sites. In built up urban/industrial areas the identification of strata is problematic as Kenyon [310] observed and it may be desirable to concentrate on semi-rural areas when undertaking surveys of this nature.

The sampling protocol described above is suitable for large scale soil trace metal surveys where it may not be economically feasible to collect more than 5 samples per $km^2$. In this instance a sampling precision better than 18% is unlikely to be achieved (Figure 9a., curve III), and the precision limits (95% confidence) would be approximately ±36% of the average measured trace metal concentration (i.e. ±2s about the mean reported concentration.). Taking more samples would obviously provide better precision, for 10 samples the precision limits would be ±22%, and for 25 samples it would be around ±10%.

The approach to sampling described is different to that of McBratney and Webster [298], who effectively stratified a region into small cells and based the overall sampling variance on the within-cell variance. They assumed all cells had a within cell variance, which was a reasonable approximation since the cells were small. Whilst their method, which allows for the spatial dependence of concentration, would probably lead to better sampling precision, for simplicity the approach described above assumes no spatial dependence within strata, but takes account of the differing variances between strata.

A paper on this approach to soil sampling was presented at the 4th International Environment and Safety Conference in 1984 (see list of publications and conference papers, no. 7). A paper describing the sampling protocol has also been accepted for publication and will be published shortly in the journal of 'Soil Science'.

# CHAPTER 4. THE DISTRIBUTION OF LEAD AND OTHER HEAVY METALS IN THE SOILS OF NORTH EAST DERBYSHIRE, ENGLAND.

## 4.1. Introduction.

The use of soil surveys to provide background data on regional soil contamination has been employed by several authors [62,95,134,265] and its value in providing data on background metal contamination levels for regional planning and policy making has been recognised [35,135,136,260]. Unfortunately little work has been carried out by these authors on the sampling precision and accuracy of their survey methods. As a result it is impossible to make direct comparisons between the data presented in one study with that of another study. In order to overcome this problem the work described in Chapter 2 and 3 was carried out, enabling some measure of sampling and analytical precision to be placed on the soil survey now presented.

The investigation presented in this chapter was carried out in cooperation with North East Derbyshire (NED) District Council and North East Derbyshire Environmental Health Department. Interest in the survey was initiated in response to local concerns in 1981 over potential lead pollution from the reprocessing of waste road surface materials near the village of Eckington, North East Derbyshire. An area of 24 $km^2$ was investigated but no significant increase in the total soil lead levels was found for the area. The Environmental Health Department and District Council subsequently expressed an interest in conducting a larger scale survey to investigate the background levels of lead and other heavy metals in

the soils of the whole North East Derbyshire region. The investigation had three aims;

a) to provide baseline data on the levels of metal in soils which could be used in future monitoring and pollution studies,
b) to identify possible point sources of soil contamination,
c) to provide an input into planning decisions.

NED district covers an area 370 $km^2$ and is administered from the town of Chesterfield. Chesterfield was excluded from the survey since it was part of a separate regional authority and was considerably more urban in its nature than semi-rural North East Derbyshire. Work by Kenyon (310) has shown that a much greater variability of concentrations of heavy metals occurs in urban areas and necessitates a different sampling procedure. The survey boundary overlaps the actual regional administrative boundary of North East Derbyshire District. Figure 10 illustrates the survey area boundary which reaches the southern boundary of the city of Sheffield and the eastern boundary of the Matlock area. The grid references shown on the map relate directly to those of the National Grid and the area may be examined in greater detail by reference to Ordnance Survey (1:50,000 second series) map sheets 110, 111, 119 and 120.

4.1.1. Geology.

A generalised map of the geology of the region is shown in Figure 11. North East Derbyshire lies on the eastern margin of the South

Figure 10. Survey area features, North East Derbyshire.

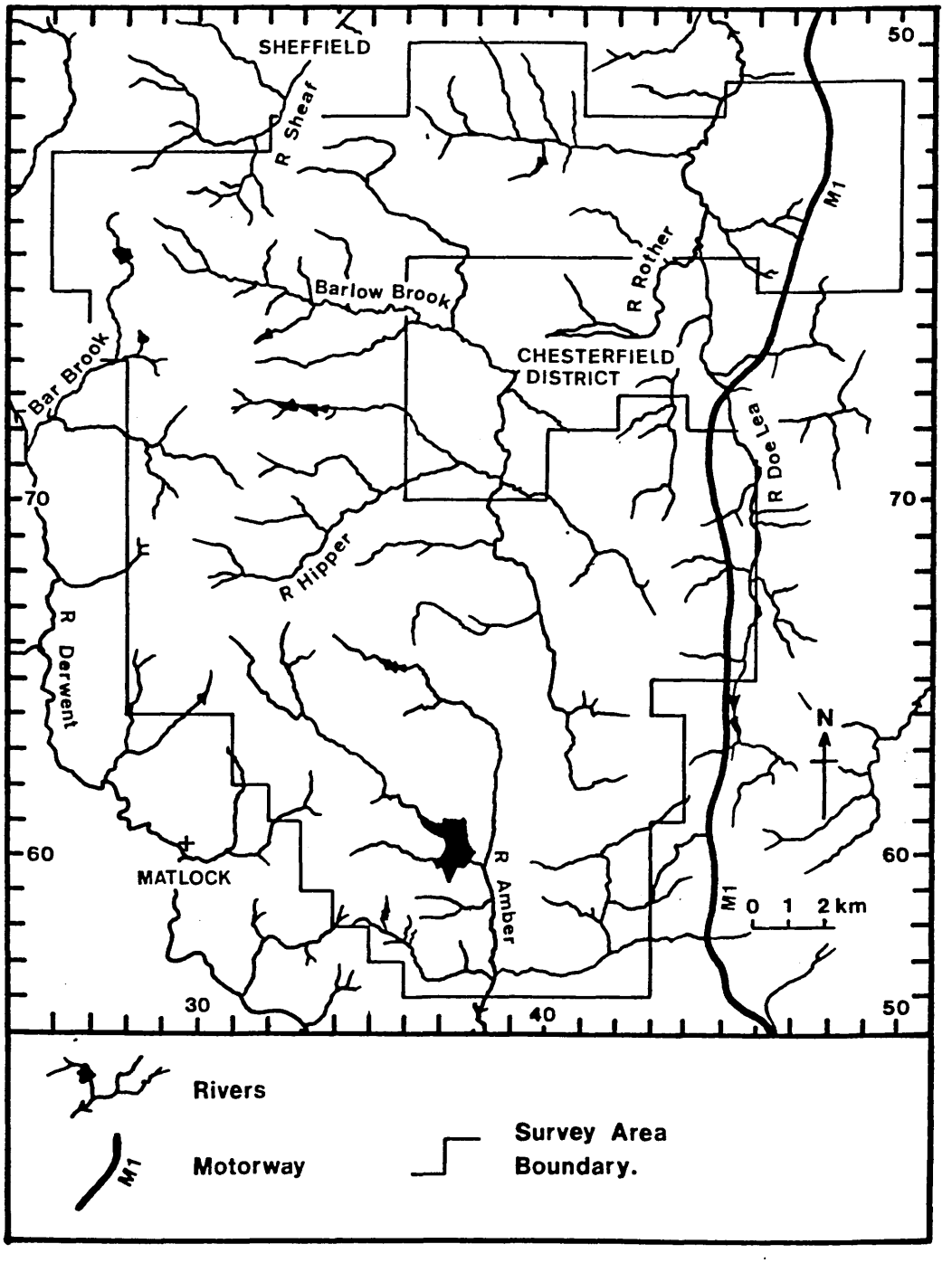
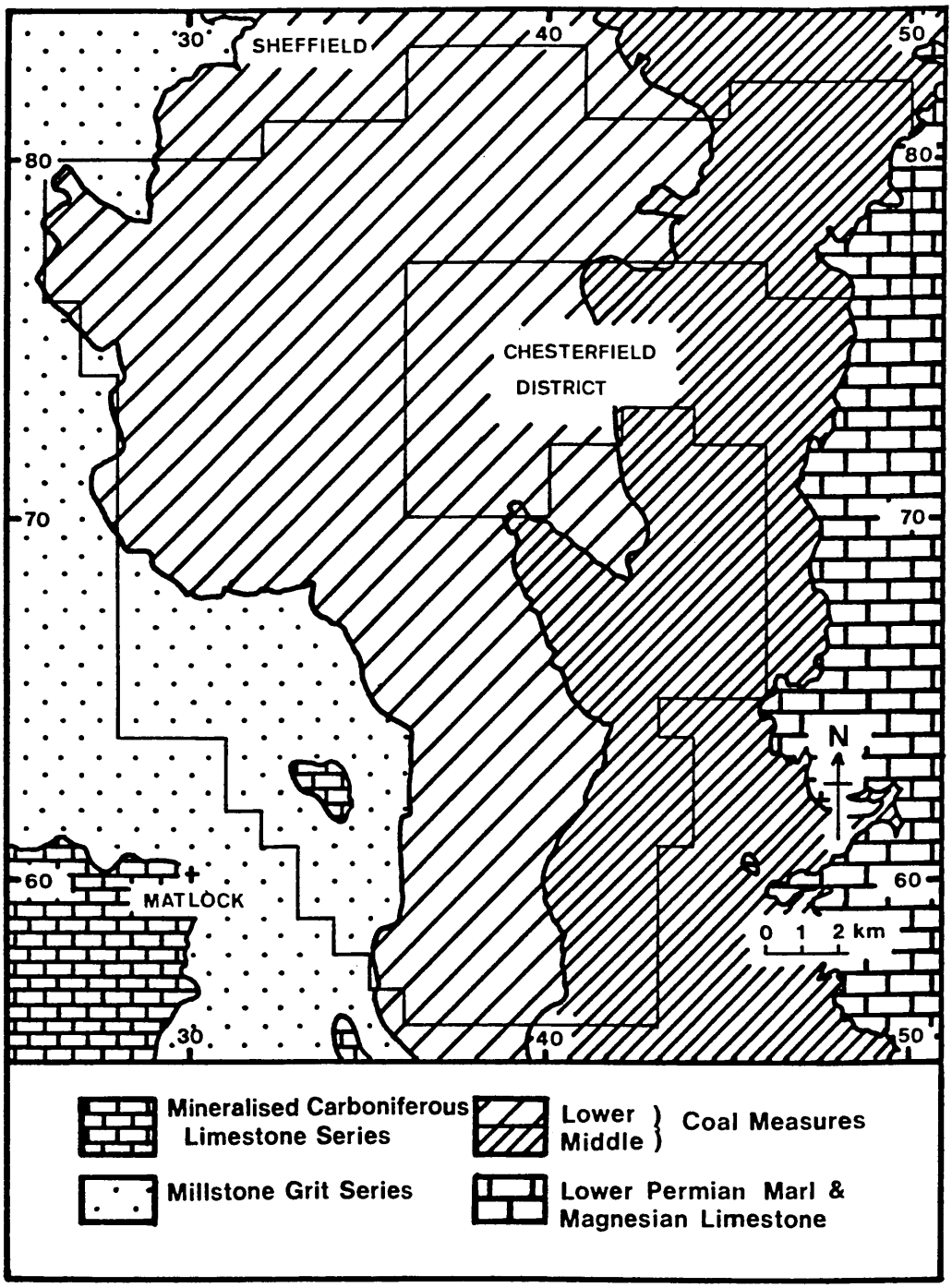


Figure 11. Generalised geology of the survey area, North East Derbyshire.



Pennine anticline where there are exposures of Namurian gritstones, shales and sandstones of the Lower Coal Measures which overlie the Carboniferous limestones. In the Ashover area (GR:3362) there is a dome of exposed limestone which has been mineralised. Generally the rock strata dip gently eastwards at an angle of 15° and this coupled to the action of rivers and weathering has lead to the development of a series of escarpments. The steep edges and gentle dip slopes have a variety of soils and plant communities which have developed from the interactions of the parent rock, climate, subsequent land use patterns, and several other environmental factors (eg. relief, drainage, organic composition, time span, etc.).

4.1.2. Soils.

Soil types vary considerably over the region and range from podsolic peaty soils on gritstone moors which are highly acidic, to less acidic, more fertile brown earths and rendzinas on the shales and limestones respectively. Retention and movement of heavy metals is highly influenced by these factors which will considerably affect the local distribution and availability of metals for plant uptake. Measurement of available lead was impractical since it would be impossible to record all the necessary soil data, pH, organic matter, etc., required to interpret the available lead figures, although it has been used by Parry, et al. [35]. Examination of total lead distribution was preferred, giving a better indication of overall background soil lead concentrations. Once high concentrations of total lead had

been found, subsequent follow up local surveys could be undertaken to assess its local availability, if required.

### 4.1.3. Other factors of potential influence.

Apart from localised concentrations of heavy metals in soils formed on mineralised rocks or by migration in solution through rock strata, the major cause of anomalously-high levels was expected to be due to human activities. Therefore, high background soil lead concentrations could be either natural or anthropogenic in origin. The human activities could include mining, processing and smelting of ores, aerial emissions from motor vehicles and industry, or dumping of wastes on land (sewage sludge, domestic or industrial waste).

## 4.2. Pilot Survey.

Two pilot surveys were carried out, the initial survey in the Eckington area and the intensive study of a semi rural 1 $km^2$ area typical of the survey region. The latter survey was conducted near the village of Wentworth, South Yorkshire (Grid Ref: 3898, 10 miles due north of the survey area boundary). This detailed survey enabled the development of a sampling procedure, and subsequent determination of sampling precision, suitable for use in the North East Derbyshire soil survey and has been described in detail in Chapter 3.

## 4.3. Experimental.

### 4.3.1. Equipment and reagents.

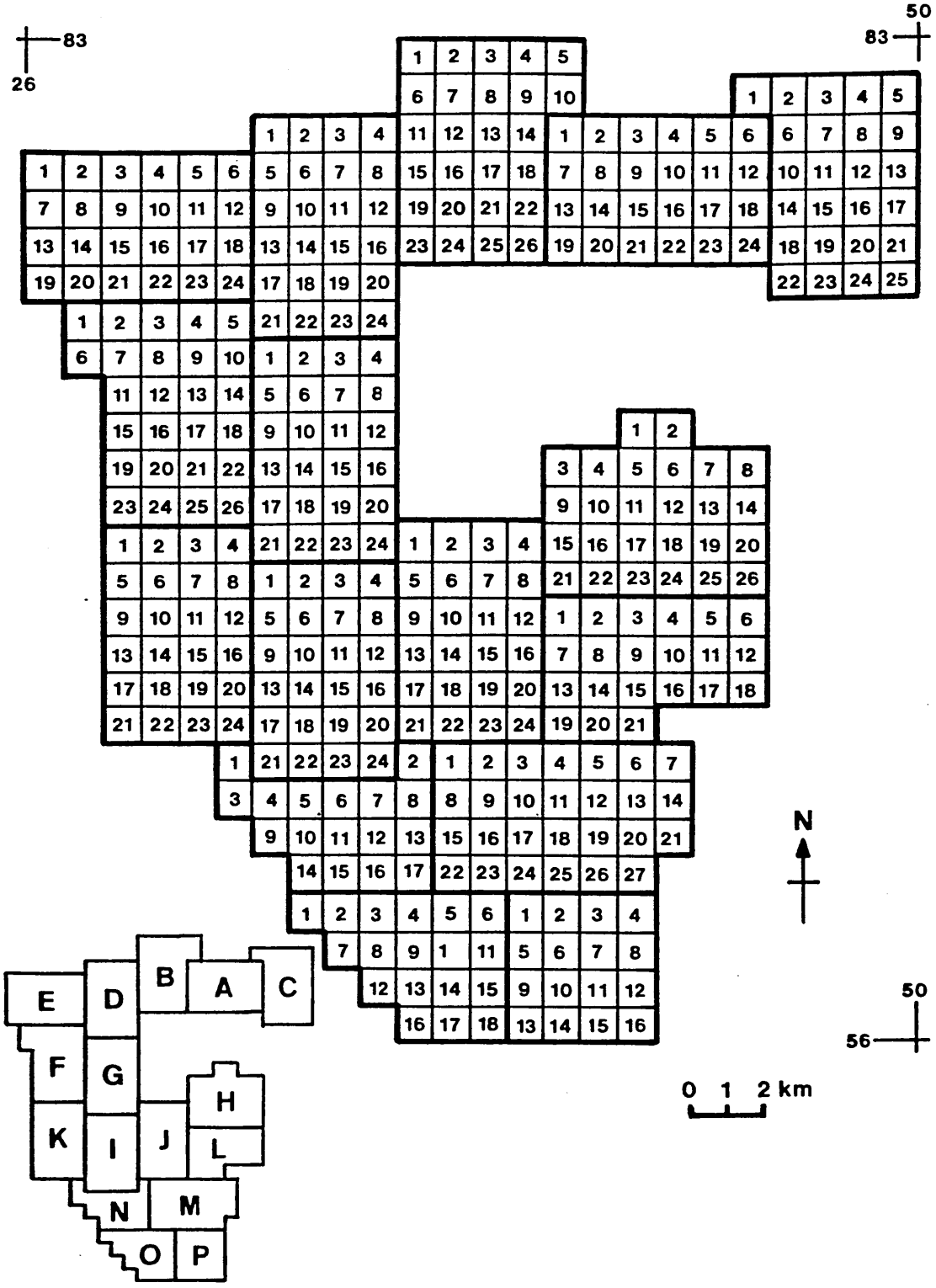
The equipment and reagents described in sections 2.2.1 and 2.2.2. in Chapter 2. were used throughout the survey.

### 4.3.2. Sample collection and preparation.

The sampling programme adopted involved the collection of five samples from five sites within a 1 $km^2$ area, taking into account the conclusions drawn from the sampling work reported in Chapter 3. The sample locations chosen were at least 50 m away from roads, buildings and tracks and were randomly chosen within identifiable strata which reflected the landscape of each individual 1 $km^2$ grid square. Ordnance Survey maps at a scale of 1:25,000 were considered appropriate for this procedure. The whole 370 $km^2$ area was divided into subregions A - P (Figure 12.), and the five site locations identified on 1:25,000 scale maps of each subregion.

At each of the five sample locations the soil collectors were further instructed to avoid obviously contaminated land and 5 subsamples were collected (approximately 100 $cm^3$ each) from within a 10 m radius, giving a total of 25 subsamples per $km^2$. The samples were collected using a clean stainless steel trowel from a depth of 5 cm below the root layer of surface vegetation. All 25 subsamples were pooled in one clean plastic bag, coded appropriately for the grid square and returned to the laboratory. The estimated sampling precision limits for collecting 25 samples

Figure 12. Subregions A - P used in the sampling programme.



per $km^2$ is around 9% (from Figure 9a, curve III, Chapter 3.) which is at least equivalent to ± 20% about any mean concentration reported for each $km^2$ (i.e., 95% confidence, ±2 standard deviations about the mean reported concentration). Therefore, if the concentration reported for a kilometre square was 100 mg/kg Pb the error limits we can place on the result would be between 80 and 120 mg/kg Pb. Whilst this seems large it is probably considerably better than other authors have achieved, had they quoted error limits for their sampling technique.

The intensive sampling programme took about 18 months (between 1981 and 1983) to complete and was only possible because of the invaluable assistance of teams of Community Service Agency (CSA) workers from North East Derbyshire. The teams of CSA workers, financed under the Manpower Services Commission Community Programme, were instructed in the sampling procedures required and worked under supervision in the field. Since North East Derbyshire District Council was supporting the project most land owners gave permission for their land to be sampled, with the exception of one kilometre square almost entirely the property of a private estate (Square A.16). A letter of authorisation, made available by North East Derbyshire District Council, helped overcome most of the problems of access to land.

Once samples had been returned to the laboratory they were prepared for analysis as described in section 3.2.3. All samples were digested in duplicate and each batch contained in-house laboratory reference control samples. These were the soil samples used

earlier for the interlaboratory survey, and ensured batch to batch reproducibility throughout the soil survey.

4.3.3. Determination of total lead, zinc, copper and cadmium.

The digest was nebulised into an air/acetylene flame of a flame atomic absorption spectrometer. Lead was determined at 283.3 nm, zinc at 213.9 nm, copper at 324.7 nm and cadmium at 228.8 nm. Freshly prepared acid-matched aqueous standards were used through out. If duplicate samples did not agree, within precision limits, then the complete procedure was repeated (in duplicate) and the outlier result rejected. The results were reported as a mean of either 2 or three analyses for each kilometre grid square.

4.4. Results and data presentation.

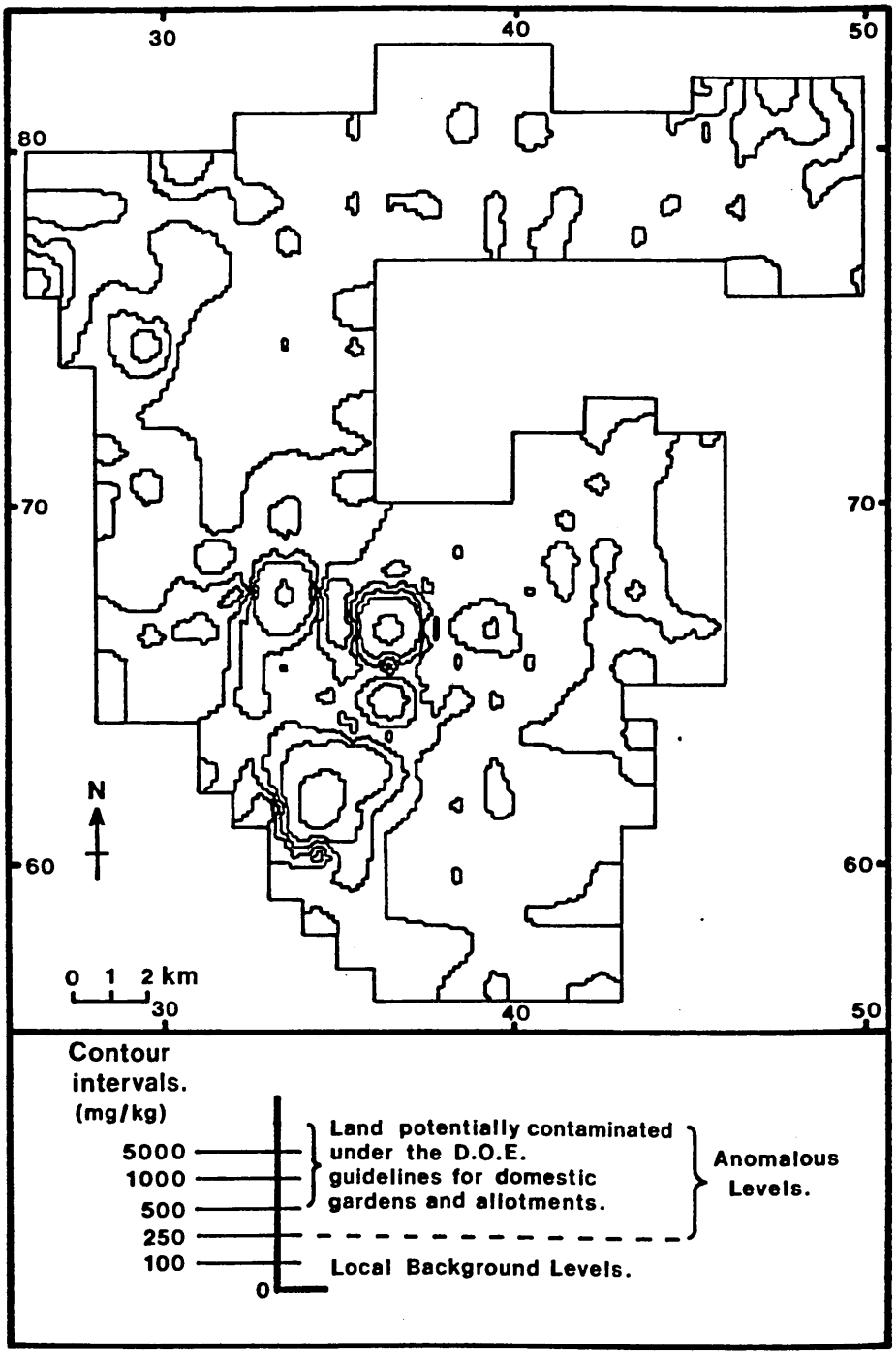
It should be remembered at all times that the estimated precision limits for the sampling technique employed are ±20% of the mean concentration reported. The complete list of results, upon which the mean reported concentrations were based, are listed in Appendix 4. a. (lead), 4. b. (zinc), 4. c. (copper) and 4. d. (cadmium). A statistical summary of all results is listed in Table 20. During the survey some 1198 individual digestions were performed on the 369 samples. This amounted to around 894 lead determinations, 960 zinc determinations, 830 copper determinations and 575 cadmium determinations, some 3259 individual analytical determinations (including initial duplicate analyses and any subsequent repeats).

Table 20. Summary of total heavy metals in soil for complete survey area (n = 369). (mg/kg).

| Element. | Mean. (mg/kg) | Maximum. (mg/kg) | Minimum. (mg/kg) | Range. (mg/kg) | Std. Dev. (mg/kg) |
|---|---|---|---|---|---|
| Lead | 339.0 | 16460.0 | 30.0 | 16430.0 | 1062.5 |
| Zinc | 196.0 | 4261.0 | 10.0 | 4251.0 | 257.0 |
| Copper | 35.0 | 241.0 | 5.0 | 226.0 | 21.0 |
| Cadmium | 1.4 | 50.0 | <1.0 | 49.0 | 3.2 |

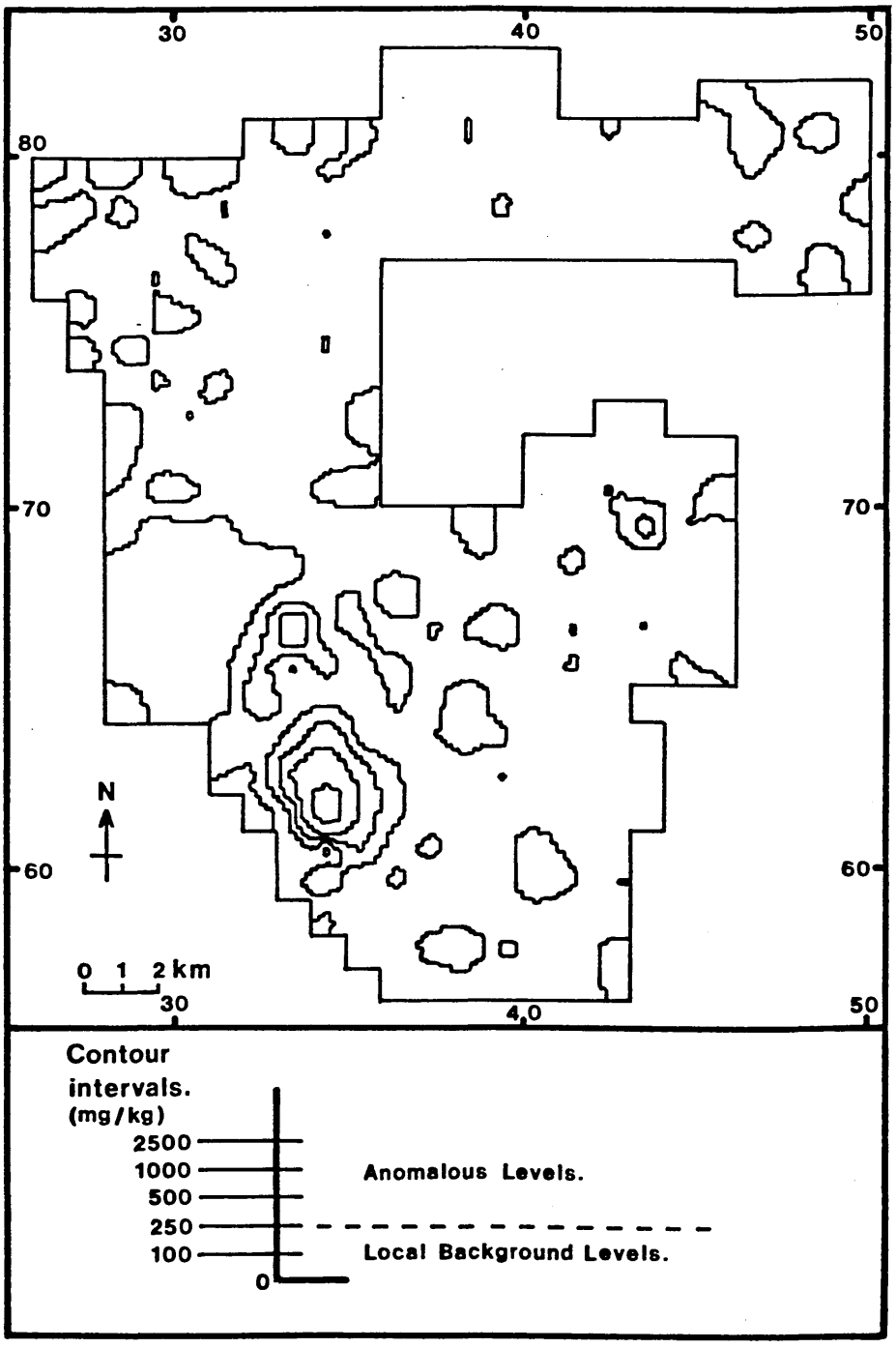
The mean concentration reported for lead, zinc and copper in each grid square was mapped using the SYMAP [301] computer mapping routine. This enabled the preparation of isarithmic contour maps showing the distributional patterns of each of the elements. The maps so produced are presented in Figure 13 (Lead), Figure 14 (Zinc) and Figure 15 (Copper). SYMAP has the advantage of producing a contour map in which the contours have been drawn without any bias that may arise from human interpolation of the contours. In order that the magnitude of variation between low and high concentrations could more easily be seen 3-dimensional plots were prepared of the survey area. The G3D computer plotting routine available under the Statistical Analysis System (SAS)[302] was used to produce the 3-D map projections which are shown in Figures 16a and 16b (Lead), Figure 17 (Zinc) and 18 (Copper). The two plots in Figure 16 were produced by rotating the image though several degrees in order that small peaks masked behind larger peaks could be seen more easily. The cadmium results were not subjected to the mapping procedure as very little variation was

Figure 13. Total lead in soil distribution.



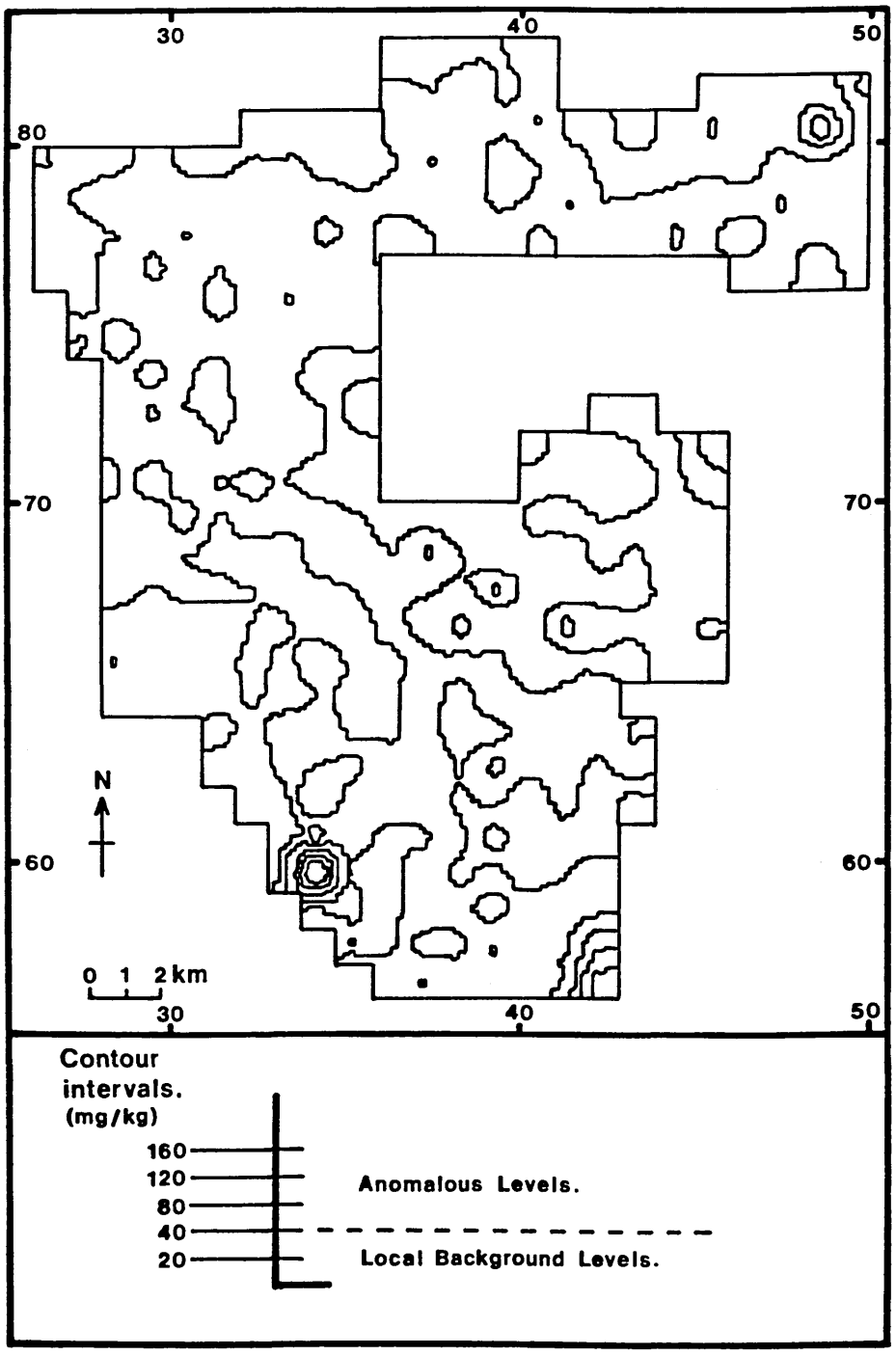

(N.B.- Refer to Appendix 4.e. showing anomalous levels highlighted)

Figure 14. Total zinc in soil distribution.




(N.B.- Refer to Appendix 4.f. showing anomalous levels highlighted)

Figure 15. Total copper in soil distribution.




(N.B.- Refer to Appendix 4.g. showing anomalous levels highlighted)

Figure 16. 3-Dimensional map of the distribution of lead in soil
A) viewed from the west.
B) viewed from the south west.

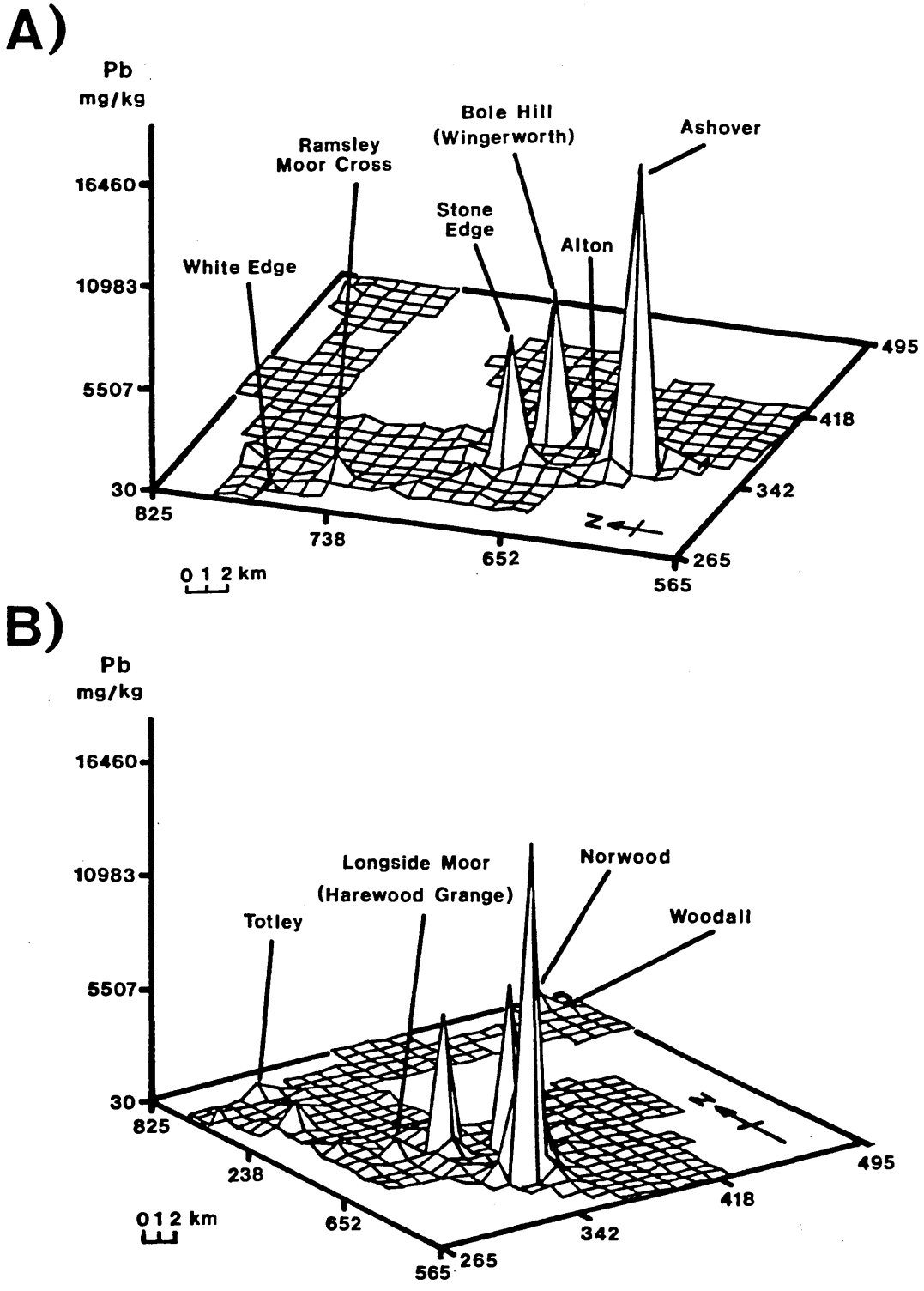


Figure 17. 3-Dimensional map of the distribution of zinc in soil viewed from the west.

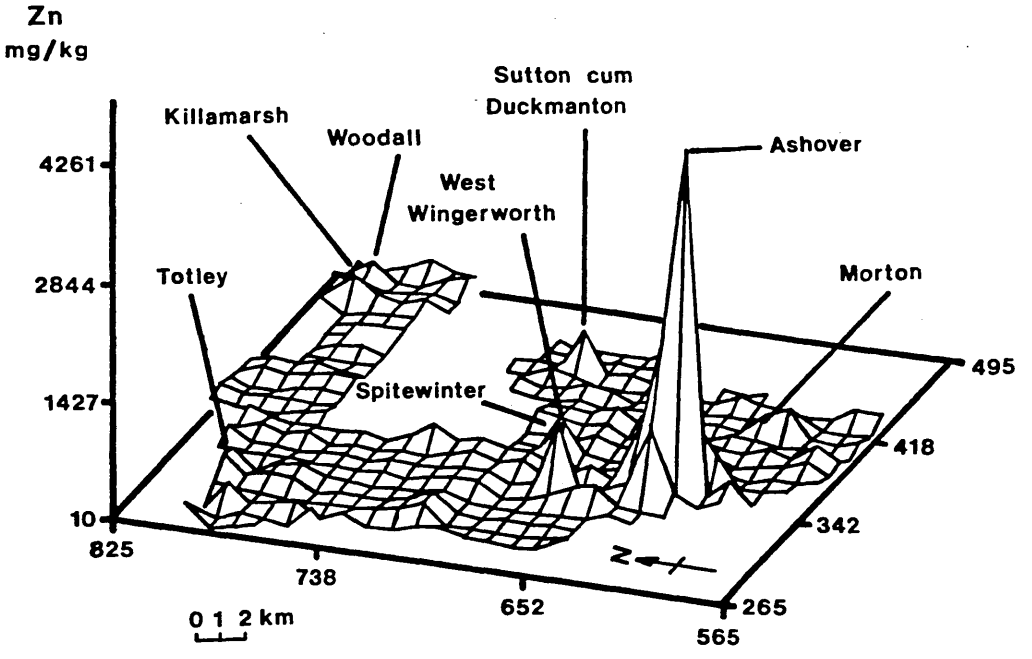
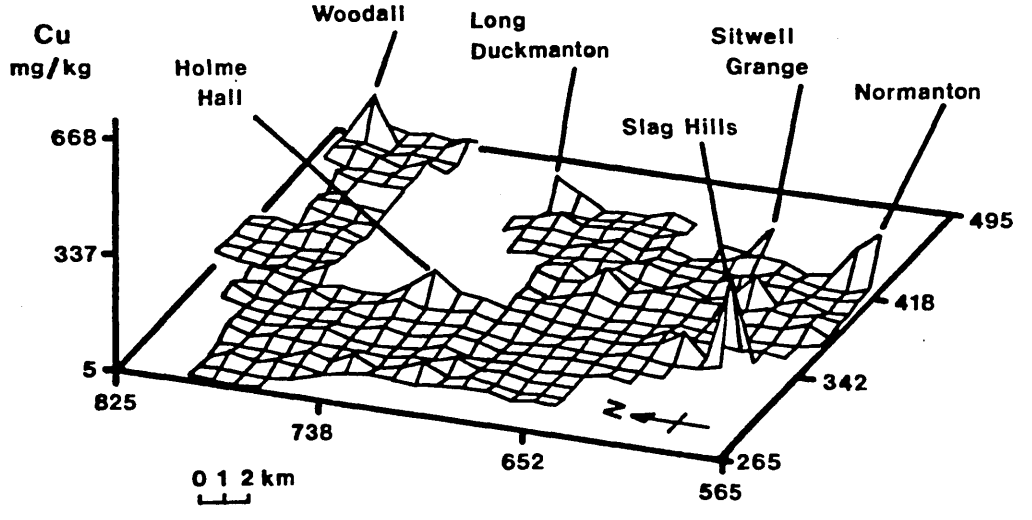



Figure 18. 3-Dimensional map of the distribution of copper in soil viewed from the west.



observed, most results being reported as a <1 mg/kg concentration. This was an interesting contradistinction to the results obtained by JURUE in a modern industrial area where metal working has taken place for many years ([118]). However, the results were of a similar magnitude to those reported by Davies and Paveley ([134]). Where a few anomalously high concentrations of cadmium have been found they are discussed in section 4.4.4. The uses and values of these types of computer maps have been discussed in detail by Davies and Roberts ([137]), Teicholz and Berry ([138]) and Peucker ([311]).

4.4.1. Lead.

It is apparent from Figures 13 and 16a and b that the distribution of total lead in soil varies considerably over the survey area. The survey was designed to observe only background levels of heavy metals in soil, with samples taken 50 m away from roads, avoiding most soils potentially contaminated by motor vehicle lead emissions. Precautions were taken in the field to avoid sampling areas which were potentially contaminated, i.e., samples were taken away from walls, buildings footpaths, etc. Therefore the variations that exist in the background concentrations could reflect the following;

a) areas of naturally low background soil lead
   (i.e., geologically relatively free from lead),
b) areas of naturally high background soil lead
   (i.e., geologically high concentrations where mineral
   veins have been weathered to form soils and subsequently
   mobilised in water and air),

c) areas of anthropogenically high background soil lead (i.e., brought about by the activities of man, including mining and processing of lead ores, smelting of lead, dumping of wastes/sewage sludge and deposition of emissions from industrial activities).

It is virtually impossible to identify which of the three groups might be attributed to a particular grid square and in reality it is probable that the concentration of lead for any grid square will reflect the interaction of a, b, and c.

The natural background levels of lead in soils have been put at between 10 and 200 mg/kg by Harrison and Laxen-Duncan (79). Davies (60) has reported that a typical background level might be below 110 mg/kg. However, studies in rural areas of the West Midlands (136) indicate background levels of between 40 and 60 mg/kg lead in soil. Burek and Cubitt (11) have reported that total soil lead concentrations found in North Derbyshire are rarely below 200 mg/kg. It is clear that for North East Derbyshire much of the area is well in excess of these levels, with only 61 out of the 369 grid squares having concentrations of lead in soil below 100 mg/kg (lowest 30 mg/kg). It is apparent that for the North East Derbyshire area the natural background levels are either naturally high or have been raised by human activities. Typical background soil lead levels for the North East Derbyshire area are between 30 and 250 mg/kg, based on comparisons between reported values for other regions of the United Kingdom (20) and the data obtained during the North East Derbyshire survey. Concentrations above this 'typical' background level may be taken as being anomalously high

and some 25% of the survey area falls into this category. The 250 mg/kg contour has been highlighted on the map in Appendix 4.e. to enable this distinction to be identified.

Using the Department of the Environment (D.O.E.) guidelines [306] for the redevelopment of contaminated land, the 500 mg/kg contour has also been highlighted in Appendix 4.e. This indicates that some 10% of the survey area identified by the contour could probably exceed the 500 mg/kg guideline if the land were to be used as a domestic garden or allotment, within the precision limits of the sampling technique. Only 5 grid squares (I6, J13, N6, N7, N11) were found to exceed the 2000 mg/kg guideline for parks, playing fields and open spaces, with the highest concentration in the survey at N11 of 16,460 mg/kg. There are many parts of the White Peak area of Derbyshire where soil lead levels of this magnitude are found [205], primarily because of lead mining activities.

For many years crops have been grown and animals grazed on the land associated with lead mining and several instances of lead poisoning, or 'bellanding', of cattle and sheep have been reported [313,314,]. This is possibly as a result of direct ingestion of soil [315,316], from contaminated pasture [317], which varies seasonally and according to farm management [316]. It is estimated that grazing cattle involuntarily ingest from 1% to nearly 18% of their daily matter intake as soil, while sheep may ingest up to 30% [316]. This represents a major potential pathway of exposure to animals and might be significant in the areas identified as having elevated levels of soil lead. Cattle poisoning may also occur as a result of the application of contaminated sewage sludge to land

(315) though it is possible to reduce this potential pathway of exposure (319). Whether such high background concentrations exert any effect on the human population is difficult to establish. At the moment no apparent problems exist and 'acceptability' of the levels is largely defined in terms of human health or impact on agriculture (320). However it has been demonstrated that high levels of lead in soil and dust correlate with the blood lead level of the residents of Halkyn, North Wales (321). Davies and White (53) have described the movement of dusts from spoil heaps over a distance of 1800 m down a valley. They concluded that such dust presented an immediate environmental hazard through deposition on plants and through direct inhalation by animals and humans.

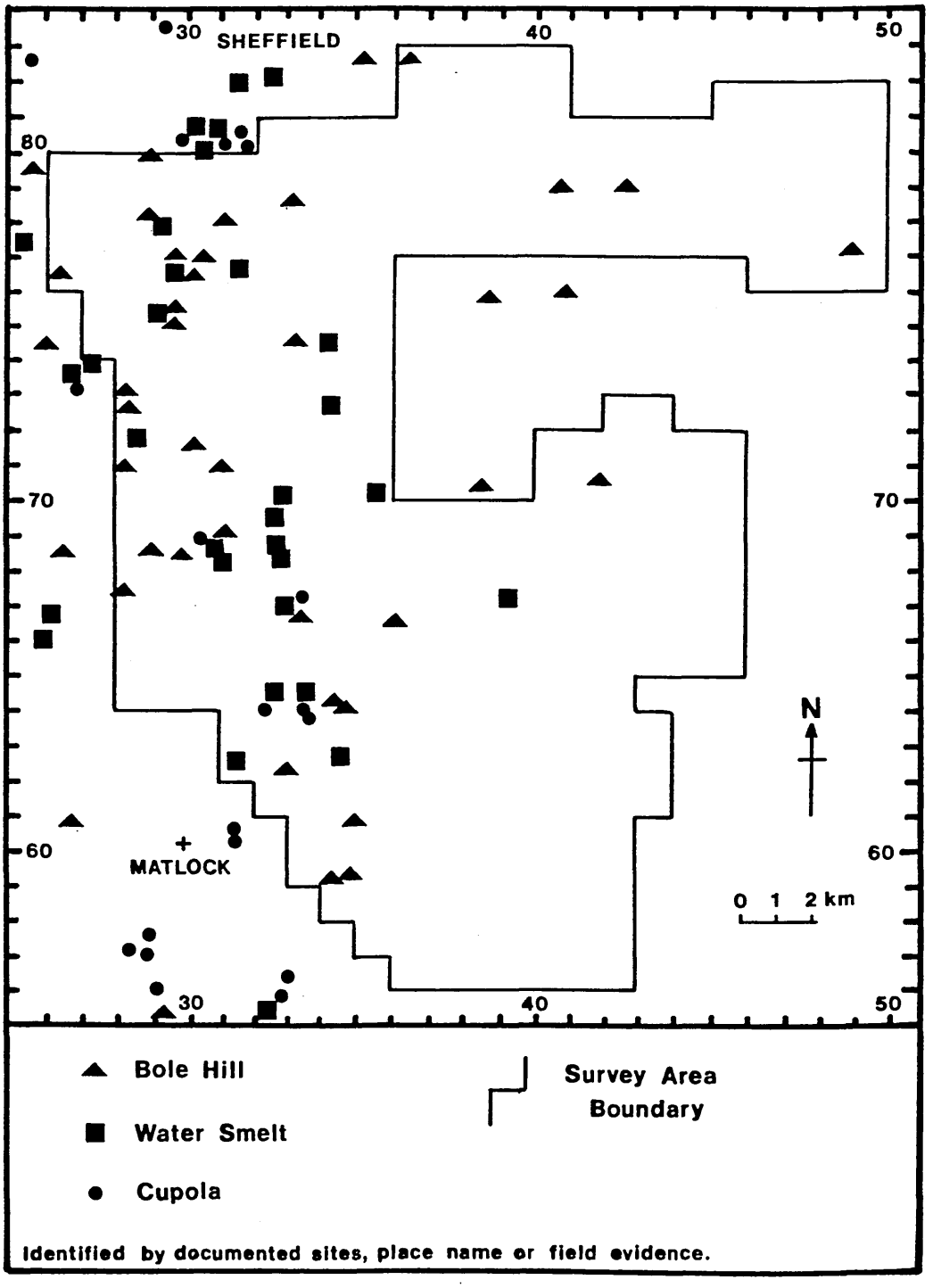
The high concentrations of lead observed for the Ashover area (Figure 16a) are probably due to high natural background sources coupled with extractive processes in the past. The area is located on a dome of Carboniferous limestone (Figure 11.) which has been mineralised and subsequently weathered to produce the soil. Where high concentrations of soil lead exist there is always the potential for highly contaminated dusts to be remobilised by the wind. These already high concentrations have been further increased by mining and smelting activities in the area. Mining and smelting operations have been well documented for the Ashover area and spoil tips are a common feature in some locations. Historically the area has been used for lead smelting since the Romano-British period (322) and a considerable amount of lead was smelted on the high land to the east of the main orefield in Derbyshire. The natural configuration of the landscape provided plenty of wood, high windy locations, fast flowing streams required

to power water bellows and isolated sites which could be used causing the minimum harm to animals and people. As wood became scarce coal was readily available locally for use in cupolas [323]. Finally the close proximity to the markets of Chesterfield and Sheffield made Ashover an ideal location for early lead processing operations.

The early sites for lead smelting occurred on windy scarps called 'bolehills', although bole hills were also places of iron smelting. They were gradually replaced by 'orehearths' often powered by water driven bellows and were sometimes referred to as 'water smelts'. They continued to be used until the development of the reverberatory cupola furnace, introduced in the 18th Century [322]. Some water smelts continued to operate for the extraction of lead from some of the large slag heaps produced by earlier operations. Most of the lead smelting in the region came to an end in the 1820's [323].

It is probable that the distribution of lead revealed by the survey map reflects a legacy of pollution from this bygone industrial age. After the survey maps had been produced, further investigations using field evidence, map place names and discussions with other workers in this field [323,324,325], revealed the location of some known and previously unknown sites of smelting activity (Figure 19). Comparison of Figures 13 and 19 indicates a clear relationship between historical smelting activities and the presentday background levels of soil contamination. This was the case in areas well away from the mineralised limestone, where high natural background lead levels can mask the effects of industrial

Figure 19. Sites of historical lead smelting and processing activity.



activity. Perhaps the best example is at Stone Edge (Grid square I7) where considerable smelting activity took place (see Plate 2) resulting in the very high concentrations of lead in soil (Figure 16a). Not all the high concentrations could be explained in this way. For example, the high lead concentrations in the north east of the survey area were not near a known smelting site. It is possible that it may be a result of modern industry, the influence of the M1 motorway or even caused by migration of minerals through rock strata into the nearby Magnesian limestone ([320]). A research investigation is currently being undertaken in the Department of Recreation and Environmental Studies at Sheffield City Polytechnic into the distribution of Romano-British smelting hearths on the Magnesian limestone in the north east of the survey area ([325]). A possible methodology has been proposed ([326]) by which this soil geochemical survey procedure as described in this chapter could be used to locate and identify sites of industrial archeological interest and is summarised in Figure 20.

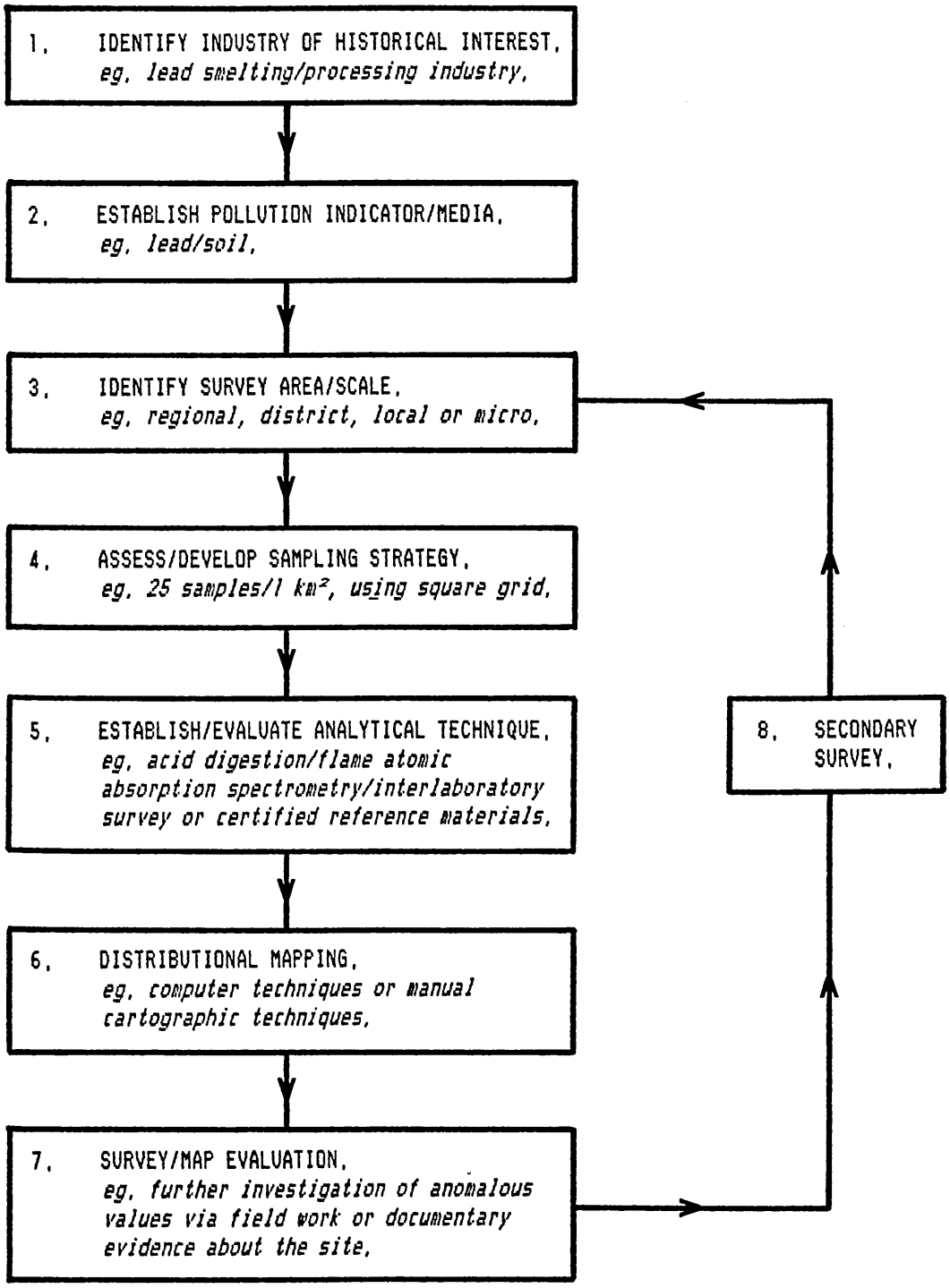
4.4.2. Zinc.

There has been considerable debate over the normal concentration of total zinc expected in soils ([20]), values ranging from 10-300 mg/kg to 1-900mg/kg (with a median of 90 mg/kg). Archer ([327]), working on 748 top soils from England and Wales put the range at 5-816 mg/kg with a median of 77 mg/kg. The range observed for North East Derbyshire is given in Table 20, with the mean concentration for the survey of 196 mg/kg. On the basis of this data a concentration of 250 mg/kg was taken as the cut off point between local background levels and anomalously high background levels of zinc in

PLATE II.

Stone Edge cupola
- a site of historical lead smelting activity
producing a contaminated rural environment.

Figure 20. Industrial Archaeological Geochemical Prospecting.



soil. Approximately 10% of the survey area falls into this category of 'anomalously high' zinc concentrations.

Comparison of Figure 13 and 14 reveals a close relationship between the distributional pattern of lead and zinc, particularly in the areas where mineralised limestone is found and lead mining took place, for example, in the Ashover area. The same cannot be said for areas where the the soil lead concentration has risen near historic smelting sites, with the exception of the major smelter site of Stone Edge cupola (grid square I7, 6767 mg/kg). The Stone Edge cupola has been investigated in some detail by Quayle [328] who has demonstrated that lead fallout from the chimney fell to background levels of <250 mg/kg Pb, within about ½-1 km of the chimney. The levels of zinc around the smelter site ranged between 110-20,000 mg/kg. These are similar to levels observed by Nichol, et al. [329] who observed zinc elevations where lead smelting had occurred. It is possible that some of the anomalous levels of zinc of smaller magnitude may be due to the application of contaminated sewage sludge to land by farmers.

There are no D.O.E. guidelines applicable to total zinc in soil, though they do exist for available zinc [306]. Zinc is recognised as a potential phytotoxin and combined with the additive effects of the phytotoxins copper and nickel could represent a potential hazard to plants. The phytotoxic effect of these metals cannot be assessed for the region since available concentrations have not been assessed, but in areas of high total zinc it is probable that some phytotoxicity may occur. Nriagu [330] has reviewed much of the literature relating to zinc in the soil ecosystem.

4.4.3. Copper.

As for zinc it is difficult to estimate the normal levels of copper in soils. The average total copper concentration in 7819 uncontaminated soils from various parts of the world has been reported as 25.8 mg/kg [20]. This has been compared with results reported by other authors analysing 46 and 751 soils from Great Britain with corresponding medians of 14 mg/kg and 17 mg/kg respectively. The overall mean total copper concentration for North East Derbyshire was 35 mg/kg. On the basis of this information a cut off value for local background copper levels was set at 40 mg/kg see Figure 15 and is highlighted in Appendix 4.g. Approximately 25% of the survey area exceeds the 'local background' level with only 5 grid squares exceeding 100 mg/kg (C8, G12, M21, M24, O2, P12, P16) with the highest concentration at O2 of 241 mg/kg. These anomalies possibly result from one or more of the following; soot and coal ash, crop and soil chemical treatment agents, municipal compost and the application of sewage sludge to land [331]. Nriagu [332] has reviewed much of the literature relating to copper distribution in soils.

4.4.4. Cadmium.

Cadmium is normally found in association with zinc [333] and consequently it was not surprising to find that the Ashover area contained high contamination levels. It is a relatively rare element which is normally only present in soils at levels <1 mg/kg, with concentrations ranging from 0.08-10.0 mg/kg in agricultural soils [327]. In North East Derbyshire some 70% of the area was

found to be <1 mg/kg with only eight grid squares (I23, N5,6,7,11,12,16, O15) exceeding the D.O.E. [306] guidelines for total cadmium in soil of 3 mg/kg (domestic gardens and allotments). Since the significant variation in distribution was confined to the Ashover area the results were not subjected to the mapping procedures described earlier. Of the eight grid squares only two exceeded the guidelines for parks, playing fields and open space of 15 mg/kg, with N8 = 18.8 mg/kg and N11 = 49.9 mg/kg.

These high concentrations are almost certainly due to the natural high background contamination that would be expected in an area of mineralised limestone, as was the case in Shipham, Somerset, where soil concentrations ranged from 2-520 mg/kg [334]. In the rest of the area there appears to be no significant increase in soil cadmium levels from any other source.

In terms of the potential influence on animal and human health lead and cadmium would appear to be of importance, with perhaps lead of more significance. Despite the much greater concentrations of cadmium in soil in Shipham, the Survey of Cadmium in Food [334] has indicated that the dietary cadmium concentrations are on average nearly double those found in the national diet, with only 4% of the local population likely to consistently exceed the recommended dietary intake of 400-500 μg Cd per week. Whilst there may be cause to monitor the situation in Ashover, it is unlikely that the population is at any great risk from cadmium exposure.

As far as lead is concerned most of the elevated concentrations are probably due to either historic polluting activities or naturally

high background levels. In both instances there is probably very little remedial action that could be taken on a wide scale to reduce exposure to the population. Where soil lead levels are high the land is often described as 'bellanded' and of little use for animal grazing and fodder crops. Ineson [320] has discussed this in detail and makes several recommendations on action that could be taken to alleviate any local problems.

In humans, blood lead level is generally accepted as an indicator of exposure to lead in the environment. Barltrop [335] has stated that the blood lead of pre-school children increases by about 0.6 µg/dl for every 1000 mg/kg of lead in soil. Results for the 1979 European Economic Community Blood Lead Survey (UK) [12] for Sheffield show the mean blood lead level for Inner City dwellers and Outer City dwellers to be 14.6 µg/dl and 13.2 µg/dl respectively. If we assume that a typical blood lead concentration for rural North East Derbyshire 'may' be 13 µg/dl, then the maximum increase in blood lead caused by soil would be 9.9 µg/dl (based on the highest soil concentration observed 16460 mg/kg), then the maximum expected resultant increase in blood lead level would be 13 + 9.9 = 22.9 µg/dl in pre-school children. Whilst this is a large increase resulting from one pollution source, it is below the maximum permissible blood lead level of 35 µg/dl, defined by the European Community Directive 77/312/EEC [336]. Nevertheless, should a child be exposed to additional sources, within this high soil lead area, there is potential risk of this safety level being exceeded.

Such a link between blood lead and elevations in soil lead has been demonstrated in Halkyn, North Wales [321]. There is evidence that in urban and rural areas of high soil lead levels, the soil may be transported into the home to produce elevated levels of lead in house dust [337,338,339,340]. In urban areas it has been found that houshold floordusts are enriched relative to soils by factors ranging from 1.5 - 6, with floordusts in 10% of homes containing in excess of 2,000 μg/g Pb [340]. It is reasonable to suggest that in an area such as Ashover similar elevations in houshold dust might be expected and may constitute a significant pathway of exposure of lead to young children.

## 4.5. Conclusions and Recommendations.

The survey procedure which was developed and described in Chapters 2 and 3 has fulfilled its initial aims 4.1. and on the basis of the survey the following general conclusions were made and reported to North East Derbyshire District Council [341].

a) Conclusions.

i) North East Derbyshire has areas in which soils show elevated concentrations of heavy metals, the most significant soil contaminant being lead.

ii) Within a kilometre grid square described as containing 'anomalously elevated' levels there are likely to be areas of both higher and lower concentrations of the metal contaminant, subject to the sampling precision of the survey technique.

iii) The causes of the anomalously high concentrations may be attributed to;

a) geological structures in the Ashover region,

b) historical mining and smelting activities,

c) local remobilisation of this primary material.

iv) In the 'urban' areas of North East Derbyshire there was no apparent elevation of background soil lead concentrations above those found in the more 'rural' areas. This indicates that modern industry and transport have not significantly influenced the soil quality. That is not to say that soil within 50 m of roads is free of lead contaminated from motor vehicle emissions, since this portion of the landscape was not included in the survey. The historic distribution of soil lead contamination does put modern industrial pollution in the area into some sort of historical perspective.

v) Some 10% of the District shows a high probability of contamination levels in excess of the D.O.E. ([306]) guidelines for soils being developed for an alternative use.

vi) There is apparently little risk of direct exposure of the heavy metals surveyed to the local population unless old tips, dumps and sites suspected of contamination are reworked or redeveloped. Normally vegetation has evolved tolerance to heavy metals and effectively covers contaminated sites. This is also the case for the contamination of plants and livestock since bellanding is only likely to occur on disturbed spoil heaps. If development

must be carried out, then it should cover the costs of remedial action required for land reclamation and restoration.

vii) The survey has provided the District with one of the most detailed baseline surveys in the United Kingdom, of background heavy metal soil contamination, upon which future local surveys can be based. Information obtained will enable future monitoring to be directed towards the 'hot' spots of contamination which have been identified and may therefore represent a considerable financial saving in the future.

b) Recommendations.

The following recommendations were made to North East Derbyshire District Council;

i) Any planning applications for land development in the areas identified as being potentially in excess of the D.O.E. guidelines should be given careful consideration, and if necessary local field contamination surveys and/or historical documentary research should be carried out to establish historical pollution sources.

ii) Enquiries should be made to determine if there have been any cases of damage to animal or human health which might be linked to the survey distribution maps.

iii) There is possible value in conducting a pilot local blood lead survey, particularly for pre-school children living in the Ashover region and other 'hot' spots of contamination.

iv) Any gardens and/or allotments in 'suspect' areas would be well worth further monitoring for potentially hazardous levels of metals exposure.

Some of these recommendations were implemented by the District Council through the Environmental Health Department and the area medical officer instructed the investigation of records for medical complaints which could be linked to the survey data. Dust deposit guages were deployed to monitor lead in aerially deposited dust though no significant results were obtained. The dust monitoring will be repeated again in 1987 since during the first survey damp weather conditions prevailed possibly resulting in low dust deposition results. The Planning Department was also provided with a copy of the lead in soil map and planning applications are checked as a matter of routine for potential problems resulting from movement of earth.

This work was published as a report and presented to a full meeting of North East Derbyshire District Council - Environmental Health Sub Committee ([341]). The work has also formed the basis of a paper published in a local history journal proposing a possible methodology for the use of soil contamination surveys in locating areas of potential industrial archaeological interest ([326]). It has generated considerable local interest and a research project by a student registered for MPhil (part-time).

# CHAPTER 5. THE DETERMINATION OF LEAD IN PLANT MATERIAL BY ATOMIC ABSORPTION SPECTROMETRY.

## 5.1. Introduction.

There are many pathways by which lead might enter the population. Details of food as a potential pathway are, however, obscure despite it being considered the major pathway of lead uptake for most people [17]. It is likely that much of the lead in food owes its origin to lead either entering through the roots from soil or into the foliage from dust and aerial particulate emissions [338].

It has been estimated that some 775 $km^2$ of agricultural land in England and Wales is contaminated by the lead emitted from petrol engined motor vehicles, most of this being confined to a strip 20 m each side of motorways, trunk and principal roads [17]. This is a relatively small area compared with the estimated 4,000 $km^2$ area contaminated by historical metal mining and smelting activities [204,316,342]. In some of these areas the concentration of lead found in the soils of rural villages has been reported at 28,000 µg/g [343]. The concentrations of lead in gardens in such areas is high and the effect on the lead content of vegetables grown on these soils is considerable [157,158,338]. In Ashover and other parts of North East Derbyshire total soil lead concentrations in excess of 5,000 mg/kg were observed and the potential effects of consuming vegetables grown on such high soil concentrations are uncertain. The Ninth Royal Commission on Environmental Pollution [17] called for further research into this pathway of lead exposure and for further research into the significance of dust as a pathway.

Generally plants grown in 'high' concentrations of soil lead show higher concentrations in plant tissues. The extent to which this may be taken up via the roots, absorbed from the atmospheric deposition of locally remobilised contaminated soil or from air deposition of particulates from motor vehicles onto leaves is uncertain. There have been many studies of the concentration and distribution of lead in various plants (eg.[156,338,344,345, 346]), but a major obstacle has been the limitation of analytical sensitivity ([347]). The result has been that many workers have had to resort to either bulking individual plant samples together or to artificially dosing the plant with high concentrations of lead salts.

Often samples from several individual plants are bulked together to form a large composite sample, which is then digested in a variety of acids prior to lead determination by flame atomic absorption spectrometry (eg.[142,348,349]) and by using graphite furnace AAS ([350,351,352,353,354,355]), differential pulse anodic stripping voltammetry ([169]) and inductively coupled plasma spectroscopy ([193,356,357]). Whilst this is an adequate approach for finding the overall concentration in several bulked plants, such as might be eaten domestically, it means that actual variations within parts of individual plants cannot be observed. Additional problems occurring during wet ashing procedures include contamination from reagents, high analytical blanks and potential risk of explosion if perchloric acid is used ([347]). Wet ashing and the associated problems can be avoided by using dry ashing techniques ([166]), normally at 450°C ([347]), though it is time consuming and volatilisation losses during ashing can be a problem.

In order to study the distribution of lead through the tissue of a single plant, a technique is required which can be used to analyse very small portions (a few milligrams) of a single plant at 'normal' concentrations of lead. Electron microscopy with x-ray micro-analysis is capable of yielding values for samples of this size, but limited sensitivity necessitates artificially dosing plants with high concentrations of lead salt solutions.

Elias and Croxdale [257] concluded that the inability to find lead particles on the needles of the Virginia Pine growing by roadsides was due to lack of sensitivity of the electron microscopy technique. Bewley and Campbell [358] studying the surface of oak leaves near a lead zinc smelter also found difficulty in locating metal containing particles at normal environmental concentrations. However, Malone et al. [230] have grown corn plants in hydroponic solutions of lead salts with concentrations up to 1000 mg/l and demonstrated that lead accumulated in cell walls of roots. Ophus and Gullvag [359] using similar procedures demonstrated lead accumulations in leaves. Using a scanning electron microscopy technique, Jensen, et al. [360] exposed algal cells to $PbCl_2$ for 96 hours and on this basis suggested that compartmentalisation of lead into phosphate bodies and cell walls was a possible mechanism by which some algae limit potential toxicity. They went on to propose that sequestering metals in this way may be a significant means by which large amounts of heavy metal can move in the food chain. They also observed similar accumulations in Anabaena variabilis (Cyanophyceae)[361]. Sharpe and Denny [362] using the scanning electron microscopy technique, have examined the leaves of Potamogeton pectinatus L. finding similar accumulations in the

cells of the leaf. Whilst studies using lead solutions are useful in attempting to describe the activity at a cellular level, it is questionable if these findings reflect what occurs in natural environmental conditions.

Haque and Subramanian [6] have criticised the artificial dosing of plants with lead salts, during greenhouse and laboratory studies, in order to gain the sensitivity required to study metal uptake. They suggested that "there are clear indications that laboratory results or results obtained from glasshouses cannot be compared with those in field conditions", calling for more work to be carried out under actual field environmental conditions. This will inevitably require that more sensitive techniques are employed and solid sampling approaches may at least provide a movement in this direction.

### 5.1.1. Solid sample microsampling cup flame AAS.

In order to overcome some of the problems of wet and dry ashing there has been a trend towards direct analysis of solid samples. Whilst several solid sampling techniques have been described for the analysis of lead in environmental samples, the term solid is often somewhat misleading in that it is used to refer to a ground or slurried sample, rather than a whole solid sample. Investigating dry ground solid samples generally involves the weighing of individual micro samples, which can introduce weighing errors and present problems of obtaining a representative sample. Several workers have analysed environmental samples using solid (ground/slurried) sample introduction with graphite furnace AAS.

These have included soil (Pb) [267,268,352,363], orchard leaves, bovine liver, oysters, wheat flour, pine needles (Pb,Cd)[354], seaweed, vine leaves, mussel (Pb) [364], food (Pb,Cd) [353], hay (As,Cd,Cr,Cu,Pb) [363], maize roots (Mn,Cu) [353], hair, nail, skin (Pb,Ni) [365], orchard leaves (Cd,Cu,Pb,Zn) [366] and environmental samples (Pb) [367].

A microsampling cup system, primarily developed for rapid analysis [175] has been sucessfully used for mass screening of lead in blood [368,369,370], though it has been demonstrated that contamination by environmental lead within the laboratory can produce erroneous results [275]. Since then it has been adapted for the analysis of lead in other matrices, paint [371], pencil paint [372], urine [373], seaweed [374], seawater [374], sewage sludge [376] and for the determination of cadmium in biological tissue [370,377]. The use of microsampling cup flame AAS for the determination of lead in kidney, liver and lung tissue has been described by Jackson, et al. [174].

More recently the microsampling cup flame AAS procedure was adapted by Jackson, et al. for the analysis of lead in vegetation [159]. Samples of vegetation were dried and ground in a tungsten carbide mill and 0.5 g weighed into a 25 ml beaker. A suspension was prepared by the addition of 10 ml of deionized water to the sample which was stirred magnetically. Aliquots (20 µl) of the suspension were transferred using a micro pipette into nickel microsampling cups. Sample standards were prepared and 20 µl of each standard pipetted, in triplicate, into cups containing the sample suspension. The cups containing the sample and standard were

dried at 110°C for 10 min and inserted into a stoichiometric air-acetylene flame of an atomic absorption spectrometer fitted with an absorption tube and microsampling cup rig. Peak absorbance at 283.3 nm was read from a recorder and the lead content of the sample determined from the resulting standard additions calibration graph. The graph served as the calibration graph for subsequent samples. Any non-specific absorption was time resolved making background correction unnecessary. Good agreement was found with certified reference materials and replicates of the suspension revealed a precision of 4.9%. The detection limit was reported at 72 pg for a 20 µl aliquot. Suitable dilutions of the suspensions provided a linear range of 0.072 - 240 µg Pb/g of dry weight vegetation. Jackson, et al. [159] concluded that the method could be scaled down for smaller sample weights and that it should then be useful where the uptake of lead by plants has to be investigated, as different parts of the same plant could be individually analysed for lead.

In order to determine lead in whole solid samples of vegetation from individual parts of a single plant it was necessary to demonstrate that whole solid samples perform in the same way as a slurried solid sample. If that were the case then calibration graphs based on homogeneous slurry samples, prepared as described above, could be used as a calibration procedure for whole solid samples of plant tissue.

It is the further development of this method and its subsequent application to the analysis of lead in individual samples of vegetation from a single plant, that is presented in this chapter.

An investigation into the contribution of lead from soil and aerial sources to the distribution of lead in individual plants growing in the field environment is discussed in Chapter 6.

5.1.2. Equipment and reagents.

Sampling: - Stainless steel scissors,
- polyethylene bags,
- labels.

Sample preparation:
- polyethylene bags,
- paper tissues,
- stainless steel disc punch,
- stainless steel reverse action forceps,
- stainless steel scalpel and razor blade,
- bunsen burner,
- pyrex 250 ml flat bottomed flasks,
- automatic 250 ml flask shaker,
- pyrex glass petri dishes,
- glass tiles,
- oven,
- agate mortar and pestle,
- Spex high speed tungsten carbide mixer mill,
- pressure cooker,
- pyrex 25 ml flat bottomed flasks,
- magnetic stirrer,
- 'Brand Transferpettor' micropipette,
- Oertling 147 micro balance,

- nickel microsampling cups,
- nickel microsampling cup carrying/furnace tray
- 50 ml volumetric flasks,
- muffle furnace,
- Perkin Elmer Model 103 atomic absorption spectrometer fitted with microsampling cup rig,
- triple slot Boling-type burner,
- ceramic absorption tube,
- Gallenkamp Euroscribe chart recorder.

Reagents:
- tap water,
- distilled water,
- 'Calgon' ringer solution (1% sodium hexametaphosphate),
- 5% $H_2SO_4$
- Pb standard solution (B.D.H.)

5.1.3. Sample collection.

Samples collected for use in the development of the method included leaves from a single specimen of a dandelion (Taraxacum officinale Weber) and a broad dock (Rumex obtusifolius L.) growing near a major road, and also leaves from an indoor rubber plant (Ficus robusta). The leaves were removed from the plant using a stainless steel scalpel, placed in labelled polyethylene bags and returned to the laboratory for treatment. A single potato tuber Solanum tuberosum (Pentland Javelin) was also collected from a domestic garden in a similar manner. A single specimen of cowslip (Primula veris L.) was collected using this procedure from an area of high soil lead associated with mineral veins in the Carboniferous

limestone of Derbyshire, England (Grid Ref: 173748). Permission was obtained for the collection of this sample from the Nature Conservancy Council.

5.1.4. Sample preparation procedures.

All glassware contacting the plant material was soaked in 5% $H_2SO_4$ rinsed in distilled water and dried before sealing in polyethylene bags ready for use. Prolonged exposure to the air after cutting was avoided in order to reduce water loss, cell disruption and possible aerial contamination. All plants were washed using the following procedure, based on methods evaluated by Saiki and Maeda [162] and Sonneveld and van Dijk [163], designed to remove as much surface contamination as possible. This was desirable since true variations within the plant, rather than variations due to surface contamination, were being sought.

Plant material was washed under running tap water for 2 minutes, rinsed in distilled water and blotted dry with a clean paper tissue. The plant samples were placed in a flat bottomed flask containing 200 ml 'Calgon' Ringer solution and shaken for 2 minutes on an auto shaker. The Ringer solution was subsequently drained off and the vessel flushed with distilled water. Then 200 ml of 0.2 M HCl was transferred into the flask which was shaken for a further 2 minutes. The plant parts were immediately rinsed under running tap water for 1 minute and then rinsed four times for 2 minute periods in a large volume (approximately 5 l) of distilled water. Whilst this procedure seemed rigorous, to the extent that

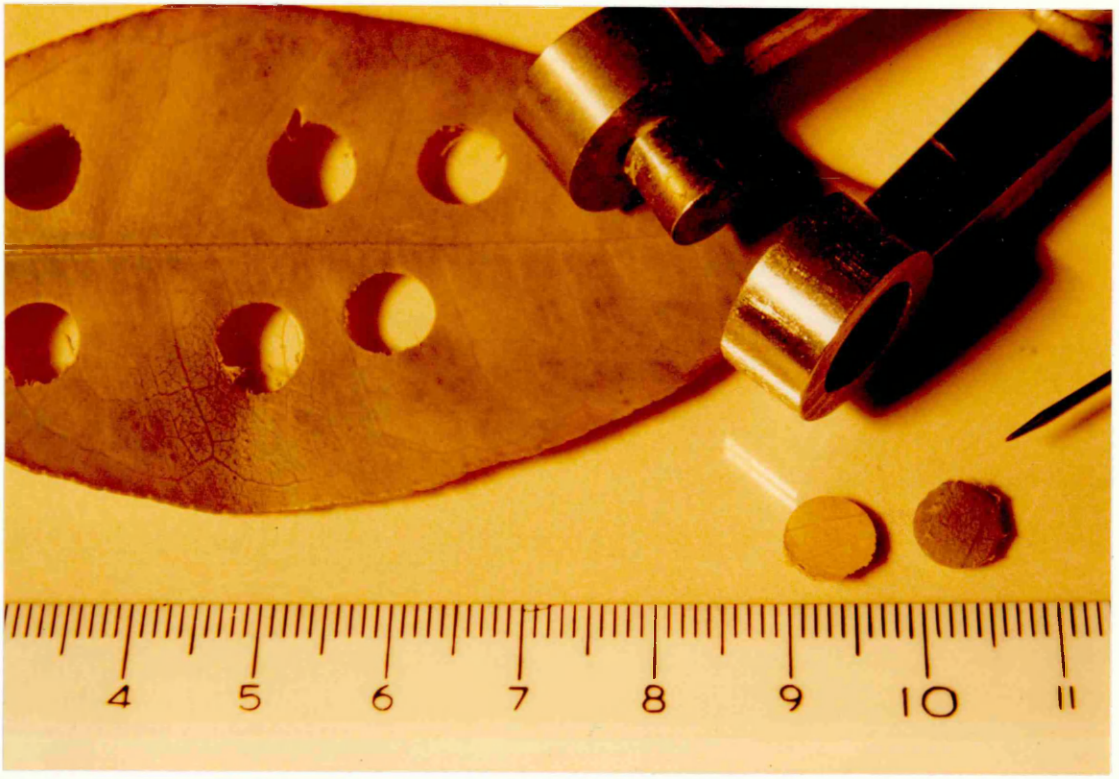
some loss of lead from cells was possible, it was essential in order to reduce potential contamination from surface particles.

For the potato tuber work a single potato tuber was washed using the same procedure as above though rather than shaking in the washing solutions the surface was gently scrubbed using a soft nylon tooth brush. Once cleaned thin cross-sectional slices, <1 mm thick, were taken using a lead-free blade. Each slice was subsequently subsampled using an acid washed stainless steel punch to obtain discs (7 mm diameter). Punched discs of leaf material were obtained, after washing the leaf, using the acid washed stainless steel (7 mm diameter) punch illustrated in Plate 3. The stainless steel punch was manufactured in workshops at Sheffield City Polytechnic.

For the analysis of a whole plant (cowslip), the sample was split into stem, flower, roots and leaves prior to washing in these groups. This was to prevent contamination of the upper parts from the highly contaminated roots. The washed plant parts were subsequently cut into small sections ready for analysis. The washed samples must not be handled unless flamed lead-free forceps are used, and it is advisable to wear disposable polyethylene gloves in order to reduce contamination by the hands. At all times after washing, the samples must be protected from aerial contamination and this was achieved by keeping samples in clean polyethylene bags.

Since the samples are small in size it is difficult to label each individual section of punch. Consequently the washed subsamples

PLATE III.




Sampling leaf discs using a stainless steel punch.

were placed directly on to acid washed glass petri dishes or tiles. The samples were labelled by writing a reference code which identified the sample on the underside of the petri dish or tile.

Once this had been done, punches and samples were dried in an oven at 102 ± 2°C for 18 hours [128]. The dry samples were then accurately weighed into lead-free nickel microsampling cups. The samples were handled using lead-free stainless steel forceps; these were flamed for 1 minute between samples in order to prevent cross contamination between samples.

Slurried samples were prepared using a similar procedure to that described by Jackson, et al. [159]. Samples of vegetation were ground in a Spex high speed mixer mill and approximately 0.3 g of sample was normally mixed with 10 ml distilled water to prepare a slurry. The slurry was stirred using a magnetic stirrer and 50 µl aliquots were pipetted into the microsampling cups and then dried on a hot plate. Spiked calibration standards were prepared by taking 50 µl aliquots of the usual range of lead standards 0.0, 0.1, 0.3, 0.5, 0.6, 1, 2, 3 mg/l, and pipetting them into successive cups containing the slurry.

During preliminary work on the whole plant samples difficulty was found in resolving the ash peak from the lead peak for unashed whole solid samples of vegetation. It was also observed that unashed solid samples resulted in a signal which was between 2/3 and 1/2 that obtained for an unashed slurry. Apparently the lead was too tightly bound in the solid plant matrix and required some form of disruption. Grinding the small solid samples in the cup

was attempted but resulted in the loss of sample and represented a potentially high source of contamination error. Ashing the sample seemed to provide an improved signal response and this approach has been investigated and the findings are presented below for dandelion leaves, dock leaves and potato tuber. The cups containing the dry samples and slurried samples were placed on a lead free holder tray and ashed at 440°C for 12 hours in a muffle furnace. A white ash could be observed in the cups after ashing.

The microsampling cups containing the whole ashed samples and ashed slurry standards were inserted into the air-acetylene flame of an atomic absorption spectrometer fitted with a triple slot burner and having a ceramic absorption tube. The nickel cup insertion system was based on that developed by Delves [175]. Peak absorbance at 283.3 nm was read from a chart recorder and any residual non-specific absorption was time resolved from the lead atomic absorption signal. The lead content of the slurried samples was determined from the standard additions calibration curve. Hence the total concentration of lead in each calibration standard (residual lead plus spiked amount) was known, and the standard additions graph then served as a calibration graph for the whole plant samples.

The inclusion of a pre-ashing step prior to analysis removed any residual non-specific absorption and disrupted the plant matrix sufficiently to allow the determination of lead in the whole solid sample. To demonstrate that whole ashed punches gave the same response as ashed slurries and consequently that slurry calibration

curves can be used for the analysis of whole plant samples the following experiments were carried out.

## 5.2. Ashed slurried samples compared with ashed whole punches.

### 5.2.1. Dandelion leaf.

Punched discs were taken from the tissue between the major veins of a single leaf which had been prepared as described above. The population of punches was divided into two, 30 punches being ground by hand using an agate mortar and pestle to provide a dry powder to prepare a slurry, the remaining 24 punches kept as whole samples. An acid washed agate mortar and pestle was used to reduce the possibility of contamination errors due to grinding the leaves. Slightly more punches were selected for grinding since sample losses were expected to occcur during grinding. Replicate slurry microsamples were ashed as described above together with the 24 whole punches. All the ashed samples prepared in this way were analysed using the procedure described above. As a check on accuracy and for quality control purposes an ashed slurry sample of Pepperbush (dry powder) Certified Reference Material ($^{376}$) was included with each of the sample runs.

The results are presented in Table 21.A. It is clear from the results that the mean concentration for the 24 ashed whole punches was in good agreement with the concentration obtained for the ashed slurry. It can be concluded that in using the ashing procedure, whole solid samples can be analysed by microsampling cup flame AAS. However, whilst the precision of the ashed slurried samples gives

Table. 21. Comparison of ashed slurried punches (X) with ashed whole punches (Y). a) Dandelion. b) Broad Dock. (µg/g Pb).

| Vegetation type. | Ashed slurried leaf punches. | | Ashed whole leaf punches. | | | Ashed slurry quality control. | |
|---|---|---|---|---|---|---|---|
| | n | conc. (µg/g) Pb | n | Mean conc. (µg/g) Pb | R.S.D. (%) | NIES SRM No1 Pepperbush 5.5 ± 0.8 µg/g | |
| | | | | | | Conc. | RSD. |
| A. | 30 | 3.78 | 24 | 3.85 | 52 | 5.55 | 6% |
| B. | 30 | 5.22 | 24 | 5.36 | 30 | 5.75 | 5% |

Where: n = the number of punches in sample population.

R.S.D. = Relative Standard Deviation.

A. = Dandelion (Taraxacum officinale weber.)

B. = Broad Dock (Rumex obstusifolius L.)

an RSD of 5-6%, in good agreement with 4.9% reported by Jackson, et al. ([159]), the RSD for replicate whole punches is 52%. Whilst this appears poor it may represent the actual variation that occurred in the leaf together with a proportion of analytical imprecision since the overall concentrations were similar. The result obtained for the Pepperbush Reference Material (5.55 μg/g) was in good agreement with the published certified concentration (Pb = 5.5 ± 0.8 μg/g). This indicates that accuracy was being achieved and that there were no significant losses during ashing of the slurries and solid vegetation samples.

5.2.2. Broad dock leaf.

The procedures carried out in 5.2.1. were repeated for a broad dock leaf. The results are presented in Table 21.B. and similar observations can be made for the broad dock as were made for the dandelion leaf. Again good agreement was found for the slurried and whole solid samples, though the precision was considerably better in the case of the broad dock (RSD = 30%). It is impossible to say whether the poor precision is due to analytical imprecision or if it reflects the actual variations that exist within the leaves. The smoother and more waxy leaf cuticle of the broad dock may provide fewer sites for surface contamination and potential leaf uptake which may explain the better precision compared with that of the dandelion leaf (RSD = 52%). Other factors such as distribution and density of leaf veins, leaf hairs and stomatal openings may also have an influence upon the relative precision for dock and dandelion leaves. The true precision for the technique cannot be assessed since a truly homogeneous solid

plant sample does not exist for evaluation purposes [379]. Since potato tubers are not influenced by factors such as veins, leaf hairs and stomatal openings, it might be reasonable to expect a better measure of precision for tubers and this is illustrated in 5.2.3.

The results for dandelion and dock leaves demonstrate that ashed whole and ashed slurried samples give the same mean result. Hence we can use an ashed slurry calibration curve for the analysis of ashed whole punches. However in order to obtain an accurate result for a leaf a number of replicates must be taken to calculate the mean, the poorer the precision the greater the number of punches required. Good agreement was also obtained between the certified reference value for the Pepperbush Reference Material and the concentration obtained using the ashed slurry procedure indicating negligible volatilisation losses during ashing.

5.2.3. Potato tuber - Pentland Javelin.

Since it was envisaged that potato tubers would be investigated the procedures were carried out on a slice of a large tuber (tuber A.). A population of 80 punched samples was collected from the slice of potato tuber. The population was split into 40 samples for grinding to produce the slurry and into 40 for analysis as whole solid samples, subsequently reduced to 39 because of contamination of one sample. Attempts to grind the hard samples by hand using the agate mortar and pestle proved impossible since the samples once dry were too hard. As a result a mixer mill was used to grind the samples. The slurries and solid samples were ashed and

analysed as described above. The results obtained for a slice of potato A are given in Table 22. Good agreement was found for the quality control certified reference material, but there was a considerable difference between the slurried punches and the whole punches. It was thought that this might be due to contamination from the mixer mill since the lead concentration of the potato samples was low. Contamination problems were not detected in the case of the leaf samples for which the concentration of lead was much higher, masking any negligible contamination from the agate mortar and pestle.

A slice of tuber was obtained from another potato (tuber B) and 48 punches obtained. A slurry was prepared from 24 punches which were ground together in the mixer mill. The remaining 24 punches were placed in a 10 ml volumetric flask and pressure cooked for 20 minutes at 15 p.s.i. This had the effect of breaking down the structure of the tuber to form a 'mash' which was sufficiently broken up to form a slurry on stirring. Both slurries prepared in this way were ashed and analysed using the procedure described above. The results for potato slice B are given in Table 22. It was apparent from the results that the higher concentrations obtained for the samples ground in the mixer mill were probably due to contamination during the grinding process.

A slice of tuber was obtained from a third potato (tuber C) and 72 punched discs were sampled using the stainless steel disc punch. The mixer mill was used to grind 24 of the discs, and a further 24 discs were pressure cooked as described above. The homogenised samples were used to prepare slurry samples which were ashed

Table. 22. Comparison of ashed slurried punches (pressure cooked vs. mixer mill ground) vs. ashed whole punches, for potato tuber slices. (µg/g Pb).

| Potato, | Ashed slurried punches, | | | | Ashed whole punches, | | | Ashed slurry quality control, NIES SRM No1 Pepperbush 5,5 ± 0,8 µg/g | |
|---|---|---|---|---|---|---|---|---|---|
| | Pressure cooked, | | Mixer mill ground, | | | | | | |
| | n | conc, µg/g Pb, | n | conc, µg/g Pb, | n | Mean conc, µg/g Pb, | R,S,D, % | Conc, µg/g, | R,S,D, % |
| A, | ND | ND | 40 | 0,31 | 39 | 0,09 | 17 | 5,58 | 4,5 |
| B, | 24 | 0,29 | 24 | 1,44 | ND | ND | ND | 5,9 | 6 |
| C, | 24 | 0,12 | 24 | 1,47 | 24 | 0,12 | 19 | 5,9 | 7 |

Where: n = number of tuber punches in sample population.

ND = no data.

R.S.D. = Relative Standard Deviation.

A. = slice of potato A.

B. = slice of potato B.

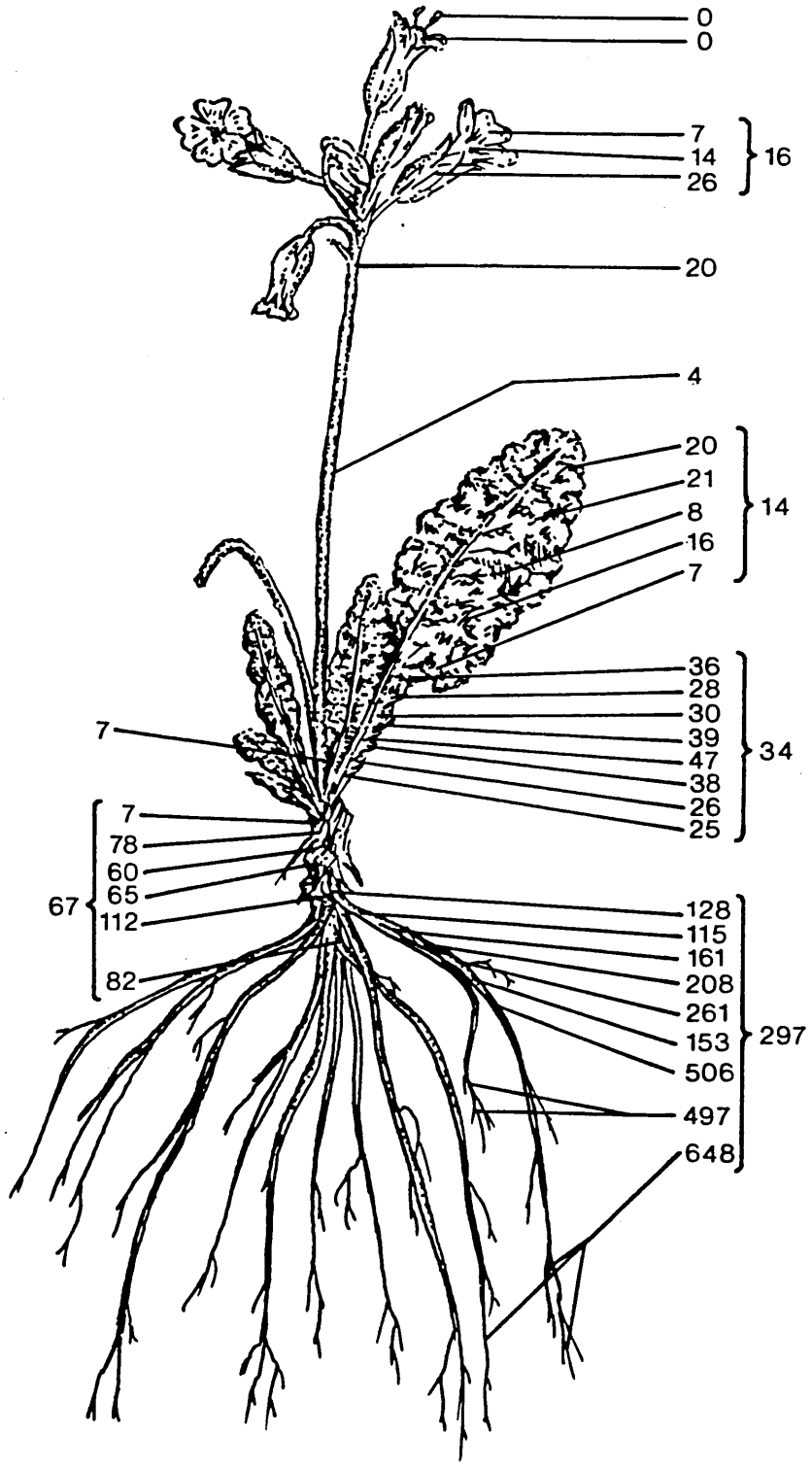
C. = slice of potato C.

together with the remaining 24 whole samples. The lead was determined in the ashed samples using the procedure described above. The results are shown in Table 22. This data confirms that contamination was occuring during grinding of low concentration samples in the mixer mill. Again good agreement was found between the ashed slurries and whole ashed punches confirming that whole solid plant samples performed in the same way as slurried ashed samples. The precision for ashed whole samples was still relatively poor at 17% and 19%, potato A and B respectively. This was a considerable improvement over the precision observed for leaf samples, as might be expected for the more homogeneous tuber material. Throughout this work good agreement was found between the certified value of the reference material and the concentration obtained using the ashed slurry procedure. This confirms that there was no evidence of volatilisation losses during ashing of the samples at 440°C for 12 hours.

## 5.3. Whole plant analysis - Cowslip.

The procedure was applied to an analysis of the distribution of lead in a single plant specimen. The plant was sectioned as described above and the solid whole ashed plant sections calibrated against an ashed spiked slurry. The resulting distribution of lead obtained has been indicated on Figure 21 for the relevant plant parts sampled. It should be remembered that the plant had been growing in a high lead environment and the results are reported on a dry weight basis. Since dilutions were not possible for solid samples where concentrations were expected to be high ie. roots, a small sample was obtained (about 0.5 mg) and larger samples (about

Figure 21. Distribution of lead in Primula veris L. (x 1) (µg/g Pb dry wt.)



10 - 20 mg) from areas expected to be low in lead concentration eg. petal. When a sample response was outside the calibration range it was rejected and the sampling repeated. It was not always possible to repeat samples. When this was the case concentrations were reported as a 'greater than' value (see Chapter 6).

From Figure 21, despite the apparently poor precision of the analytical method, it is clear that there is considerable variation in the overall distribution of lead though the plant with more present in the roots than the stems. The high lead concentrations in the roots may be explained by possible residual surface contamination after washing. Since the soil was of a high lead content it would only take a few particles to produce contamination. The much higher concentrations towards the root tips may reflect an increased possibility for surface contamination since root hairs increase the surface area and provide potential sites for particles to become trapped. There are generally lower concentrations in the flower, leaf, and leaf petiole. The lower lead concentrations in aerial plant parts may reflect the relatively short exposure time for different plant parts. The flower will have been exposed to dust contamination for a shorter period of time than the stem and leaves. Looking at the range of values obtained for the petiole it is clear that there is a considerable variation in lead concentration over a relatively short section of a single plant. It is impossible to say whether this is due to analyical imprecision or if it reflects the actual variations that exist within the plant as a result of local changes in plant structures eg. veins, stomata and leaf cuticle. The true precision for the technique cannot be assessed since a truly

homogeneous solid plant sample does not exist for evaluation purposes.

## 5.4. Conclusions.

The precision of the microsampling cup technique for solid samples is unknown but is probably in the range 15-20%, since the RSD for relatively homogeneous potato tuber has been found to be 17-19%. Unfortunately plant material such as leaves and tubers does not contain a truely homogeneous distribution of lead. Concentrations of lead may be stratified in the tuber material and leaves will vary due to differences in leaf cuticle characteristics eg, surface wax, number of stomata and their distribution, vein structure and absence or presence of surface hairs, over a single leaf [9]. The absence of naturally occurring solid homogeneous plant reference materials [379], which could be used to assess precision, means that an accurate evaluation of the precision of this technique is impossible.

The results obtained for a dandelion leaf, broad dock leaf and potato tuber demonstrate that ashed whole and ashed slurried samples give the same mean result. Consequently we can use an ashed slurry calibration curve for the analysis of whole plant samples. However in order to get accurate results a number or replicates have to be taken to calculate a mean concentration, the worse the precision the greater the number of replicates required.

The procedure represents a considerable development of the microsampling cup technique and opens up a range of new

applications in the field of environmental monitoring, particularly in the study of lead uptake and distribution in plants grown in normal environmental conditions. In addition to the uncertainty of the analytical precision the major disadvantages of the technique are concerned with the considerable time and effort required to weigh the individual plant samples into the microsampling cups, together with the necessary introduction of an ashing step and the possibility that volatilisation losses could occur. It is also essential that every precaution is taken to provide lead-free sample handling, preparation and analytical conditions. Consequently the technique is very costly which limits its use as a routine procedure.

However, the technique does offer a reagent-free procedure with sufficient sensitivity to enable the analysis of lead in milligram samples of solid vegetation, without the need to bulk or dose samples in order to gain sensitivity. It has been shown for the first time that analysis of the distribution of lead through a single plant specimen grown in normal field conditions is possible. The effectiveness of the procedure is limited by the precision. Despite this imprecision, however, for the analysis of a single cowslip it could be confidently demonstrated that there was a significant gradient throughout a single plant because the variation from root to leaf was so large. Some of this work formed the basis of a paper presented at the 5th International Environment and Safety Conference in 1985 (see list of publications and conference papers, no. 9).

The work presented in the following chapter is a study of the distribution of lead through potato plants grown in field conditions. The successful analysis of whole solid samples has enabled an assessment to be made of the relative contribution of aerial and soil sources to the distribution of lead in plants.

# CHAPTER 6. AN ASSESSMENT OF THE CONTRIBUTION OF SOIL AND AERIALLY DEPOSITED LEAD TO THE DISTRIBUTION OF LEAD IN POTATO PLANTS.

## 6.1. Introduction.

In Chapter 1 some of the previous work on the distribution of lead in the soil and plant environments was examined. However, as the Ninth Royal Commission on Environmental Pollution ([17]) stated, more research is needed to gain a better understanding of the relative contribution that different sources and pathways can make to lead in dust and also the pathways and mechanisms by which food is subsequently contaminated. This echoed the findings of the Survey of Lead in Food ([360]) which had identified lead in food as the major source of lead intake for the general population. Although current levels of dietary lead presented no proven toxic hazard ([361]), it was suggested that the margin of safety resulting from the combined exposure levels which may occur from all sources is relatively small. Consequently it was felt prudent to ensure the widest possible safety margin by reducing the levels of lead in food and the environment generally.

The procedure developed in Chapter 5 provides the opportunity to investigate the relative contributions of lead from aerial and soil sources to the final distribution of lead in individual plant specimens. It is possible to carry out investigations of a similar nature using $Pb^{210}$ isotope studies ([156]), though they rely on the assumption that $Pb^{210}$ enters food in exactly the same way as lead from dusts, particulates, and soil ([350]). This is a major assumption which has not been proved. Isotopic ratios have also

been used to indicate the contribution of lead from various sources to the levels of lead in blood [382], though the same basic assumption had to be made.

Perhaps one of the most interesting food plants commonly grown in the United Kingdom is the potato and it has received little attention [160]. Potato consumption in the United Kingdom is fairly consistent from year to year at 75-85 kg/head [383]. Most researchers have concentrated on fast growing plants, such as radish and lettuce, which, whilst they are easy to grow, are eaten in much smaller quantities than are potatoes. Consequently radish [384] and lettuce [384,385,386,387], in terms of dietary influence, may be of little significance. Some concentrations of lead which have been reported in various studies on potatoes are summarised in Table 23. The concentrations are wide ranging and comparisons cannot easily be made since various analytical methods are used, soil lead concentrations are not always reported and plant tissue concentrations are reported on both a wet (fresh) or dry weight (dwt) basis.

A study of potatoes was carried out by Harris, et al. [160], who studied concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in six potato cultivars. Tubers of all cultivars showed low metal concentrations, with varietal differences occurring for all metals except Cd and Cr. Higher concentrations of lead were reported in the roots of early cultivars compared with maincrop varieties. In the haulms of the early cultivars stem zinc was always greater than foliar zinc whereas the converse was reported for Cd, Cu, Ni and Pb. The results for lead are reported in Table 23. The

Table 23. Summary of concentrations reported for lead in potatoes.

| Tuber, (µg/g) dwt, | Plant Parts, (µg/g) dwt, | | | | | Total Pb in soil, (mg/kg) | Available Pb in soil, (mg/kg) | Author, (Ref,) |
|---|---|---|---|---|---|---|---|---|
| | Whole plant, | Leaf, old, | Leaf, new, | Stem, base, | Stem, top, | Root, | | | |
| 2,72 | | | | | | | | 273,0(b) | (73) |
| 1,34 | | | | | | | | 65,0(b) | (73) |
| 12,5 | | | | | | | 127 | 6,4(a) | (388) |
| 6,3 | 15,0 | | | | | | 124 | | (388) |
| 12,5-7,5 | | | | | | | | | (388) |
| V 0,41 | | 5,61 | 2,74 | 0,74 | 0,80 | 11,59 | 871 | | (160) |
| P 0,55 | | 6,25 | 3,27 | 2,14 | 1,27 | 14,14 | 871 | | (160) |
| H 0,26 | | 6,77 | 3,53 | 1,72 | 1,30 | 10,48 | 871 | | (160) |
| M 0,29 | | 4,75 | 4,40 | 2,35 | 1,11 | 6,76 | 871 | | (160) |
| D 1,04 | | | | | | 8,55 | 871 | | (160) |
| K 0,66 | | | | | | 7,51 | 871 | | (160) |
| 1,53 | | | | | | | 1409 | | (390) |

Data reported for Tuber only (µg/g Pb);

| No, samples, | Mean, | Range, | Sample location, | |
|---|---|---|---|---|
| | | 0,3 - 14 * | Market basket sample, | (15) |
| | 1,3 | 0,7 - 1,7 * | Odda, Norway, | (389) |
| 62 | 0,14 | 0,02 - 0,39 ** | Shipham study, | (380) |
| 7 | 0,04 | 0,02 - 0,08 ** | Market garden | (380) |
| 19 | <0,04 | <0,01 - 0,14 ** | Background levels, | (380) |
| 17 | 0,16 | 0,03 - 0,4 ** | Results by Public Analyst | (380) |
| 96 | 0,052* | | Holland, | (391) |
| 96 | 0,6 * | | Holland, | (391) |
| | | 0,11 - 0,24 ** | Norway, | (392) |
| | 0,16 | 0,01 - 0,56 | Australia, | (16) |

* = dry weight basis,
** = fresh weight basis,
(a) = acetic acid extractable lead,
(b) = EDTA extractable lead,

POTATO VARIETIES:
V = Vanessa (early)
P = Pentland Javelin (early)
H = Home Guard (early)
D = Desiree (maincrop)
K = King Edward (maincrop)
M = Majestic (maincrop)

contribution of lead from aerial sources was not assessed during the study. Similar varietal differences have been noted for lettuce [384].

Whilst an attempt was made to show the distribution of lead throughout the potato plants it must be remembered that the samples analysed consisted of bulked plant material from at least six different plants. This results in a loss of information regarding the variations within individual plant specimens. It was envisaged that the application of the microsampling cup procedure, together with conventional soil and extraction procedures, would permit an assessment of the relative contribution of lead from soil and aerial sources to the distribution of lead in individual potato plants growing in the field environment. In order to carry out this investigation a series of field trials was conducted, as described in detail below.

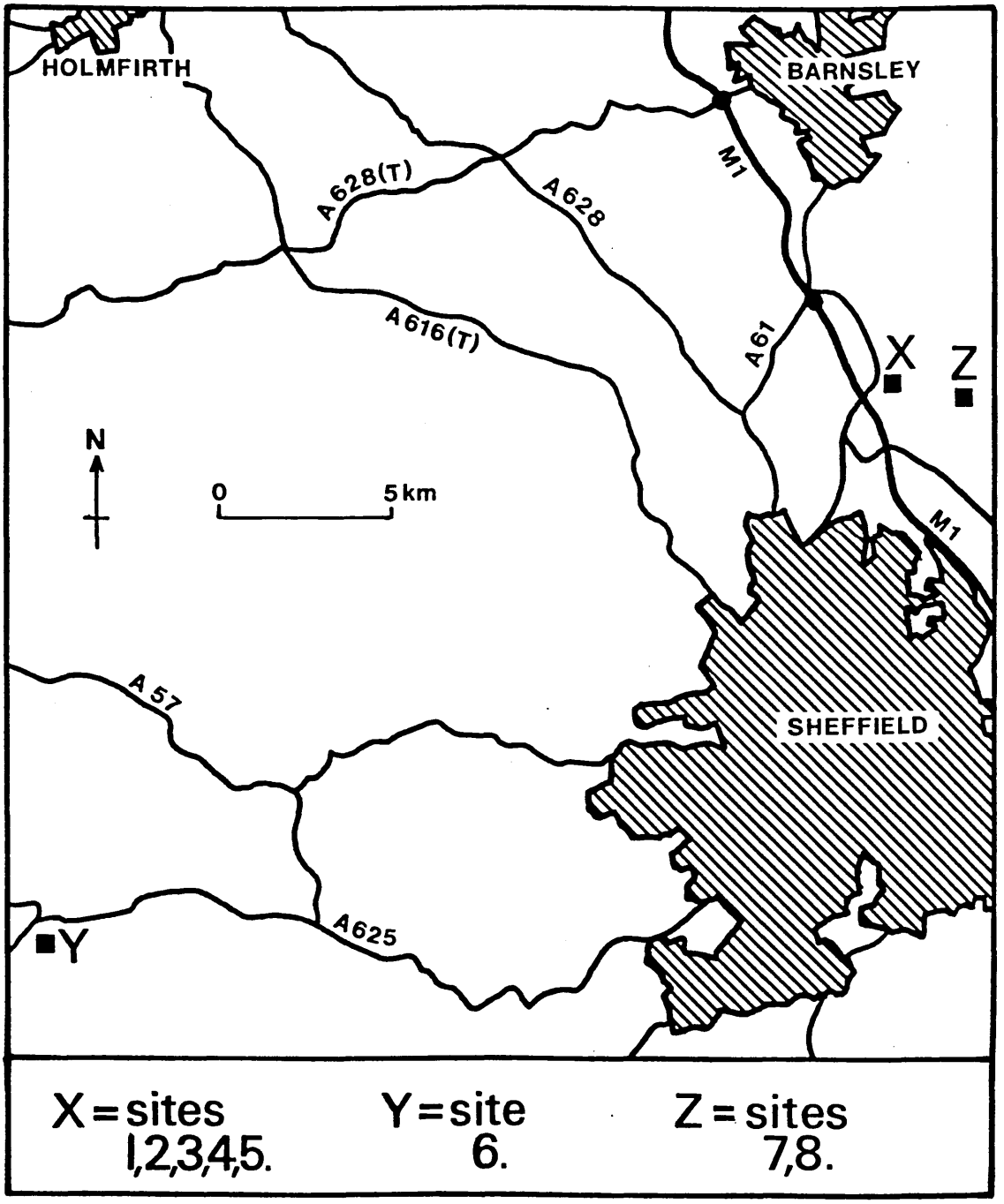
### 6.1.1. Selection of study site locations.

In order to assess the contribution from aerial lead deposition a series of differing field locations was chosen for the study. Each location was expected to have varying aerial lead depsition regime. Eight field sites were selected and each given a code number 1 to 8, the locational details of each study site being summarised in Table 24 and discussed below. The locations are identified in Figure 22.

Table 24. Summary of field study site locations.

| SITE LOCATION CODE. | DESCRIPTION OF SITE LOCATION. |
|---|---|
| 1 | Transect from A 6135, roadside site I. (Ordnance Survey [1:50,000 series] Sheet 110 - G.R. 365987.) |
| 2 | Transect from A 6135, roadside site II. (Ordnance Survey [1:50,000 series] Sheet 110 - G.R. 365987.) (20m from site 1) |
| 3 | Transect from A 6135, field site I. (Ordnance Survey [1:50,000 series] Sheet 110 - G.R. 365987.) (18m from site 1) |
| 4 | Transect from A 6135, field site II. (Ordnance Survey [1:50,000 series] Sheet 110 - G.R. 365987.) (48.6m from site 3) |
| 5 | Transect from A 6135, field site III. (Ordnance Survey [1:50,000 series] Sheet 110 - G.R. 366987.) (91.5m from site 4) |
| 6 | Site near Rowter Farm, Derbyshire. (Ordnance Survey [1:50,000 series] Sheet 110 - G.R. 133819.) |
| 7 | Site at Wentworth Woodhouse, South Yorks. (Ordnance Survey [1.50,000 series] Sheet 110 - G.R. 393979.) |
| 8 | Laboratory Greenhouse Site. (Ordnance Survey [1.50,000 series] Sheet 110 - G.R. 393979.) |

Figure 22. Field study site locations.



Site numbers 1 to 5 were chosen because of their proximity to the main A 6135 trunk road running from Barnsley to Sheffield. Sites 1 and 2 were in similar locations but 20 m apart and each was 2.0 m from the edge of the main road, but within an agricultural field used for hay production. At Site 1 there was no barrier between the roadside and the field, consequently the site was clearly visible to passing pedestrians and could potentially be disturbed. Site 2 was protected from view by a low wall (0.9 m high). Whilst this had the advantage of protection from potential vandalism, it had the disadvantage of shielding from the particulate emissions from the road. In the event the duplication of sites proved useful since on two occasions ground level deposit gauges were disturbed.

Sites 3, 4 and 5 formed a transect perpendicular to the road at distances of 20 m, 68.6 m and 160.1 m from the road respectively and are identified in more detail in Figure 23. The location of these sites was partly dictated by the requirements of the farmer who had given permission for the use of his land. The field was ideal in that at these distances from the road there was a tree and two telegraph poles, each rendering an area of land useless for tractor operation. Site 3 was under a large oak tree, Sites 3 and 4 next to the telegraph poles. It was envisaged that this arrangement would allow an assessment of the changes in lead exposure which take place with distance from road sides [393]. The roadside transect area is shown in Plate IV.

Site 6 was located in a potentially high lead environment, a partly exposed lead rake in Derbyshire. The major source of

Figure 23. Map of roadside transect study area.

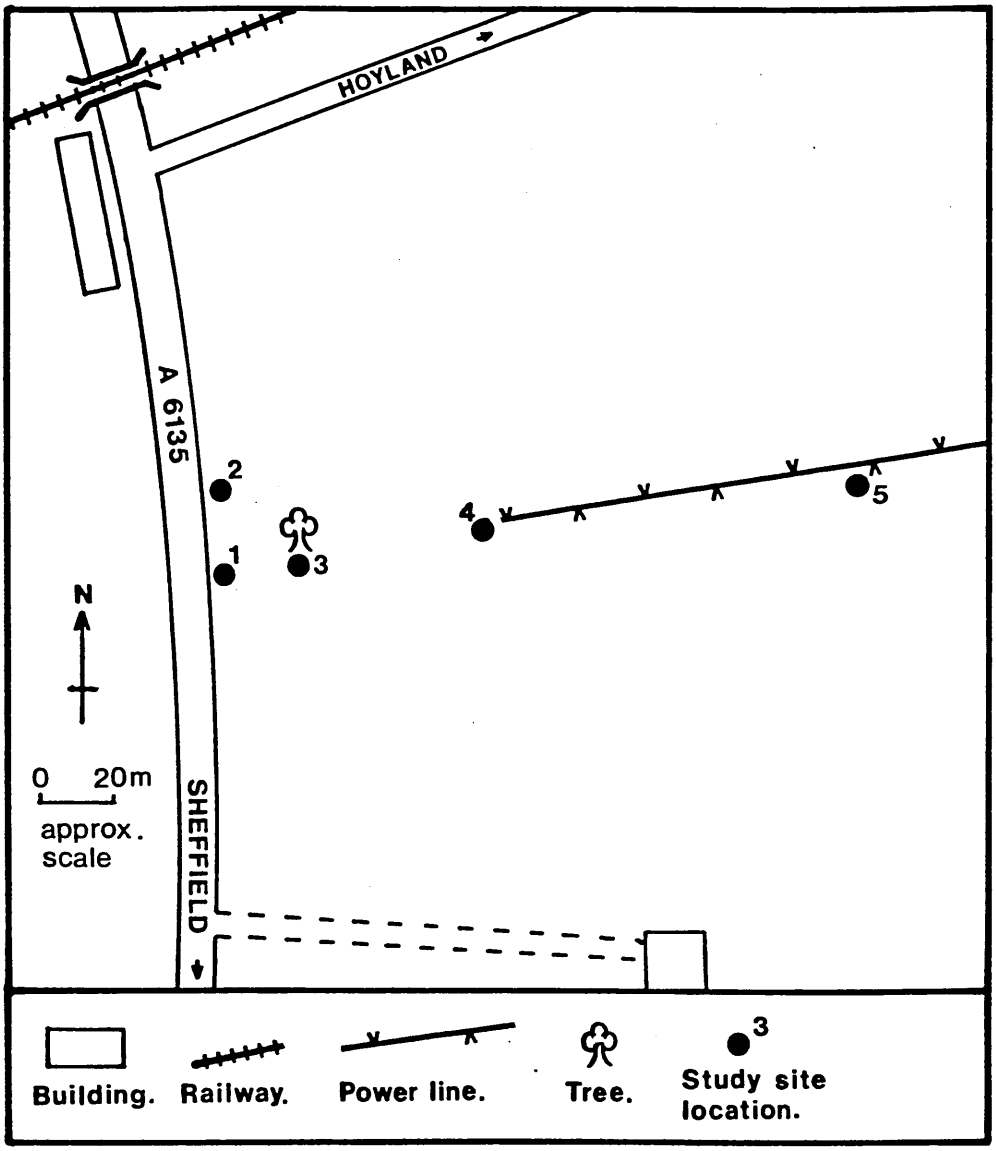
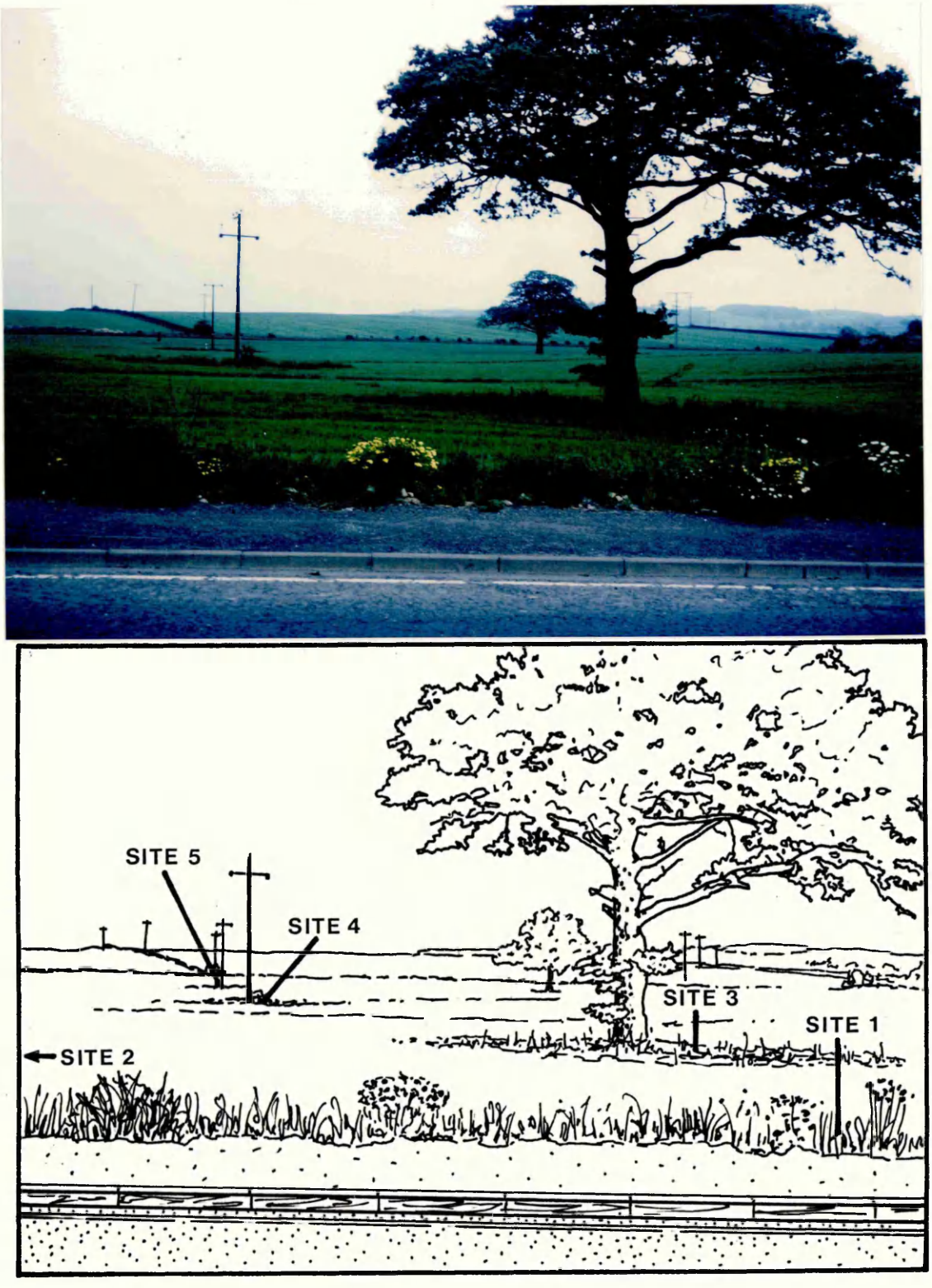


PLATE IV




Transect sites 1,3,4,5, used during the roadside study next to the A6135.

aerially-deposited lead was expected to be from the exposed spoil heaps within 15 m of the station. No other major sources, such as emissions from motor vehicles, existed in the area. It was necessary to fence off the study area using galvanised wire fence since a footpath ran 30 m from the site and there was evidence of rabbits in the location which could have caused damage to plants. Despite its high lead concentration, the area was periodically grazed by cattle and sheep which might also have damaged the station. Site 6 is shown in Plate V.

Site 7 was designed as a control, in what was expected to be an area of low aerial contamination, in the rural parkland of Wentworth Woodhouse. It was situated 7 m from a group of lecture rooms on an isolated lawned area and is shown in Plate VI. Site 8 was also designed as a control but in this instance the location was a laboratory greenhouse. This provided a means for comparing the data observed in the field with that which could be obtained under greenhouse conditions. It was expected that plants would grow in the greenhouse with more vigour than plants growing out in the field.

A ground level dust deposit gauge (GLDDG) was installed at each of the Sites 1 to 7. In addition at Sites 5, 6, 7 British Standard dust deposit gauges (BSDDG) were deployed to monitor general levels of dust deposition during the growth period. The gauges are illustrated and discussed in more detail in section 6.3.

PLATE V.

Study site 6, near Rowter Farm, Derbyshire.

PLATE VI.

Study site 7, at Wentworth Woodhouse, South Yorkshire.

6.1.2. Preparation of experimental soil media.

Whilst the eight study sites provided a variety of aerial lead exposures it was necessary to produce a series of homogeneous growing media in order to assess contributions from soil to the plants growing in the study areas.

Three soil media were prepared for the study by collecting a large quantity of soil, approximately 250 l, and returning it to the laboratory for treatment. Soil medium X was collected from an area of parkland known to be low in lead contamination (394). Soil medium Y consisted of a well developed top soil from a location 10 m away from a lead rake. Soil medium Z was obtained from a poorly developed top soil found on a lead rake and associated spoil heaps. During sampling sections of turf and vegetation were removed and the soil collected from beneath the sods. This reduced local ecological damage, particularly important in the area of the lead rake. In collecting the soils from these locations it was hoped that the soils X, Y and Z would contain a 'naturally' low, medium and high concentration of lead respectively, without the need for artificial dosing with lead solutions.

Once the large volumes of soil were returned to the laboratory they were homogenised using a portable cement mixer (see Plate VII). The cement mixer was initially cleaned using water, coarse silica gravel and sharp sand. Cleaning was carried out between production of each of the three media to reduce cross contamination. Initially the large sample was divided into 8

PLATE VII.

The use of a portable cement mixer in homogenisation of the soil growing media X, Y and Z.

cones, and half of each soil cone was sequentially mixed with half of the neighbouring cone until all cones had been mixed with each other. The moist soil was tumble mixed each time for no more than 3 minutes, longer then five minutes usually resulting in unwanted clodding. Large stones and any other foreign material were removed during this process.

The homogenisation process was carried out in order to reduce variability between and within pots once they were in the field trial. In order to establish whether soil homogeneity had been achieved all pots were tested for a number of soil parameters reported in section 6.2. The bases of 24 new polypropylene pots (25 l) were drilled to allow for drainage and then lined with a 2 inch thick fibreglass mat, which acted as a porous barrier between the contents in the pot and the surrounding environment. Eight pots each were filled with 25 l of the soil types X, Y and Z. The prepared pots were allowed to stand in the greenhouse, for two weeks watering every three days, to allow them to stabilise prior to planting.

### 6.1.3. Selection and cultivation of potato plants.

There are many varieties of potato and as has been demonstrated [160] variations will occur between varieties. Pentland Javelin was chosen since it is moderately scab free, has a round shape, is virus free, resistant to potato cyst nematode and is also a first early variety [395,396,397]. An early variety was chosen due to the constraints of time. Good quality seed potatoes, 15 kg were

obtained directly from the producer, Mr D MacLean, Dornock Farm, Crieff, Perthshire, Scotland.

The seed potatoes were chitted (ie. sprouted prior to planting) in a ventilated light cabinet under fluorescent tubes for 5 weeks, at a temperature of about 16°C until sprouts 1-2 cm had been obtained [383,398]. The chitted potatoes were graded according to size and 72 of the middle sized potatoes chosen randomly for planting into the 24 pots. Three chitted potatoes were planted per pot in a prepared furrow, 12 cm deep, 15 cm apart, and gently covered over. The pots were retained in the laboratory greenhouse for two weeks until sprouts emerged from the soil. Due to a series of late frosts the pots had to be retained for a further week in the greenhouse before distribution to the study sites. This was essential to prevent frost damage to plants, particularly those growing at Site 6 which was subject to rather late frosts. Prior to distribution of the pots to the sites each pot was given an application of an N.P.K. (7%:7%:7%) fertiliser ('pbi' Growmore) at the manufacturer's recommended standard application rate of 19 g per 0.093 $m^2$. This was raked in and the earth ridged up over the shoots.

At each site three holes had been dug, 23 cm deep in the proportions of the pots, and were used to sink the pots into the ground. This enabled the plants to grow at normal ground level and kept the soil at normal ground temperatures reducing water losses from the pots. The pots were distributed to the sites in late May, one of each soil type at each site. The immediate area surrounding the pots was treated every other week with ICI. Slug

Pellets, in order to reduce potential slug attack. The surrounding grass was periodically cut to prevent shielding of the growing plants. During the growth period drought conditions occured from the middle of June until the end of July. This resulted in the need to water pots at intervals of three days. Distilled water from a single source was used in order to prevent any discrepancies which might occcur if tap water from different sources had been used. Approximately 4 l was given to each pot directly to the soil without washing the leaves. The plants were grown to maturity until the beginning of August 1984.

6.1.4. Sample collection.

The mature plants were collected intact, within the pot, and returned to the laboratory for treatment. The sampling of the plant materials is discussed below in Sections 6.5 and 6.6. Soil samples were collected from each pot by lifting each potato plant from the pot and shaking the soil surrounding the root systems of the three plants into a polyethylene bag. The soil samples, approximately 1.5 kg, were air dried at 30°C ($^{128}$) for 3 days and then hand ground with a porcelain mortar and pestle until they passed through a 2 mm nylon sieve, excluding any stones and root debris. The sample was then coned and divided into two subsamples, one being sealed in a plastic bag the other subject to further preparation. The latter sample was dried in an oven at 100°C for 48 hours and treated as described in Section 2.2.3.1. It was necessary to produce air-dried soil samples and oven-dried soil samples in order to carry out the soil analyses described in section 6.2.

## 6.2. Analysis of soils after harvesting potato plants.

In order to be able to assess the possible reasons for the distribution of lead in plant material growing on the soil types it was necessary to have a knowledge of some of the properties of each soil which might have an influence on the plant's development. It was assumed that initially the soils (X, Y and Z) in different locations were homogeneous after tumble mixing. The degree of homogeneity of the soil growing media was tested by analysing the soil in each of the pots for a series of parameters at the end of the field study. This was carried out after the field trial in order to assess any losses from the pots which may have occurred by leaching. It is accepted that during the growth period plants will have utilised minerals from the soil, but this loss should be constant between pots of a particular soil type. Therefore, it was of interest to establish the final concentrations of elements after harvesting the plants.

Some of the factors which govern the movement of heavy metals from soils to plants have been discussed earlier in Section 1.6.1. Total and available lead concentrations were determined in each of the soil samples collected from the pots together with total and available concentrations of other metals including, Cd, Cu, Ca, Cr, Fe, Mg, Mn, Ni and Zn, which are known to exert a phytotoxic effect on some plants at various concentrations [6].

The 1 + 1 nitric acid digestion procedure was used to determine 'total' lead in the soil samples. It has been illustrated in Chapter 1 that a wide variety of extraction techniques have been

used in the literature to assess 'available' levels of metals in soils, though the suitability of the extractant in predicting plant available concentrations of metals is questionable. Available concentrations of lead and other metals were determined using three extraction procedures 0.5 M acetic acid; 0.05 M ammonium EDTA; and 1 M ammonium nitrate. These extractants are normally used by MAFF ([128]) to determine extractable levels of Pb, Cd, Ni, Zn; Cu; and Mg, K, in soil respectively.

Once an extract was prepared it was analysed for 'all' elements under consideration, in order to provide comparative data on the relative extraction efficiencies of the three extractants for the different elements. However the extractants did not always extract sufficient levels of the metals to be determined by flame AAS and in such case no data is reported. An estimation of the percentage of organic matter present was obtained, by simple loss on ignition, together with measures of pH, N, P and K status of the soils. The procedures and results are presented below in sections 6.2.1. to 6.2.7. and discussed in more detail in section 6.2.8.

### 6.2.1. 1 + 1 nitric acid extraction.

This extraction procedure was used to obtain the total concentrations of the metals Cd, Cu, Ca, Cr, Fe, Mg, Mn, Ni, Pb and Zn in each of the soil samples. The procedure has been described in detail in Chapter 2, and the metals were determined in the digests by flame AAS at the following wavelengths; Cd (228.8 nm), Cu (324.7 nm), Ca (422.7 nm), Cr (357.9 nm), Fe (248.3

nm), Mg (285.2 nm), Mn (279.5 nm), Ni (232.0 nm), Pb (283.3 nm) and Zn (213.9 nm). A releasing agent (strontium chloride: MAFF Method 12 ([128])) was used (10% V/V) during the analyses of Ca and Mg in order to overcome phosphate interferences. All analyses were carried out in duplicate and the mean results for each soil medium and site location are reported in Appendices 6.a. to 6.j., under extraction procedure A.

6.2.2. 0.5 M acetic acid extraction.

The 0.5 M acetic acid extraction procedure was based on a procedure normally used by MAFF ([128]) to determine extractable lead, cadmium, nickel and zinc in soils, and was modified to suit the apparatus available in the laboratory. For the procedure a 10 ml scoop of the air dried soil sample, struck off level without tapping, was transferred into a 500 ml polypropylene bottle. Then 50 ml of the extactant was added to the bottle which was stoppered and shaken by hand for a few minutes releasing any pressure built up. The bottles were placed on an automatic bottle shaker, together with blanks, and shaken for 1 hour at room temperature. The resulting slurry was filtered through a Whatman No. 40 filter paper into 50 ml volumetric flasks ready for analysis by flame AAS. Diluted samples were prepared as required. Acid matched standards were prepared and 0.5 M acetic acid extractable Cd, Cu, Ni, Pb and Zn determined at the wavelengths given in 6.2.1. Background correction was used for the determination of Cd, Ni, and Zn. All analyses were carried out in triplicate and the mean results are reported for each soil media and site location in the respective columns of Appendices 6.a, b, c, i, and j.

6.2.3. 0.05 M ammonium EDTA extraction.

This procedure was based on one normally used by MAFF [128] for the determination of extractable copper in soil, although it is often used for the determination of plant available lead and other heavy metals in soil [73]. For the procedure a 20 ml scoop of the air dried soil sample, struck off level without tapping, was transferred into a 500 ml polypropylene bottle. Then 100 ml of the extractant (adjusted to pH 7 using M nitric acid and M ammonia) was added to the bottle which was stoppered and placed on an automatic shaker, together with blanks, and shaken for 1 hour at room temperature. The resulting slurry was filtered through Whatman No. 40 filter paper into 50 ml volumetric flasks ready for analysis by flame AAS. Diluted samples were prepared as required. Matched standards were prepared and 0.05 M ammonium EDTA extractable Cd, Cu, Ni, Pb and Zn determined at the wavelengths given in 6.2.1. Background correction was used for the determination of Cd, Ni and Zn. All analyses were performed in triplicate and the mean results are reported for each soil media and site location in the respective columns of Appendices 6.a, b, c, i, and j.

6.2.4. 1 M ammonium nitrate extraction.

This extractant is normally used in the determination of extractable magnesium in soil [128]. A 10 ml scoop of air dried soil sample, struck off level without tapping, was transferred into a 500 ml polypropylene bottle and 50 ml of M ammonium nitrate added. The bottle was stoppered and shaken on an automatic

shaker, together with blanks, for 30 minutes. The resulting slurry was then filtered through a Whatman No. 2 filter paper into 50 ml volumetric flasks ready for analysis by flame AAS. Diluted samples were prepared as required. Matched standards were prepared and 1 M ammonium nitrate extractable Ca, Fe, Mg, Mn, and Pb determined at the wavelengths in 6.2.1. A releasing agent (strontium chloride: MAFF Method 12 ([128])) was used (10% V/V) during the analysis of Ca and Mg in order to overcome possible phosphate interferences. All analyses were performed in triplicate and the mean results are reported for each soil media and site location in the respective columns of Appendices 6.a, d, f, g, and h.

6.2.5. N, P, K status.

The water soluble nitrate/nitrogen concentrations were determined using a standard Wescan Ion Analyser procedure and samples were submitted for analysis. A 20 ml scoop of air dried soil, struck off level without tapping, was transfered into a 500 ml polypropylene bottle containing 50 ml of distilled water and shaken on an automatic stirrer for 30 minutes. The resulting slurry was filtered through a Whatman No. 2 filter paper and the filtrate injected into the ion analyser for analysis. All analyses were carried out in duplicate and the mean concentration is reported for each soil sample in Appendix 6.k.

Extractable phosphorus was determined in the soil samples using a similar procedure to the standard MAFF method 65 ([128]). A 10 ml scoop, struck off level without tapping, of air dried soil sample

was transfered into a 500 ml polypropylene bottle. Then 100 ml of sodium bicarbonate, buffered to pH 8.5 was added and the bottle shaken for 30 minutes on an automatic shaker at room temperature. The slurry was filtered through a Whatman No. 2 filter paper and the filtrate retained for determination of phosphorus using the standard MAFF procedure. Phosphate was measured spectrophotometrically at 880 nm. All analyses were carried out in duplicate and the mean concentration is reported for each soil sample in Appendix 6.k.

Extractable potassium was determined in the soil samples using the standard MAFF method 68 ([128]). A 10 ml scoop, struck off level without tapping, of air dried soil sample was transferred into a 500 ml polypropylene bottle. Then 50 ml of 1 M ammonium nitrate was added and the bottle shaken for 30 minutes on an automatic shaker at room temperature. The slurry was filtered through a Whatman No. 2 filter paper and the filtrate retained for determination of extractable potassium by the standard flame photometric procedure. All analyses were carried out in triplicate and the mean concentration is reported for each soil sample in Appendix 6.k.

### 6.2.6. Organic content (% loss on ignition)

An approximate indication of the amount of organic matter present in the soil was determined by loss on ignition ([393]). The procedure is often used ([160]), though it is not a true measure of organic matter since at the normal ashing temperature some bound water is lost from the clay minerals and is included in the

overall loss. Considerable discrepancies can result in calcareous soils because of the loss of $CO_2$ from $CaCO_3$ on ignition. Allen [399] suggests an ashing temperature of 450°C since volatile minerals may be lost at higher temperatures and incomplete combustion may occur at lower temperatures. For the procedure approximately 4 g of oven dried soil sample was accurately weighed into a large dry crucible. It was then placed in a muffle furnace and the temperature allowed to rise slowly to 450°C and kept at this temperature for four hours. The sample was then cooled and reweighed and the percentage loss on ignition calculated from the weight loss during combustion. The complete results are reported for each soil sample in Appendix 6.k.

6.2.7. pH.

The pH of each soil sample was determined using a procedure similar to the standard MAFF method 34 ([126]). A 20 ml scoop, filled and struck off level, of air dried soil sample was transferred to a 500 ml polypropylene bottle and 50 ml distilled water added. The bottle was shaken for 30 minutes on an automatic shaker and the resulting suspension used for the determination of soil pH. All analyses were carried out in duplicate. An E.I.L 7020 pH meter was used for the determinations together with buffer solutions pH 4 and pH 7. The complete results are reported in Appendix 6.k.

6.2.8. Results and discussion.

It should be emphasised that it is not possible to make direct comparisons between the three soil media X, Y and Z, since they are of completely different origins and hence different overall matrix. A summary of the variations in the composition of different parameters measured in the three soils from pots in the 8 site locations is given in Table 25. Whilst the concentration of 'total' lead in soils X, Y and Z (73 μg/g, 4120 μg/g and 38000 μg/g respectively) provides a spectrum of possible natural soil lead levels, the variation in the component structure of each soil, pH, organic composition and synergistic effects of other elements within them prohibits any direct comparison in terms of uptake of lead by the potato plants.

For example it can be seen from Table 25 that soil Z was higher in calcium (553100 μg/g) and lower in iron (5828 μg/g) when compared with soil X which was lower in calcium (2996 μg/g) and higher in iron (40708 μg/g). Similarly soils X and Y have a higher percentage of organic material (13% and 16.4% respectively) than soil Z (4.2%), whilst pH is relatively similar at 5.4, 4.7 and 5.6 for the soils X, Y and Z respectively. Clearly such differences would have an impact upon the way in which plants might take up lead from the three different soil types. Consequently only generalised observations can be made between plants grown in the three different soils at the different study sites. The important point is that the results relating to the three soils demonstrate the way plants grown in these soils (of differing matrix and lead concentration) have responded to exposure in environments subject

Table 25. Summary of the concentrations and RSDs** of some components of soil media X, Y and Z. (ALL SITES)

| SOIL COMPONENT. | SOIL MEDIA. | | | | | |
|---|---|---|---|---|---|---|
| | X. | | Y. | | Z. | |
| | Mean. | % RSD. | Mean. | % RSD. | Mean. | % RSD. |
| * Lead (µg/g) | 73 | 13 | 4120 | 6 | 38000 | 3 |
| * Cadmium (µg/g) | 1,7 | 17 | 1,5 | 17 | 1,4 | 19 |
| * Copper (µg/g) | 22 | 3,8 | 34 | 4,1 | 38 | 4,1 |
| * Calcium (µg/g) | 2996 | 13 | 5679 | 26 | 553100 | 2,4 |
| * Chromium (µg/g) | 10,4 | 7,1 | 18,5 | 5,8 | 9,9 | 10 |
| * Iron (µg/g) | 40708 | 4,7 | 8029 | 9 | 5828 | 2,5 |
| * Magnesium (µg/g) | 1707 | 6 | 1480 | 20 | 376 | 5,8 |
| * Manganese (µg/g) | 1070 | 6,4 | 70 | 45 | 126 | 5,5 |
| * Nickel (µg/g) | 17 | 4,8 | 27 | 8,9 | 38 | 5 |
| * Zinc (µg/g) | 108 | 5,3 | 160 | 10,2 | 319 | 6,9 |
| *** N (mg/l) | 24,3 | 83,5 | 15,1 | 67,5 | 30 | 69,6 |
| *** P (mg/l) | 20,4 | 20,6 | 16,9 | 15 | 47 | 6,3 |
| *** K (mg/l) | 192 | 15,5 | 167 | 15,2 | 68 | 20,5 |
| % loss on ignition. | 13 | 8,3 | 16,4 | 3,8 | 4,2 | 12 |
| pH | 5,4 | 5,7 | 4,7 | 9,2 | 5,6 | 4,3 |

* 1 + 1 $HNO_3$ extraction, ie. 'total' concentration.

** RSD = % Releative Standard Deviation based on all results from soils at site locations 1 to 8.

*** Extractable.

to various aerial depositions and different climates (sites 1 to 8).

A spectrum of lead concentrations could have been obtained for a single soil by additions of lead or by using solution culture techniques. However, the resulting soils or growth medium would not be 'natural' in structure and may not have exerted the same effect upon plants as for those grown in natural soils.

During laboratory greenhouse studies it is possible to control to some extent environmental factors which may be acting upon an individual experiment. However, the results obtained under such conditions may not be the same as those which would have occurred under field conditions. Consequently for any field investigation the greatest limiting factor is the ability to control all other influential environmental parameters, in order to examine the effects of only one or two parameters of interest, e.g. the contribution of aerial and soil lead to the distribution of lead in potato plants. Control of all these factors in the field is impossible. Normally the best alternative is to measure parameters of potential influence then to use the data retrospectively in interpreting the results of field observations.

In the study every effort was made to homogenise the three soil media so that the plants grown in each of the pots containing either soil X, Y or Z were growing in similar soil conditions. Theoretically, variable factors for each pot containing a particular soil still existed; for instance its location, its climate, its height above sea level and subsequent aerial lead

exposure. Use of homogenised soil media, in theory, meant that all the measured constituents (Cd, Cu, Ca, Cr, Fe, Mg, Mn, Ni, Pb, Zn, N, P, K, pH and organic content) and hence the overall matrix in each of the three soil media, should have been constant. The actual variations that occurred within each soil type are illustrated in Table 25. (The complete data are contained in Appendices 6.a. to 6.k.).

In practice it appears that for 1 + 1 $HNO_3$ extractable ('total') levels of metals measured, organic content and pH the soils were relatively homogeneous. This assertion is based on an acceptable precision limit (RSD) for soil medium homogeneity of 20%. This is generally supported by the data in Tables 25 for all components, with the one exception of soil medium Y where calcium has an RSD of 26% and manganese of 45%. The complete data for lead in the three soil media, at all site locations, are given in Table 26 and confirm that for lead all three soils were of an acceptable degree of homogeneity

In terms of 'extractable' levels of N, P and K poorer site-to-site precision was observed (eg. RSD of up to 83.5% for N levels in soil medium X, Table 25). Whilst a proportion of the variability from site to site could possibly be attributed to field variations, some of the variation may also be attributed to the analytical precision of the extraction technique. Poor precision might have been expected since pots containing the same soil in different field locations may have been subject to different leaching rates, or different rates of removal and uptake by plants growing in the soil.

The latter is a possible explanation for the highly variable N results at each of the study sites 1 to 8 for each of the three soil media, particularly since concentrations were measured after the growth period and the soils had initially been given a standard fertiliser application. Nitrate levels however, are notoriously unpredictable from day to day as a result of oxidation, reduction, temperature, moisture, pH and other factors within the soil sample [400]. MAFF/ADAS [405] recognise this problem and often use past cropping history rather than soil analysis. The mean concentration of N in soil media X was 24.3 mg/l (Table 25), however low N levels were observed at sites 6, 7 and 8 (7.5 mg/l, 8.2 mg/l and 4.7 mg/l respectively, see Appendix 6.k.). Similar trends occurred for soil media Y and Z, though Z7 did have 23.5 mg/l N. The apparent N loss was possibly due to leaching during watering since there is no obvious evidence from the data on plant yield (see section 6.4.) to suggest that nitrogen was utilised in increased biomass production. This cannot be confirmed since the N content of the biomass was not determined. Despite lower levels of soil N at Sites 6 and 7 this appears to have had little effect upon the tuber yield and stem growth of the plants (see section 6.4.), since they are neither significantly higher nor lower than the respective measurements for plants at the other sites. However, plants grown at Site 8 were consistently taller than the other sites, presumably due to the warmer and lighter growth conditions afforded by the greenhouse [401]. Possible reasons for higher N concentrations at Sites 1 to 5 are that the soil surrounding the pots either dried out to a lesser extent resulting in a lower potential loss by leaching or, possibly even due to absorption of N from the

surrounding local soil. Alternatively it might suggest that N had not been used for plant growth though the data on plant yield does not support this since plants did not have a smaller yield than at the other sites.

The complete data giving the concentrations of 'total' and 'available' lead in soil at all sites for soils X, Y, and Z are given in Table 26. The mean concentrations of 'total' lead in soil X, Y, and Z were 73 µg/g, 4120 µg/g and 38000 µg/g respectively, with the greatest variation between the 8 pots occuring for soil medium X (RSD = 13%). The table also contains results for 'extractable' lead determined using three different extractants. Various extraction procedures have different extraction efficiencies when used on different soils. The extractant 0.05 M ammonium EDTA it typically extracted 38%, 65% and 85% of the total lead in soils X, Y and Z respectively. However, 0.5 M acetic acid extracted 0.5%, 3% and 19% respectively, and M ammonium nitrate extracted 0.5%, 5.4% and 8.1% from soils X, Y and Z respectively. The acetic acid and ammonium EDTA procedures have been used by several authors to determine lead available to plants, though clearly different results would be obtained using each technique with ammonium EDTA extracting considerably more lead than acetic acid. The relative extraction efficiencies of the three extractants for selected elements are summarised in Table 27. In this study the ammonium EDTA extractable results are used when referring to lead available to plants since this method has been preferred by several authors. Therefore the concentrations of available lead in soils X, Y and Z are taken to be 28 mg/l, 2690 mg/l and 32200 mg/l respectively.

Table 26. Lead in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | EXTRACTION PROCEDURE | | | |
|---|---|---|---|---|
| | TOTAL LEVELS. (µg/g) A. | AVAILABLE LEVELS. (mg/l) B. | (mg/l) C. | (mg/l) D. |
| X 1 | 70 | 0.5 | 0.6 | 26 |
| X 2 | 76 | 0.4 | 0.4 | 30 |
| X 3 | 77 | 0.4 | 0.3 | 31 |
| X 4 | 66 | 0.4 | 0.3 | 25 |
| X 5 | 75 | 0.4 | 0.4 | 28 |
| X 6 | 84 | 0.4 | 0.5 | 31 |
| X 7 | 54 | 0.4 | 0.4 | 24 |
| X 8 | 78 | 0.5 | 0.4 | 31 |
| Mean = | 73 | 0.4 | 0.4 | 28 |
| Std. Dev. = | 9 | 0.05 | 0.1 | 3 |
| RSD% = | 13 | 11 | 24 | 10 |
| Y 1 | 4194 | 192 | 128 | 2867 |
| Y 2 | 3990 | 170 | 132 | 2688 |
| Y 3 | 4329 | 177 | 116 | 2771 |
| Y 4 | 4327 | 148 | 107 | 2863 |
| Y 5 | 3738 | 184 | 106 | 2392 |
| Y 6 | 3901 | 164 | 114 | 2542 |
| Y 7 | 4075 | 84 | 188 | 2617 |
| Y 8 | 4407 | 676 | 110 | 2762 |
| Mean = | 4120 | 224 | 125 | 2690 |
| Std. Dev. = | 235 | 186 | 27 | 164 |
| RSD% = | 6 | 83 | 22 | 6 |
| Z 1 | 39931 | 3227 | 7708 | 33292 |
| Z 2 | 39553 | 3476 | 7267 | 33458 |
| Z 3 | 38661 | 3643 | 7525 | 34708 |
| Z 4 | 37791 | 3294 | 7242 | 33208 |
| Z 5 | 36514 | 3598 | 7833 | 33000 |
| Z 6 | 37127 | 2472 | 7858 | 31708 |
| Z 7 | 37622 | 2637 | 6800 | 32875 |
| Z 8 | 37140 | 2306 | 5767 | 25333 |
| Mean = | 38000 | 3080 | 7250 | 32200 |
| Std. Dev. = | 1200 | 531 | 697 | 2890 |
| RSD% = | 3 | 17 | 10 | 9 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = M Ammonium Nitrate Extraction
(mean result of 3 determinations)
C. = 0.5 M Acetic Acid Extraction
(mean result of 3 determinations).
D. = 0.05 M Ammonium E.D.T.A. Extraction
(mean result of 3 determinations).

Table 27. The relative extraction efficiencies of the three soil extractants used. (% of 'total' element extracted by each extractant).

| Element. | % of 'total' conc. extracted by extractant. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Soil medium X. | | | Soil medium Y. | | | Soil medium Z. | | |
| | Extractant | | | Extractant | | | Extractant | | |
| | A. | B. | C. | A. | B. | C. | A. | B. | C. |
| Lead | 0,5 | 0,5 | 38 | 5,4 | 3,0 | 65 | 8,1 | 19 | 85 |
| Copper | ND | ND | 31 | ND | ND | 43 | ND | 5,5 | 68 |
| Calcium | 54 | ND | ND | 39 | ND | ND | 0,2 | ND | ND |
| Magnesium | 18 | ND | ND | 5,3 | ND | ND | 6,7 | ND | ND |
| Nickel | ND | ND | 16 | ND | ND | 21 | ND | ND | 5,3 |
| Zinc | ND | 2,8 | 7,5 | ND | 9,2 | 25 | ND | 3,1 | 15 |

Where;

ND = No Data.

A = M Ammonium Nitrate Extractant.

B = 0,5 M Acetic Acid Extractant.

C = 0,05 M Ammonium EDTA Extractant.

The variations of the different components of each soil type make comparisons of the data from site to site difficult since as demonstrated above parameters of potential influence on lead uptake vary, even within a homogenised soil, after allowing the soil to stand through a growth season. Since this is the case, evaluation of the synergistic effects of the soil components upon one another and their effect on lead accumulation by plants is difficult to assess on the limited information available and this should be remembered when considering the following data.

## 6.3. Determination of lead in dust deposited material.

Dust samples were collected using three procedures, British Standard Dust Deposit Gauges (BSDDG) [402], Ground Level Dust Deposit Gauges (GLDDG) and Leaf Capture. The latter procedure is discussed in more detail in Section 6.5. BSDDG's are often used to determine the amount of dry matter which falls into a 315 mm collecting bowl over a period of 1 month. The quantity of deposited material is normally expressed as milligrams dry deposited material per metre square per day ($mg/m^2/day$). The concentration of lead in the dust deposited material can be determined after suitable acid dissolution and analysis to give $\mu g\ Pb/mg/m^2/day$. The usefulness of gauges of this nature is questionable since sampling errors of 40% are common [403]. These variations are mainly caused by fluctuations in meterological factors such as rainfall, wind speed and wind direction, together with particle blow-out. The data obtained can only serve as a general guide to particle fall out since the surface of the bowl in no way resembles the particle capturing surfaces of leaves.

Consequently caution must be exercised in using these results as a measure of the direct aerial contamination of the plants.

A single BSDDG was deployed at Sites 5, 6 and two (A and B) at Site 7. Only 4 gauges could be obtained for use during the study and these locations gave the best possible coverage for monitoring purposes. It would have been desirable to have a BSDDG at Site 1 or Site 2 next to the road, though it would have been at risk of vandalism. The gauges can be seen in their respective locations in Plates V and VI. Gauge A. at Site 7 was used for a period of six months and the remaining three gauges for a three month period during the field trial. The samples were collected on a monthly basis and the dust in the collecting bowl was rinsed into the collecting bottle and returned to the laboratory. The water and particulate material was filtered through a Whatman No 2 filter paper and the total mass of solid material determined. The filter paper and residue were digested in 10 ml of 1 + 1 $HNO_3$ using the procedure described in Chapter 2. The volume of acid was reduced to 5 ml and the liquid filtered and made up to 10 ml in a volumetric flask. Total lead in dust deposited material was determined by flame AAS at 217.0 nm using background correction. The results are presented in Table 28 and are illustrated in Figure 24.

The GLDDG's were designed to sample the deposition of particulate matter at near ground level and are illustrated in Figure 25. Using these gauges it was hoped that a better estimate of the dust mobilised near plants could be obtained. A GLDDG was located at each study Site 1 - 7, with duplicate gauges at Sites 6 and 7.

Table 28. Results for lead in dust deposited material using British Standard Dust Deposit Gauges (BSDDGs). (µg Pb/mg/m²/day). (Feb. - July 1984)

| Site. | Month | | | | | |
|---|---|---|---|---|---|---|
| | FEB. | MAR. | APRIL | MAY | JUNE | JULY |
| 5 | ND | ND | ND | 0.13 | 0.48 | 0.14 |
| 6 | ND | ND | ND | 1.17 | 0.36 | 0.13 |
| 7A | 0.16 | 0.15 | 0.30 | 0.12 | 0.26 | 0.05 |
| 7B | ND | ND | ND | 0.15 | 0.10 | 0.04 |

ND = No data.

Table 29. Results for lead in dust deposited material using Ground Level Dust Deposit Gauges during two sampling periods. (µg Pb/mg/m²/day).

| Time period. | Site locations. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6a | 6b | 7a | 7b |
| I | ND | ND | 0.37 | 1.51 | 4.64 | 1.79 | 9.28 | 1.61 | 0.75 |
| II | 0.54 | 0.65 | 0.31 | 0.14 | 0.35 | 1.92 | 3.17 | 0.37 | 0.43 |

ND = No data.

Time Period I = 21st May to 17th June 1984.

Time Period II = 18th June to 1st August 1984.

Figure 24. Deposition of lead in dust for sites 5,6, and 7 during February to July 1984 using British Standard Dust Deposit Gauges (BSDDGs).

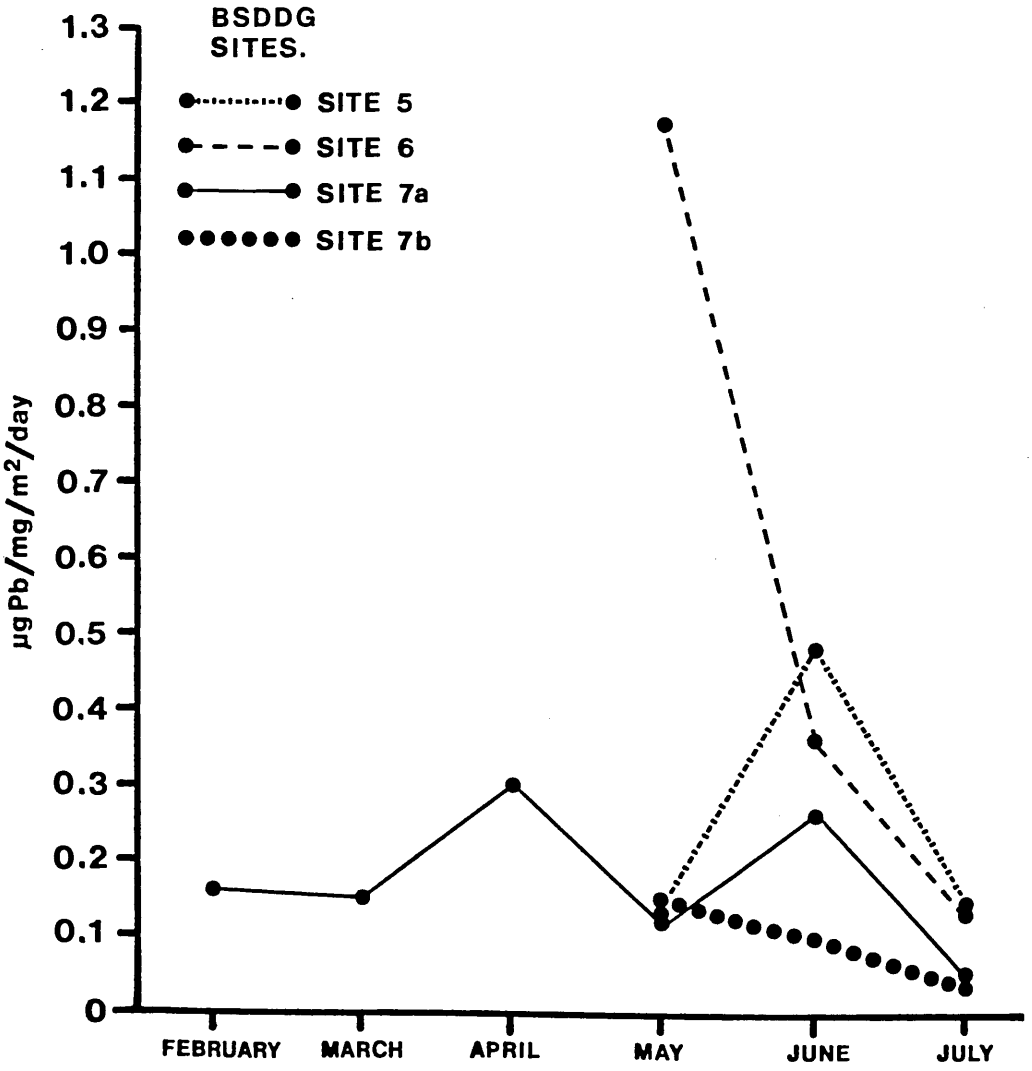
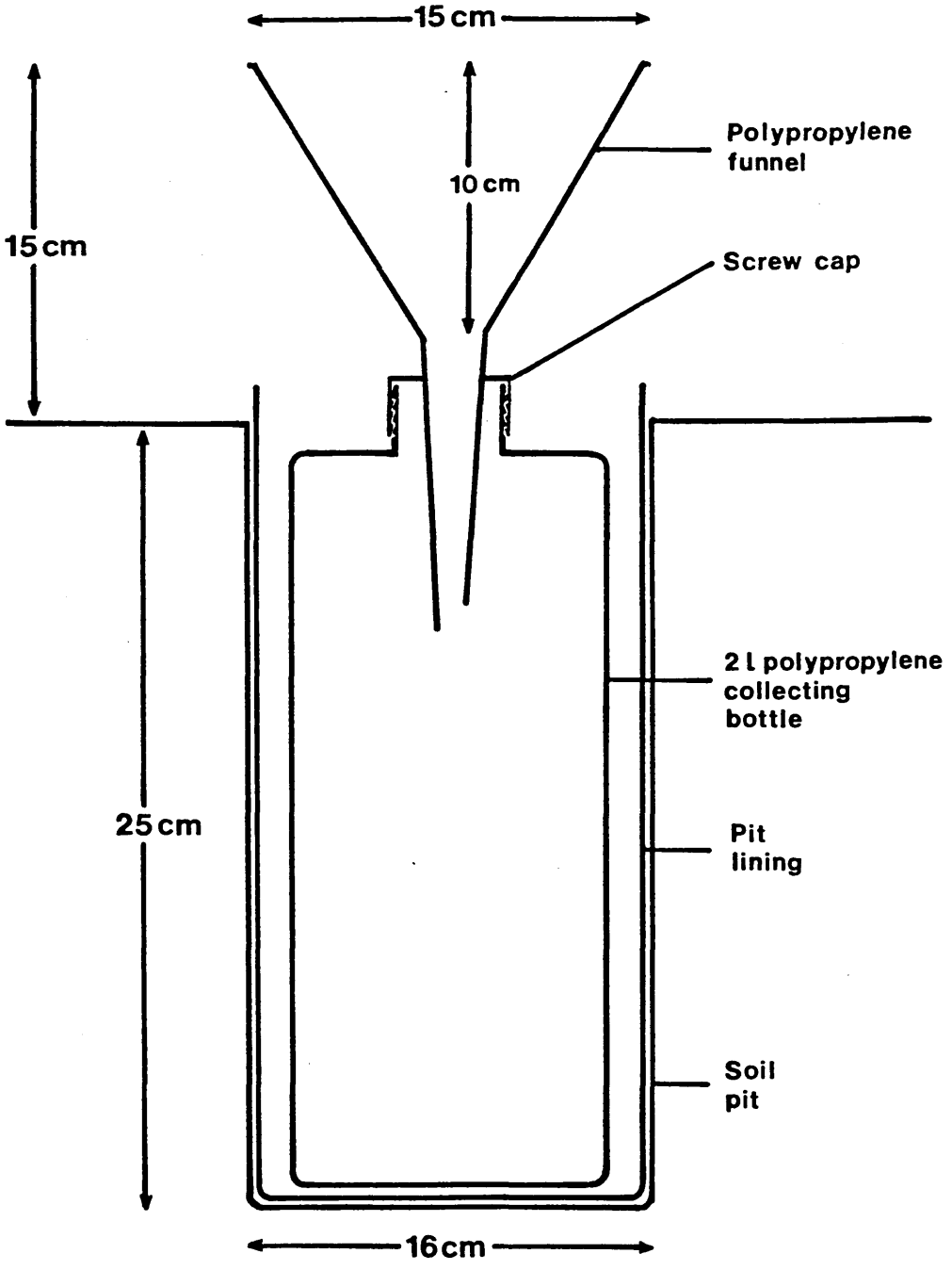


Figure 25. Diagram of Ground Level Dust Deposit Gauge (GLDDG) used during the study to estimate ground level aerial dust exposure.



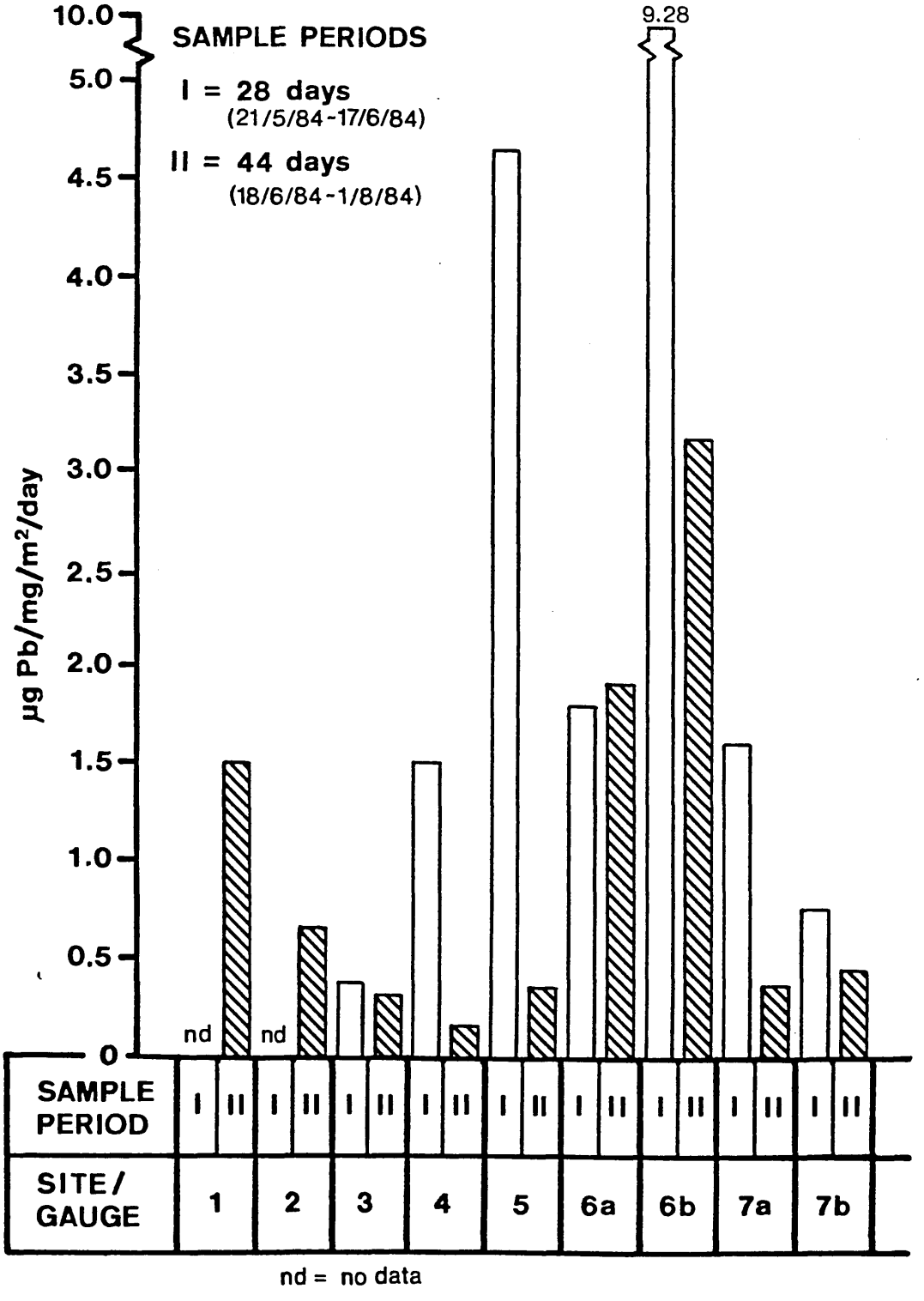
The duplicate gauges at Sites 6 and 7 provide an indication of the reproducibility of the gauges in terms of their ability to monitor dust deposition. Dust deposited material was collected and analysed for lead in the same way as for the BSDDG. The results are presented in Table 29 and illustrated in Figure 26.

6.3.1. Discussion.

Measurement of the aerial exposure to lead of the plant at the different study sites was problematic. Whilst the BSDDG gives a general indication of the extent of aerial contamination in the local area this concentration in no way relates to the levels of exposure for the potato plants. From the data in Table 28, illustrated in Figure 24, it is apparent that plants growing at Site 6 near the lead rake should have had the greatest aerial lead exposure in May (1.17 μg Pb/mg/$m^2$/day), the roadside transect Site 5 the second largest exposure in June (0.48 μg Pb/mg/$m^2$/day) and Site 7 the Wentworth control site the lowest aerial exposure in July (0.04 μg Pb/mg/$m^2$/day). It is interesting to note how unreliable the BSDDG results can be by comparing the results for sites 7A and 7B during May, June and July. Whilst May and July give acceptable comparable rates of dust deposition, gauge 7A produced a rate 1.5 times higher than gauge 7B during June despite the gauges being only 1 metre apart.

Similar trends are also reflected in the data (Table 29) obtained using the GLDDG illustrated in Figure 26, though the GLDDGs show considerably higher dust deposition rates. The collecting bowl of the BSDDG is approximately 1.2 m above the ground whereas the

Figure 26. GLDDG results showing lead deposition/day at sites 1 to 7 during two sampling periods.



GLDDGs are only 15 cm above the ground and may be capturing dust from a level at which the plants are exposed to aerial dust deposition locally remobilised at ground level. Apparently the greatest rate of dust deposition was in the early period (Figure 26, period I.) of plant growth, possibly due to high winds during May which may have mobilised more material. During the second period the data shown in Figure 26 clearly illustrates the distance decay of exposure from roadside (Sites 1 and 2) to the centre of the field at Site 5. The lower level at Site 2 is possibly due to shielding effects of the field boundary wall at this site location. Unfortunately the samples for period I at Sites 1 and 2 were lost due to vandalism. The very high dust deposition rate at Site 5, period I (4.64 μg Pb/mg/$m^2$/day, implies even higher levels for the lost data, if the distance decay pattern observed for period II occurred in period I. Again Site 6 near the lead rake shows some of the highest dust deposition rates, though deposition rates at Site 7 were higher than might have been expected. Comparison of the results for duplicate GLDDGs at Sites 6a/6b and 7a/7b suggest poor reproducibility of the gauge results over a short distance. Perhaps due to different rates of particle blow out from the collecting funnel.

Since the capture surface of the dust deposit gauges in no way simulates the capture surface of a leaf the procedure described in section 6.5 (ie. involving cutting exposed leaves in half down the central vein, one half washed, the other left unwashed and lead in dust deposition determined) may provide a better estimate of the actual exposure of the plants. However the dust deposit gauges do

give a general indication of lead in dust deposition at the study sites.

## 6.4. Estimation of tuber yield, plant growth and moisture content.

To assess the tuber yield on harvesting all the tubers from each pot were washed using the procedure described previously and weighed. The results are given in Table 30 and are reported on a wet weight basis per row (3 potato plants) together with soil lead concentrations for purposes of comparison. The tuber crops for all sites were photographed. Three of the photographs are presented in Plates VIII, IX and X, showing the relative tuber yield for plants growing at Site 1 (Roadside), Site 6 (Rowter Farm) and Site 8 (Greenhouse), respectively. The tubers are grouped according to soil growth media and labelled L (soil medium X), M (soil medium Y) and H (soil medium Z). L, M and H indicate if the soil was of a 'low', 'medium' or 'high' soil lead concentration.

An estimate of overall plant growth (aerial parts) was obtained by washing and drying all the stem material from all plants in each pot. The plant material was oven dried and the combined dry weight stem yield calculated for each pot. The height of each stem was also measured and the mean stem height together with combined dry weight of stem material from each pot is reported in Table 31. The measured stem height gives an indication of plant stunting.

Table 30. Tuber yield (ALL SITES)

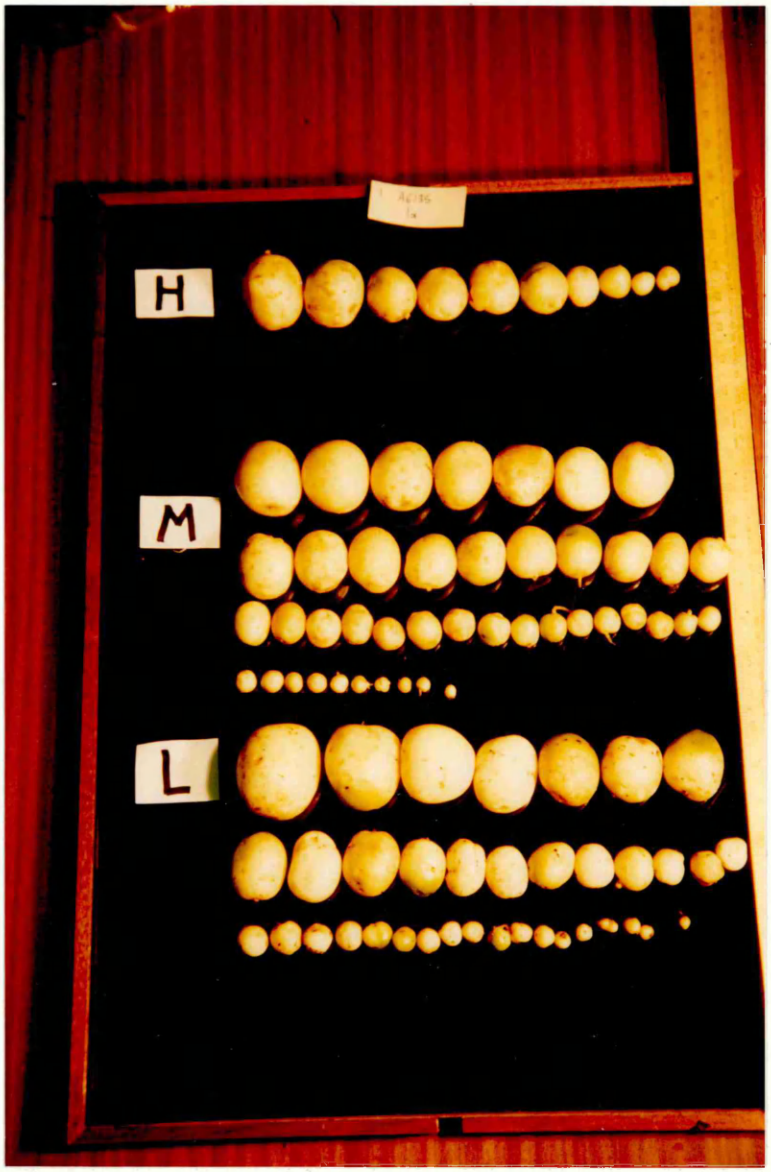
| SOIL MEDIUM/ SITE LOCATION. | | TUBER YIELD. (g. wet Wt. per row) |
|---|---|---|
| X 1 | | 538 |
| X 2 | | 364 |
| X 3 | | 442 |
| X 4 | | 528 |
| X 5 | | 584 |
| X 6 | | 666 |
| X 7 | | 410 |
| X 8 | | 472 |
| Mean | = | 501 |
| Std. Dev. | = | 98 |
| RSD.% | = | 20 |
| Y 1 | | 506 |
| Y 2 | | 445 |
| Y 3 | | 542 |
| Y 4 | | 628 |
| Y 5 | | 700 |
| Y 6 | | 757 |
| Y 7 | | 540 |
| Y 8 | | 567 |
| Mean | = | 586 |
| Std. Dev. | = | 103 |
| RSD.% | = | 18 |
| Z 1 | | 195 |
| Z 2 | | 141 |
| Z 3 | | 197 |
| Z 4 | | 191 |
| Z 5 | | 203 |
| Z 6 | | 185 |
| Z 7 | | 123 |
| Z 8 | | 142 |
| Mean | = | 173 |
| Std. Dev. | = | 30 |
| RSD.% | = | 17 |

---

Mean soil lead concentrations:

| | 'Total' (µg/g). | 'Available' (mg/l). |
|---|---|---|
| Soil Medium X | 73 | 28 |
| Soil Medium Y | 4120 | 2690 |
| Soil Medium Z | 38000 | 32200 |

PLATE VIII.




Tuber yield at site 1 (Roadside) for soil media X, Y and Z.
L = 'low' lead concentration, soil medium X
M = 'medium' lead concentration, soil medium Y
H = 'high' lead concentration, soil medium Z

PLATE IX.


Tuber yield at site 6 (Rowter Farm) for soil media X, Y and Z.
L = 'low' lead concentration, soil medium X
M = 'medium' lead concentration, soil medium Y
H = 'high' lead concentration, soil medium Z

PLATE X.


Tuber yield at site 8 (Greenhouse) for soil media X, Y and Z.
L = 'low' lead concentration, soil medium X
M = 'medium' lead concentration, soil medium Y
H = 'high' lead concentration, soil medium Z

Table 31. Stem yield (ALL SITES)

| SOIL MEDIUM/ SITE LOCATION. | STEM YIELD. (Washed stems per row) (g. dry Wt.) | (Mean stem height) (cm.) | MASS PER UNIT HEIGHT ie. (Wt. of Washed dry stem ÷ mean stem height) (g/cm x $10^{-3}$) |
|---|---|---|---|
| X 1 | 1.7 | 22 | 77 |
| X 2 | 0.6 | 19 | 32 |
| X 3 | 1.7 | 18 | 94 |
| X 4 | 1.1 | 14 | 78 |
| X 5 | 2.0 | 26 | 77 |
| X 6 | 0.8 | 8 | 100 |
| X 7 | 0.7 | 10 | 70 |
| X 8 | 5.3 | 46 | 115 |
| Mean = | 1.7 | 20.4 | 80.4 |
| Std. Dev. = | 1.5 | 12 | 25 |
| RSD.% = | 89 | 59 | 31 |
| Y 1 | 2.1 | 23 | 91 |
| Y 2 | 1.4 | 23 | 61 |
| Y 3 | 3.0 | 29 | 104 |
| Y 4 | 1.1 | 16 | 69 |
| Y 5 | 2.0 | 27 | 74 |
| Y 6 | 0.7 | 9 | 78 |
| Y 7 | 1.7 | 15 | 113 |
| Y 8 | 3.8 | 43 | 88 |
| Mean = | 1.98 | 23.1 | 84.6 |
| Std. Dev. = | 1 | 10 | 18 |
| RSD.% = | 51 | 43 | 21 |
| Z 1 | 0.6 | 20 | 30 |
| Z 2 | 0.6 | 14 | 43 |
| Z 3 | 0.2 | 8 | 25 |
| Z 4 | 0.5 | 10 | 50 |
| Z 5 | 0.5 | 10 | 50 |
| Z 6 | 0.1 | 2 | 50 |
| Z 7 | 0.3 | 5 | 60 |
| Z 8 | 0.9 | 18 | 50 |
| Mean = | 0.46 | 10.9 | 44.8 |
| Std. Dev. = | 0.26 | 6.2 | 12 |
| C.V.% = | 56 | 57 | 27 |

---

Mean soil lead concentrations:

| | 'Total' (µg/g). | 'Available' (mg/l). |
|---|---|---|
| Soil Medium X | 73 | 28 |
| Soil Medium Y | 4120 | 2690 |
| Soil Medium Z | 38000 | 32200 |

Division of the weight of dry stem material by the mean stem height gives an estimate of plant mass per unit height, with 'leggy' plants having a low value and compact strong growth having a high value. This may be indicative of variations in local environmental factors such as temperature and light, for a given soil medium, and may be significant in terms of dilution of the lead distribution in leggy plants compared with compact plants.

In order to allow comparisons of the dry weight data with the fresh weight concentrations often reported in the literature an estimate of the percentage water loss on drying was obtained by drying bulked samples of plant material. Bulked samples of leaf, petiole, stem, and root tissue were dried at 102°C ± 2°C for 18 hours, together with a bulked sample of tuber material dried at 60°C for 24 hours followed by 18 hours at 102°C ± 2°C [128]. The percentage water loss on drying is shown in Table 32.

Table 32. Percentage water loss on drying parts of a potato plant.
(For conversion of Dry wt. to Wet wt.)

| PLANT TISSUE. | % WATER LOSS ON DRYING. |
|---|---|
| Leaf. | 91 |
| Petiole. | 95 |
| Stem. | 91 |
| Roots. | 91 |
| Tuber (peeled). | 81 |

6.4.1. Discussion.

It might be expected that with available lead concentrations in the three soils X, Y and Z of 28 mg/l, 2690 mg/l and 32200 mg/l respectively tuber yield would be affected. From Table 30 it can be seen that for tubers grown in soil medium X the mean yield was 501 g. wet wt./row with an RSD between the 8 study sites of 20%. However for tubers grown in soil media Y and Z the mean yield and (RSD%) were 586 g. wet wt./row (18%) and 173 g. wet wt./row (17%). It is apparent that tuber yield is not directly linked to available lead in soil since soil medium Y had the best overall yield despite an available lead concentration of 2690 mg/l. However tuber yield was considerably reduced for plants growing in soil medium Z with an available lead concentration of 32200 mg/l. It is interesting that the plants grew at all considering the potential for plant toxicity from the lead and possible synergistic effects of other elements. This may be in part due to the standard fertiliser application given to all pots.

It is impossible to state categorically that the reduction in tuber yield for plants grown in soil Z was a result of lead toxicity alone since in comparison with the other two soil media X and Y, concentrations of Fe, Mg and Mn were low and for the phytotoxins Cu, Ni and Zn high (see Table 25). In addition it can be seen from Table 25 that final levels of N and P were high in soil medium Z (30 mg/l and 47 mg/l) compared with soil media X and Y (N = 24.3 mg/l and 15.1 mg/l, and P = 20.4 mg/l and 16.9 mg/l respectively). This also suggests that for plants growing in soils X and Y, N and P were utilised in production of biomass (ie.

as storage organs such as tubers). However toxicity resulted in an apparent reduction in the utilisation of N and P in the case of plants growing in soil medium Z. This is possible since lead is known to be actively sequestered in the roots of plants, competing with phosphates and other nutrients for binding sites within cells ([361]). Active transport mechanisms may also suffer from enzyme inactivation. The organic content 13%, 16.4% and 4.2% (loss on ignition, Table 25) for soil media X, Y and Z respectively may also be related to the tuber yield. The differences in tuber yield can be seen quite clearly in plates VIII, IX and X.

A similar variation in yield can be seen for the aerial parts of plants (see Table 31). The mean stem height for plants growing in soil medium X was 20.4 cm, soil medium Y 23.1 cm and soil medium Z only 10.9 cm. This is also reflected in the data indicating stunting, (Column 4, Table 31.) with plants growing in soil media X, Y and Z having means of 80.4, 84.6 and 44.8 g/cm x $10^{3}$. This is best shown in Plate XI where the relative stunting of plants at Site 7 after 6 weeks in the field is displayed. The effect of stunting can have implications for the exposure of the aerial plant parts to lead. Stunted plants may be susceptible to further lead exposure not just from dust deposition but also the additional inputs from rainsplash due to their closer proximity to the ground. This would exert a 'multiplier effect' and is discussed in more detail in the following sections.

PLATE XI.

Relative stunting of plants after 6 weeks in the field (Site 7.).
Left = plants in soil medium X.
Middle = plants growing in soil medium Y.
Right = plants growing in soil medium Z.

## 6.5. Distribution of lead in potato plants using a perchloric/nitric acid extraction procedure.

Whilst dust deposit gauges (discussed in section 6.3.) give an indication of the general dust deposition in a specific location they in no way represent the extent of exposure of individual plants. The amount of lead incident on plant surfaces is governed by many factors in the micro environment of a leaf or stem surface. These include cuticular factors such as roughness, hairyness, waxy texture, sticky surface, vein structure and surface shape [9]. Consequently measurement of direct dust exposure is problematic since it is well nigh impossible to replicate the particle capturing ability of a surface even if that surface were homogeneous. Little [231,254] overcame this problem to a certain extent by cutting leaves down the central leaf vein and analysing washed and unwashed bulked halves to test washing efficiency and plant exposure. Cataldo, et al. [255] however, have reported that even with diligent washing techniques it is unlikely that all particles can be removed and some may become embedded in the cuticular structure [256].

In order to assess the direct exposure of the aerial parts of the plants to dust deposition, bulked washed and unwashed plant samples were analysed for lead using the procedure described next. Subtraction of the washed concentration from the unwashed concentration gives an estimate of the surface dust exposure. It should be remembered that this only gives an indication of the actual surface contamination on the date of sampling. During the growth period this exposure will have fluctuated due to periodic removal of dust and re-addition of new particulate material by

wind and rain. The analytical procedure was also applied to root, tuber and tuber peel tissue in order to provide data for comparison with the distributions observed using the solid sample microsampling cup procedure.

6.5.1. Sampling, sample preparation and analysis.

Once the plant material required for the analytical procedure employing the microsampling cup discussed in section 6.6, had been selected the remaining vegetation in each pot was divided into leaf, stem, root, tuber and tuber peel tissue. All the leaves and stems from each of the three plants in the pots were cut in half, down the central leaf vein and across the diameter of the stem respectively. One half was retained unwashed and the other half, together with root, tuber peel and tuber material, subjected to the vigorous washing procedure described previously in section 5.1.4.

The plant tissues were then dried in an oven as described above in section 6.4. The dried samples were then ground, using a mixer mill, to pass through a 1 mm nylon sieve ready for digestion. A plant digest was prepared, using the following procedure, based on the standard MAFF method 4 for plant materials ([128]) and the 1 + 1 $HNO_3$ block digestion procedure described earlier in Chapter 2.

For each of the plant samples, approximately 2 g of the dried sample (ground to pass a 1 mm sieve) was added to acid washed pyrex digestion tubes. In the case of the peeled tuber material 4 g of sample was used in anticipation of a low lead

concentration. Then 15 ml of digestion acid (1 vol. 60% $HClO_4$ to 4 vol. 70% $HNO_3$) was added to the tubes which were covered and left to stand overnight. The tubes were heated using the block digestion procedure until the initial reaction started at approximately 100°C. The temperature was then increased and the contents allowed to gently reflux in the tall digestion tubes for about 2 hours until oxidation was complete. The digest should be a clear red brown liquid, but in the unwashed samples the presence of dust caused the digest to be darker in appearance. When oxidation was complete the temperature of the aluminium heating blocks was raised causing the tubes to produce white fumes and the volume of acid to be reduced to about 5 ml. If the solution darkened considerably on reducing the volume, the tubes and contents were cooled and a further 1 - 2 ml of $HNO_3$ were added to the tubes and re-heated. The final contents are usually colourless, unless as in the case of the unwashed samples iron and other minerals are present. The digest in the tubes was heated further until all the perchloric acid was volatilised and the tube contained a dry residue. When the tube was cool, 5 ml 2 M HCl was added, brought to the boil and simmered gently for 5 minutes.

Without delay the contents of the tubes were quantitatively transferred into a 25 ml volumetric flask and diluted to 25 ml. The samples were then filtered through a Whatman No. 541 filter paper and acid matched lead standards prepared. Total lead in leaf, stem, tuber peel and root tissue was determined at 283.3 nm, and tuber tissue at 217.7 nm, by flame AAS using a Varian Model 1275 with background correction.

6.5.2. Results and discussion.

The contribution of lead from aerial and immediate soil sources to the distribution of lead observed in plants growing in the three soils is difficult to assess. This is primarily due to problems in assessing the actual level of aerial contamination incident on each plant and the synergistic effects of the different soil components in the three different soil media upon plant uptake. However the following general observations may be made from the data.

The results obtained using the conventional nitric/perchloric procedure provide comparative data for use with results obtained using the micro sampling cup procedure. The nitric/perchloric digestion results also enable an estimate to be made of the amount of surface contamination of leaf and stem tissue at each of the study sites. The concentration of total lead in washed and unwashed leaf material is given in Table 33 and subtraction of column B from column A gives an estimate of leaf surface contamination at each site for the three soil media X, Y and Z. Similarly the results for stem material are presented in Table 34. Table 35 gives the mean total concentrations of lead found in duplicate analyses of roots, tuber peel and tubers using the acid digestion procedure. The mean soil lead concentrations have been included in these tables for ease of comparison of the data.

The overall mean concentrations for sites 1 - 7, are summarized together with the relevant soil and aerial contamination data in Table 36. Site 8 (the greenhouse) has been left out of the

Table 33. Lead in potato plants by acid digestion procedure. Results for leaves (ALL SITES) (µg/g dwt)

| SOIL MEDIUM/ SITE LOCATION. | | LEAF UNWASHED. (A)* | LEAF WASHED. (B)* | LEAF SURFACE. CONTAMINATION. (A-B)* |
|---|---|---|---|---|
| X 1 | | 140 | 23 | 117 |
| X 2 | | 110 | 8 | 102 |
| X 3 | | 48 | 9 | 39 |
| X 4 | | 26 | 8 | 18 |
| X 5 | | 34 | 8 | 26 |
| X 6 | | 65 | 30 | 35 |
| X 7 | | 51 | 9 | 42 |
| X 8 | | 12 | 5 | 7 |
| Mean | = | 60.8 | 12.5 | 48.3 |
| Std. Dev. | = | 44 | 8.9 | 40 |
| RSD.% | = | 72 | 71 | 82 |
| Y 1 | | 175 | 69 | 106 |
| Y 2 | | 141 | 51 | 90 |
| Y 3 | | 95 | 48 | 47 |
| Y 4 | | 75 | 60 | 15 |
| Y 5 | | 70 | 43 | 27 |
| Y 6 | | 190 | 133 | 57 |
| Y 7 | | 102 | 51 | 51 |
| Y 8 | | 32 | 26 | 6 |
| Mean | = | 110 | 60 | 49.9 |
| Std. Dev. | = | 55 | 32 | 35 |
| RSD.% | = | 50 | 53 | 70 |
| Z 1 | | 1236 | 67 | 1169 |
| Z 2 | | 765 | 54 | 711 |
| Z 3 | | 1142 | 78 | 1064 |
| Z 4 | | 1150 | 280 | 870 |
| Z 5 | | 2057 | 142 | 1915 |
| Z 6 | | 4110 | 302 | 3808 |
| Z 7 | | 1591 | 92 | 1499 |
| Z 8 | | 651 | 19 | 632 |
| Mean | = | 1588 | 129 | 1458 |
| Std. Dev. | = | 1112 | 106 | 1039 |
| RSD.% | = | 70 | 82 | 71 |

(* = Results based on 1 analytical determination.)

---

Mean soil lead concentrations:

| | 'Total' (µg/g) | 'Available' (mg/l) |
|---|---|---|
| Soil Medium X | 73 | 28 |
| Soil Medium Y | 4120 | 2690 |
| Soil Medium Z | 38000 | 32200 |

Table 34. Lead in potato plants by acid digestion procedure. Results for stems (ALL SITES) (µg/g dwt)

| SOIL MEDIUM/ SITE LOCATION. | | STEM UNWASHED. (A)* | STEM WASHED. (B)* | STEM SURFACE CONTAMINATION. (A-B)* |
|---|---|---|---|---|
| X 1 | | 26 | 4 | 22 |
| X 2 | | 24 | 9 | 15 |
| X 3 | | 15 | 3 | 12 |
| X 4 | | 18 | 4 | 14 |
| X 5 | | 15 | 4 | 11 |
| X 6 | | 33 | 8 | 25 |
| X 7 | | 17 | 3 | 14 |
| X 8 | | 9 | 5 | 4 |
| Mean | = | 19.6 | 5.0 | 14.6 |
| Std. Dev. | = | 7.6 | 2.3 | 6.5 |
| RSD.% | = | 39 | 45 | 45 |
| Y 1 | | 300 | 300 | 0 |
| Y 2 | | 358 | 364 | -6 |
| Y 3 | | 312 | 349 | -37 |
| Y 4 | | 476 | 518 | -42 |
| Y 5 | | 313 | 322 | -9 |
| Y 6 | | 512 | 431 | 81 |
| Y 7 | | 338 | 390 | -52 |
| Y 8 | | 250 | 250 | 0 |
| Mean | = | 357 | 366 | -8.1 |
| Std. Dev. | = | 91 | 83 | - |
| RSD.% | = | 25 | 23 | - |
| Z 1 | | 1447 | 131 | 1316 |
| Z 2 | | 1110 | 225 | 885 |
| Z 3 | | 1235 | 132 | 1103 |
| Z 4 | | 807 | 227 | 580 |
| Z 5 | | 1254 | 212 | 1042 |
| Z 6 | | 3108 | 396 | 2712 |
| Z 7 | | 1927 | 390 | 1537 |
| Z 8 | | 212 | 304 | -92 |
| Mean | = | 1388 | 252 | 1135 |
| Std. Dev. | = | 853 | 103 | 808 |
| RSD.% | = | 62 | 41 | 71 |

(* = Results based on 1 analytical determination)

---

Mean soil lead concentrations:

| | 'Total' (µg/g) | 'Available' (mg/l) |
|---|---|---|
| Soil Medium X | 73 | 28 |
| Soil Medium Y | 4120 | 2690 |
| Soil Medium Z | 38000 | 32200 |

Table 35. Lead in potato plants by acid digestion procedure. Results for roots, tuber peel and tuber (peeled) (ALL SITES) (µg/g dwt)

| SOIL MEDIUM/ SITE LOCATION. | | ROOTS.** (Washed) | TUBER PEEL.** (washed) | TUBER.** (peeled) |
|---|---|---|---|---|
| X 1 | | 18 | 6.0 | 1.4 |
| X 2 | | 32 | 3.1 | 1.2 |
| X 3 | | 28 | 2.7 | 1.1 |
| X 4 | | 21 | 2.4 | 1.4 |
| X 5 | | 23 | 3.7 | 1.0 |
| X 6 | | 45 | 3.8 | 3.0 |
| X 7 | | 21 | 2.6 | 1.2 |
| X 8 | | 15 | 2.2 | 1.0 |
| Mean | = | 25.4 | 3.31 | 1.41 |
| Std. Dev. | = | 9.6 | 1.2 | 0.7 |
| RSD.% | = | 38 | 37 | 47 |
| Y 1 | | 835 | 19.4 | 5.8 |
| Y 2 | | 761 | 15.1 | 5.7 |
| Y 3 | | 762 | 15.8 | 5.2 |
| Y 4 | | 718 | 27.8 | 5.2 |
| Y 5 | | 630 | 26.6 | 4.8 |
| Y 6 | | 865 | 21.6 | 4.0 |
| Y 7 | | 714 | 17.5 | 5.2 |
| Y 8 | | 1416 | 23.4 | 7.5 |
| Mean | = | 837.6 | 20.9 | 5.42 |
| Std. Dev. | = | 245 | 4.8 | 1 |
| RSD.% | = | 29 | 23 | 19 |
| Z 1 | | 8321 | 164 | 6.2 |
| Z 2 | | 8086 | 199 | 4.1 |
| Z 3 | | 8618 | 216 | 4.2 |
| Z 4 | | 10979 | 235 | 4.6 |
| Z 5 | | 10751 | 503 | 7.7 |
| Z 6 | | 9628 | 378 | 7.6 |
| Z 7 | | 6451 | 233 | 5.0 |
| Z 8 | | 5138 | 437 | 7.6 |
| Mean | = | 8496 | 296 | 5.88 |
| Std. Dev. | = | 2007 | 126 | 1.6 |
| RSD.% | = | 24 | 42 | 27 |

(** = Results based on mean of 2 analytical determinations.)

---

Mean soil lead concentrations:

| | 'Total' (µg/g) | 'Available' (mg/l) |
|---|---|---|
| Soil Medium X | 73 | 28 |
| Soil Medium Y | 4120 | 2690 |
| Soil Medium Z | 38000 | 32200 |

Table 36. Summary of the mean lead concentrations for sites 1 - 7 for soil media X, Y and Z.
(Acid digestion procedure results)

| | | SOIL MEDIA. | | |
|---|---|---|---|---|
| | | X | Y | Z |
| | | Pb Conc. µg/g | Pb Conc. µg/g | Pb Conc. µg/g |
| Leaf surface contamination. (Column 4, Table 33) | = | 54 | 56 | 1580 |
| Leaf tissue concentration. (Column 3, Table 33) | = | 14 | 65 | 145 |
| Stem tissue concentration. (Column 3, Table 34) | = | 5.0 | 382 | 245 |
| Tuber tissue concentration. (Column 4, Table 35) | = | 1.5 | 5.1 | 5.6 |
| Tuber peel concentration. (Column 3, Table 35) | = | 3.5 | 21 | 275 |
| Root tissue concentration. (Column 2, Table 35) | = | 27 | 755 | 8980 |
| EDTA extractable in soil (mg/l) (Column 5, Table 26) | = | 28 | 2680 | 32900 |
| Total Pb in soil. (Column 2, Table 26) | = | 72 | 4080 | 38200 |

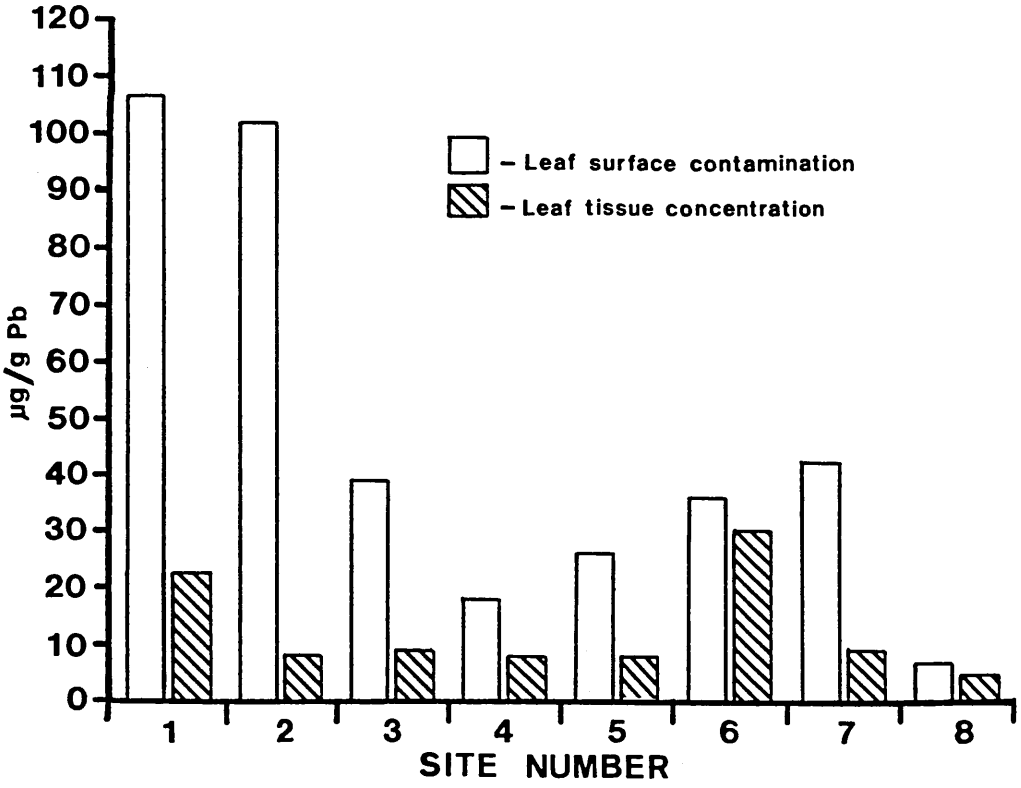
(N.B. - Site 8, Greehouse excluded from calculations)

calculations in Table 36 since the plants were not grown under field conditions. It is apparent from Tables 33 and 34 that aerial contamination resulting from periodic ventilation of the greenhouse was low compared with the other sites and this resulted in reduced aerial upake under these conditions.

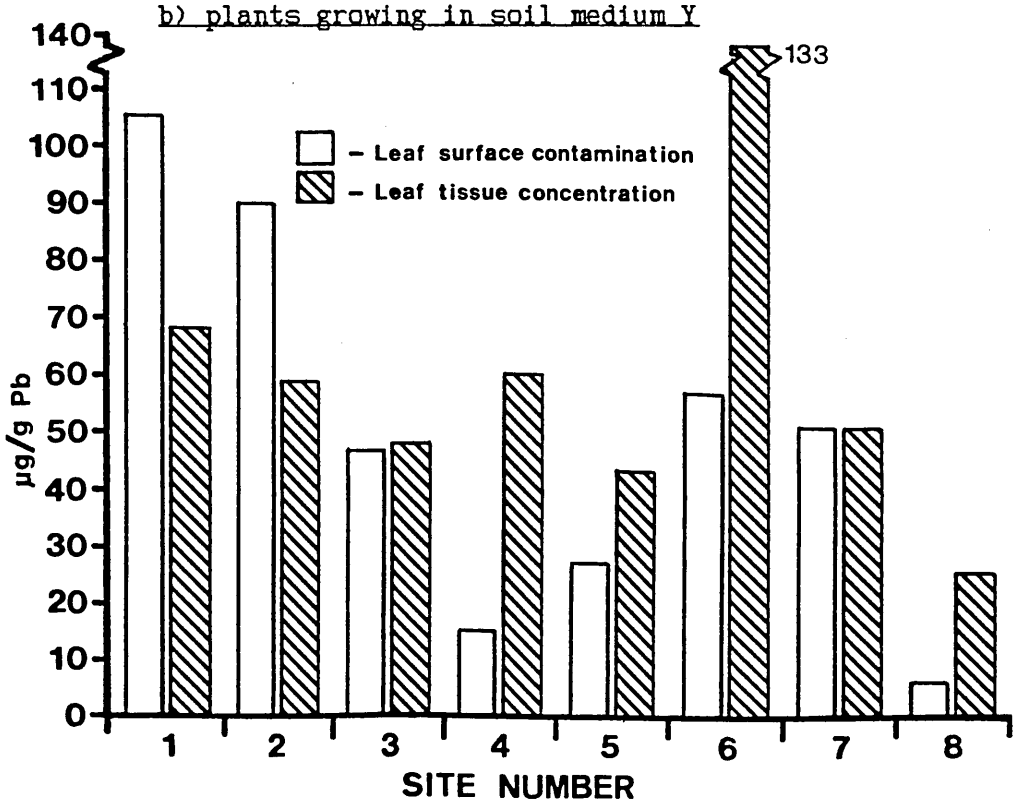
From the data in Table 33 it is not possible to establish a direct relationship between high surface contamination and increased concentration in leaf tissue. This is best illustrated for soil media X and Y in Figures 27 a. and b. The results relating to soil media Z have not been illustrated but are discussed below. Examination of Figure 27 a. shows that leaf tissue concentration (ie. washed) is not significantly increased with an increase in surface lead contamination. However at Site 6 the aerial contamination of the leaf surface level is consistently high for all plants (35, 57 and 3808 μg/g for soil media X, Y and Z respectively, Table 33.) resulting in higher leaf tissue concentrations of 30, 133 and 302 μg/g respectively (Table 33.). Examination of Table 31 (See section 6.4.1.) shows that all plants grown at Site 6 were considerably stunted when compared with the other sites, making the plants more susceptible to contamination by rain splash from the soil media. This stunting may have been due to phytotoxicity resulting from metals in the soils surrounding the pots leaching into the soils or being blown onto plants. However the former can be discounted since there is no appreciable increase in the measured levels of EDTA extractable lead in any of the soils at Site 6 compared with the other sites. It is suggested therefore that the stunting is most likely due to the effects of the local climate at Site 6 since the plants were

Figure 27. Comparison between leaf concentration and surface contamination at all sites for:

a) plants growing in soil medium X




b) plants growing in soil medium Y



considerably exposed to the effects of wind, cooler temperature and higher altitude.

Different rates of lead accumulation for plants growing in colder conditions have been observed by Waughman, et al. [401]. They noted that plants grown in cold frames had a greater growth rate but did not take up lead and zinc to the same extent as plants grown outside cold frames. This may explain the differences observed for plants grown at Site 6 near an exposed lead rake and Site 8 within a greenhouse. Plants growing in soils X and Y in the greenhouse grew to 46 cm and 43 cm respectively (Table 31). However at the cooler exposed Site 6 the mean stem heights were only 8 cm and 9 cm respectively. The corresponding effects on lead uptake and accumulation in the leaves of these plants can be seen in Figure 27. Plants from Site 6 have consistently higher accumulations of lead in leaf tissue than those at Site 8.

Generally, for soil X the leaf lead concentration is stable, the overall mean for sites 1-7 being 14 μg/g with a mean surface contamination level of 54 μg/g (Table 36). Comparison of the histograms showing leaf surface contamination in Figure 27 for soil media X and Y indicates an almost identical pattern of surface contamination for Sites 1 - 8. This suggests that the procedure used was reasonably accurate in estimating the exposure of leaves to aerial contamination. The general trends between the eight sites are similar to those identified using the GLDDGs. If leaf surface contamination were the only source of lead in the leaf it would have been expected that the leaves of the plants growing in soil Y would have had the same lead concentration of

those grown in soil X since they have similar surface contamination levels. Clearly the leaf tissue concentrations of the plants, illustrated in Figure 27, are consistently higher for plants grown in soil medium Y than those grown in soil medium X. The overall differences are highlighted in Table 36 where for soil media X and Y the mean leaf surface contamination (sites 1-7) is 54 and 56 μg/g respectively. However the mean leaf tissue concentrations are 14 and 65 μg/g. Clearly the higher concentration of lead in leaf tissue observed for plants growing in soil medium Y must be partly due to surface uptake from aerial contamination combined with a much greater uptake from soil by translocation from the roots to the leaves.

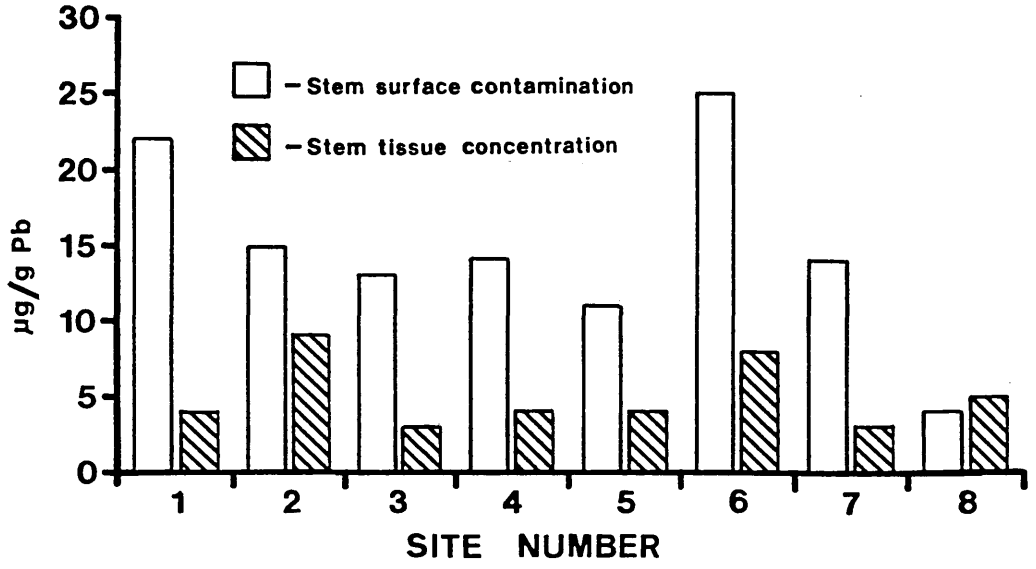
This suggestion is supported further by the results for the leaves of plants growing in soil Z. On first consideration the data for soil media Z could seem erroneous since the plants were grown in the same locations as the other plants. The very high surface contamination may be explained by the fact that all the plants grown in soil Z were considerably stunted with a mean stem height less than half of that of the plants growing in soils X and Y (Table 31). The stems on average achieved a height of about 10 cm and it is suggested that rain splash, with the exception of Site 8 (greenhouse), has contaminated the leaves with the highly contaminated soil. It is also possible that some of the highly contaminated soil may have been left on leaf surfaces as a residual deposit from early emergence of the shoots from the soil. This latter effect could explain how the leaves of the plants grown in the greenhouse (Site 8) became contaminated even though they were not subjected to rain splash.

The surface contamination, though very great (1580 µg/g, Table 36) presumably as a result of stunting and the accentuated impact of rain splash, has not apparently increased the leaf tissue concentration to the extent that might have been expected, with an increase to only 145 µg/g. This not only suggests that lead may be taken up from the roots of the potato plant into the leaf, but that at the leaf surface there appears to be a considerable barrier to foliar entry and uptake. This supports the findings of Arvik and Zimdahl [69] who suggested that only extremely small amounts of lead could penetrate cuticles of leaves. The amount of lead absorbed through the leaves and transported to other parts of a plant may vary considerably between plant species. Dollard [156] using Pb210 found the amount transported to the storage organs from leaf absorption was 0.05 - 0.28% in radish and 0.43% in carrots. In terms of total root burden, foliar absorption accounted for about 35% in radish and only 3% in carrots. It is possible that leaf structure may be significant in producing these variations between plants.

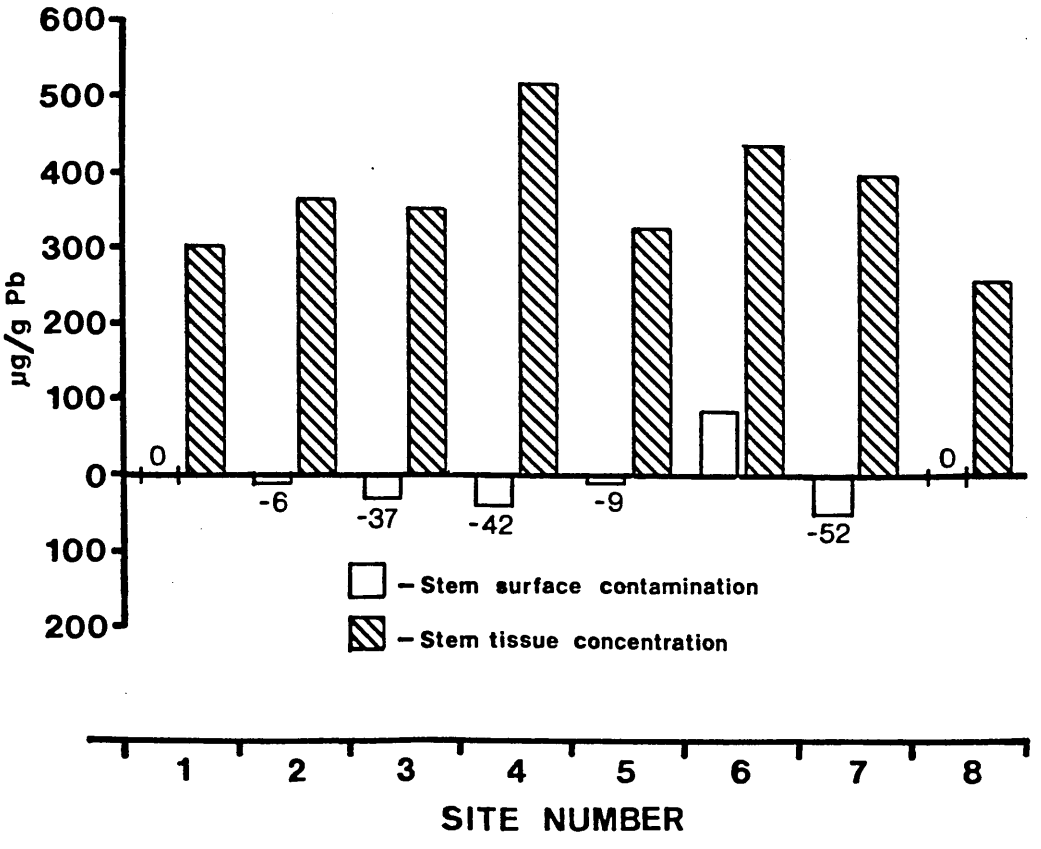
Further evidence of uptake from the roots and transport in the vascular tissue into the upper parts of the plants can be seen in the results for stem lead concentrations in Table 34. For instance, whilst there is little evidence of any appreciable accumulation in the stems of plants growing in soil X (mean stem concentratration 5 µg/g, Table 36), there is a considerable accumulation in the stems of plants grown on soils Y and Z (382 and 245 µg/g respectively, Table 36). The magnitude of difference in stem concentrations for plants growing in soil media X and Y is best seen in Figure 28 a. and b. The tissue levels are so high in

Figure 28. Comparison between stem concentration and surface contamination at all sites for:

a) plants growing in soil medium X




b) plants growing in soil medium Y



the stems of the plants grown on soil Y that surface contamination is masked and could not be detected, with the exception of Site 6 where the plants were stunted and a measurable increased surface contamination was found. This is best illustrated in Figure 28 b. and explains the reason for the apparent negative results for stem surface contamination.

In the case of the plants growing in soil medium Z it has already been shown that these plants were stunted, leading to probable increased surface contamination from rain splash. This resulted in a very high mean level of stem surface contamination for sites 1 - 7 of 1310 μg/g (Table 34). Site 8 (greenhouse) is rejected from this calculation since it did not suffer rain splash with a negative stem surface contamination -92 μg/g (Table 34.). Despite these high contamination levels there appears to be less lead accumulated in the stems of plants grown at Sites 1 - 7 on soil Z (245 μg/g) compared with those growing in soil Y (383 μg/g). This suggests that lead is not absorbed across the stem tissue from the cuticle to inner tissue to any great extent. If it was, then it might have been reasonable to expect the stem tissue concentration of plants growing in soil medium Z to be higher than those in soil Y where the mean stem contamination was negligible at -9.3 μg/g (Sites 1 - 7, Table 34). In reality the mean stem tissue concentration for sites 1 - 7 was lower for plants growing in soil medium Z (245 μg/g) than for plants growing in soil medium Y (382 μg/g, Table 36). It is suggested that lead is therefore transported from the roots, via the vascular system into the stem and ultimately the leaves, with only small contributions via the

stem or leaf tissue and that less active uptake has occurred in the stunted plants on soil Z.

Given the mean EDTA extractable soil lead levels (Table 36) of 2680 µg/g and 32900 µg/g, for soils Y and Z respectively, it might have been expected that the stem tissue lead concentration for plants grown in soil Z would be higher than those grown in soil Y. From the results the reverse is true which suggests that lead was possibly actively sequestered in the root sytems of the plants growing on soil Z causing some toxicity and reduced nutrient demand or may have competed with phosphates and other nutrients, accounting for the low utilisation of N, P and K in this soil (Table 25). This would also explain the stunting of the plants growing in soil medium Z.

The possibility that lead was sequestered in the root system may explain the very high concentrations of lead in the roots of plants grown in soil Z Sites 1 - 7 (8980 µg/g, Table 36) compared to only 27 µg/g and 755 µg/g in the roots of plants grown in soil media X and Y respectively. Site 8 is excluded from these calculations since the roots may have developed in a different way to plants growing in the field (eg. the greenhouse was warmer). It must be stressed, as already stated, that it is uncertain that all the lead external to the root tissue had been removed despite the vigorous washing procedure. Therefore it could be high by virtue of 'uptake' from soil and/or root surface contamination. The mean concentration of lead in the roots of plants grown in soil X (27 µg/g) was about equal to the mean EDTA extractable lead concentration in the soil. However, for the roots of plants grown

in soils Y and Z the lead concentrations represented 28% and 27% of the EDTA extractable lead concentrations in the respective soils.

If lead were being actively transported from the roots into the stem and to the leaves in the vascular system it might be expected that the concentrations of lead in the tubers would be similar to the levels in the stem tissue if the tuber were supplied with minerals by the xylem. However, since a tuber is a storage vessel composed of a swollen underground stem or rhizome which accumulates materials derived from photosynthetic processes in the leaves, the major route by which a tuber becomes filled must be via the phloem ([160]). It would be reasonable to suggest that for lead to enter the tuber there would either have to be a mechanism of exchange between the phloem and the xylem, and/or that lead would have to cross the foliar barrier into the phloem and negotiate the transport conduits before accumulating in the tuber. At present there is no evidence for either of these pathways being a direct route for lead entering potato tubers, though Dollard ([156]) using Pb 210 has shown that lead applied to the foliage of radish and carrots will enter the swollen storage organ. Harris, et al. ([160]) suggested that the metal content of potato tubers is independent of both soil levels and the metal content of the rest of the plant body, and they did not rule out elevated foliar metal levels as having an influence on tuber development.

The results of the field work reported in this study suggest that lead transported from the roots must be entering the tuber tissue by some mechanism. Even in the lower aerial lead environments

(eg. Site 8, the greenhouse) appreciable increases in levels of lead were found in the tubers grown in the highly contaminated soils Y and Z (7.5 and 7.6 μg/g respectively, Table 35), the source of this lead is more likley to be via the roots rather than the leaves. If aerial deposited lead had been the major source of lead in tuber tissue then for Site 8 Soils Y and Z the tuber concentrations should have been significantly lower than at Sites 1 - 7 since the dust contamination was lower at Site 8. This was not the case suggesting that it is more probable that the source of lead in tubers is related to the roots rather than via the leaves. Excluding Site 8 (greenhouse), there is clearly a significant difference between the mean concentration of lead in tubers grown in soil X (1.5 μg/g) compared with soils Y and Z (5.1 and 5.6 μg/g respectively, Table 36.) and this would appear to be more closely related to soil concentrations rather than changes in aerial lead exposure.

This may have implications, in terms of the health for people if they grow and eat potato tubers from contaminated domestic garden soils. However, even in the extreme cases of soils Y and Z the internal lead levels in the tuber tissue do not exceed the 1 ug/g (wet weight) limit for lead in food ([72]). Perhaps the greatest potential danger to health is from eating jacket potatoes grown in lead contaminated soils, since much larger concentrations are found in the tuber peel 3.5, 21 and 275 μg/g (Table 36) for tubers grown out doors (ie. excluding Site 8) in soils X, Y and Z respectively. Previous investigations by Davies and Crews ([404]) found however, that for potatoes grown in soil contaminated by lead and zinc smelter fumes the contribution of peel to diet

conferred no risk. It must be remembered that this must be seen in the light of the potential additive effects from other sources and their contribution to total exposure for an individual. The elevations in the tuber peel are thought to be caused by the simple inclusion of soil particles within the tissue surface during tuber growth, cork being a dead and passively absorbing tissue with a suberin layer that prevents water loss and may limit transport to the inner tissue.

It has been demonstrated above that the conventional acid digestion procedure provides useful data for assessing the relative contributions from soil and aerial sources to the distribution of lead in bulked samples of plant material. However this masks information on the variations which may occur in a single plant specimen and between individual plant specimens. The microsampling cup procedure used in the next section allows these variations to be examined in normal field samples and provides comparative data for use in the interpretation of the contributions from aerial and soil sources to the distribution of lead in potato plants.

## 6.6. Distribution of lead in potato plants using solid sample microsampling cup flame AAS procedure.

The distribution of lead throughout a single plant specimen growing in each pot has been studied using the solid sample microsampling cup procedure described in Chapter 5. This data together with the environmental and plant tissue digestion data obtained in sections 6.2. to 6.5. enables an assessment of the contribution that lead from soil and aerial sources makes to the

distribution of lead in individual potato plants grown in a variety of field environments.

Whilst the results obtained in Section 6.5., using the acid digestion procedure, give a general indication of the distribution of lead in the various plant parts it is not possible to see how variable the concentrations are within individual plant specimens. The solid sample microsampling procedure has been used to measure the actual concentrations in individual plants growing in each of the study locations.

### 6.6.1. Sampling and sample preparation.

Once the pots had been returned to the laboratory from the field study sites a single specimen, the middle plant of the three potato plants in each pot, was selected for sample preparation. From this plant the tallest stem was selected together with a single leaf, leaf petiole, tuber and root for sample treatment. These were selected in such a way that all parts had been continuous from leaf to root.

It is accepted that all roots, stems, petiole, leaves, etc. from the same plant will vary in concentration of lead to some degree. The samples studied however represent a semi-random selection, since the largest stem was selected in all cases to introduce some standardisation between the sampling locations for plants from different pots.

Each plant specimen was divided into leaf, petiole, stem, tuber and root subsamples and washed separately using the washing procedure described in Section 5.1.4. The washed samples were then sectioned to provide the subsamples indicated in Figure 29. The subsamples were then dried using the drying procedure described in section 5.1.4.

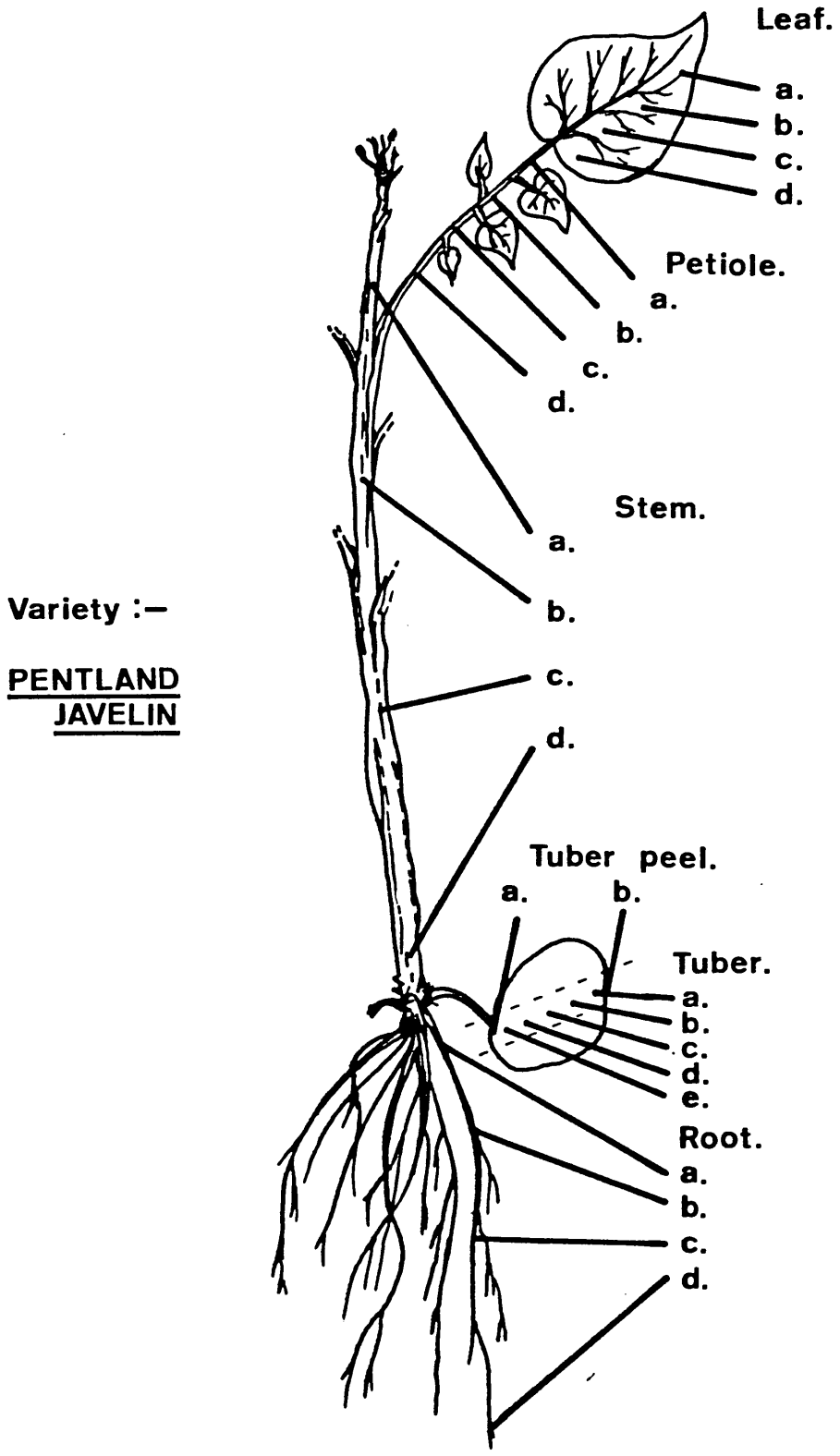
6.6.2. Solid sample microsampling cup procedure.

The dried samples were accurately weighed into nickel microsampling cups, ashed at 440°C for 12 hours and the lead determined using the procedure described in Section 5.1.4. Samples were treated in batches of leaves, stems, roots etc and slurried NIES Pepperbush material was used for quality control of batches.

6.6.3. Results and discussion.

To assess the distribution of lead in the plants growing in the soils at the study sites two analytical procedures were used, perchloric/nitric acid digestion (discussed in section 6.5) and the whole solid sample microsampling cup procedure. Acid digestion of the bulked plant material provided a general idea of the overall concentrations of lead in the various parts of the potato plants. The microsampling cup procedure enabled, for the first time, the examination of the variability that exists within single milligram, whole, solid samples of plant tissue in a part of an individual plant specimen.

Figure 29. The location of plant sample sections used during the micro sampling cup procedure.



The individual results obtained for each of the whole solid microsamples taken from single plants grown in soil media X, Y and Z are given in Appendices 6 p, 6 q and 6 r respectively. The letters (a,b,c, etc.) correspond to the sampling locations indicated in Figure 29. It should be remembered that the data represent a continuous sequence of lead concentrations through an individual plant. In some instances, particularly samples from roots grown in highly contaminated soil media, the results are reported as a greater than (>) concentration, indicating that the absorption signal went over the standard calibration range and the figure reported is a minimum concentration. Since the micro samples are individual to a particular location on a plant and the technique is destructive repetition of such samples was not possible. The mean lead concentration for each of the sections of plant material (leaf, petiole, stem, tuber, tuber peel and root) has been calculated and is given for plants grown in soil media X, Y and Z in Tables 37, 38 and 39 respectively. The Tables also contain the overall means for Site locations 1 - 7 together with the corresponding overall mean obtained using the acid digestion procedure, for purposes of comparison. Site 8 was excluded from calculation of the mean values since these samples were grown under greenhouse conditions and samples grown under natural environmental conditions were of prime interest.

Figures 30, 31 and 32 have been prepared from the complete results given in appendices 6 p, 6 q and 6 r. They illustrate examples of the actual concentrations of lead observed in the micro samples taken at each of the plant sample locations (Figure 29). Just two sites are presented for each of the soil media X, Y and Z, Site 1

Table 37. Mean concentration of lead in potato plant sections grown in soil medium X (ALL SITES)(µg/g dwt).

| PLANT SECTIONS/ CONTAMINANTS, | SITE LOCATIONS, | | | | | | | | OVERALL MEAN SITES 1 - 7, | |
|---|---|---|---|---|---|---|---|---|---|---|
| | X1 | X2 | X3 | X4 | X5 | X6 | X7 | X8 | A. | B. |
| Leaf surface contamination | 117 | 102 | 39 | 18 | 26 | 35 | 42 | 7 | 54 | |
| Leaf | 6,46 | 1,67 | 3,50 | 1,66 | 3,90 | 5,64 | 1,38 | 1,10 | 3,5 | 14 |
| Petiole | 9,50 | 2,11 | 4,31 | 1,08 | 2,78 | 2,56 | 2,97 | 0,91 | 3,6 | ND |
| Stem | 11,54 | 3,31 | 4,96 | 2,84 | 2,85 | 2,81 | 5,43 | 1,31 | 4,8 | 5,0 |
| Tuber | 0,18 | 0,08 | 0,09 | 0,06 | 0,10 | 0,08 | 0,04 | 0,06 | 0,1 | 1,5 |
| Tuber peel | 2,17 | 1,06 | 1,20 | 0,63 | 0,69 | 0,82 | 0,52 | 0,91 | 1,0 | 3,5 |
| Roots | 15,6 | 31,4 | 97,9 | 33,8 | 17,4 | 63,7 | 20,9 | 16,4 | 40 | 27 |
| Available Pb in soil (mg/l) | 26 | 30 | 31 | 25 | 28 | 31 | 24 | 31 | 28 | |
| Total Pb in soil (µg/g) | 70 | 76 | 77 | 66 | 75 | 84 | 54 | 78 | 72 | |

Where: A = Microsampling cup procedure,

B = Acid digestion procedure,

Table 38. Mean concentration of lead in potato plant sections grown in soil medium Y (ALL SITES)(µg/g dwt).

| PLANT SECTIONS/ CONTAMINANTS. | SITE LOCATIONS. | | | | | | | | OVERALL MEAN SITES 1 - 7. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Y1 | Y2 | Y3 | Y4 | Y5 | Y6 | Y7 | Y8 | A. | B. |
| Leaf surface contamination | 106 | 90 | 47 | 15 | 27 | 57 | 51 | 6 | 56 | |
| Leaf | 52,1 | 25,1 | 77,5 | 185,8 | 55,9 | 132,3 | 34,1 | 77,4 | 80 | 65 |
| Petiole | 160,3 | 59,0 | 103,6 | 218,8 | 97,9 | 229,2 | 200,7 | 22,1 | 150 | ND |
| Stem | >269,2 | >153,8 | >296,0 | >622,0 | >414,4 | 420,6 | >399,0 | 72,8 | >370 | 382 |
| Tuber | 2,1 | 1,5 | 2,2 | 1,9 | 2,1 | 1,2 | 2,4 | 3,6 | 1,9 | 5,1 |
| Tuber peel | 31,4 | 67,1 | 46,9 | 17,7 | 68,9 | 60,6 | 20,9 | 75,8 | 45 | 21 |
| Roots | >1615 | 649 | 1440 | >901 | 256 | 344 | >1433 | >1856 | >950 | 755 |
| Available Pb in soil (mg/l) | 2867 | 2688 | 2771 | 2863 | 2392 | 2542 | 2617 | 2762 | 2680 | |
| Total Pb in soil (µg/g) | 4194 | 3990 | 4329 | 4327 | 3738 | 3901 | 4075 | 4407 | 4080 | |

Where: A = Microsampling cup procedure.

B = Acid digestion procedure.

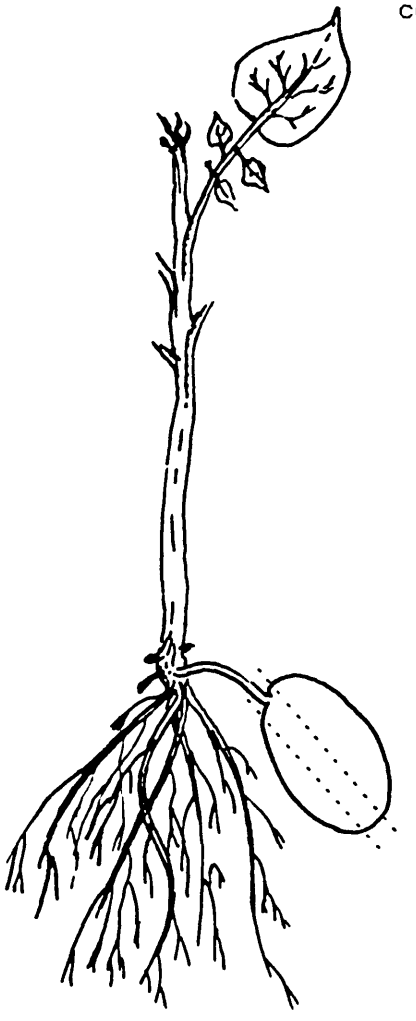
Table 39. Mean concentration of lead in potato plant sections grown in soil medium Z (ALL SITES)(µg/g dwt).

| PLANT SECTIONS/ CONTAMINANTS, | SITE LOCATIONS, | | | | | | | | OVERALL MEAN SITES 1 - 7, | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Z1 | Z2 | Z3 | Z4 | Z5 | Z6 | Z7 | Z8 | A, | B, |
| Leaf surface contamination | 1169 | 711 | 1064 | 870 | 1915 | 3808 | 1499 | 632 | 1580 | |
| Leaf | 89,5 | 20,9 | 33,7 | 30,8 | 29,5 | 55,2 | 21,7 | 10,5 | 40 | 145 |
| Petiole | 52,6 | 22,0 | 113,1 | 221,7 | 155,6 | 162,6 | 188,4 | 19,8 | 130 | ND |
| Stem | 109,3 | 192,1 | >441,4 | 639,3 | 182,0 | >412,7 | >796,3 | 58,7 | >400 | 245 |
| Tuber | 1,7 | 1,6 | 1,6 | 1,0 | 1,4 | 2,1 | 2,1 | 2,9 | 1,6 | 5,6 |
| Tuber peel | >280 | >297 | >206 | >157 | >330 | >173 | >230 | >220 | >240 | 275 |
| Roots | >1467 | >1732 | >1796 | >1194 | >1797 | >2587 | >1560 | >1520 | >1700 | 8980 |
| Available Pb in soil (mg/l) | 33300 | 33500 | 34700 | 33200 | 33000 | 31700 | 32900 | 25300 | 32900 | |
| Total Pb in soil (µg/g) | 39900 | 39600 | 38700 | 37800 | 36500 | 37100 | 37600 | 37100 | 38200 | |

Where: A = Microsampling cup procedure,

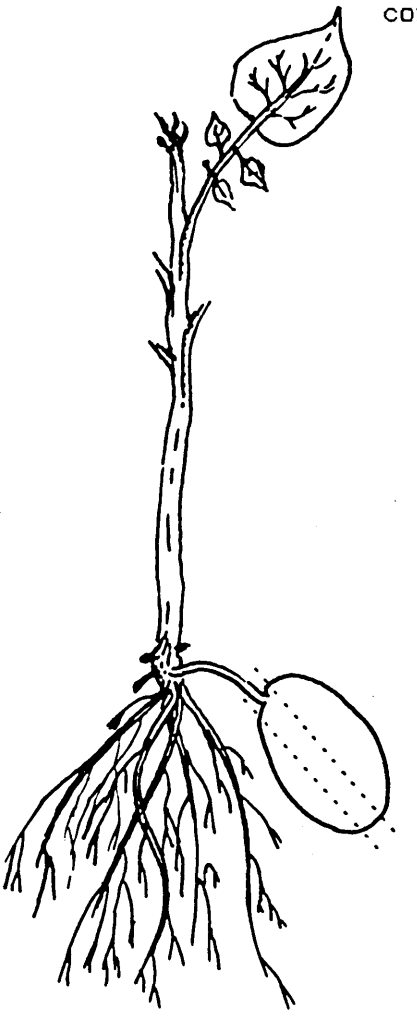
B = Acid digestion procedure,

Figure 30. Comparison of results obtained using the microsampling cup procedure on a single specimen grown in soil medium X at Site 1 (Roadside) and Site 8 (Greenhouse) (Pb µg/g dwt)



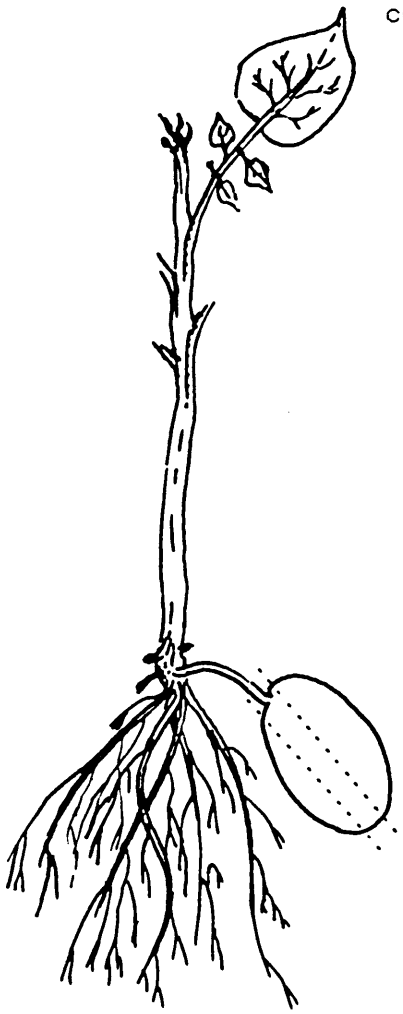
| | | SITE 1. (Roadside) | SITE 8. (Greenhouse) |
|---|---|---|---|
| Surface leaf contamination. | | 117 | 7 |
| **Leaf** | -a. | 4.94 | 0.28 |
| | b. | 9.01 | 1.44 |
| | c. | 8.75 | 1.19 |
| | d. | 3.15 | 1.48 |
| **Petiole** | -a. | 9.27 | 0.46 |
| | b. | 2.19 | 0.87 |
| | c. | 24.85 | 1.82 |
| | d. | 1.70 | 0.51 |
| **Stem** | -a. | 5.00 | 0.82 |
| | b. | 4.88 | 0.53 |
| | c. | 33.90 | 0.74 |
| | d. | 2.37 | 3.15 |
| **Tuber peel** | -a. | 2.35 | 0.94 |
| **Tuber** | -a. | 0.10 | 0.07 |
| | b. | 0.13 | 0.05 |
| | c. | 0.16 | 0.08 |
| | d. | 0.41 | 0.06 |
| | e. | 0.11 | 0.06 |
| **Tuber peel** | -b. | 3.07 | 0.88 |
| **Root** | -a. | 7.9 | 8.0 |
| | b. | 9.5 | 7.4 |
| | c. | 16.3 | 17.5 |
| | d. | 28.8 | 32.7 |
| Available lead in soil. (EDTA extraction) | | 26 | 31 |
| Total lead in soil. | | 70 | 78 |

Figure 31. Comparison of results obtained using the microsampling cup procedure on a single specimen grown in soil medium Y at Site 1 (Roadside) and Site 8 (Greenhouse) (Pb µg/g dwt)



| | | SITE 1. (Roadside) | SITE 8. (Greenhouse) |
|---|---|---|---|
| Surface leaf contamination. | | 106 | 6 |
| Leaf | -a. | 50.3 | 84.1 |
| | b. | 50.8 | 73.0 |
| | c. | 59.6 | 75.1 |
| | d. | 44.3 | 77.4 |
| Petiole | -a. | 161.1 | 20.0 |
| | b. | 93.8 | 17.7 |
| | c. | 169.0 | 26.1 |
| | d. | 217.5 | 24.7 |
| Stem | -a. | 59.4 | 16.1 |
| | b. | 99.6 | 21.6 |
| | c. | >549 | 114 |
| | d. | >369 | 139 |
| Tuber peel | -a. | 18.8 | 86.6 |
| Tuber | -a. | 0.56 | 2.94 |
| | b. | 2.14 | 3.21 |
| | c. | 3.77 | 2.23 |
| | d. | 2.65 | 7.13 |
| | e. | 1.21 | 2.28 |
| Tuber peel | -b. | 44.0 | 65.0 |
| Root | -a. | 1420 | >1720 |
| | b. | >962 | >2130 |
| | c. | 2280 | >2300 |
| | d. | 1800 | >1208 |
| Available lead in soil. (EDTA extraction) | | 2870 | 2760 |
| Total lead in soil. | | 4190 | 4410 |

Figure 32. Comparison of results obtained using the microsampling cup procedure on a single specimen grown in soil medium Z at Site 1 (Roadside) and Site 8 (Greenhouse) (Pb µg/g dwt)



| | | SITE 1. (Roadside) | SITE 8. (Greenhouse) |
|---|---|---|---|
| Surface leaf contamination. | | 1169 | 632 |
| **Leaf** | -a. | 60.2 | 5.3 |
| | b. | 47.8 | 20.1 |
| | c. | 46.4 | 8.3 |
| | d. | 203.6 | 8.5 |
| **Petiole** | -a. | 45.2 | 19.0 |
| | b. | 74.2 | 28.0 |
| | c. | 63.5 | 9.4 |
| | d. | 27.6 | 22.8 |
| **Stem** | -a. | 65.6 | 26.1 |
| | b. | 31.6 | 27.1 |
| | c. | 79.1 | 79.8 |
| | d. | 261.1 | 101.7 |
| **Tuber peel** | -a. | >383 | >261 |
| **Tuber** | -a. | 1.29 | 3.13 |
| | b. | 1.68 | 4.07 |
| | c. | 2.78 | 3.58 |
| | d. | 1.13 | 2.86 |
| | e. | 1.46 | 0.89 |
| **Tuber peel** | -b. | >178 | >178 |
| **Root** | -a. | >1680 | >992 |
| | b. | >1160 | >1290 |
| | c. | >1700 | >1680 |
| | d. | >1330 | >2130 |
| Available lead in soil. (EDTA extraction) | | 33300 | 25300 |
| Total lead in soil. | | 39900 | 37100 |

(roadside) and Site 8 (laboratory greenhouse). It is clear from the data presented in Figures 30, 31 and 32 that even within a single leaf specimen the concentration of lead can vary considerably. Whilst some of this variation is due to the imprecision of the analytical technique estimated to be between 30% and 50% for leaves (see Chapter 5), the vast majority of variation observed is probably due to actual fluctuations in tissue lead. The fluctuations may be due to minute changes in the surface structure, for example the veins in leaves may contain more or less lead than the surrounding tissue. Local variations in the number of stomata which may contain inclusions of trapped particulate lead not removed during washing may occur, or dead cells may accumulate more lead than living cells ([208]). These large fluctuations within a particular tissue type (eg. leaf) can be observed throughout the results for all parts of the plants, leaf, stem, petiole, tuber and roots.

In the root sections considerably greater variability can be seen (eg. Figure 30 Site 1: 7.9, 9.5, 16.3 and 28.8 μg/g). For plants grown in soil X it is apparent that samples from the lower parts of roots (plant sections c. and d.) contain more lead than the upper parts of roots. Whilst it would be possible to suggest that these higher lead concentrations were in the tissue it is more probable that the elevations are due to residual surface contamination remaining despite the extremely vigorous washing procedure used to clean the samples. In this area the root hairs produce a large surface area increasing the potential for surface contamination and even if damaged during washing some may remain producing apparent large elevations in tissue concentration.

The problem of obtaining a clean plant sample may explain some of the large variations which occur in the tissue concentrations of the plants grown in the highly contaminated soils Y and Z (Figures 31 and 32 respectively). Given that the mean total soil lead concentration for soils Y and Z were 4120 µg/g and 38000 µg/g (Table 26) respectively it would need only a few minute particles to contaminate a milligram plant sample. This is a possible reason why it is difficult to detect a gradation down the root in the case of root sections shown in Figures 31 and 32.

This leads me to question whether contamination observed using the microsampling procedure is being missed by other authors reporting concentrations of lead in plant material determined by grosser methods such as acid digestion. Clearly bulked tissue samples subsequently digested in acid must contain an element of contamination due to inadequate washing. In soils of high lead concentration, as for soils Y (4120 µg/g) and Z (38000 µg/g), this contamination may cause highly significant variations when it comes to interpreting data on the uptake of lead by plants grown in natural soils. The question whether the lead concentration observed is 'in' or 'on' the plant tissue cannot be easily answered for either the microsampling technique or the conventional acid digestion procedures. However, with the microsampling procedure it is possible at least to observe the variations which occur. Consequently, the microsampling technique may be better suited to uptake experiments on individual plants grown in hydroponic solutions where particular contamination would not present a problem. This is a possible area for its application in future research.

It is apparent from the mean concentrations given in Tables 37, 38 and 39 that for plants grown in the same soil medium, at different sites, there is considerable variability from plant to plant. Whilst this may be partly due to the differing site loctions and subsequent aerial exposure, the magnitude of variation between the leaves of plants growing in a particular soil medium seems to be unrelated to the level of aerial contamination at each site. This suggests that the variation is a facet of sampling variability within a single leaf, stem, root, etc. from an individual plant. Consequently the microsampling procedure could be used to examine variations that occur within a single plant stem, leaves, etc, and it is possible to study the detailed distribution throughout a whole single plant specimen, perhaps charting variations that occur between different stems and leaves of an individual plant.

In Tables 37, 38 and 39 the overall mean lead concentration of the plants growing at Sites 1 - 7 has been calculated for all plant parts using the microsampling cup procedure. Similarly the mean concentrations for lead in plants (and plant parts) grown at these sites, analysed using the acid digestion procedure, has also been included for comparison. The overall mean results obtained using the two analytical procedures are summarised in Table 40. The data for site 8 were not included in this Table since these plants were grown under laboratory greenhouse conditions. It is not entirely correct to compare these two sets of data since effectively the samples were drawn from considerably different population sizes and the lead determined by two completely different preparation and analytical procedures. It is reasonable

Table 40. Summary of overall mean lead concentrations for sites 1 - 7 for soil media X, Y and Z.
A) Micro sampling cup procedure results. (µg/g)
B) Acid digestion procedure results. (µg/g)

| | SOIL MEDIA. | | | | | |
|---|---|---|---|---|---|---|
| | X | | Y | | Z | |
| AERIAL CONTAMINATION, (leaf only) (µg/g) | 54 | | 56 | | 1580 | |
| ANALYTICAL PROCEDURE - | A | B | A | B | A | B |
| Leaf sections, | 3,5 | 14 | 80 | 65 | 40 | 145 |
| Leaf petiole sections, | 3,6 | ND | 150 | ND | 130 | ND |
| Stem sections, | 4,8 | 5,0 | >370 | 380 | >400 | 245 |
| Tuber sections, | 0,1 | 1,5 | 1,9 | 5,1 | 1,6 | 5,6 |
| Tuber peel sections, | 1,0 | 3,5 | 45 | 21 | >240 | 275 |
| Root sections, | 40 | 27 | >950 | 755 | >1700 | 8980 |
| SOIL CONTAMINATION, - EDTA extractable in soil (mg/l), | 28 | | 2680 | | 32900 | |
| - Total Pb in soil(µg/g) | 72 | | 4080 | | 38200 | |

Where: A = Microsampling cup procedure results,

B = Acid digestion procedure results,

to suggest that the mean concentration of lead in other leaves on the same stem as the leaf that was analysed using the micro sampling cup procedure might have been higher or lower. The same could be said for petiole, stem, tuber and root sections. Therefore in order to obtain a more accurate picture of the distribution through a plant many more samples may be desirable. This may be one reason why the overall mean concentrations for various plant parts observed using the micro sampling cup procedure are not the same as those obtained using the acid digestion procedure (See columns in Tables 37, 38 and 39 giving overall mean concentrations for different plant parts using the two procedures). Obviously the different analytical precisions of the two techniques also accounts for a proportion of the variation. Similarly there are two different regimes of risk of contamination and sample handling errors for the two techniques. The acid digestion procedure, for example may be susceptible to reagent and sample grinding contamination whilst the micro sampling technique could suffer from volatilisation losses or contamination during intricate handling of micro samples.

Nevertheless comparison of the two sets of data reveals that in nearly all instances the overall mean concentration for all sites obtained by the two different analytical methods was of a similar magnitude. The most consistently differing results were those obtained for tuber samples. The results obtained using the acid digestion procedure were considerably higher than those obtained using the microsampling cup procedure, the latter concentrations being more comparable with those reported in the literature by other authors (see Table 23). It is suggested that the results

obtained by the acid digestion procedure may have been influenced by contamination during the grinding process. The possibility for contamination of low concentration plant samples during grinding has already been discussed in Chapter 5. Despite the relatively poor precision of the micro sampling cup procedure it is still possible to see similar trends in the data identified already using the acid digestion procedure. Consequently many of the observations made already for the acid digestion procedure results could be repeated for the results obtained using the micro sampling cup procedure.

In terms of plant uptake of lead the data obtained by the microsampling cup procedure cannot easily be used to assess the relative contribution from aerial and soil sources. This is because of the considerable variability of the results within and between individual plants growing in a particular soil medium, together with the inability to obtain a measure of the level of aerial lead incident upon the individual milligram sample of plant tissue analysed. Consequently the results obtained by the acid digestion procedure may enable a better estimate to be made of the contribution from aerial and soil sources to the distribution of lead in the plants grown in the three soils at the eight experimental locations.

## 6.7. Conclusions.

It is difficult to draw firm conclusions on the contribution of lead from aerial and soil sources to its distribution in plants from the limited data, and more work is required using much larger populations of plants. However, some general conclusions can be made for the plants grown in the three soil media X, Y and Z during this study.

Comparisons of the data suggests that the major source of lead in potato plants grown in highly contaminated soils is from the soils via the roots by transport in the vascular tissues. This could best be confirmed using radio isotope studies similar to the approach published recently by Dollard ([156]), though this would necessitate the use of a greenhouse study and might not reflect the processes occuring in the natural environment.

It is apparent that inputs from aerial sources via the leaves have a comparatively negligible effect on the overall distribution of lead in the potato plants studied. However, for plants grown in soil with low lead concentrations it is possible to distinguish slight elevations in leaf tissue lead in contaminated aerial lead environments after the leaves have been washed. Surface contamination of plants is significant but potato leaves are not consumed, however other vegetable leaves are and care should be taken to remove outer leaves or wash carefully if they are for human consumption.

There is evidence that soil lead as a contamination source contributes more to the level of lead in potato tubers than lead entering the plant through the leaves from aerial sources. Whilst lead can be elevated in the inner tissue tubers it occurs to a lesser extent than in any other part of the plant. It is interesting that potato plants were able to grow, and produce edible tubers (after peeling), in such high levels of soil lead contamination. The possibility exists of using potatoes as a means for introducing organic material into developing soils on spoil heaps, though fertiliser applications may be necessary.

The solid sample microsampling cup procedure was successfully used to identify for the first time the distribution of lead throughout individual plant specimens grown at lead levels which exist in the natural environment and under field conditions. However, in order to be able to make firmer conclusions on lead uptake by plants using this procedure a much larger number of specimens and samples would have to be studied. It is known that differences in trace metal partitioning occur between plant varieties ($^{160}$) and this may need further investigation using the microsampling cup procedure.

Problems of surface contaminations of the small samples, particularly in the case of root samples, due to incomplete removal of particles during washing results in apparently poor sampling precision. This makes interpretation of the data difficult particularly for plants grown in highly contaminated environments.

It is suggested that because of the cost incurred and the problems of surface contamination the microsampling technique could best be applied to a study of the uptake of lead in individual plants grown in hydroponic solutions. The problem of contamination by residual soil particles would be considerably reduced, though it would reintroduce the problem of growing plants in unnatural environments.

The question of the cleanliness of a plant sample prior to its analysis, casts a doubt on the results of much work that has been carried out in the past and that which may be carried out in the future. It is impossible to state categorically that in plants, samples such as roots are totally free of surface contamination being covered as they are by fine root hairs or mycorrhizae. More research is required into methods of adequately cleaning plant tissues if future work is to produce accurate measurement of the different contributions of lead from soil and aerial sources in individual sections of plants grown under field conditions.

REFERENCES.


(1) Gilfillan, S. C., (1965) Lead poisoning and the fall of Rome. *J. of Occupational Med.*, 7, 53 - 60.

(2) Health and Saftey Commission, (1980) *Control of lead at work: approved code of practice.* H.M.S.O.

(3) Hepple, P., (Ed) (1972) *Lead in the Environment.* Applied Science Pub.

(4) Zimdahl, R.L. & Arvik, J.H., (1973) Lead in soils and plants: a literature review. *CRC Critical Reviews in Environmental Control*, 3, 2, 213 - 224

(5) Zimdahl, R.L. (1976) Entry and movement in vegetation of lead derived from air and soil sources, *J. of the Air Pollution Control Assoc.*, 26, 7, 655 - 660.

(6) Lepp, N. W. (1981) *Effect of Heavy Metal Pollution on Plants, Volume 1 - Effects of trace metals on Plant Function,* Applied Science Pub.

(7) Lepp, N. W. (1981) *Effect of Heavy Metal Pollution on Plants, Volume 2 - Metals in the environment,* Applied Science Pub.

(8) Haque, A. Md. & Subramanian, V. (1982) Copper, Lead and Zinc Pollution of Soil Environments, *CRC Critical Reviews in Environmental Control*, 12, 1, 13 - 69.

(9) Martin, M. H. & Coughtrey, P. J. (1982) *Biological Monitoring of Heavy Metal Pollution (Land and Air)*, Applied Science Pub.

(10) Manning, W. J. and Feder, W. A. (1980) *Biomonitoring Air Pollutants with Plants.* Applied Science Pub.

(11) Royal Commission on Environmental Pollution (1974) *Pollution control: progress and problems.* Fourth Report, Cmnd. 5780. H.M.S.O.

(12) Department of Health and Social Security (1980) *Lead and Health: the report of a DHSS working party on lead in the environment.* H.M.S.O.

(13) Bryce-Smith, D. and Stephens, R. (1980) *Lead or Health,* (2nd Edition). Conservation Society Pollution Working Party, London.

(14) Wilson, D. (1982) *Lead-free air...a legacy for our children.* C.L.E.A.R.

(15) National Research Council. (1980) *Lead in the Human Environment.* National Academy of Sciences, Washington D. C.

(16) Australian Academy of Sciences. (1981) *Health and environmental lead in Australia.* Australian Academy of Sciences, Canberra.

(17) Royal Comission on Environmental Pollution (1983) *Lead in the Environment.* Ninth Report, Cmnd. 8852. H.M.S.O.

(18) Department of the Environment (CDEP). (1983) *Lead in the Environment.* (The Government response to the Ninth Report of the Royal Commision on Environmental Pollution), Pollution Paper No.19, H.M.S.O.

(19) *The Guardian*, 18th March 1987, 1-2.

(20) Royal Society of Chemistry. (1982) *Environmental Chemistry (Volume 2).* Royal Society of Chemistry.

(21) Nriagu, J. O. (1979) Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature*, 279, 409-411.

(22) Nriagu, J. O.(Ed) (1978) *The biogeochemistry of lead in the environment.* Elsevier/North-Holland Biomedical Press.

(23) Waldron, H. A. (1981) Lead in the environment. *Environmental Pollution Management*, Jan./Feb., 16-18 & 29.

(24) Settle, D. M. and Patterson, C. C. (1980) Lead in albacore: guide to lead pollution in Americans. *Science*, 207, 1167-1176.

(25) Lee, J. A. and Tallis, J. H. (1973) Regional andhistorical aspects of local lead pollution in Britain. *Nature*, 245, 216-218.

(26) Murzumi, M., Chow, T. J. and Patterson, C. C. (1969) Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Arctic snow strata. *Geochimica et Cosmochimica Acta*, 33, 1247-1294.

(27) Patterson, C. C. (1965) Contaminated and Natural Lead Environments of Man. *Archives of Environmental Health*, 11, 344-360.

(28) Agrawal, Y. K., Patel, M. P. & Merh, S. S. (1981) Lead in soils and plants. It's relationship to traffic volume and proximity to Highway Lalbag, Baroda City, India. *International Journal of Environmental Studies*, 16, 222-224.

(29) Barnes, D., Hamada, M. A. & Ottaway, J. M. (1976) The lead, copper and zinc content of tree rings and bark. *Science of the Total Environment*, 5, (1), 63-67.

(30) Byrd, D. S., Gilmore, J. T. & Lea, R. H. (1983) Effect of decreased use of lead in gasoline in the soil of a highway. *Environmental Science and Technology*, 17, (2), 121.

(31) Chow, T. J. (1970) Lead accumulation in roadside soil and grass. *Nature*, 17, 295.

(32) Hassett, J. J. & Miller, J. E. (1977) Uptake of lead by corn from roadside soil samples. *Communications in Soil Science and Plant Analysis*, 8, (1), 49-55.

(33) Lau, W. M. & Wong, H. M. (1982) An ecological survey of lead contents in roadside dusts and soils in Hong Kong. *Environmental Research*, 28, 39-54.

(34) Maclean, R. O. & Shields, B. (1977) A study of the factors causing changes in the lead levels of crops growing besides roadways. *Environmental Pollution*, 14, 267-273.

(35) Parry, G. D. R., Johnson, M. S. & Bell, R. M. (1981) Trace metal surveys of soil as a component of strategic and local planning policy development. *Environmental Pollution (Series B)*, 2, 97-107.

(36) Polemio, M., Senesi, N. & Bufo, S. A. (1982) Soil contamination by metals: survey in industrial and rural areas of Southern Italy. *Science of the Total Environment*, 27, 71-79.

(37) Preer, J. R. Sekhon, H. S., Stephens, B. R. & Collins, H. S. (1980) Factors affecting heavy metal contents of garden vegetables. *Envrionmental Pollution (Series B)*, 1, 95-104.

(38) Ratcliffe, D. & Beeby, A. (1980) Differential accumulation of lead in living and decaying grass on roadside verges. *Environmental Pollution (Series A)*, 23, (4), 279-286.

(39) Wheeler, G. L. & Rolfe, G. L. (1979) The relationship between daily traffic volume and the distribution of lead in roadside soil and vegetation. *Environmental Pollution*, 18, 265-274.

(40) Atkins, D. P., Trueman, I. C., Clarke, C. B. & Bradshaw, A. D. (1982) The evolution of lead tolerance by festuca rubra on a motorway verge. *Environmental Pollution (Series A)*, 27, 3, 233-241.

(41) Nasralla, M. M. & Ali, E. A. (1985) Lead accumulation in edible portions of crops grown near Egyptian roads. *Agricultural Ecosyst. Environ.* 13, 1, 73-82.

(42) Lu, S. C., Hong, C. C. & Liu, C. J. (1985) Study of lead pollution of Taiwan area national freeway. *Proc. 78th APCA Annual Meeting*, 5, 85-59, B2. 1-2.

(43) Gulson, B. L., Tiller, K. G., Mizon, K. J. & Merry, R. H. (1981) Use of lead isotopes in soils to identify the source of lead contamination near Adelaide, S. Australia. *Environmental Science and Technology*, 15, (6), 691-696.

(44) Garcia-Miragaya, J., Castro, S. & Paolini, J. (1981) Lead and zinc levels and chemical fractionation of roadside soils of Caracas, Venezuela. *Water Air and Soil Pollution*, 15, 285-297.

(45) Wong, M. H. & Tam, F. Y. (1978) Lead contamination of soil and vegetables grown near motorways in Hong Kong. *Journal of Environmental Science and Health*, A13, 13-22.

(46) Beavington, F. (1973) Contamination of soil with zinc, copper, lead and cadmium in the Wollongong City area. *Australian Journal of Soil Reasearch*, 11, 27-31.

(47) Beavington, F. (1975) Heavy metal contamination of vegetables and soil in domestic gardens around a smelting complex. *Environmental Pollution*, 9,211-217.

(48) Bisessar, S (1982) Effects of heavy metals on micro-organisms in soils near a secondary smelter. *Water Air and Soil Pollution*, 17, (3), 305-308.

(49) Czuba, M. & Hutchinson, T. C. (1980) Copper and lead levels in crops and soils of the Holland Marsh area, Ontario. *Journal of Environmental Quality*, 9, (4), 567-575.

(50) Godzik, S., Florkowski, T., Piorek, S. & Sassen, M. M. A. (1979) An attempt to determine the tissue contamination of Quercus robur and Pinus sylvestris foiliage by particulates from zinc and lead smelters. *Environmental Pollution*, 18, 97-106.

(51) Lynch, A. J., McQuaker, N. R. & Brown, D.F. (1980) Inductively coupled plasma atomic emission spectrometer analysis and the composition of airborne and soil materials in the vicinity of a lead-zinc smelter complex. *Journal of Air Pollution Control Association*, 30, (3), 257-260.

(52) Nakos, G. (1979) Fate of lead in the soil and its effects on Pinu halperms (pine needles). *Plant and Soil*, 53, (4), 427-443.

(53) Schmitt, N., Philion, J. J., Larsen, A. A., Harnadek, M. & Lynch, A. J. (1979) Surface soil as a potential source of lead exposure to young children. *Canadian Medical Associaion Journal*, 121, 1474-1478.

(54) Brabec, E., Cudlin, P., Raugh, O. & Skoda, M. (1983) Lead budget in a smelter adjacent grass stand. *Proc. 4th Int. Conf. on Heavy Metals in the Environment*. 2, 1150-1153, CEP Consult. Edinburgh.

(55) Mankovska, B. (1986) Accumulation of arsenic, antimony, sulfur and lead in soil and pine forests. *Ecologica*, 5, 1, 71-79.

(56) Ward, T. J., Correl, R. L. & Anderson, R. B. (1986) Distribution of cadmium, lead and zinc among the marine sediments, sea grasses and fauna and the selection of sentinel accumulators near a lead smelter in Southern Australia. *Australian J. of Marine and Freshwater Research*. 37, 5, 567-585.

(57) Barry, S. A. S. & Clark, S.G. (1978) Problems of interpreting the relationship between the amounts of lead and zinc in plants and soil on metalliferous wastes. *New Phytologist*, 81, 773-783.

(58) Callio, S. (1980) Lead by flameless atomic absorption with phosophate matrix modification. *Atomic spectroscopy*, 1, (3), 80-81.

(59) Davies, B. E., Ginnever, R. C. & Lear, J. M. (1980) Cadmium and lead contaminated soils in some British metal mining areas. In *Reclamation of Contaminated Land*, Proceedings of a Society of Chemical Industry Conference, Eastbourne, England, October 22-25 1979 London: Society of Chemical Industry.

**(60)** Davies, B. E. (1983) A graphic estimation of the normal lead content of some British soils. *Geoderma*, 29, (1), 67-75.

**(61)** Davies, B. E. & Roberts, L. J. (1975) Heavy metals in soils and radish in a mineralised limestone area of Wales, Great Britain. *Science of the Total Environment*, 4, (3), 249-261.

**(62)** Davies, B. E. & Roberts, L. J. (1978) The distribution of heavy metals contamination in North East Clwyd, Wales. *Water, Air and Soil Pollution*, 9, 507-511.

**(63)** Davies, B. E. & White, H. M. (1981) Environmental pollution by wind-blown leadmine wastes: a case study in Wales (UK). *Science of the Total Environment*, 20, (1), 57-74.

**(64)** Johnson, M. S. & Eaton, J. W. (1980) Environmental contamination through residual trace metal dispersal from a derelict lead-zinc mine. *Journal of Environmental Quality*, 9, (2), 175-180.

**(65)** Palmer, K. T. & Kucera, C. L. (1980) Lead contamination of sycamore and soil from lead mining and smelting operations in Eastern Missouri. *Journal of Environmental Quality*, 9, (1), 106-111.

**(66)** Robert, R. D., Johnson, M. S. & Hutton, M. (1978) Lead contamination of small mammals from abandoned metalliferous mines. *Environmental Pollution*, 15, 61-69.

**(67)** Simon, E. (1978) Heavy metals in soils, vegetation development and heavy metal tolerence in plant populations from metalliferous areas. *New Phyologist*, 81, 175.

**(68)** Gatz, D. F., Bartlett, J. & Hassett, J. J. (1981) Metal pollutants in agricultural soils and the St. Louis, Illinois, U.S.A. urban rainfall anomely. *Water, Air and Soil Pollution*, 15, (1), 61-76.

**(69)** Liukkonen-Lilja, H., Kuusi, T., Laaksourata, K., Lodenius, M. & Piepponen, S. (1979) The effects of lead processing works on the lead, cadmium and mercury contents of fungi. *Zeitschrift fur Lebensmittel Untersuchung und Forschung*. 176, (2), 120-123.

**(70)** Miller, W. P. & McFee, W. W. (1983) Distribution of cadmium, zinc, copper, and lead in soils of industrial Northwestern Indiana. *Journal of Environmental Quality*, 12, (1), 29-34.

**(71)** Davies, B. E. (1983) Lead in city soils and vegetables-a London Case Study. *CLEAR*, (3), 7-70.

**(72)** *The Lead in Food Regulations* (1979) SI 1979 - No 1254, HMSO.

**(73)** Davies, B. E. (1978) Plant available lead and other metals in Britishh garden soils. *Science of the Total Environment*, 9, 243.

**(74)** Davies, B. E., Conway, D. & Holt, S. (1979) Lead pollution of London soils: a potential restriction on their use for growing

vegetables. *Journal of Agricultural Science (Cambridge)*, 93, 749-752.

**(75)** Nicklow, C. W., Norvell, W. A. & Spittler, T. (1981) Predicting total soil lead from acetic acid sodium acetate buffered solution. *Communications in Soil Science and Plant Analysis*, 12, (3), 239-245.

**(76)** Preer, J. R. & Rosen, W. G. (1977) Lead and cadmium content of urban garden vegetables. Annual Conference on Trace Substances In *Environmental Health Proceedings*, No. 11, 399-405.

**(77)** Preer, J. R., Sekhon, H. S., Stephens, B. R. & Collins, H. S. (1980) Factors affecting heavy metal contents of garden vegetables. *Environmental Pollution (series B)*, 1, 95-104.

**(78)** Spittler, T. M. & Feder, W. A. (1979) A study of soil contamination and plant lead uptake in Boston urban gardens. *Communications in Soil Science and Plant Analysis*, 10, (9), 1195-1210.

**(79)** Harrison, R. M. & Laxen-Duncan, P. H. (1981) *Lead pollution: causes and control*. London, Chapman and Hall.

**(80)** Zimdahl, R. L. & Skogerboe, R. K. (1977) Behaviour of lead in soil. *Environmental Science and Technology*, 11, 1202-1207.

**(81)** Swaine, D. J. & Mitchell, R. L. (1960) Trace element distribution in soil profiles. *Journal of Soil Science*, 11, 347

**(82)** Lagerwerff, J. V. & Specht, A. W. (1970) Contamination of roadside soil with cadmium, nickel, lead and zinc. *Environmental Science and Technology*, 4, 583-586.

**(83)** Motto, H. L., Daines, R. H., Chilko, D. M. & Motto, C. K. (1970) Lead in soils and plants: its relationship to traffic volume and proximity to highways. *Environmental Science and Technology*, 14, 231-235.

**(84)** Khan, D. H. (1980) *Lead in the soil environment*. Monitoring Assessment Research Centre, Chelsea College, University of London.

**(85)** Demayo, A., Taylor, M. C., Taylor, K. W. & Hodson, P. V. (1982) Toxic effects of lead and lead compounds on human health, aquatic life, wildlife, plants and livestock. *CRC Critical Reviews in Environmental Control*, 12, (4), 301-364.

**(86)** Brummer, G. W., Gerth, J. & Herms, U. (1986) Heavy metal species, mobility and availability in soils. *Z. Pflanzenernaehr. Bodenkd*, 149, 4, 382-398.

**(87)** Ter Haar, G. (1970) Air as a source of lead in edible crops. *Environmental Science and Technology*, 4, 226-229.

**(88)** Vestergaard, P. (1979) A study of the indication of trace metal pollution of marine areas by analysis of salt marsh soils. *Marine Environment Research*. 2, (1), 19-32.

(89) Arvik, J. H. & Zimdahl, R. L. (1974) Barriers to foliar uptake of Pb. *Journal of Environmental Quality*, 3, (4), 369-374.

(90) Miller, J. E., Hassett, J. J. & Koeppe, D. E. (1975) The effect of soil properties and extractable lead levels on the lead uptake by soybeans. *Communications in Soil Science and Plant Analysis*, 6, 339.

(91) Neuhauser, E. F. Hartenstein, R. (1980) Efficiencies of extractants used in the analysis of heavy metals in sludges. *Journal of Environmental quality*, 9, (1), 21-22.

(92) Petrov, I. I., Tsalev, D. L. & Bareev, A. I. (1980) Atomic absorption spectrometric determination of cadmium, cobalt, copper, manganese, nickel, lead and zinc in acetate soil extracts. *Atomic Spectroscopy*, 1, (2), 47-51.

(93) Crump, D. R. & Barlow, P. (1982) Factors controlling the lead content of pasture grass. *Environmental Pollution (Series B)*, 3, (3), 181-192.

(94) Glenn, R. C. (1983) Reliability of volumetric sampling as compared to weighed samples in quantitative soil test interpretations. *Communications in Soil Science and Plant Analysis*, 14, (3), 199-208.

(95) Davies, B. E. (1984) Soil and plant analysis for heavy metals and the quality of our environment. *ESN - European Spectroscopy News*, 56, 19-22.

(96) Andersson, A. (1975) Relative efficiency of nine different soil extractants. *Swedish J. Agricultural Research*. 5, 125-135.

(97) Karamanos, R, E., Bettany, J. R. & Stewart, J. W. B. (1976) The uptake of native and applied lead by alfalfa and bromograss from soil. *Canadian Journal of Soil Science*, 56, 485.

(98) Clayton, P. M. & Tiller, K. G. (1979) A chemical method for the determination of the heavy metal content of soils in environmental studies. *CSIRO Aust. Div. Soils Tech. Paper*, No 41, 1-17.

(99) Anon. (1980) *Analytical Atomic Absorption Spectroscopy*. Ed. J. C. van Loon, Academic Press, Inc.

(100) Karamanos, R. E., Bettany, J. R. & Rennie, D. A. (1976) Extractability of added lead in soils using lead-210. *Canadian Journal of Soil Science*, 56, 37-42.

(101) Lau, C. M., Ure, A.M. & West, T.S. (1983) The determination of lead and cadmium in soils by atom trapping atomic absorption spectrometry. *Analytica Chimica Acta*, 146, 171-179.

(102) Ure, A. M., Hernandez-Artiga, M. P. & Mitchell, M. C. (1978) A carbon rod atomiser for the determination of cadmium and lead in plant materials and soil extracts. Part III. Simultanious determination of cadmium by atomic fluorescence and lead by atomic absorption spectrometry. *Analytica Chimica Acta*, 96, 37-43.

**(103)** Issac, R. A. (1980) Atomic absorption methods for analysis of soil extracts and plant tissue digests. *Journal of the Association of Official Analytical Chemists*, 63, 788-796.

**(104)** John, M. K. (1972) Lead availability related to soil properties and extractable lead. *Journal of Environmental Quality*, 1, 295-298.

**(105)** Johnston, W. R. & Proctor, J. A. (1977) A comparative study of metal levels in plants from two contrasting lead mining sites. *Plant and Soil*, 46, 251-257.

**(106)** Misra, S. G. & Pandey, G. (1976) Evaluation of suitable extractants for available lead in soils. *Plant and Soil*, 45, 693-696.

**(107)** Bajo, S. & Wyttenbach, A. (1979) Lead, cadmium and zinc Bis (diethldithiocarbanate) and diethldithiocarbamic acid as reagents for liquid-liquid extraction. *Analytical Chemistry*, 51, (3), 376-378.

**(108)** Pedersen, B., Willems, M. & Jorgensen, S. S. (1980) Determination of copper, lead, cadmium, nickel and cobalt in EDTA extracts of soil by solvent extraction and graphite furnace atomic absorption spectrophotmetry. *Analyst*, 105, 119-124.

**(109)** Patke, S.K. & Agarawal, Y. K. (1980) Extraction and spectrophotometric determination of lead in the environment. *International Journal of Environmental Analytical Chemistry*, 8, (1), 67-73.

**(110)** Azarez, J., Palacios, F. & Vidal, J. C. (1982) Determination of lead in environmental samples by electrothermal A.A. spectrophotometry after extraction with pyrrolidine dithocarbonate. *Atomic Spectroscopy*, 3, 192.

**(111)** Hannaker, P. & Hughes, T. C. (1977) Multielement trace analysis of geological materials with solvent extraction and flame atomic absorption spectrometry. *Analytcial Chemistry*, 49, (11), 1485-1488.

**(112)** Personal communication (7/4/82) - Dr. A. M. Ure, Macaulay Institute for Soil Research.

**(113)** Edmonds, T. E., Gvogang, P. & West, T. S. (1980) The differential pulse anodic stripping voltammetry of copper and lead and their determination in EDTA extracts of soils with mercury glassy carbon electrode. *Analytica Chimica Acta*, 120, 41-53.

**(114)** Pribil, R. (1972) *Analytical applications of EDTA and related compounds.* (International series of Monographs in Analytical Chemistry, V. 52), Pergammon.

**(115)** Harrison, R. M. & Laxen-Duncan, P. H. (1977) Comparative study of methods of soil analysis of total lead in soils. *Water, Air and Soil Pollution*, 8, (4), 387-392.

**(116)** Johnson, M., Roberts, D. & Firth, N. (1978) Lead and zinc in the terrestrial environment around derelict metalliferous mines in Wales (UK). *Science of the Total Environment*, 10, (1), 61-78.

**(117)** Scott, D. & Thomas, J. H. (1977) Comparative efficiencies of various methods for extracting trace heavy metals from soils. *Soil Science*, 124, (6), 319-322.

**(118)** Stevenson, F. J. & Welch, L. F. (1979) Migration of applied lead in a field soil. *Environmental Science and Technology*, 13, (10), 1255-1259.

**(119)** Baker, D. E. & Chesnin, L. (1975) Chemical monitoring of soils for environmental quality and animal and human health. *Advances in Agronomy*, 27, 305.

**(120)** Veneman, P. L. M., Bodine, S. M., Murray, J. R. & Baker, J. H. (1982) Effectiveness of three repid digestion methods to estimate total lead in orchard soils. *Communications in Soil Science and Plant Analysis*, 13, (8), 585-592.

**(121)** Chowdhury, A. N. & Bose, B. B. (1982) Study of the method of decomposition of samples of soil for repid geochemical analysis by atomic absorption spectrometry. *Spec. Pub. Ser. - Geological Survey of India*, 8, 195-200.

**(122)** Heinrichs, H. (1979) Determination of lead in geological and biological materials by graphite furnce atomic absorption spectrometry. *Fresenius Zeitschrift fur Analtische Chemie*, 295, 355-358.

**(123)** Bryce-Smith, D. (1982) Environmental lead and the analyst. *Trends in Analytical Chemistry*, 1, 199-203.

**(124)** Markunas, L. D., Barry, E. F., Giuffre, G. P. & Litman, R. (1979) An improved procedure for the determination of lead in environmental samples by atomic absorption spectroscopy. *Journal of Environmental Science*, 14, (6), 501-506.

**(125)** Stoeppler, M., Valenta, P. & Nurnberg, H. W. (1979) Application of independent methods and standard materials : and effective approach to reliable trace and ultratrace analysis of metals and metalloids in environmental and biological matrices. *Fresenius Zeitschrift fur Analytische Chemie*, 297, 22-34.

**(126)** Kosta, L. (1982) Contamination as a limiting parameter in trace analysis. *Talanta*, 29, (11B), 985-992.

**(127)** Severson, R. C., McNeal, J. M. & Dickinson, J. J. (1979) Effects of soil preparation on DTPA - extratable elements in soils of the Northern Great plains. *Soil Science*, 128, (2), 70-79.

**(128)** MAFF/ADAS, (1981) *The analysis of agricultural materials*. (2nd Ed), HMSO.

**(129)** Bartlet, R. & James, B. (1980) Studying dried, stored soil samples - some pitfalls. *Soil Science of America Journal*, 44, (4), 721-724.

(130) Hamilton, E. I. (1980) Analysis of trace elements I: sample treatment and laboratory quality control. In *Applied soil trace elements*. (Ed. B. E. Davies), John Wiley and Sons Ltd.

(131) Rother, J. A., Millbank, J. W. & Thornton, I. (1982) Seasonal fluctuations in nitrogen fixing (acetylene reduction) by free-living bacteria in soils contaminated with cadmium, lead and zinc. *Journal of Soil Science*, 33, (1), 101-113.

(132) Andersen, A. M., Johnson, A. H. & Siccama, T. G. (1980) Levels of lead, copper and zinc in the forest floor in Northeastern United States. *Journal of Environmental Quality*, 9, (2), 293-297.

(133) Wilkins, C. (1978) The distribution of lead in the soils and herbage of West Pembrokshire. *Environmental Pollution*, 15, (1), 23-30.

(134) Davies, B. E. & Paveley, C. F. (1985) Baseline survey of metals in Welsh soils. *Trace Substances in Environmental Health*, 19, 87-93.

(135) Haines, R. C. & Pocock, R. L. (1980) *Heavy metal contamination: background levels and site case histories in the London Borough of Greenwich.* Research note 16. Joint Unit for Research on the Urban Environment, University of Aston.

(136) Joint Unit for Research on the Urban Environment (1982) *Background levels of heavy metal soil contamination in Walsall.* JURUE, University of Aston.

(137) Davies, B. E. & Roberts, L. J. (1976) The use of the computer in soil trace element research with special reference to SYMAP and SYMVU package programme. *University of Manchester Regional Computer Centre Journal*, 3, 14-21.

(138) Teicholz, E. & Berry, B. J. L. (1983) *Computer graphics and Environmental Planning.* Prentice Hall Inc.

(139) MAFF/ADAS. (1979) *Sampling of soils, soilless growing media, crop plants and miscellaneous substances for chemical analysis.* MAFF Publications.

(140) Harris, M. R., Harrison, S. J., Wilson, N. J. & Lepp, N. W. (1983) Elemental composition of fruit crops and their use as bio-indicators of reclamation treatment performance on metal contaminated land. *Proc. 4th Int. Conf. on Heavy Metals in the Environment*, 2, 1162-1165. CEP Consult., Edinburgh.

(141) Baumhardt, G. R. & Welch, L. F. (1972) Lead uptake and corn growth with soil applied lead. *Journal of Environmental Quality*, 1, 92.

(142) Cox, W. J. & Rains, D. W. (1972) Effects of lime on lead uptake by five plant species. *Journal of Environmental Quality*, 1, 167-169.

**(143)** Harris, M. R. (1981) Distribution of lead in winter wheat plants grown in the vicinity of a lead smelter. *Environmental Technology Letters*, 2, (6), 243-252.

**(144)** Jarvis, S. C., Jones, L. P. H. & Clement, C. R. (1972) Uptake and transport of lead by perennial rye grass from flowing solution culture with a controlled concentration of lead. *Plant and Soil*, 46, 371-379.

**(145)** John, M. K. & Van Laerhoven, C. (1972) Lead uptake by lettuce and oats as affected by lime, nitrogen and sources of lead. *Journal of Environmental Quality*, 1, 169-171.

**(146)** Khan, D. H. & Frankland, B. (1983) Effects of cadmium and lead on radish plants with particular reference to movement of metals through the soil profile and plant. *Plant and Soil*, 70, (3) 335-346.

**(147)** Lee, K. C., Cunningham, B. A., Chung, K. H., Paulsen, G. M. & Liang, G. H. (1976) Lead effects on several enzymes and nitrogen compounds in soybean leaf. *Journal of Environmental Quality*, 5, 357-359.

**(148)** Rolfe, G. L. (1973) Lead uptake by selected tree seedlings. *Journal of Environmental Quality*, 2, 153-157.

**(149)** Leblova, S., Mucha, A. & Spirhanzlova, E. (1986) Compartmentation of Cd, Cu, Pb and Zn in seedlings of maize (Zea mays L.) and introduction of metallothionein. *Biologia (Bratislava)*, 41, 8, 777-785.

**(150)** Juwarker, A. S. & Shende, G. B. (1986) Interaction of Cd, Pb: effect on growth yield and content of Cd, Pb in Barley (Hordeum vulgare). *Indian J. Environmental Health*, 28, 3, 235-243.

**(151)** Van Driel, W., Smilde, K. W. & Van Luit, B. (1985) Comparison of the heavy metal uptake of Cyprus esculentus and of agronomic plants grown on contaminated dutch sediments. *Misc. Paper D. - U.S. Army Eng. Waterw. Exp. Stn.* D-83-1, 1-52.

**(152)** Hardiman, R. T., Jacoby, B. & Banin, A. (1984) Factors affecting the distribution of Cd, Cu & Pb and their effect upon yeild of zinc content in bush beans. *Plant Soil*, 81, 1, 17-27.

**(153)** Wong, M. K., Hew, C. S. & Lee, Y. H. (1982) Uptake of lead by Brassice chinensis. *J. Singapore National Acad. Sci.*, 9, 46-48.

**(154)** Nicklow, C. W., Comas-Haezebrouck, P. H. & Feder, W. A. (1983) Influence of varying soil lead levels on lead uptake in leafy and root vegetables. *J. American Soc. Horticultural Sci.*, 108, 2, 193-195.

**(155)** Arvik, J. H. & Zimdahl, R. L. (1974) The influence of temperature, pH and metabolic inhibitors on uptake of lead by plant roots. *Journal of Environmental Quality*, 3, (4), 374-376.

(156) Dollard, G. S. (1986) Glasshouse experiments on the uptake of foliar applied lead. *Environmental Pollution (Series A)*, 40, 109-119.

(157) Davies, B. E. & White, H. M. (1980) Cadmium and lead contamination of soils and vegetables in relation to historic base metal mining. In *Reclamation of Contaminated Land*, Proceedings of a Society of Chemical Industry Conference, Eastbourne, England, Oct. 22-25, 1979. London: Society of Chemical Industry.

(158) Davies, B. E. & Ginnever, R. C. (1979) Trace metal contamination of soils and vegetables in Shipham, Sommerset. *Journal of Agricultural Science (Camb.)*, 93, 754-756.

(159) Jackson, K. W., Ebdon, L., Webb, D. C. & Cox, A. E. (1981) Determination of lead in vegetation by a rapid microsampling-cup atomic absorption procedure with soilid sample introduction. *Analytica Chimica Acta*. 128, 67-74.

(160) Harris, M. R., Harrison, S. J. Wilson, N. J. & Lepp, N. W. (1981) Varietal differences in trace metal partitioning by six potato cultivars grown on contaminated soil. In *Proc. 3rd Int. Conf. Heavy Metals in the Environment (Amsterdam)*, 3, 399-402.

(161) Davies, B. E. (1977) Base metal mining and heavy metal contamination of agricultural land in England and Wales. In *Inorganic Pollution and Agriculture*, (Great Britain M.A.F.F. Reference Book:326), Proceedings of a Conference organised by the Agricultural Development and Advisory Service, April 1977, London, H.M.S.O. 142-156.

(162) Saiki, H, & Maeda, O. (1982) Cleaning procedures for removal of external deposites from plant samples. *Environmental Science and Technology*, 16, (8), 536-539.

(163) Sonneveld, C. & van Dijk, P. A. (1982) The effectiveness of some washing procedures on the removal of contaminants from plant tissue samples of glass house crops. *Communications in Soil Science and Plant Analysis*, 13, (7), 487-496.

(164) Ward, N. I., Reeves, R. D. & Brooks, R. R. (1975) Lead in soil and vegetation along a New Zealand state highway with low traffic volume. *Environmental Pollution*, 9, 243-251.

(165) Harris, M. R. (1981) Concentration of lead in the atmosphere and soil measured in the vicinity of a secondary lead smelter. *Environmental Science and Technology Letters*, 2, (6), 233-242.

(166) Feinberg, M & Ducauze, C. (1980) High temperature dry ashing of foods for atomic absorption spectrometric determination of lead, cadmium and copper. *Analytical Chemistry*, 52, 207-209.

(167) Holak, W. (1977) Temperature programmable furnce for ashing of foods in trace metal analysis. *Journal of the Association of Official Analytical Chemists*, 60, (1), 239-240.

(168) Berman, E. (1980) *Toxic metals and their analysis*. (Heyden International Topics in Science). Heyden and Son Ltd.

**(169)** Satzger, R. D., Glow, C. S., Bonnin, E. & Fricke, F. L. (1982) Determination of background levels of lead and cadmium in raw agricultural crops by using differential pulse anodic-stripping voltammetry. *Journal of the Association of Official Analytical Chemists*, 65, (4), 987-991.

**(170)** Dietz, M. L. Tackett, S. L. (1983) Determination of lead in plant ash by X-ray fluoresscence spectrometry. *Analytical Chemistry*, 55, (4), 812-813.

**(171)** Shamsipoor, M. & Wahdat, F. (1977) Determination of lead in plants. *Fresenius Zeitschrift fur Analytische Chemie*, 288, 191-192.

**(172)** Thornburg, W. (1982) Precautions in ashing techniques for lead determination in food. *Journal of the Association of Official Analytical Chemists*, 65, (4), 992-993.

**(173)** Van Eenbergen, A. & Bruninx, E. (1978) Losses of elements during sampling decomposition in an acid digestion bomb. *Analytica Chimica Acta*, 98, 405-406.

**(174)** Jackson, K. W., Marczak, E. & Mitchell, D. G. (1978) Rapid determination of lead in biological tissues by microsampling-cup atomic absorption spectrometry. *Analytica Chimica Acta*, 97, 37-42.

**(175)** Delves, H. T. (1970) A microsampling method for the rapid determination of lead in blood by atomic absorption spectrometry. *Analyst*, 95, 431-438.

**(176)** Stoeppler, M. & Backhaus, F. (1978) Pretreatment studies with biological and environmental materials. *Fresenius Zeitschrift fur Analytische Chemie*, 297, 116-120.

**(177)** Nichols, J. A., Jones, R. D. & Woodriff, R. (1978) Background reduction during direct atomisation of soild background samples in atomic absorption spectrometry. *Analytical Chemistry*, 50, (4), 2071-2076.

**(178)** Marr, I. L. & Cresser, M. S. (1983) *Environmental Chemical Analysis*. International Textbook Co.

**(179)** Ebdon, L (1982) *An introduction to atomic absorption spectroscopy*. Heyden.

**(180)** Regan, J. G. T. & Warren, J. (1976) A novel approach to the elimination of matrix interferences in flameless atomic absorption spectroscopy usiing a graphite furnace. *Analyst*, 101, 220-221.

**(181)** Schmidt, W. & Dietl, F. (1980) Determination of lead in digested soils and sediments and in soil and sediment extracts by flameless atomic absorption with zirconium-coated graphite tubes. *Fresenius Zeitschrift fur Analytische Chemie*, 303, 385.

**(182)** Sturgeon, R. E., Desaulniers, J. A. M., Bermen, S. S. & Russell, D. S. (1982) Determination of trace metals in esturine sediments by graphite furnce atomic absorption spectrometry. *Analytica Chimica Acta*, 134, 283-291.

(183) Ure, J. R., Bacon, M. L., Berrow, M. L. & Watt, L. (1979) The total trace element content of some Scottish soils by spark source mass spectrometry. *Geoderma*, 22, (1), 1-23.

(184) Whittman, Z. (1982) Determination of lead in oils by atomic absorption spectrometry using a modified Delves cup technique. *Acta Chimica Academica Scientanium Hungaricae*, 11, (1), 85-88.

(185) Evans, W. H., Read, J. I. & Lucas, B. E. (1978) Evaluation of a method for the determination of total cadmium, lead and nickel in foodstuffs using measurement by flame atomic absorption spectrophotometry. *Analyst*, 103, 580-594.

(186) Woodis, T. C., Hunter, G. B. & Johnson, T. J. (1977) Statistical studies of matrix effects on the determination of cadmium and lead in fertiliser materials and plant tissue by flameless atomic absorption spectrometry. *Analytica Chimica Acta*, 90, 127-136.

(187) Slavin, W and Manning, D. C. (1982) Graphite furnace interferences, a guide to the literature. *Prog. Analyt. Atom. Spectrosc.*, 5, 243-340.

(188) Ediger, R. (1975) Atomic absorption analysis with graphite furnace using matrx modification. *Atomic Absorption Newsletter*, 14, (5), 127-130.

(189) Andersson, A. (1976) Interference from sulphur in the determination of lead with graphite furnace. *Atomic Absorption Newsletter*, 15, (3), 71-72.

(190) Thompson, K. C., Wagstaff, K. & Wheatstone, K. C. (1977) Method for the minimisation of matrix interferences in the determination of Pb and Cd in non-saline waters by AAS using electrothermal atomisation. *Analyst (London)*, 102, 310-313.

(191) Manning, D. C. & Slavin, W. (1979) Determination of lead in a chloride matrix. *Atomic Absorption Newsletter*, 17, (2), 43-46.

(192) Date, A. R. & Hutchison, D. (1986) The determination of trace elements in geochemical exploration samples by ICP-MS. *Spectrochimica Acta (part B)*, 41B, 1-2, 175-181.

(193) Schramel, P. (1983) Consideration of inductively coupled plasma spectroscopy for trace element analysis in the bio-medical and environmental fields. *Spectrochimica Acta (part B)*, 38B, 1/2, 199-206.

(194) Barnes, I. L., Murphy, T. J. & Michiels, E. A. I. (1982) Certification of lead concentration in standard reference materials by isotope dilution mass spectrometry. *Journal of the Association of Official Analytical Chemists*, 65, (4), 953-956.

(195) Stoeppler, M., Duerbeck, H. W. & Nuernberg, H. W. (1982) Environmental specimen banking ; a challenge in trace metal analysis. *Talanta*, 29, (11B), 963-972.

(196) Versick, J., Barbier, F., Cornelis, R. & Hoste, J. (1982) Sample contamination as a source of error in trace element analysis of biological samples. *Talanta*, 29, (11B), 973-984.

(197) Moody, J. R. & Lindstrom, R. M. (1977) Selection and cleaning of plastic containers for storage of trace element samples. *Analytical Chemistry*, 49, (14), 2264-2267.

(198) Settle, D. M. & Patterson, C. C. (1980) Lead in Albacore: Guide to lead pollution in Americans. *Science*, 207, 14 March, 1167-1176.

(199) Guevremont, R. & Jamieson, W. D. (1982) Reference materials for marine trace analysis. *Trends in Analytical Chemistry*, 1, (5), 113-116.

(200) O'Brien, B. J. (1980) *Progress reports in environmental monitoring and assessment: 1 Lead.* Monitoring and Assessment Research Centre, Chelsea College, University of London, MARC Report 16.

(201) Antonovics, J., Bradshaw, A. D. & Turner, R. G. (1971) Heavy metal tolerance in plants. In *Advances in Ecological Research* (Ed. J. B. Cragg), 7, 1-85, Academic Press.

(202) Holl, W. & Hampp, R. (1975) Lead and plants. *Residue Rev.* 54, 79-111.

(203) Hughes, M. K., Lepp, N. W. & Phipps, D. A. (1980) Aerial heavy metal pollution and terrestrial ecosystems. *Advances in Ecological Research*, 11, 217-327.

(204) Thornton, I (1980) Geochemical aspects of heavy metal pollution and agriculture in England and Wales. In *Inorganic Pollution and Agriculture.* MAFF (ADAS) Ref. Book No. 326, HMSO London.

(205) Colbourn, P. & Thornton, I. (1978) Lead pollution in agricultural soils. *J. Soil Science*, 29, 513-526.

(206) Mizuno, N. (1968) Interaction between iron/nickel and copper/nickel: various plant species. *Nature (London)*, 219, 1271-1272.

(207) Lepp, N. W. & Eardley, G. T. (1978) Growth and trace metal content of European sycamore seedlings grown in soils amended with sewage sludges. *Journal of Environmental Quality*, 7, 413-416.

(208) Miller, J. E., Hassett, J. J. & Keoppe, D. E. (1977) Interactions of lead and cadmium on metal uptake and growth of corn plants. *Journal of Environmental Quality*, 6, 18-20.

(209) Wallace, A., Romney, E. M., Alexander, G. V., Soufi, S. M. & Patel, P. M. (1977) Some interactions in plants among cadmium and other heavy metals and chelating agents. *Agron. J.*, 69, 18-20

(210) Miles, L.J. & Parker, G. R. (1979) Heavy metal interaction for Andropogon scoparius and Rudbeckia hirta grown on soil from

urban and rural sites with heavy metal additions. *Journal of Environmental Quality*, 8, 443-449

**(211)** Page, A. L. (1981) Cadmium in soils and its accumulation by food crops. In *Proc. Int. Conf. on Heavy metals in the Environment*, 206-213, (Amsterdam), CEP Consult., Edinburgh.

**(212)** Beckett, P. H.T. & Davis, R. D. (1978) The additivity of the toxic effects of coppper, nickel and zinc in young barley. *New Phytologist*, 81, 155-173.

**(213)** Carlson, R. W. & Bazzaz, F. A. (1977) Growth reductions in American sycamore (Platanus occidentallis L.) caused by Pb-Cd interactions. *Environmental Pollution*, 12, 243-253.

**(214)** Zimdahl, R. L. & Keoppe, D. E. (1977) Uptake by plants. In *Lead in the environment*. (Ed. Boggess, W. R.) 99-104, Nat. Sci. Found., Washington D.C.

**(215)** Chaney, R. L. (1973) Crop and food chain effects of toxic elements in sludges and effluents. In *Recycling Municipal Sludges and Effluents on Land*. 129-141, EPA, Washington.

**(216)** Berrow, M. L. & Burridge, J. C. (1980) Trace element levels in soil: effects of sewage sludge. In *Inorganic Pollution and Agriculture*. MAFF Ref Book No. 326, 159-190, HMSO (London).

**(217)** Brown, J. C. & Ambler, J. E. (1973) Reductants released by roots of Fe-deficient soybeans. *Agron. J.*, 65, 311-314.

**(218)** Tanton, T. W. & Crowdy, S. M. (1971) The distribution of lead chelate in the transpiration stream of higher plants. *Pestic. Sci.*, 2, 211-212.

**(219)** Smiley, R. M. (1974) Rhizosphere pH as influenced by plants, soils and nitrogen fertilisers. *Soil Sci. Soc. Am. Proc.*, 38, 795-799.

**(220)** Thurman, D. A. (1981) Mechanism of metal tolerance in higher plants. In *Effect of heavy metal pollution on plants. V.2. Metals in the Environment* (Ed. Lepp, N. W.), 239-249, Applied Sci. Pub.

**(221)** Clarkson, D. T. (1974) *Ion Transport and Cell Structure in Plants*. McGraw-Hill.

**(222)** Tyler, G. (1976) Soil factors controlling metal ion absorption in the wood anemone Anemone nemorosa. *Oikos*, 27, 71-80.

**(223)** Andersson, A. (1977) Some aspects of the significance of heavy metals in sewage slude and related products used as fertilisers. *Swedish J. Agricultural Research*, 7, 1-5.

**(224)** Petterson, O. (1976) Heavy metal ion uptake by plants from nutrient solutions with metal ion, plant species and growth period variations. *Plant and Soil*, 45, 445-449.

(225) Petterson, O. (1977) Differences in cadmium uptake between plant species and cultivars. *Swedish J. Agricultural Research*, 7, 21-24.

(226) Jarvis, S. C. & Jones, L. P. H. (1978) Uptake and transport of cadmium by perennial ryegrass from flowing culture with constant concentration of cadmium. *Plant and Soil*, 49, 333-342.

(227) Jarvis, S. C., Jones, L. P. H. & Hopper, M. J. (1976) Cadmium uptake from solution by plants and its transport from roots to shoot. *Plant and Soil*, 44, 179-191.

(228) Hammet, F. S. (1928) Studies on the biology of metals 1. The localisation of lead by growing roots. *Protoplasma*, 4, 183-186.

(229) Tandler, C. J. & Solari, A. J. (1969) Nucleolar orthophosphate ions - electron microscope and difraction studies. *J. Cell Biology*, 41, 91-108.

(230) Malone, C. D., Keoppe, D. E. & Miller, R. J. (1974) Localisation of lead accumulated by corn plants. *Plant Physiology*, 53, 388-394.

(231) Little, P. (1974) *Airborne zinc, lead and cadmium pollution and its effects on soils and vegetation.* PhD Thesis, University of Bristol.

(232) Ellis, R. H. & Alloway, B. J. (1983) Factors affecting the availability of cadmium, lead and nickel in soils amended with sewage slude. *Proc. 4th Int. Conf. Heavy Metals in the Environment*, 1, 358-361, CEP Consult., Edinburgh.

(233) Guha, M. M. & Mitchell, R. L. (1966) The trace and major element composition of the leaves of some deciduous trees. II Seasonal changes. *Plant and Soil*, 24, 90-112.

(234) Tyler, G. (1971) Moss analysis - A method for surveying heavy metal deposition. In *Proc. 2nd Int. Clean Air Conf.*, 129-132, I.U.A.P.P., Washington.

(235) Hall, C. (1977) *A Study of certain heavy metals in woody plants.* PhD Thesis, Liverpool Polytechnic.

(236) Dollard, G. J. (1979) *Some aspects of the behaviour of heavy metal ions in the tissue of a woody plant.* PhD Thesis, Liverpool Polytechnic.

(237) MacLean, A. J., Halstead, R. L. & Finn, B. J. (1969) Extractability of added lead in soils and its concentration in Plants. *Canadian Journal of Soil Science*, 49, 327-334.

(238) Page, A. L. & Ganje, T. J. (1970) Accumulation of lead in soils for regions of high and low motor vehicle traffic density. *Environmental Science and Technology*, 4, 140-142.

(239) Aarkrog, A. & Lippert, J. (1971) Direct contamination of barley with $^{51}Cr$, $^{59}Fe$, $^{65}Zn$, $^{203}Hg$ and $^{210}Pb$, *Radiat. Bot.* 11, 463-472.

(240) Tiffin, L. O. (1972) Translocation of micronutrients in plants. In *Micronutrients in Agriculture* (Ed. Mortveldt, J. J.), 199-229, Soil Sci. Soc. Am.

(241) Tiffin, L. O. (1977) The form and distribution of metals in plants: an overview. In *Biological Implications of metals in the Environment*. 315-334, Proc. 15th Ann. Hanford Life Sci. Symp. ERDA-TIC-Conf. No. 750929, Springfield, USA.

(242) Lyon, G. L., Peterson, P. J. and Brooks, R. R. (1969) Chromium-51 distribution in tissues and extracts of Leptospermum scoparium. *Planta*, 88, 282-287.

(243) Bollard, E. G. (1953) The use of tracheal sap in the study of apple tree nutrition. *J. Experimental Botany*, 4, 363-368.

(244) Bollard, E. G. (1960) Transport in the xylem. *Annual Review Plant Physiology*, 11, 141-166.

(245) Lepp, N. W. (1975) The potential of tree ring analysis for monitoring heavy metal pollution patterns. *Environmental Pollution*, 9, 49-61.

(246) Dollard, G. J. & Lepp, N. W. (1978) Some factors affecting the transport of heavy metals in woody plant tissue. In *Trace Substances in Environmental Health* (Ed. Hemphill, D. D.), 433-439, Univ. Missouri Press.

(247) Dedolph, R. Ter Haar, G., Holtzman, R. & Lucas, H. (1970) Sources of lead in perennial rygrass and radishes. *Environmental Science and Technology*, 4, (3), 217-223.

(248) Mathy, P. (1980) Contamination of the plants by the heavy metals: Distinction of the transfers soil-plant and air-plant. In *Int. Conf. Bioindicators Deterioisationes Regionis*, Liblice, Cezch. (Ed. Spaleny, J.), 385-390, Praha, Academia.

(249) Ter Haar, G. J., Dedolph, R. R., Holtzman, R. B. & Lucas, H. F. (1969) The lead uptake by perennial ryegrass and radish from air, water and soil. *Environmental Research*, 2, 267-271.

(250) McLeod, K. W., Adriano, D.C., Boni, A. L., Corey, J. C., Horton, J. H., Paine, D. & Pinder, J. E. (1980) Influence of a nuclear fuel chemical separators facility on the plutonium contents of a wheat crop. *Journal of Environmental Quality*, 9, 306-315.

(251) Rabinowitz, M. B. (1972) Plant uptake of soil and atmospheric lead in Southern California. *Chemosphere*, 175-180.

(252) Lindberg, S. E., Turner, R. R., Shriner, D. S. & Huff, D. D. (1981) Atmospheric deposition of heavy metals and their interaction with acid precipitation in a North American deciduous forest. In *4th Int. Conf. Heavy Metals in the Environment (Amsterdam)*, 306-309, CEP Consult., Edinburgh.

(253) Carlson, R. W., Bazzaz, F. A., Stukel, J. J. & Wedding, J. B. (1976) Physiological effects, wind re-entrainment and rainwash

of lead aerosol particulate deposition on plant leaves. *Environmental Science and Technology*, 10, 1139-1142.

**(254)** Little, P. (1973) A study of heavy metal contamination of leaf surfaces. *Environmental Pollution*, 5, 159-172.

**(255)** Cataldo, D. A., Garland, T. R. and Wildung, R. B. (1981) Foliar retention and leachability of plutonium and americum particles. *Journal of Environmental Quality*, 10, 31-37.

**(256)** Roberts, T. M. (1975) A review of some biological effects of lead emissions from primary and secondary smelters. In *Proc. Int. Conf. on Heavy Metals in the Environment* (Toronto, Canada), 2, 2, 503-532.

**(257)** Elias, R. W. & Croxdale, J. (1980) Investigations of the deposition of lead-bearing aerosols on the surfaces of vegetation. *Science of the Total Environment*, 14, 265-278.

**(258)** Flanagen, J. T., Wade, K. T., Currie, A. & Curtis, D. J. (1980) The deposition of lead and zinc from traffic pollution on two roadside shrubs. *Environmental Pollution (Series B)*, 1, 71-78.

**(259)** Garber, K. (1974) Heavy metals as air pollution-lead-zinc-cadmium influence on vegetation. *Staub. Reinhault der Luft.*, 34, 1-7.

**(260)** Schuck, E. A. & Locke, J. K. (1970) Relationships of automotive lead particulates to certain consumer crops. *Environmental Science and Technology*, 4, 324-330.

**(261)** Geiger, D. R., Sovonick, S. A., Shock, T. L. & Fellows, R. J. (1974) Role of free space in translocation in sugar beet. *Plant Physiology*, 54, 892-898.

**(262)** Hemphill, D. D. & Rule, J. H. (1975) Foliar uptake and translocation of Pb210 and Cd109 by plants. In *Proc. Int. Conf. on Heavy Metals in the Environment*. 2, 1, 77-86, CEP Consult., Edinburgh.

**(263)** Pate, J. S. (1975) Exchanges of solutes between phloem and xylem and circulation in the whole plant. In *Transport in Plants*, (Ed. Zimmerman, M. H. & Milburn, J. A.), 451-473, Encyclop. of Plant Physiol. New Series V.1., Springer-Verlag.

**(264)** Lepp, N. W. & Dollard, G. J. (1974) Studies on the lateral movement of Pb210 in woody stems. *Oecologia*, 16, 179-184.

**(265)** Bradley, R. I. (1980) Trace elements in soils around Llechryd, Dyfed, Wales. *Geoderma*, 24, 17-23.

**(266)** Balraadjsing, B. D. (1974) Determination of total lead in soil by atomic absorption spectrometry. *Communications in Soil Science and Plant Analysis*, 5, 25-37.

**(267)** Jackson, K. W. & Newman, A. P. (1983) Determination of lead in soil by graphite furnace atomic absorption spectrometry with

the direct introduction of slurries. *Analyst (London)*, 108, 2611-264.

**(268)** Hinds, M. W., Jackson, K. W. & Newman, A. P. (1985) Electrothermal atomisation AAS with the direct introduction of slurries. Determination of trace metals in soil. *Analyst (London)*, 110, 947-950.

**(269)** Yamagata, N. (1982) Interlaboratory comparison study on the reliability of environmental analysis. Soil and sediment 1978-80. *Bunseki Kagaku*, 31, T1-T5.

**(270)** Davis, R. D. & Carlton-Smith, C. H. (1983) An interlaboratory comparison of metal determinations in sludge-treated soil. *Water Pollution Control*, 82, 544-456.

**(271)** Perket, C. L. & Barsotti, L. R. (1985) Multilaboratory Analysis of soils for lead. *ASTM Spec. Tech Publ.* 886, 121-138.

**(272)** Cottenie, A. (1981) Mobility of heavy metals in sludge amended soil. An interlaboratory comparison. *Comm. European Communities [Report] EUR 7076*, 251-263.

**(273)** Boyer, K. W., Horwitz, W. & Albert, R. (1985) Interlaboratory variability in trace element analysis. *Analytical Chemistry*, 57, 2, 454-459.

**(274)** Rust, R. H. & Fenton, T. E. (1983) Interlaboratory comparison of soil characterisation data - North Central States. *Soil Sci. Soc. Am. J.*, 47, 3, 566-569.

**(275)** Jackson, K. W. (1978) Interlaboratory comparison of results of erythrocyte protoporphyrin analysis. *Clinical Chemistry*. 24, 2135-2138.

**(276)** Okamoto, K. (Ed.) (1982) *Preparation, analysis and certification of PONDSEDIMENT Certified Reference Material.* Division of Chemistry and Physics, The National Institute for Environmental Studies (Japan).

**(277)** Taylor, J. K. (1986) The critical relation of sample to environmental decisions. *TrAC. Trends in Analytical Chemistry*, 5, 5, 121-123.

**(278)** Dept. of Environment (Standing Committee Analysts) (1986) (2nd Ed.) *The samples and initial preparation of sewage sludge and waterworks sludges, soils, sediments, plant materials and contaminated wildlife prior to analysis.* (Methods Exam. Water Assoc. Matter.), D.O.E.

**(279)** Melcher, R. G., Peters, T. L. & Emmel, R. W. (1986) Sampling and sample preparation of environmental material. *Top. Current Chem.*, 134, 100-123.

**(280)** Plant, J. A. (1982) *Regional geochemical maps of the United Kingdom environmental and economic applications.* Institute of Geological Sciences, Foundation Lecture, 6/2/82.

(281) Plant, J. A. & Moore, P. J. (1979) Regional geochemical mapping and interpretation in Britain. *Phil. Trans. R. Soc. London.* B 288, 95-112.

(282) Plant, J. A. (1985) Regional geochemical maps of the United Kingdom. *N.E.R.C. News Journal*, 3, 4, 5-7.

(283) Institute of Geological Science (1978) *Geochemical Atlas of Great Britain: Shetland Islands.* I.G.S. London.

(284) Institute of Geological Science (1978) *Geochemical Atlas of Great Britain: Orkney Islands.* I.G.S. London.

(285) Institute of Geological Science (1979) *Geochemical Atlas of Great Britain: Caithness and South Orkney.* I.G.S. London.

(286) Institute of Geological Science (1982) *Geochemical Atlas of Great Britain: Sutherland.* I.G.S. London.

(287) Institute of Geological Science (1982) *Geochemical Atlas of Great Britain: Hebrides.* I.G.S. London.

(288) Aljibury, F. K. & Evans, D. D. (1961) Soil sampling for moisture retention and bulk density measurements. *Soil Science Soc. Am. Proc.*, 25, 180-183.

(289) Jacob, W. C. & Klute, A. (1956) Sampling soils for physical and chemical properties. *Soil Science Soc. Am. Proc.*, 20, 170-172.

(290) Mader, D. L. (1963) Soil variability - A serious problem in soil site studies in the northeast. *Soil Science Soc. Am. Proc.*, 27, 707-709.

(291) Gerrard, J. (1982) The use of hand-operated soil penetrometers. *Area.* 14, 227-234.

(292) Hammond, L. C., Pritchett, W. L. and Chew, V. (1958) Soil sampling in relation to soil heterogeneity. *Soil Science Soc. Am. Proc.*, 22, 548-552.

(293) Khan, M. A. and Nortcliff, S. (1982) Variability of selected soil micronutrients in a single soilseries in Berkshire, England. *Journal Soil Science.* 33, 763-770.

(294) Robinson, G. W. and Lloyd, W. E. (1915) On the probable error of sampling in soil surveys. *Journal Agricultural Science.* 7, 144-153.

(295) Quenouille, M. H. (1949) Problems in plane sampling. *Ann. Math. Stat.*, 29, 355-375.

(296) Berry, B. J. L. (1962) *Sampling, coding and storing flood plain data.* Agricultural Handbook No. 237, U. S. Department of Agriculture.

(297) Webster, R. (1977) *Quantitative and numerical methods of soil classification and survey.* Oxford University Press.

(298) McBratney, A. B. & Webster, R. (1983) How many observations are needed for regional estimation of soil properties? *Soil Science*, 135, 177-183.

(299) Cochran, W. G. (1963) *Sampling techniques.* (2nd Ed) Wiley, New York.

(300) Cline, M. G. (1944) Principles of soil sampling. *Soil Science*, 58, 275-288.

(301) Harvard University. (1971) *Users reference manual for SYnagraphic computer MAPping 'SYMAP'.* Laboratory for Computer Graphics and Spacial Analysis, Cambridge, Mass., U.S.A.

(302) SAS Inst. Inc. (1981) *SAS/Graph users guide.* SAS Institute Inc., Cary., N.C., USA.

(303) Cannon, H. L. & Bowles, J. M. (1962) Contamination of vegetation by tetraethyl lead. *Science*, 137, 765-766.

(304) Daines, R. H., Motto, H. and Chilko, D. M. (1970) Atmosphereic lead: Its relationship to traffic volume and proximity to highways. *Environmental Science and Technology*, 4, 318-322.

(305) Krishnayya, N. S. R. & Bedi, S. J. (1986) Effect of automobile lead pollution on Cassia tora L. and Cassia occidentalis L. *Environmental Pollution (Series A)*, 40, 221-226.

(306) Inter Departmental Committee on the redevelopment of Contaminated land (ICRCL) (1983) *Guidance on the assessment and redevelopment of contaminated land.* ICRCL 59/83, CDEP, Dept. of the Environment.

(307) Personal communication - Prof. K. W. Jackson, Dept. Chemistry, University of Saskatchewan, Canada.

(308) Commission of the European Communities. (1975) *Proposal for a Council Directive (EEC) in air quality satndards for lead.* COM (75), 166.

(309) Mendenhall, W., Ott, L. & Scheaffer, R. L. (1971) *Elementary survey sampling.* Wadsworth Pub. Co., USA.

(310) Kenyon, A. (1984) *An investigation into the heavy metal content of soils in the Darnall area of Sheffield with particular emphasis on finding a suitable sampling technique for industrial areas.* Dissertation submitted for the CNAA Degree of B.A.(Hons) Environmental Studies, Sheffield City Polytechnic.

(311) Peucker, T. K. (1980) The use of computer graphics for displaying data in three dimensions. *Cartogrphica*, i7, 2, 59-72.

(312) Burek, C. V. & Cubitt, J. M. (1979) Trace element distribution in the superficial deposites of Northern Derbyshire, England. *Minerals and the Environment*, 1, 90-100.

(313) Allcroft, R. (1950) Lead as a nutritional hazard to farm livestock. *Journal of Comparative Pathology*, 60, 190-208.

(314) Allcroft, R. (1951) Lead poisoning in cattle and sheep. *The Veterinary Record*, 37, 63, 583-591.

(315) Karacic, V., Prpic-Majic, D. & Skender, L. (1983) Biological indicators of lead absorption in cows as a measure of ambiental lead exposure. In *Proc. 4th Int. Conf. on heavy metals in the Environment*, 2, 1071-1073.

(316) Thornton, I. & Abrahams, P. (1983) Soil ingestion - a major pathway of heavy metals. Chemical estimation, ecological and health implications (Ed. Jenne, E. A. & Wildung, R. E.). *Science of the Total Environment*, 28, 287-294.

(317) McNeilly, T., Williams, S. T. & Christian, P.J. (1984) Lead and zinc in a contaminated pasture at Minera, North Wales and their impact on productivity and organic matter breakdown. *Science of the Total Environment*, 38, 183-198.

(318) Dorn, C. R., Tuomari, D., Reddy, C. & Logan, T. J. (1986) Acute lead poisoning with eosinophilic meningoe ncephalitis in calves on a farm recieving land application of sewage sludge. *Jounal of Environmental Pathology, Toxicology and Oncology*, 6, 3-4, 305-313.

(319) Pocock, R. L. (1983) Reducing heavy metal contamination in sewage sludge. In *Proc. 4th Int. Conf. on Heavy Metals in the Environment*, 1, 338-341, CEP Consult., Edinburgh.

(320) Ineson, P. R. (1982) Belland ground in the South Pennines - causes and alleviations. *Bull. Peak District Mines Hist. Soc.*, 8, 3, 193-200.

(321) Page, R. A. & Swires-Hennessy, E. (1986) A safe level for lead in soil and dust. In *Proc. 1st Int. TNO Conf. on Contaminated Soil*. (Ed. Assink, J. W. et. al.) 232-246, Nijhaft: Dordrecht, Netherlands.

(322) Willies, L. (1982) *Lead and lead mining*. Shire Publications.

(323) Willies, L. (1969) Cupola lead-smelting sites in Derbyshire 1737-1900. *Bull. Peak District Mines Hist. Soc.*, 4, 97-144.

(324) Personal communications - Dr. L. Willies, Mr. D. Crossley and Dr. D. Kiearnan.

(325) Personal communication - Mrs. J. Lane, Research student, Sheffield City Polytechnic.

(326) Eastwood, I. W. & Wild, M. S. (1986) Industrial archeological geochemical prospecting (IAGP) : A scientific aid to the study of industrial history. *The Hallamshire Historian*, 1, 1, 17-22.

(327) Archer, F. C. (1980) Trace elements in soils in England and Wales. In *Inorganic pollution and Agriculture*, pp 184-190. MAFF Reference Book 326, London. HMSO.

(328) Quayle, D. V. (1984) Monitoring of toxic metal concentrations near a disused lead smelter site. *Paper presented at 4th International Environment and Safety Conference*, London, March 1984. I. E. S.

(329) Nichol, I., Thornton, I., Webb, J. S., Fletcher, W. K., Horsnail, R. F., Khaleelee, J. & Taylor, D. (1970) *Regional geochemical reconaissance of the Derbyshire area.* Report No. 70/2, Institute of Geological Sciences, N.E.R.C., H.M.S.O.

(330) Nriagu, J. O. (Ed) (1980) *Zinc in the evironment. Part 1: ecological cycling.* John Wiley & Sons.

(331) Purves, D. (1972) Consequences of trace element contamination of soils. *Environmental Pollution*, 3, 17-24.

(332) Nriagu, J. O. (Ed) (1979) *Copper in the environment. Part 1: Ecological Cycling.* John Wiley & Sons.

(333) Nriagu, J. O. (Ed) (1980) *Cadmium in the environment. Part 1: Ecological Cycling.* John Wiley & Sons.

(334) Twelfth Report of the Steering Group on Food Surveillance The Working Party on the Monitoring of Foodstuffs for Heavy Metals. (1983) *Survey of cadmium in food: First Supplementary Report.* Food Surveillance Paper No.12., M.A.F.F., HMSO.

(335) Barltrop, D. (1975) *Archives of Industrial Hygiene and Toxicology*, 26 (supplement), 81.

(336) *Official J. of the European Communities* (1977) L105, 10-12, 28th April.

(337) Culbard, E., Moorcroft, S., Watt, J., Thornton, I. & Thomas, J. F. A. (1983) Nationwide reconnaissance survey of metals in urban dusts and soils. *Minerals and the Environment*, 5, 2-3, 82-84.

(338) Davies, B.E. & Davies, W. L. (1983) Lead in urban soils and vegetables in Great Britian. In *Proc. 4th Int. Conf. on Heavy Metals in the Environment*, 2, 1154-1157, CEP Consult., Edinburgh.

(339) Culbard, E., Thornton, I., Watt, J., Moorcroft, S. & Brooks, K. (1983) Sources and distribution of lead and cadmium in U.K. dusts and soils. In *Proc. 4th Int. Conf. on Heavy Metals in the Environment*, 1, 426-429, CEP Consult., Edinburgh.

(340) Thornton, I., Culbard, E., Moorcroft, S., Watt, J., Wheatly, M. & Thompson, M. (1985) Metals in urban dusts and soils. *Environmental Technol. Lett.*, 6, 4, 137-144.

(341) Wild, M. S., Eastwood, I. W. and Newman, A. P. (1984) *Background distribution of some heavy metals in soils of North East Derbyshire, England. Report to: NED District Council* -

*Environmental Health Sub Committee*. Report No. (NED Cont. Surv.) 1/84. Sheffield City Polytechnic.

**(342)** Thornton, I. (1980) Regional distribution of trace element problems in Great Britain. In *Applied Soil Trace Elements* (Ed. Davies, B. E.), J. Wiley and Sons.

**(343)** Barltrop, D., Strehlow, C. D., Thornton, I. & Webb, J. S. (1975) Absorption of lead from dust and soil. *Postgraduate Medical Journal*, 51, 801-904.

**(344)** Alloway, B. J. & Davis, B. E. (1971) Heavy metal content of plants growing on soils contaminated by lead mining. *Journal of Agricultural Science*, 76, 321-323.

**(345)** Servant, J. & Delapart, M. (1981) Blood lead and lead 210 origins in residents in Toulouse. *Health Physics*, 41, 483-487.

**(346)** Martin, M. H., Duncan, E. M. & Coughtrey, P. J. (1982) The distribution of heavy metals in a contaminated woodland ecosystem. *Environmental Pollution (Series B)*, 3, 147-157.

**(347)** Hoenig, M. & De Borger, R. (1983) Particular problems encountered in trace metal analysis of plant material by atomic absorption spectrometry. *Spectrochimica Acta*, 38B, 5-6, 873-880.

**(348)** Evans, W. H. Read, J. I. & Lucas, B. E. (1978) Evaluation of a method for the determination of total cadmium, lead and nickel in foodstuffs using measurement by flame atomic absorption spectrophotometry. *Analyst*, 103, 580-594.

**(349)** Fletcher, K. (1971) Direct determination of lead in plant material by atomic absorption spectroscopy. *Journal of Science Food Agriculture*, 22, 260-261.

**350)** Carnrick, G. R., Lumas, B. K. & Barnett, W. B. (1986) Analysis of solid samples by graphite furnace A.A.S. using Zeeman background correction. *J. Analytical Atomic Spectrometry*, 1, 6, 443-447.

**(351)** Dabeka, R. W. & McKenzig, A. D. (1986) Graphite-furnace A.A.S. determination of lead and cadmium in food after nitric-perchloric acid digestion and coprecipitation with ammonium pyrrolidine dithocarbamate. *Canadian J. Soil Science*, 31, 2, 44-52.

**(352)** Stupar, J. (1986) Direct determination of lead in soils and sediments by atomic absorption spectrometry employing a graphite capsule-flame atomizer. *J. Analytical Atomic Spectrometry*, 1, 5, 373-378.

**(353)** Fagioli, F., Landi, S. & Lucci, G. (1982) Determination of manganese and copper in small amounts of maize roots by graphite -tube furnace atomic absorption spectroscopy with liquid and solid sampling techniques. *Annali di Chimica*, 72, 63-71.

**(354)** Fagioli, F., Landi, S., Locatelli, C. & Bighi, C. (1986) Determination of Pb and Cd in small amounts of biological material

by graphite furnace A.A. spectroscopy with sampling of carbonaceous slurry. *Atomic Spectroscopy*, 7, 2, 49-51.

**(355)** Hoenig, M. & Van Hoeyweghen, P. (1986) Alternative solid sampling for trace metal determination by platform electrothermal atomic absorption spectrometry- direct despensing of powdered samples suspended in liquid medium. *Analytical Chemistry*, 58, 13, 2614-2617.

**(356)** Mermet, J. M. & Hubert, J. (1982) Analysis of biological materials using plasma atomic emission spectroscopy. *Progress in Analytical Atomic Spectroscopy*, 5, 1-33.

**(357)** Pettit, W. E. & Horlick, G. (1986) An automated direct sample insertion system for the inductively coupled plasma. *Spectrochimica Acta*, 41B, 7, 699-712.

**(358)** Bewley, R. J. F. & Campbell, R. (1978) Scanning electron microscopy of oak leaves contaminated with heavy metals. *Trans. Brit. Mycol. Society*, 71, 508-511.

**(359)** Ophus, E. M. & Gullvag, B. M. (1974) Localisation of lead within the leaf cells of Rhytidiadelphus squarrosus (Hedw.) Warnst. by means of transmission electron microscopy and X-ray microanalysis. *Cytobios*, 10, 45-58.

**(360)** Jensen, T. E., Rachlin, J. W. Jani, V and Warkentine, B. (1982) An X-ray energy dispersive study of cellular compartmentalisation of lead and zinc in Chlorella saccharophilla (Chlorophyta), Navicula incerta and Nitzschia clsterium (bacillariophyta). *Environmental and Experimental Botany*, 22, 3, 319-328.

**(361)** Jensen, T. E., Rachlin, J. W. Jani, V and Warkentine, B. (1986) Heavy metal uptake in relation to phosphorus nutrition in Anabaena variabilis (Cyanophyceae). *Environmental Pollution (Series A)*, 42, 261-271.

**(362)** Sharpe, V. & Denny, P. J. (1976) Electron microscope studies on the absorption and localization of lead in the leaf tissue of Potamogeton pectinatus L. *Journal of Experimental Botany*, 27, 101, 1155-1162.

**(363)** Vollkopf, U., Grobenski, Z., Tamm, R. & Welz, B. (1985) Solid sampling in graphite furnace A.A.S. using the cup in tube technique. *Analyst*, 110, 573-577.

**(364)** Favretto, L., Marletta, G. P. & Favretto, L. G. (1981) Atomic absorption spectroscopic determination of lead in biological materials by direct solid microsampling. *Mikrochimica Acta (Wien)*, 11, 387-398.

**(365)** Alder, J. F. & Batoreu, M. C. C. (1983) Determination of lead and nickel in epithelial tissue by electrothermal atomic absorption spectrometry. *Anal. Chimica. Acta.*, 155, 199-207.

**(366)** Nichols, J. A., Jones, R. D. and Woodriff, R. (1978) Background reduction during direct atomisation of solid biological

samples in atomic absorption spectrometry. *Analytical Chemistry*, 50, 2071-2076.

**(367)** Ni, Z., Han, H. & Le, X. (1986) Determination of lead by graphite furnace atomic absorption spectrometry with argon-hydrogen as the purge gas using low temperature atomization. *J. Analytical Atomic Spectrometry*, 1, 2, 131-134.

**(368)** Mitchell, D. G., Aldous, K. M. & Ryan, F. J. (1974) Mass screening for lead poisoning. *New York State Journal of Medicine*, Aug, 1599-1603.

**(369)** Hicks, J. M., Gutierrez, A. N. & Worthy, B. E. (1973) Evaluation of the Delves micro system for blood lead analysis. *Clinical Chemistry*, 19, 3, 322-325.

**(370)** Pandya,C. B.,Patel, T. S., Shah, G. M., Sathawara, N. G., Patel, V. G., Parikh, D. J. & Chatterjee, B. B. (1986) Quality assurance of analytical data withspecial reference to the determination of lead and cadmium in biological samples. *J. Analytical Atomic Spectrometry*, 1, 5, 387-390.

**(371)** Lau, O. W. & Li, K. L. (1975) Determination of lead and cadmium in paint by atomic absorption spectrometry utilising the Delves micro sampling technique. *Analyst*, 100, 430-437.

**(372)** Mitchell, D. G., Aldous, K. M. & Ward, A. P. (1974) Determination of lead in pencil paint using a microsampling cup atomic absorption technique. *Atomic Absorption Newsletter*, 13, 5, 121-122.

**(373)** Jackson, K. W., Fuller, T. D., Mitchell, D. G. & Aldous, K. M. (1975) A rapid microsampling cup atomic absorption procedure for the determination of lead in urine. *Atomic absorption Newsletter*, 14, 5, 121-123.

**(374)** Favretto, L. (1976) Determination of lead in seaweed at the nanogram level using a microsampling system. *Atomic Absorption Newsletter*, 15, 4, 98-100.

**(375)** Gabrielli, L. F., Marletta, G. P. & Favretto, L. (1977) Rapid determination of particulate lead in sea water by a reagent free microsampling system. *Atomic Absorption Newsletter*, 16, 1, 4-6.

**(376)** Mitchell, D. G., Mills, W. N., Ward, A. F. & Aldous, K. M. (1977) The determination of cadmium, copper, and lead in sludges by microsampling cup A.A.S. in a nitrous oxide/acetylene flame. *Analytica Chimica Acta*, 90, 275-278.

**(377)** Jackson, K. W. & Mitchell, D. G. (1975) Rapid determination of cadmium in biological tissues by microsampling cup atomic absorption spectrometry. *Analytica Chimica Acta*, 80, 39-45.

**(378)** Okamoto, K. (Ed) (1980) *Preparation, analysis and certification of PEPPERBUSH standard reference material.* Research Report No. 18. The National Institute For Environmental Studies, Japan.

(379) Karwowska, R. & Jackson, K. W. (1986) Lead atomisation in the pressence of aluminium matrices by electrothermal atomic absorption spectrometry : a comparative study of slurry vs. solution sample introduction. *Spectrochimica Acta*, 41B, 9, 947-957.

(380) M.A.F.F. (1982) *Survey of lead in food: Second Supplementary Report*, Food Surveillance Paper No. 10, HMSO.

(381) Sherlock, J. C., Smart, G. A., Walters, B., Evans, W. H., McWeeny, D. J. & Cassidy, W. (1983) Dietary surveys on a population at Shipham, Sommerset, U.K. *Science of the Total Environment*, 29, 1-2, 121-142.

(382) Facchetti, S. (1979) Isotope study of lead in petrol. In *Int. Conf. Management and Control of Heavy Metals in the Environment*, 95-102, London, Sept. '79, CEP Consultants.

(383) Lockhart, J. A. R. & Wiseman, A. J. L. (1978) *Introduction to crop husbandry*. Pergamon Press.

(384) Davies, B. E. & Lewis, N. J. (1985) Controlling heavy metal uptake through choice of plant varieties. *Trace substances in Environmental Health*, 19, 102-108.

(385) Wiersma,D., van Goor, B. J. & van der Veen, N. G. (1986) Cadmium, lead, mercury and arsenic concentrations in crops and corresponding soils in the Netherlands. *J. Agricultural Food Chem.*, 34, 6, 1067-1074.

(386) Bassuk, N. L. (1986) Reducing lead uptake in lettuce. *Horticultural Science*, 21, 4, 993-995.

(387) Crews, H. M. & Davies, B. E. (1985) Hevay metal uptake from contaminated soils by six varieties of lettuce. *J. of Agricultural Science*, 105, 3, 591-595.

(388) Richardson, S. J. (1980) Composition of soils and crops following treatment with sewage sludge. In *Inorganic Pollution and Agriculture*, M.A.F.F./ADAS Reference Book 326, 1980, HMSO.

(389) Lag, J. & Elsokkary, I. H. (1978) A comparison of chemical methods for estimating Cd, Pb and Zn availability tosix food crops grown in industrially polluted soils at Odda, Norway. *Acta Agriculturæ Scandinavia*, 28, 76-80.

(390) Davies, B. E. & Ginnever, R. C. (1979) Trace metal contamination of soils and vegetables in Shipham, Sommerset. *J. of Agricultural Science*, 93, 753-756.

(391) De Haan,S. & Lubbers, J. (1983) Microelements in potatoes under conditions and as affected by microelements in municipal waste compost, sewage sludge and dredged materials from harbours. *RAPP-Inst. Bodemvruchtbaarheid*, 3-83, pp22.

(392) Baerug, R. & Martinsen, J. H. (1977) The influence of sewage sludge on the content of heavy metals in potatoes and on tuber yield. *Plant and Soil*, 47, 407-418.

(393) Harrison, R. M. & Jonhnston, W. R. (1985) Deposition fluxes of lead, cadmium, copper and polynuclear aromatic hydrocarbons (PAH) on the verge of a major highway. *Science of the Total Environent*, 46, 121-135.

(394) Jackson, K. W., Eastwood, I. W. & Wild, M. S. (IN PRESS) Stratified sampling protocol for monitoring trace metal concentrations in soil. *(To be published in 'Soil Science' 1987).*

(395) M.A.F.F./ADAS. (1983) *Cyst nematodes on potato.* Leaflet 284, HMSO.

(396) M.A.F.F./ADAS. (1980) *Potato virus diseases.* Leaflet 139, HMSO.

(397) Personal communication - Mr D MacLean (seed potato producer).

(398) M.A.F.F./ADAS. (1982) *Seed potato sprouting.* Booklet 2400. M.A.F.F. Publications.

(399) Allen, S. E. (Ed) (1974) *Chemical analysis of ecological materials.* Blackwell Scientific Publications.

(400) Dahnke, W. C. & Vasey, E. H. (1973) Testing soils for nitrogen. In *Soil Testing and Plant Analysis* (Ed. Walsh, L. M. and Beaton, J. D.) Soil Sci. Soc. Am. Inc.

(401) Waughman, G. J., Kookorinis, E. & Bellamy, D. J. (1983) Influences of climate and heavy metal concentrations in the soils on plants of grassland and flush vegetation in Upper Teesdale. *J. of Ecology*, 71, 177-187.

(402) British Standards Institution (1969) *Methods for the measurement of air pollution Part 1. Deposit gauges.* B.S. 1747., B.S.I.

(403) Tranmer, N. R. (1985) *Air pollution monitoring and modelling in North East Derbyshire.* MPhil Thesis, Dept. of Chemistry, Sheffield City Polytechnic.

(404) Davies, B.E. & Crews, H. M. (1983) The contribution of heavy metals in potato plants to dietary intake. *Science of the Total Environment*, 30, 261-264.

(405) MAFF/ADAS (1985) Fertiliser Recommendations 1985-1986, MAFF Ref. Book 209, MAFF Publications.

LECTURES AND MEETINGS ATTENDED.

1. Diploma in Chemical Pollution Monitoring. Module 5 - Trace Inorganic Determination. Department of Chemistry, Sheffield City Polytechnic. 21/1/82-18/3/82.

2. Royal Statistical Society (Local Group Meeting) - M J Quinn, 'EEC Blood Lead Surveys' & R S Pocock, 'Lead and Health: A Review', University of Sheffield, 18/3/82

3. First Biennial National Atomic Spectroscopy Symposium, Royal Soc. Chemistry (Analytical Divison - Atomic Spectroscopy Group)/Institute of Physics (Spectroscopy Group). Sheffield, 13/7/82-15/7/82.

4. Modern Methods of Analysis Group - R Jenkins, 'Pollution Analysis', Sheffield, 16/11/82.

5. Institute of Biology Lecture - Dr A Peel, 'Some recent advances in the physiology of nutrient transfer systems in higher plants.' Sheffield City Polytechnic, 24/11/82.

6. 6th Form Geographical Association Conference, held at Sheffield City Polytechnic, Totley Site, Sheffield. 25 & 2/11/83. (Lecture to Conference).

7. Visit to laboratories of Cookson Group (Formerly Lead Industries) plc., London, 23/11/83.

8. I.L. Northern User Group Meeting - D A Stewart, 'Trace metal impurities in the semiconductor industry', J F Tyson, 'Flow injection analysis techniques for flame AAS', A Batho, 'Background Correction in AAS', & M P Bertenshaw, 'Experiences using IL furnaces for lead analysis in the water industry'. Ladbrook Mercury Hotel, Huddersfield, 1/12/83.

9. 4th International Environment and Safety Conference, The Barbican Centre, London, 27/3/84-29/3/84. (Two papers presented).

10. LABORATORY '84 Exhibition (Spons. RSC, SIMA, CDG), Manchester, 12/4/84

11. Pye Unicam AA User Group Meeting - J Ottaway, 'Recent advances in electrothermal atomisation', A Taylor, 'Clinical applications of the slotted tube atom trap (STAT)', P J Whiteside, 'Graphite platforms - the answer to a maiden's prayer or much ado about nothing?', J F Tyson, 'Flame AA with flow injection sample

introduction', M Lee, 'A new vapour generation system for AA', and G J Stapleton, Continuum source background correction - state of the art. Holiday Inn, Birmingham, 16/5/84.

12. North East Derbyshire District Council - Environmental Health Sub Committee Meeting, 4/12/84. (Presented report to Council).

13. Tourism and Heritage - the practicalities. Institution of Environmental Sciences Conference, Manchester Polytechnic, 29/3/85.

14. 5th International Environment and Safety Conference, Apex Suite, Olympia, London, 16/9/85-19/9/85. (Two papers presented).

15. The British Laboratory Week Exhibition 1985 (Spons. RSC, SIMA, CDG, BLWA, ACB, IST), 17/9/85.

16. Post Graduate Certificate in Education (Further Education) Course - Science Biology Option (University of Leeds), Huddersfield Polytechnic. 10/85-7/86. (Permission obtained for concurrent registration).

PUBLICATIONS AND CONFERENCE PAPERS.

1. Eastwood, I.W. (1982) "lead in Soil - Its distribution and significance in the soils of N. W. Cheshire.", *Terre d'Eau*, Bullitin d'Information du Centre Rivage, France. No. 2 March - April pp 2-4.

2. *"Using SYMAP Under VM/CMS"* (1983) V6/3.25, Sheffield City Polytechnic, Computer Services (Internal Publication).

3. Jackson, K.W., Eastwood, I.W. and Newman, A.P. (1983) "Determination of Trace Metals in Environmental Samples by Micro Atomic Absorption Spectrometry with Solid Sample Introduction." *Paper presented at the 23rd Colloquium Spectroscopium International*, Amsterdam.

4. Wild, M.S. and Eastwood, I.W. (1983) "The ecology of polluted soils." *Presented at 6th Form Geographical Conference*, Nov. '83, Sheffield.

5. Eastwood, I.W. and Jackson, K.W. (1984) "Interlaboratory Comparison of Soil Lead Determinations." *Environmental Pollution (Series B)*, 8, pp 231-243.

6. Eastwood, I.W., Wild, M.S. and Newman, A.P. (1984) "Distribution of soil heavy metal concentrations in an area contaminated by historical smelting and extractive processes." (*Poster Paper presented at 4th International Environment and Safety Conference*, London, March 1984)

7. Eastwood, I.W., Jackson, K.W. and Wild, M.S. (1984) "Evalution of sampling errors when monitoring trace metal concentrations in soil." (*Paper presented at the 4th International Environment and Safety Conference*, London, March 1984)

8. Wild, M.S., Eastwood, I.W. and Newman, A.P. (1984) "*Background distribution of some heavy metals in soils of North East Derbyshire, England.*" (Report to North East Derbyshire District Council - Environmental Health Sub Committee) Rep. No. (NED Cont. Surv.) 1/84, Sheffield City Polytechnic.

9. Eastwood, I.W., Wild, M.S., Newell, P.S. and Jackson, K.W. (1985) "Determination of lead in vegetation by a direct solid sampling microsampling-cup atomic absorption procedure and its application in environmental monitoring." (*Paper presented at the 5th International Environment and Safety Conference*, London, September 1985)

10. Eastwood, I.W., Newman, A.P., Jackson, K.W. and Hinds, M.W. (1985) "Atomic absorption spectrometry - determination of heavy metals in soil and plants without prior dissolution of the sample." (*Poster Paper at 5th International Environment and Safety Conference*, London, September 1985)

11. Eastwood, I.W. and Wild, M.S. (1986) "Industrial Archeological Geochemical Prospecting (IAGP): A Scientific Aid to the Study of Industrial History.", *The Hallamshire Historian*, Vol. 1, No. 1 Autumn), pp 17-22.

12. Jackson, K.W., Eastwood, I.W. and Wild, M.S. (IN PRESS) "Stratified Sampling Protocol for Monitoring Trace Metal Concentrations in Soil." (*To be published in Soil Science.*)

APPENDIX 1.a.

Some extraction/digestion techniques used by various authors in the analysis of 'total' and 'available' lead in soil.

| TECHNIQUE | AUTHORS |
|---|---|
| $HNO_3$ | 59,100,120,161 |
| Dry ashed at 430°C, followed by addition of hot conc. $HNO_3$ | 60,62 |
| Dry ashed at 500°C, followed by addition of 20 ml 4 N $HNO_3$ | 115 |
| Heated for 30 minutes in $HNO_3$, evaporated to dryness; repeat | 61 |
| Sample in 5 ml of 0,5 N, 0,25 N, 0,1 N $HNO_3$ for 30 mins. | 104 |
| Extracted in hot $HNO_3$, evaporated, reextracted with 0,1 M $HNO_3$ | 63 |
| 2,5 g sample digested in 1 N $HNO_3$; repeat 3 X. | 44 |
| 1,0 g sample digested in $HNO_3$ at 25°C for 48 hours | 67 |
| 0,5 g sample digested in 25% $HNO_3$ at 90-95°C | 57,90 |
| 5,0 g sample digested in 20 ml 4 N $HNO_3$, at 80-90°C for 4 hours | 68 |
| 0,4 g sample digested in 8 N $HNO_3$ at 70-90°C for 2 hours | 115 |
| 0,5-2g sample digested in 15 ml $HNO_3$ on a hotplate; $H_2O_2$ added | 76 |
| Boiled overnight | 115 |
| $HNO_3$:$HClO_4$ | |
| 4:1 $HNO_3$:$HClO_4$, boiled for 6 hours at 120°C | 116 |
| 4:1 " " , wet oxidation at 140°C | 49,64 |
| 4:1 " " , wet oxidation at 120°C | 66 |
| 4:1 " " , diluted with $HNO_3$ (0,5 N) | 165 |
| 1:1 " " , 0,1 g sample in 10 ml, dried, taken up in HCl | 28 |
| 5 ml $HNO_3$(70%) + 3 ml $HClO_4$(70%) | 120 |
| Predigested in 10 ml $HNO_3$, then 5,5 ml of 70% $HClO_4$ | 53 |
| 1,0 g in 15 ml on hotplate | 124 |
| $HNO_3$:HCl (Aqua Regia) | |
| 1 g sample extracted in 10 ml $HNO_3$ | 115 |
| Heated to ash in silica crucible then 15-20 g digested in $HNO_3$:HCl | 109 |
| 1 g added to 1:3 aqua regia, repeat 3 X, then digest in 6 M HCl | 101 |
| 10 g in aqua regia | 65 |
| Digested in hot $HNO_3$ followed by aqua regia | 146 |
| $HNO_3$:HF | 43 |
| 0,2 g added to 1:1 $HNO_3$:HF (40%), taken up in 2 ml 2 N HCl | 115 |
| 0,1 g digested in 1:1 $HNO_3$:HF, dried over water bath | 164 |
| $HNO_3$:HF:$HClO_4$ | 51 |
| 1,0 g in 10 ml $HNO_3$:10 ml HF:5 ml $HClO_4$, digest overnight. | 120 |

| TECHNIQUE | AUTHORS |
|---|---|
| $HNO_3$:HF:HCl | |
| Soil oxidised with $HNO_3$:$HClO_4$, evap. to dryness with $HNO_3$:HF:HCl | 182 |
| $HNO_3$:$H_2SO_4$:$HClO_4$ | |
| Wet digestion 10:1:4 mixture with low temp. control | 117 |
| 0,5 g in 6,5 ml 5:0,5:1,5 mixture | 33 |
| HF:$HClO_4$ | 122 |
| 5 ml 48% HF + 0,5 ml 70% $HClO_4$ heated at 200°C | 117 |
| HF:HCl Ignition of sample in platinum crucible 900°C, digestion | 103,118 |
| HCl:$H_2SO_4$ 5 g digested for 20 mins. | 84 |
| HCl (total Pb) | 106,120 |
| Various weights added to 25 ml 7 N HCl, leached with 25 ml N HCl | 31 |
| 2 g sample dry ashed 490°C, digested in 10 ml 6 N HCl at 55°C | 118 |
| 1 g sample heated to 490°C (muffle furnce) 5 hours, digested for 3 hours at 80-90°C in 1:1 HCl:$H_2O$ | 39 |
| HCl (available) | 43 |
| 10 g shaken with 20 ml of 1 N HCl for 1 hour | 115 |
| ACETIC ACID/ACETATE EXTRACTIONS | |
| 20 g sample in 800 ml 0,5 M acetic acid | 102 |
| Extract from acetic acid into EDTA | 101 |
| 5 g sample in 3% acetic acid for 12 hours | 65 |
| Sample shaken for 4 hours with 0,5 N acetic acid | 46,47 |
| Air dried sample extracted in 0,5 N acetic acid | 35 |
| 5 hr leach with 25 ml in 1 N ammonium acetate | 84,103 |
| 1 N ammonium acetate | 33,104,105,106 |
| 10 g in ammonium acetate at pH 7 for 12 hr, percolated for 3 hours | 67 |
| 100 g sodium acetate in 50 ml of water + 30 ml glacial acetic acid at pH 4,8, to predict total lead. | 15 |
| Griggs - acid ammonium oxalate | 106 |

| TECHNIQUE. | AUTHORS. |
|---|---|
| EDTA | |
| Sample shaken with 0,2 M EDTA | 59,100,106 |
| Sample shaken with 0,02 M EDTA for 24 hours | 88 |
| 15 g sample shaken with 0,5 M EDTA for 1 hour (pH 7) | 61 |
| 15 g sample shaken with 0,05 M EDTA for 1 hour (pH 7) | 73 |
| 15 ml of EDTA + 15 ml acetate buffer + 60 ml $H_2O$ extr. into xylene | 108 |
| 15 g sample shaken 1 hour at 20°C with 0,05 M EDTA, then digested | 113 |
| 0,5 M EDTA at pH 7 for 30-60 mins. | 74,146 |
| LIQUID/LIQUID extractions | |
| 1-pyrrolidine dithiocarbamate into chloroform at pH 4,0 | 110 |
| Comparison of HMA HMDC/n-butylactate; DEDTC/MIBK; APPC/MIBK | 92 |
| Extraction in PBHA by chloroform at ph 9,5 | 109 |
| APDC/MIBK, re-extracted into $HNO_3$ | 181 |
| PBHA | 104 |
| 30 ml of DTPA sol. + 15 g soil shaken 2 hours, buffered pH 3 | 127 |
| OTHERS | |
| Sodium carbonate fusion | 117 |
| Calcium chloride 0,05 M , also Barium Chloride 0,5 M. | 100 |
| 10 g soil in water for 48 hours at 25°C | 67 |
| SOME COMPARATIVE STUDIES | 100,104,106,109,115 117,120 |

APPENDIX 1.b.

Some soil and plant sampling techniques used by various authors.

| TECHNIQUE. | SOIL LEAD DETERMINATION. | PLANT LEAD DETERMINATION. |
|---|---|---|
| TRANSECTS | 28,34,39,48,68,71,74,164,247 | 28,34,39,65,116,164 |
| SAMPLING GRIDS | 35,46,51,61,62,63,94,116 | |
| SOIL DEPTH PITS | 28,33,35,39,44,45,46,47,48,49,50, 60,61,63,66,68,71,88,105,106,116, 120,125,127,143,161,164,247 | |
| AUGERS | 36,43,46,48,60,62,70,74,106,116, 161,164 | |
| SOME MENTION OF REPRESENTATIVE SAMPLING | 30,44,45,46,52,57,59,70,83,88, 161,169 | 45,49,52,61,66,74,83,132,161,169 |
| RANDOM SAMPLING | 32,33,36,49,53,64,65,73,78,105, 115,127,183 | 59,69,77,105,168 |

(Numbers refer to reference number in 'list of references')

APPENDIX 1.c.

Some vegetation samples studied by various authors

| VEGETATION. | AUTHORS. | VEGETATION. | AUTHORS. |
|---|---|---|---|
| Aleppo Pine | 52 | Oats | 34,104,142,145 |
| Alfalfa | 97 | Onion | 49 |
| Autumn Olive | 148 | Parsnip | 49,74 |
| Barley | 62 | Peanuts | 169 |
| Beet | 37,76,78 | Perennial Ryegrass | 144,247 |
| Black Locust | 148 | Pine | 50 |
| Bromegrass | 28 | Poke | 76 |
| Cabbage | 45,47,49,74,159 | Potato | 49,73,169 |
| Carrots | 49,74,77,78 | Radish | 59,61,73,74,78, 146,247 |
| Cauliflower | 49 | Red Oak | 50,148 |
| Celery | 49 | Short leaf pine | 148 |
| Chard | 57,76,110 | Soybeans | 47,90,161,169 |
| Clover | 159 | Spinach | 170 |
| Collards | 37,77 | Sweet Corn | 169 |
| Corn | 31,32,46 | Sycamore | 65 |
| Cottonwood | 148,164 | Tomatoes | 77 |
| Fungi | 69 | Tree rings/bark | 29 |
| Garlic leaves | 47 | Turnips | 78 |
| Grasses | 116,159 | Wheat | 106,143,169 |
| Kale | 76 | White Oak | 148 |
| Koramiko | 164 | Yellow poplar | 148 |
| Lettuce | 37,47,49,76,78,104 145,159,169 | Various/grab samples | 28,39,64,132,161 |
| Loblolly pine | 148 | | |
| Mint | 42 | | |
| Mustard | 37 | | |

(Numbers refer to reference number in 'list of references')

APPENDIX 1.d.

Some techniques used in the preparation of plant samples.

| TECHNIQUE. | AUTHORS. |
|---|---|
| ACID DIGESTION AND WET ASHING. | 69,77,116 |
| $HNO_3$ | 62,105 |
| 10 M $HNO_3$ for 1 hour | 38 |
| $HNO_3$:$HClO_4$ taken up in 3 N $HNO_3$ | 46,104,141,145,155 |
| $HNO_3$:$HClO_4$:$H_2SO_4$ | 45,106 |
| 6 M HCl for 15 minutes | 57 |
| $HNO_3$:$HClO_4$(:H2O) | 49,52,64,65,66,67,97, 103,143,144,147,247 |
| DRY ASHING. | 247 |
| 430°C - taken up in $HNO_3$ | 59,61,73,74,161 |
| 430°C - 5 g sample taken up in HCl then $HNO_3$ | 47 |
| 450°C - taken up in HCl | 28,29,102,146,164 |
| 450°C - for 5 hours taken up in 6 N HCl | 148 |
| 450°C - for 30 mins. with $H_2SO_4$:$H_2O$ ash aid, taken up in $HNO_3$ | 169 |
| 470°C - for 5 hours | 186 |
| 475°C - 2 g taken up in hot $HNO_3$ over 30 mins. | 132 |
| 475-500°C - taken up in 2 N HCl | 103 |
| 490°C - for 4 hours, taken up in 3 N HCl | 32,90 |
| 490°C - for 5 hours, taken up in HCl:$H_2O$ | 39 |
| 500°C - for 2 hours | 75 |
| 510°C - for 10-16 hours, taken up in HCl | 76 |
| 560°C - for 16 hours, taken up in $HNO_3$:HCl | 37,77 |
| ACID DIGESTION BOMB | |
| $HNO_3$:$HClO_4$ | 122,173 |
| SOLID SAMPLING | 159,177,353 |

(Numbers refer to reference number in 'list of references').

APPENDIX 1.e.

Some analytical techniques employed by various authors in the analysis of lead in soil and plant samples.

| TECHNIQUE. | SOIL LEAD DETEMINATION. | PLANT LEAD DETERMINATION. |
|---|---|---|
| FLAME ATOMIC ABSORPTION SPECTROSCOPY | 28,30,33,36,39,44,45,46,47,49, 57,59,60,61,62,63,65,67,70,73, 74,84,88,90,92,103,104,105,109, 113,115,116,117,118,124,125, 127,146,161,164,165, | 28,32,34,37,38,39,45,46,47,49, 52,57,59,61,62,65,66,67,73,76, 77,90,103,104,105,129,132,143, 144,145,146,147,155,159,161, 164,171 |
| FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY | 64,74,92,101,102,103,108,110, 122,146,181,182 | 29,64,74,103,122,146,177,186 |
| SPECTROPHOTOMETRY/ COLORIMETRY | 31,106,109 | 106,141,247 |
| DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY | 102,113 | 169 |
| MASS SPECTROMETRY | 43,183 | |
| X-RAY FLUORESCENCE | 75,78,182,184 | 50,78,170 |
| POLOROGRAPHY | | 29 |
| INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY | 51,75,182 | |

(Numbers refer to reference number in 'list of references')

APPENDIX 1.f.

Quality control techniques used by some investigators

| TECHNIQUE | SOIL LEAD DETERMINATION | PLANT LEAD DETERMINATION |
|---|---|---|
| SOME MENTION OF TESTS ON PRECISION AND ACCURACY | 30,49,66,70,74,92,102,108,110, 113,115,118,124, | 29,32,37,38,49,50,66,67,77,78, 102,144,146,155,159,169,170,186 |
| STANDARD ADDITIONS | 29,30,35,49,51,66,67,73,78,101, 103,108,109,113,115,116,117, 124,127 | |
| STANDARD REFERENCE MATERIALS | 36,66,78,102,122,182,183 | 37,66,77,78,102,159,169,173,177 |
| INTER-LABORATORY COMPARISONS | 70,78,124,182 | 38,67 |

(Numbers refer to reference number in 'list of references')

APPENDIX 2.a.

Replicate results for lead in soil sample α using conc. nitric acid and 1 + 1 nitric acids digests.

| n | SOIL SAMPLE α, (conc, µg/g) 1 + 1 $HNO_3$ digestion, | SOIL SAMPLE α (conc, µg/g) Conc, $HNO_3$ digestion, |
|---|---|---|
| 1 | 99 | 101 |
| 2 | 83 | 62 |
| 3 | 104 | 65 |
| 4 | 92 | 66 |
| 5 | 91 | 59 |
| 6 | 94 | 63 |
| 7 | 90 | 77 |
| 8 | 96 | 66 |
| 9 | 89 | 80 |
| 10 | 175 | 78 |
| 11 | 91 | 64 |
| 12 | 97 | 86 |
| 13 | 99 | 71 |
| 14 | 97 | 59 |
| 15 | 96 | 67 |
| 16 | 87 | 67 |
| 17 | 111 | 81 |
| 18 | 96 | 83 |
| 19 | 100 | 71 |
| 20 | 98 | 61 |
| 21 | 120 | 87 |
| n | 21 | 21 |
| Mean | 100 | 72 |
| Std Dev | 18,9 | 11,3 |
| RSD % | 18,9 | 15,6 |

APPENDIX 2.b.

Replicate results for lead in soil sample ß using conc. nitric acid and 1 + 1 nitric acids digests.

| n | SOIL SAMPLE ß. (conc. µg/g) 1 + 1 $HNO_3$ digestion. | SOIL SAMPLE ß (conc. µg/g) Conc. $HNO_3$ digestion. |
|---|---|---|
| 1 | 628 | 543 |
| 2 | 612 | 551 |
| 3 | 621 | 564 |
| 4 | 612 | 546 |
| 5 | 647 | 540 |
| 6 | 662 | 530 |
| 7 | 648 | 568 |
| 8 | 633 | 541 |
| 9 | 593 | 551 |
| 10 | 598 | 552 |
| 11 | 607 | 549 |
| n | 11 | 11 |
| Mean | 624 | 548 |
| Std Dev | 22,1 | 10,7 |
| RSD % | 3,54 | 1,96 |

APPENDIX 2.c.

Replicate results for lead in soil sample Y using conc. nitric acid and 1 + 1 nitric acids digests.

| n | SOIL SAMPLE Y, (conc, µg/g) 1 + 1 $HNO_3$ digestion, | | SOIL SAMPLE Y (conc, µg/g) Conc, $HNO_3$ digestion, |
|---|---|---|---|
| 1 | 3634 | 3704 | 3085 |
| 2 | 3603 | 3582 | 3188 |
| 3 | 3596 | 3589 | 3194 |
| 4 | 3582 | 3638 | 3088 |
| 5 | 3537 | 3585 | 3147 |
| 6 | 3533 | 3520 | 3137 |
| 7 | 3505 | 3540 | 3176 |
| 8 | 3561 | 3478 | 3128 |
| 9 | 3520 | 3505 | 3179 |
| 10 | 3505 | 3488 | 3154 |
| 11 | 3474 | 3478 | 3138 |
| 12 | 3471 | 3512 | 3103 |
| 13 | 3516 | 3485 | 3016 |
| 14 | 3596 | 3526 | 3100 |
| 15 | 3481 | 3495 | 3150 |
| 16 | 3561 | 3540 | 3153 |
| 17 | 3519 | 3502 | 3160 |
| 18 | 3548 | 3512 | 3128 |
| 19 | 3547 | 3492 | 3103 |
| 20 | 3429 | 3467 | 3135 |
| 21 | | | 3141 |
| 22 | | | 3135 |
| 23 | | | 3123 |
| n | 40 | | 23 |
| Mean | 3534 | | 3133 |
| Std Dev | 55,4 | | 39,0 |
| RSD % | 1,57 | | 1,25 |

APPENDIX 3. Replicate results (a, b and c) for lead and copper at each of the 121 sample locations.

| Grid location. | Lead in soil (µg/g). | | | Copper in soil (µg/g) | | |
|---|---|---|---|---|---|---|
| | a. | b. | c. | a. | b. | c. |
| A 1 | 236.5 | 224 | - | 53.0 | 52.4 | 51.2 |
| A 2 | 99 | 101 | - | 52.0 | 54.4 | - |
| A 3 | 53 | 53 | - | 25.6 | 25.4 | - |
| A 4 | 66 | 65 | - | 26.7 | 26.6 | - |
| A 5 | 61 | 66 | - | 24.6 | 23.2 | - |
| A 6 | 50 | 53 | - | 22.0 | 20.4 | - |
| A 7 | 49 | 48 | - | 23.5 | 23.2 | - |
| A 8 | 63 | 64 | - | 25.5 | 25.0 | - |
| A 9 | 274.5 | 279.5 | - | 63.9 | 65.8 | - |
| A10 | 312 | 304 | - | 68.8 | 69.8 | - |
| A11 | 250 | 249 | - | 50.8 | 50.2 | - |
| B 1 | 71 | 72 | - | 31.1 | 31.9 | - |
| B 2 | 369 | 364.5 | - | 51.2 | 52.7 | - |
| B 3 | 105 | 108 | - | 38.7 | 39.8 | - |
| B 4 | 51 | 46 | - | 24.4 | 24.3 | - |
| B 5 | 77 | 71 | - | 24.3 | 23.7 | - |
| B 6 | 61 | 54 | - | 22.1 | 21.8 | 21.2 |
| B 7 | 89 | 83 | - | 27.6 | 25.0 | - |
| B 8 | 52 | 42 | - | 24.5 | 24.1 | 24.3 |
| B 9 | 54.5 | 48 | - | 22.0 | 15.9 | - |
| B10 | 55 | 47 | - | 21.8 | 18.1 | - |
| B11 | 137 | 134 | - | 32.3 | 33.3 | 33.4 |
| C 1 | 63 | 56 | - | 23.9 | 17.9 | - |
| C 2 | 66.5 | 62 | - | 28.3 | 20.6 | - |
| C 3 | 349.5 | 332 | - | 53.4 | 44.9 | - |
| C 4 | 74 | 70 | - | 34.6 | 32.1 | - |
| C 5 | 80 | 71 | - | 29.6 | 28.2 | - |
| C 6 | 73 | 69 | - | 26.9 | 24.9 | - |
| C 7 | 73 | 66 | - | 25.4 | 19.0 | - |
| C 8 | 80 | 82 | - | 28.2 | 21.2 | - |
| C 9 | 110.5 | 112 | - | 27.5 | 26.4 | 24.4 |
| C10 | 60 | 52 | - | 20.3 | 17.6 | - |
| C11 | 57 | 50 | - | 25.0 | 22.0 | - |
| D 1 | 74 | 67 | - | 25.2 | 19.9 | - |
| D 2 | 92 | 81 | - | 35.3 | 35.0 | - |
| D 3 | 89.5 | 87 | - | 35.3 | 35.9 | - |
| D 4 | 112 | 119 | - | 42.4 | 42.7 | - |
| D 5 | 94 | 90 | - | 29.7 | 30.5 | - |
| D 6 | 69 | 65 | - | 26.4 | 26.8 | - |
| D 7 | 66 | 56 | - | 26.1 | 26.1 | - |
| D 8 | 73 | 77 | - | 24.4 | 21.6 | - |
| D 9 | 69 | 77 | - | 27.7 | 24.9 | - |
| D10 | 34 | 35 | - | 15.6 | 14.4 | - |
| D11 | 43 | 33 | - | 24.0 | 22.1 | - |
| E 1 | 70 | 77 | - | 29.2 | 26.6 | - |
| E 2 | 58 | 65 | 69 | 61.6 | 58.7 | 59.2 |
| E 3 | 72 | 61 | - | 28.5 | 25.5 | - |
| E 4 | 332 | 327 | 375 | 88.9 | 90.9 | - |
| E 5 | 104 | 91 | - | 35.5 | 28.4 | - |
| E 6 | 46 | 48 | - | 22.5 | 18.6 | - |
| E 7 | 78 | 87 | - | 31.7 | 29.4 | - |
| E 8 | 60 | 66 | - | 23.7 | 19.9 | - |
| E 9 | 66 | 77 | - | 22.1 | 18.1 | - |
| E10 | 58 | 46 | - | 21.6 | 17.3 | - |
| E11 | 47 | 38.5 | - | 22.6 | 19.0 | - |

APPENDIX 3. Continued.

| Grid location. | Lead in soil (µg/g). | | | Copper in soil (µg/g) | | |
|---|---|---|---|---|---|---|
| | a. | b. | c. | a. | b. | c. |
| F 1 | 62 | 50 | 53 | 23.2 | 19.9 | - |
| F 2 | 78 | 87 | - | 29.7 | 26.9 | - |
| F 3 | 111 | 118 | - | 29.2 | 25.8 | - |
| F 4 | 59 | 70 | - | 31.6 | 28.5 | - |
| F 5 | 195 | 192 | 215 | 47.9 | 47.5 | - |
| F 6 | 92 | 100 | - | 33.8 | 31.3 | - |
| F 7 | 200 | 202 | - | 74.9 | 61.7 | - |
| F 8 | 121 | 131 | - | 36.7 | 34.7 | - |
| F 9 | 49 | 60 | - | 26.7 | 24.6 | - |
| F10 | 48 | 50 | - | 22.3 | 18.0 | - |
| F11 | 71 | 74 | - | 27.3 | 24.1 | - |
| G 1 | 280 | 272 | 275 | 78.7 | 71.2 | - |
| G 2 | 118 | 116 | - | 42.2 | 38.0 | - |
| G 3 | 72 | 75 | - | 30.6 | 27.7 | - |
| G 4 | 63 | 67 | - | 25.7 | 22.3 | - |
| G 5 | 164 | 154 | - | 53.2 | 49.9 | - |
| G 6 | 85 | 89 | - | 35.1 | 33.1 | - |
| G 7 | 69.5 | 77 | - | 31.1 | 27.6 | - |
| G 8 | 81 | 89 | - | 31.7 | 28.2 | - |
| G 9 | 110 | 110 | - | 35.6 | 32.9 | - |
| G10 | 118 | 115 | - | 32.0 | 26.9 | - |
| G11 | 124 | 121 | - | 37.3 | 33.4 | - |
| H 1 | 66 | 77 | - | 27.3 | 24.7 | - |
| H 2 | 60 | 67 | - | 21.9 | 16.9 | - |
| H 3 | 38 | 34 | - | 25.2 | 23.0 | - |
| H 4 | 136 | 125 | - | 91.4 | 84.3 | - |
| H 5 | 735 | 763 | - | 36.8 | 39.7 | - |
| H 6 | 519 | 527 | - | 58.1 | 57.7 | - |
| H 7 | 74 | 78 | - | 32.3 | 33.6 | - |
| H 8 | 122 | 124 | - | 39.4 | 39.8 | - |
| H 9 | 96.5 | 101 | - | 32.8 | 34.6 | - |
| H10 | 92.5 | 95 | - | 35.6 | 38.3 | - |
| H11 | 71 | 74 | - | 27.0 | 26.4 | - |
| I 1 | 27 | 22 | - | 29.6 | 30.0 | - |
| I 2 | 40 | 31 | - | 25.9 | 26.0 | - |
| I 3 | 31 | 30 | - | 28.3 | 27.6 | - |
| I 4 | 147 | 149 | - | 38.3 | 40.4 | - |
| I 5 | 123 | 123 | - | 33.8 | 34.5 | - |
| I 6 | 928 | 920 | - | 39.2 | 40.1 | - |
| I 7 | 914 | 971 | - | 68.1 | 68.7 | - |
| I 8 | 335 | 332 | - | 76.6 | 77.9 | - |
| I 9 | 180.5 | 188 | - | 46.4 | 48.1 | - |
| I10 | 209 | 209 | - | 60.8 | 61.1 | - |
| I11 | 197 | 192 | - | 41.7 | 42.7 | - |
| J 1 | 71 | 73 | - | 34.4 | 34.2 | - |
| J 2 | 51 | 55 | - | 26.9 | 26.4 | - |
| J 3 | 71 | 70 | - | 26.9 | 28.0 | - |
| J 4 | 173 | 169 | - | 38.7 | 39.5 | - |
| J 5 | 83 | 85 | - | 31.0 | 31.5 | - |
| J 6 | 150 | 145 | - | 44.6 | 45.6 | - |
| J 7 | 106 | 108 | - | 41.8 | 41.8 | - |
| J 8 | 199 | 198 | - | 70.3 | 67.7 | - |
| J 9 | 231 | 235.5 | - | 47.4 | 47.3 | - |
| J10 | 260 | 270 | - | 75.1 | 76.3 | - |
| J11 | 116 | 120 | - | 49.7 | 49.3 | - |
| K 1 | 46 | 48 | - | 23.5 | 23.8 | - |
| K 2 | 27 | 26 | - | 20.9 | 23.5 | - |
| K 3 | 29 | 30 | - | 17.4 | 16.5 | - |
| K 4 | 36 | 44 | - | 23.8 | 23.0 | - |
| K 5 | 19 | 25 | - | 14.9 | 15.2 | - |
| K 6 | 46 | 46 | - | 19.8 | 18.1 | - |
| K 7 | 24 | 25 | - | 23.4 | 23.9 | - |
| K 8 | 112 | 114 | - | 24.1 | 24.7 | - |
| K 9 | 132 | 134 | - | 35.1 | 36.4 | - |
| K10 | 149 | 160 | - | 41.8 | 42.9 | - |
| K11 | 129 | 136 | - | 40.5 | 41.3 | - |

APPENDIX 4.a. Complete data results for total lead in soil for the North East Derbyshire Soil Survey (µg/g).

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| A 1 | 405805 | 65 | 63 | - | - | 64 |
| A 2 | 415805 | 130 | 165* | 136 | 132 | 133 |
| A 3 | 425805 | 202.5 | 204 | - | - | 203 |
| A 4 | 435085 | 111 | 110 | - | - | 110 |
| A 5 | 445805 | 251 | 266 | - | - | 258 |
| A 6 | 455805 | 84 | 88 | 92 | 89 | 88 |
| A 7 | 405795 | 118.5 | 130 | - | - | 124 |
| A 8 | 415795 | 159 | 158 | - | - | 158 |
| A 9 | 425795 | 168 | 166 | - | - | 167 |
| A 10 | 435795 | 182 | 186.5 | - | - | 184 |
| A 11 | 445795 | 173 | 173 | - | - | 173 |
| A 12 | 455795 | 122 | 121 | - | - | 122 |
| A 13 | 405785 | 148 | 155 | - | - | 152 |
| A 14 | 415785 | 70 | 68 | - | - | 69 |
| A 15 | 425785 | 126 | 123 | - | - | 124 |
| A 16 | 435785 | ND | ND | ND | ND | ND |
| A 17 | 445785 | 92 | 95 | - | - | 94 |
| A 18 | 455785 | 104 | 110 | - | - | 107 |
| A 19 | 405775 | 95 | 97 | - | - | 96 |
| A 20 | 415775 | 92 | 161* | 101 | 100 | 98 |
| A 21 | 425775 | 186 | 195 | - | - | 190 |
| A 22 | 435775 | 95 | 96 | - | - | 96 |
| A 23 | 445775 | 132 | 131.5 | - | - | 132 |
| A 24 | 455775 | 115.3 | 184* | 116 | 119 | 116 |
| B 1 | 365825 | 238 | 261* | 231.5 | 229 | 233 |
| B 2 | 375825 | 180 | 118* | 180.5 | 182 | 181 |
| B 3 | 385825 | 235 | 239 | - | - | 237 |
| B 4 | 395825 | 109 | 138* | 111 | 113 | 111 |
| B 5 | 405825 | 131 | 133.5 | - | - | 132 |
| B 6 | 365815 | 175 | 137 | - | - | 156 |
| B 7 | 375815 | 194 | 190 | - | - | 192 |
| B 8 | 385815 | 113 | 101 | - | - | 107 |
| B 9 | 395815 | 113 | 126 | 124.5 | 119 | 121 |
| B 10 | 405815 | 136 | 127 | - | - | 132 |
| B 11 | 365805 | 104 | 99 | - | - | 102 |
| B 12 | 375805 | 143.5 | 134 | - | - | 139 |
| B 13 | 385805 | 93* | 69 | 70 | 72 | 70 |
| B 14 | 395805 | 142 | 137 | - | - | 140 |
| B 15 | 365795 | 145 | 150 | - | - | 148 |
| B 16 | 375795 | 191 | 196 | - | - | 194 |
| B 17 | 385795 | 141.5 | 148 | - | - | 145 |
| B 18 | 395795 | 116 | 107 | - | - | 112 |
| B 19 | 365785 | 105 | 89.5 | - | - | 97 |
| B 20 | 375785 | 84 | 75 | - | - | 80 |
| B 21 | 385785 | 143 | 124* | 141 | 140 | 141 |
| B 22 | 395785 | 302 | 267 | - | - | 284 |
| B 23 | 365775 | 252.5 | 235 | - | - | 244 |
| B 24 | 375775 | 118 | 112.5 | 112 | 119 | 115 |
| B 25 | 385775 | 116 | 111 | - | - | 114 |
| B 26 | 395775 | 280 | 287 | - | - | 284 |
| C 1 | 455815 | 476 | 669* | 542 | 453 | 490 |
| C 2 | 465815 | 178 | 147 | 151 | 166 | 160 |
| C 3 | 475815 | 828 | 853 | - | - | 180 |
| C 4 | 485815 | 162 | 156 | 156 | 174 | 162 |
| C 5 | 495815 | 88 | 85 | - | - | 86 |
| C 6 | 465805 | 288.5 | 251* | 279 | 303.5 | 290 |
| C 7 | 475805 | 468* | 231 | 244 | 253 | 243 |
| C 8 | 485805 | 409* | 339 | 351.5 | 351 | 347 |
| C 9 | 495805 | 102 | 102 | - | - | 102 |
| C 10 | 465795 | 260 | 240 | - | - | 250 |
| C 11 | 475795 | 185.5 | 182 | - | - | 184 |
| C 12 | 485795 | 82 | 72 | - | - | 77 |
| C 13 | 495795 | 87 | 82 | - | - | 84 |
| C 14 | 465785 | 98 | 93 | - | - | 96 |
| C 15 | 475785 | 171 | 155 | - | - | 163 |
| C 16 | 485785 | 96 | 98 | 97 | 97 | 97 |
| C 17 | 495785 | 146 | 141 | - | - | 144 |
| C 18 | 465775 | 115 | 110 | - | - | 112 |
| C 19 | 475775 | 124 | 127 | 116 | 116 | 121 |
| C 20 | 485775 | 192 | 193 | - | - | 192 |
| C 21 | 495775 | 127 | 122 | - | - | 124 |
| C 22 | 465765 | 88 | 88 | - | - | 88 |
| C 23 | 475765 | 91 | 89 | - | - | 90 |
| C 24 | 485765 | 186 | 182.5 | - | - | 184 |
| C 25 | 495765 | 101 | 102 | - | - | 102 |
| D 1 | 325805 | 215 | 219 | - | - | 217 |
| D 2 | 335805 | 183 | 172 | 157 | 164 | 169 |
| D 3 | 345805 | 165 | 161 | - | - | 163 |
| D 4 | 355805 | 290 | 261 | 374* | 262 | 271 |
| D 5 | 325795 | 160.5 | 158 | 155 | 151 | 156 |
| D 6 | 335795 | 161 | 154 | - | - | 158 |
| D 7 | 345795 | 218 | 206* | 208 | 215 | 214 |
| D 8 | 355795 | 150 | 125 | - | - | 138 |
| D 9 | 325785 | 241 | 254 | - | - | 374 |
| D 10 | 335785 | 252 | 235 | - | - | 244 |
| D 11 | 345785 | 141 | 145 | - | - | 143 |
| D 12 | 355785 | 264 | 280 | - | - | 272 |
| D 13 | 325775 | 186 | 171 | - | - | 178 |
| D 14 | 335775 | 67 | 65 | - | - | 66 |
| D 15 | 345775 | 133 | 134 | - | - | 134 |
| D 16 | 355775 | 179 | 179 | - | - | 176 |
| D 17 | 325765 | 154 | 128 | - | - | 141 |
| D 18 | 335765 | 156 | 162 | - | - | 159 |
| D 19 | 345765 | 145 | 146 | - | - | 146 |

APPENDIX 4.a. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| D 20 | 355765 | 152 | 153 | - | - | 152 |
| D 21 | 325755 | 172 | 164 | - | - | 168 |
| D 22 | 335755 | 167 | 170 | - | - | 168 |
| D 23 | 345755 | 178 | 175 | - | - | 176 |
| D 24 | 355755 | 443 | 426 | - | - | 434 |
| E 1 | 265795 | 190 | 186 | - | - | 188 |
| E 2 | 275795 | 180 | 174 | - | - | 177 |
| E 3 | 285795 | 128 | 118 | - | - | 123 |
| E 4 | 295795 | 165 | 161 | - | - | 163 |
| E 5 | 305795 | 708 | 997 | 810.5 | 824 | 835 |
| E 6 | 315795 | 436 | 420 | - | - | 428 |
| E 7 | 265785 | 299 | 295 | - | - | 297 |
| E 8 | 275785 | 315 | 297 | - | - | 306 |
| E 9 | 285785 | 317 | 322 | - | - | 320 |
| E 10 | 295785 | 176 | 179 | - | - | 178 |
| E 11 | 305785 | 180 | 192 | - | - | 186 |
| E 12 | 315785 | 107.5 | 122 | 110 | - | 113 |
| E 13 | 265775 | 219 | 214 | - | - | 216 |
| E 14 | 275775 | 230 | 226 | - | - | 228 |
| E 15 | 285775 | 156 | 150 | - | - | 153 |
| E 16 | 295775 | 251 | 242 | - | - | 246 |
| E 17 | 305775 | 404 | 386 | - | - | 395 |
| E 18 | 315775 | 261 | 248 | - | - | 254 |
| E 19 | 265765 | 1252 | 1213 | - | - | 1232 |
| E 20 | 275765 | 125 | 158 | - | - | 141 |
| E 21 | 285765 | 232 | 228 | - | - | 230 |
| E 22 | 295765 | 144 | 128 | - | - | 136 |
| E 23 | 305765 | 454 | 510 | - | - | 482 |
| E 24 | 315765 | 374 | 789* | 326 | 315 | 338 |
| F 1 | 275755 | 145 | 207* | 129 | 137 | 137 |
| F 2 | 285755 | 491 | 506 | - | - | 498 |
| F 3 | 295755 | 424 | 416 | - | - | 420 |
| F 4 | 305755 | 294 | 282 | - | - | 288 |
| F 5 | 315755 | 208 | 199 | - | - | 204 |
| F 6 | 275745 | 240 | 238 | - | - | 239 |
| F 7 | 285745 | 529 | 512 | - | - | 520 |
| F 8 | 295745 | 1569 | 1027* | 1537 | 1519 | 1542 |
| F 9 | 305745 | 258 | 237 | - | - | 248 |
| F 10 | 315745 | 178 | 164 | - | - | 171 |
| F 11 | 285735 | 329 | 323 | - | - | 326 |
| F 12 | 295735 | 398 | 385 | - | - | 392 |
| F 13 | 305735 | 122 | 112 | - | - | 117 |
| F 14 | 315735 | 120 | 109 | - | - | 114 |
| F 15 | 285725 | 318 | 118* | 276 | 301 | 298 |
| F 16 | 295725 | 244 | 164* | 210.5 | 212 | 230 |
| F 17 | 305725 | 202 | 222 | - | - | 212 |
| F 18 | 315725 | 126 | 282* | 113 | 116 | 119 |
| F 19 | 285715 | 667 | 551 | 641 | 606 | 616 |
| F 20 | 295715 | 377* | 324 | 306 | 308 | 313 |
| F 21 | 305715 | 358 | 324 | - | - | 341 |
| F 22 | 315715 | 178 | 109* | 148 | 152 | 147 |
| F 23 | 285705 | 187 | 174 | - | - | 180 |
| F 24 | 295705 | 681 | 635 | - | - | 658 |
| F 25 | 305705 | 328 | 312 | - | - | 320 |
| F 26 | 315705 | 233 | 226 | - | - | 230 |
| G 1 | 325745 | 120 | 121 | 112 | 112 | 116 |
| G 2 | 335745 | 101 | 106 | 92 | 96 | 98 |
| G 3 | 345745 | 119 | 116 | 117 | - | 117 |
| G 4 | 355745 | 88 | 136* | 84 | - | 86 |
| G 5 | 325735 | 166 | 154 | 159 | - | 160 |
| G 6 | 335735 | 158 | 135 | 148 | - | 147 |
| G 7 | 345735 | 153 | 136 | 119 | - | 136 |
| G 8 | 355735 | 213 | 195 | 196 | - | 201 |
| G 9 | 325725 | 148 | 138 | 142 | - | 143 |
| G 10 | 335725 | 160 | 142 | 148 | - | 150 |
| G 11 | 345725 | 223 | 112* | 204 | - | 214 |
| G 12 | 355725 | 337 | 329 | 314 | - | 327 |
| G 13 | 325715 | 204 | 248 | 187 | - | 213 |
| G 14 | 335715 | 252 | 116* | 236 | - | 244 |
| G 15 | 345715 | 214 | 190 | 200 | - | 201 |
| G 16 | 355715 | 237 | 211 | 221 | - | 223 |
| G 17 | 325705 | 272 | 241 | 258 | - | 257 |
| G 18 | 335705 | 440 | 423 | 420 | - | 428 |
| G 19 | 345705 | 460 | 451 | 445 | - | 452 |
| G 20 | 355705 | 670 | 665 | 650 | - | 662 |
| G 21 | 325695 | 308 | 263 | 262 | - | 277 |
| G 22 | 335695 | 733 | 674 | 715 | - | 707 |
| G 23 | 345695 | 300 | 283 | 304 | - | 296 |
| G 24 | 355695 | 426 | 349* | 400 | - | 413 |
| H 1 | 425725 | 67 | 71 | - | - | 69 |
| H 2 | 435725 | 92 | 97 | - | - | 94 |
| H 3 | 405715 | 172 | 152 | 164 | - | 163 |
| H 4 | 415715 | 135 | 133 | - | - | 134 |
| H 5 | 425715 | 106 | 78 | 93 | - | 92 |
| H 6 | 435715 | 183 | 220 | 202 | - | 202 |
| H 7 | 445715 | 109 | 90 | 100 | - | 100 |
| H 8 | 455715 | 97 | 101 | - | - | 99 |
| H 9 | 405705 | 191* | 160 | 166 | - | 163 |
| H 10 | 415705 | 219 | 197 | 214 | - | 210 |
| H 11 | 425705 | 302 | 289 | 255 | - | 282 |
| H 12 | 435705 | 116 | 108 | 118 | - | 115 |
| H 13 | 445705 | 91 | 90 | - | - | 90 |
| H 14 | 455705 | 73 | 73 | - | - | 73 |
| H 15 | 405695 | 138 | 127 | 139 | - | 135 |
| H 16 | 415695 | 82 | 73 | - | - | 78 |
| H 17 | 425695 | 145 | 139 | 142 | - | 142 |

APPENDIX 4.a. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| H 18 | 435695 | 129 | 129 | 127 | - | 128 |
| H 19 | 445695 | 84 | 75 | - | - | 80 |
| H 20 | 455695 | 78 | 73.5 | - | - | 76 |
| H 21 | 405685 | 168 | 193 | - | - | 180 |
| H 22 | 415685 | 339 | 329 | 314 | - | 327 |
| H 23 | 425685 | 63 | 58 | - | - | 60 |
| H 24 | 435685 | 131 | 134 | - | - | 132 |
| H 25 | 445685 | 90 | 86 | - | - | 88 |
| H 26 | 455685 | 66 | 61 | 71 | - | 66 |
| I 1 | 325685 | 273 | 276 | - | - | 274 |
| I 2 | 335685 | 495 | 497 | - | - | 496 |
| I 3 | 345685 | 313 | 321.5 | - | - | 317 |
| I 4 | 355685 | 268 | 289 | - | - | 278 |
| I 5 | 325675 | 152 | 144.5 | - | - | 148 |
| I 6 | 335675 | 6799 | 6735 | - | - | 6767 |
| I 7 | 345675 | 143 | 139 | - | - | 141 |
| I 8 | 355675 | 130 | 126 | - | - | 128 |
| I 9 | 325665 | 660 | 604.5 | - | - | 632 |
| I 10 | 335665 | 1101 | 1247.5 | - | - | 1174 |
| I 11 | 345665 | 173 | 176 | - | - | 174 |
| I 12 | 355665 | 116 | 116 | - | - | 116 |
| I 13 | 325655 | 599 | 580.5 | - | - | 590 |
| I 14 | 335655 | 264 | 253 | - | - | 258 |
| I 15 | 345655 | 354 | 433* | 312 | 331 | 332 |
| I 16 | 355655 | 179 | 187 | - | - | 183 |
| I 17 | 325645 | 690 | 630 | - | - | 660 |
| I 18 | 335645 | 376 | 358 | - | - | 367 |
| I 19 | 345645 | 258 | 308.5* | 234 | 245 | 246 |
| I 20 | 355645 | 346 | 354 | - | - | 350 |
| I 21 | 325635 | 299 | 331 | - | - | 315 |
| I 22 | 335635 | 587 | 557 | - | - | 572 |
| I 23 | 345635 | 650 | 649 | 634 | 627 | 640 |
| I 24 | 355635 | 260 | 257 | 235 | 252 | 251 |
| J 1 | 365695 | 219 | 211 | - | - | 215 |
| J 2 | 375695 | 203 | 210 | 198 | - | 204 |
| J 3 | 385695 | 239 | 238.5 | - | - | 239 |
| J 4 | 395695 | 196 | 179.5 | - | - | 188 |
| J 5 | 365685 | 117 | 114 | - | - | 116 |
| J 6 | 375685 | 132 | 135 | - | - | 134 |
| J 7 | 385685 | 240 | 297 | 213.5 | - | 250 |
| J 8 | 395685 | 164.5 | 149 | - | - | 157 |
| J 9 | 365675 | 349 | 342 | 370 | 367 | 357 |
| J 10 | 375675 | 97 | 93 | - | - | 95 |
| J 11 | 385675 | 160 | 147 | - | - | 154 |
| J 12 | 395675 | 177 | 166 | - | - | 172 |
| J 13 | 365665 | 7870 | 7803 | - | - | 7836 |
| J 14 | 375665 | 218 | 221 | 220 | 222 | 220 |
| J 15 | 385665 | 350 | 353 | - | - | 352 |
| J 16 | 395665 | 565.5 | 564 | - | - | 565 |
| J 17 | 365655 | 128 | 137 | 131 | - | 132 |
| J 18 | 375655 | 140 | 132 | 126 | - | 132 |
| J 19 | 385655 | 93 | 90 | 94 | 96 | 93 |
| J 20 | 395655 | 161 | 152 | - | - | 156 |
| J 21 | 365645 | 1938 | 1890 | - | - | 1959 |
| J 22 | 375645 | 218 | 219.5 | - | - | 219 |
| J 23 | 385645 | 337 | 341 | 314 | - | 340 |
| J 24 | 395645 | 78 | 81 | - | - | 80 |
| K 1 | 285695 | 233 | 236 | - | - | 234 |
| K 2 | 295695 | 384 | 386 | - | - | 385 |
| K 3 | 305695 | 434 | 402 | - | - | 418 |
| K 4 | 315695 | 106 | 106 | - | - | 106 |
| K 5 | 285685 | 282 | 283.5 | 271 | - | 279 |
| K 6 | 295685 | 386 | 389.5 | 372 | - | 382 |
| K 7 | 305685 | 304 | 311 | - | - | 308 |
| K 8 | 315685 | 892 | 896 | - | - | 894 |
| K 9 | 285675 | 264 | 264 | - | - | 264 |
| K 10 | 295675 | 450 | 408 | - | - | 429 |
| K 11 | 305675 | 192 | 150 | - | - | 171 |
| K 12 | 315675 | 157 | 133 | - | - | 145 |
| K 13 | 285665 | 157 | 130 | - | - | 144 |
| K 14 | 295665 | 93 | 74 | - | - | 84 |
| K 15 | 305665 | 98 | 75 | - | - | 86 |
| K 16 | 315665 | 111 | 85 | - | - | 98 |
| K 17 | 285655 | 363 | 285* | 342 | 345 | 350 |
| K 18 | 295655 | 151 | 113 | - | - | 132 |
| K 19 | 305655 | 241 | 154.5* | 215 | 215 | 224 |
| K 20 | 315655 | 105.5 | 106 | - | - | 106 |
| K 21 | 285645 | 298 | 301 | - | - | 300 |
| K 22 | 295645 | 174 | 157 | - | - | 166 |
| K 23 | 305645 | 98 | 110 | - | - | 104 |
| K 24 | 315645 | 150 | 143 | - | - | 146 |
| L 1 | 405675 | 95.5 | 97 | - | - | 96 |
| L 2 | 415675 | 271 | 306 | - | - | 288 |
| L 3 | 425675 | 70 | 64 | - | - | 67 |
| L 4 | 435675 | 298 | 292 | - | - | 295 |
| L 5 | 445675 | 92.5 | 96 | - | - | 95 |
| L 6 | 455675 | 77 | 76.5 | - | - | 77 |
| L 7 | 405665 | 134.5 | 150 | 121 | 150 | 139 |
| L 8 | 415665 | 158 | 148 | 155 | 154 | 154 |
| L 9 | 425665 | 64 | 65 | 69 | - | 66 |
| L 10 | 435665 | 28 | 31.5 | - | - | 30 |
| L 11 | 445665 | 110 | 112 | - | - | 111 |
| L 12 | 455665 | 104 | 108 | - | - | 106 |
| L 13 | 405655 | 258 | 244 | - | - | 251 |
| L 14 | 415655 | 164 | 158.5 | - | - | 161 |
| L 15 | 425655 | 90 | 91.5 | - | - | 91 |

APPENDIX 4.a. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| L 16 | 435655 | 144 | 151 | - | - | 148 |
| L 17 | 445655 | 75.5 | 67 | - | - | 71 |
| L 18 | 455655 | 45 | 35 | - | - | 40 |
| L 19 | 405645 | 166 | 174 | - | - | 170 |
| L 20 | 415645 | 91 | 85 | - | - | 88 |
| L 21 | 425645 | 61 | 43 | - | - | 52 |
| M 1 | 375635 | 323 | 312 | - | - | 318 |
| M 2 | 385635 | 167 | 160.5 | - | - | 164 |
| M 3 | 395635 | 152 | 144.5 | - | - | 148 |
| M 4 | 405635 | 85 | 74 | - | - | 80 |
| M 5 | 415635 | 88 | 71.5 | - | - | 80 |
| M 6 | 425635 | 63 | 37* | 57.5 | 57 | 59 |
| M 7 | 435635 | 121 | 114 | - | - | 118 |
| M 8 | 375625 | 148 | 151 | - | - | 150 |
| M 9 | 385625 | 223 | 207 | - | - | 215 |
| M 10 | 395625 | 83 | 82 | - | - | 82 |
| M 11 | 405625 | 213 | 202 | - | - | 208 |
| M 12 | 415625 | 129 | 124 | - | - | 126 |
| M 13 | 425625 | 171.5 | 163 | - | - | 167 |
| M 14 | 435625 | 70 | 56 | - | - | 63 |
| M 15 | 375615 | 225 | 211.5 | - | - | 218 |
| M 16 | 385615 | 261 | 267 | - | - | 264 |
| M 17 | 395615 | 66 | 47 | - | - | 56 |
| M 18 | 405615 | 116 | 105 | - | - | 110 |
| M 19 | 415615 | 147 | 136 | - | - | 142 |
| M 20 | 425615 | 124 | 121 | - | - | 122 |
| M 21 | 435615 | 190 | 172 | 171 | - | 178 |
| M 22 | 375605 | 111 | 108 | 109 | - | 109 |
| M 23 | 385605 | 232* | 140 | 146 | - | 143 |
| M 24 | 395605 | 226 | 197 | 210 | - | 211 |
| M 25 | 405605 | 173 | 168.5 | 157 | - | 166 |
| M 26 | 415605 | 139 | 134 | 124 | - | 134 |
| M 27 | 425605 | 162 | 163 | 142 | - | 152 |
| N 1 | 315635 | 430 | 411 | - | - | 420 |
| N 2 | 365635 | 220 | 207 | - | - | 214 |
| N 3 | 315625 | 523 | 505 | - | - | 514 |
| N 4 | 325625 | 211 | 209 | - | - | 210 |
| N 5 | 335625 | 1063 | 1074.5 | - | - | 1069 |
| N 6 | 345625 | 5017 | 4961 | - | - | 4989 |
| N 7 | 355625 | 4026.5 | 4311 | 4339 | 4623.5 | 4325 |
| N 8 | 365625 | 1015 | 1062 | - | - | 1038 |
| N 9 | 325615 | 128 | 128 | - | - | 128 |
| N 10 | 335615 | 261 | 246 | - | - | 254 |
| N 11 | 345615 | 16376 | 16545 | - | - | 16460 |
| N 12 | 355615 | 1206 | 1210 | - | - | 1208 |
| N 13 | 365615 | 462 | 442 | - | - | 452 |
| N 14 | 335605 | 182 | 191.5 | - | - | 187 |
| N 15 | 354605 | 220.5 | 212 | - | - | 216 |
| N 16 | 355605 | 1062 | 940 | - | - | 1001 |
| N 17 | 365605 | 214.5 | 208 | - | - | 211 |
| O 1 | 335595 | 370 | 359 | - | - | 364 |
| O 2 | 345595 | 492 | 502 | - | - | 497 |
| O 3 | 355595 | 614 | 592 | - | - | 603 |
| O 4 | 365595 | 248 | 237 | - | - | 242 |
| O 5 | 375595 | 155 | 138 | - | - | 146 |
| O 6 | 385595 | 266 | 249 | - | - | 258 |
| O 7 | 345585 | 224 | 209 | - | - | 216 |
| O 8 | 355585 | 275 | 286 | - | - | 280 |
| O 9 | 365585 | 248 | 232 | - | - | 240 |
| O 10 | 375585 | 220 | 230 | - | - | 225 |
| O 11 | 385585 | 199 | 202 | - | - | 200 |
| O 12 | 355575 | 271 | 262 | - | - | 266 |
| O 13 | 365575 | 349 | 341 | - | - | 345 |
| O 14 | 375575 | 317 | 294 | - | - | 306 |
| O 15 | 385575 | 323 | 324 | - | - | 324 |
| O 16 | 365565 | 274 | 264 | - | - | 269 |
| O 17 | 375565 | 303 | 380* | 254 | 251.5 | 270 |
| O 18 | 385565 | 215 | 224 | - | - | 220 |
| P 1 | 395595 | 130 | 128 | - | - | 129 |
| P 2 | 405595 | 231 | 284* | 194 | 211 | 212 |
| P 3 | 415595 | 208 | 199.5 | - | - | 204 |
| P 4 | 425595 | 81 | 80 | - | - | 80 |
| P 5 | 395585 | 211 | 206 | - | - | 208 |
| P 6 | 405585 | 87 | 83 | - | - | 85 |
| P 7 | 415585 | 75 | 75.5 | - | - | 75 |
| P 8 | 425585 | 69 | 64 | - | - | 66 |
| P 9 | 395575 | 168 | 157 | - | - | 162 |
| P 10 | 405575 | 151 | 147 | - | - | 149 |
| P 11 | 415575 | 159 | 154 | - | - | 156 |
| P 12 | 425575 | 161 | 165 | - | - | 163 |
| P 13 | 395565 | 75 | 75.5 | - | - | 75 |
| P 14 | 405565 | 141 | 133 | - | - | 137 |
| P 15 | 415565 | 97 | 106 | - | - | 102 |
| P 16 | 425565 | 89 | 98 | - | - | 90 |

APPENDIX 4.b. Complete data results for total zinc in soil for the North East Derbyshire Soil Survey (µg/g).

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| A 1 | 405805 | 98.5* | 147 | 157 | - | 152 |
| A 2 | 415805 | 153 | 118 | 120 | - | 130 |
| A 3 | 425805 | 178* | 90 | 97 | - | 94 |
| A 4 | 435805 | 125 | 135 | 131 | - | 130 |
| A 5 | 445805 | 317* | 124 | 109 | - | 116 |
| A 6 | 455805 | 147 | 96 | 103.5 | - | 116 |
| A 7 | 405795 | 173 | 130* | 253 | 261 | 229 |
| A 8 | 415795 | 128 | 103* | 127 | 133 | 129 |
| A 9 | 425795 | 193 | 179 | 164 | - | 179 |
| A 10 | 435795 | 198 | 152 | 170 | - | 173 |
| A 11 | 445795 | 198 | 169 | 161.5 | - | 176 |
| A 12 | 455795 | 163 | 163 | 159 | - | 162 |
| A 13 | 405785 | 183 | 152 | 147 | - | 161 |
| A 14 | 415785 | 118 | 111 | 111 | - | 113 |
| A 15 | 425785 | 209 | 184 | 186.5 | - | 193 |
| A 16 | 435785 | ND | ND | ND | ND | ND |
| A 17 | 445785 | 206 | 173 | 149 | - | 175 |
| A 18 | 455785 | 211 | 178 | 183.5 | - | 190 |
| A 19 | 405775 | 103 | 116.5 | 104 | - | 108 |
| A 20 | 415775 | 123 | 120 | 117 | - | 120 |
| A 21 | 425775 | 105 | 118 | 93 | - | 105 |
| A 22 | 435775 | 125 | 151 | 128 | - | 135 |
| A 23 | 445775 | 198 | 180 | 200.5 | - | 193 |
| A 24 | 455775 | 318* | 198 | 206 | - | 202 |
| B 1 | 365825 | 284* | 224 | 206 | 195 | 208 |
| B 2 | 375825 | 255 | 234 | - | - | 244 |
| B 3 | 385825 | 208 | 216 | 188 | - | 204 |
| B 4 | 395825 | 152 | 127 | 144 | - | 141 |
| B 5 | 405825 | 152 | 116 | 134 | - | 134 |
| B 6 | 365815 | 133 | 135 | 127 | - | 132 |
| B 7 | 375815 | 158 | 161 | 161 | - | 160 |
| B 8 | 385815 | 112 | 108 | 102 | - | 107 |
| B 9 | 395815 | 217 | 258 | - | - | 238 |
| B 10 | 405815 | 227 | 198 | - | - | 212 |
| B 11 | 365805 | 154 | 110 | - | - | 132 |
| B 12 | 375805 | 176 | 188 | - | - | 182 |
| B 13 | 385805 | 89 | 83 | 95 | - | 89 |
| B 14 | 395805 | 184 | 145 | - | - | 164 |
| B 15 | 365795 | 148 | 102.5 | 107 | - | 119 |
| B 16 | 375795 | 168 | 165 | 161.5 | - | 165 |
| B 17 | 385795 | 156 | 158 | - | - | 157 |
| B 18 | 395795 | 204 | 196 | - | - | 200 |
| B 19 | 365785 | 147 | 165 | - | - | 156 |
| B 20 | 375785 | 138 | 135 | - | - | 136 |
| B 21 | 385785 | 216 | 194 | 194 | - | 201 |
| B 22 | 395785 | 251 | 276 | - | - | 264 |
| B 23 | 365775 | 229 | 255 | - | - | 242 |
| B 24 | 375775 | 159 | 216* | 135 | 172 | 155 |
| B 25 | 385775 | 158 | 180 | - | - | 169 |
| B 26 | 395775 | 256 | 231 | - | - | 244 |
| C 1 | 455815 | 489* | 362 | 252.5 | 220.5 | 278 |
| C 2 | 465815 | 256 | 268 | - | - | 262 |
| C 3 | 475815 | 511.5* | 129.5 | 130 | 126 | 128 |
| C 4 | 485815 | 170 | 206 | - | - | 188 |
| C 5 | 495815 | 210 | 185 | - | - | 198 |
| C 6 | 465805 | 431 | 457 | - | - | 444 |
| C 7 | 475805 | 224 | 249 | - | - | 236 |
| C 8 | 485805 | 335 | 397 | - | - | 366 |
| C 9 | 495805 | 410* | 166 | 106 | 107 | 126 |
| C 10 | 465795 | 297 | 250 | - | - | 274 |
| C 11 | 475795 | 147 | 191 | - | - | 169 |
| C 12 | 485795 | 134 | 156 | - | - | 146 |
| C 13 | 495795 | 192 | 231 | - | - | 212 |
| C 14 | 465785 | 179 | 220 | - | - | 200 |
| C 15 | 475785 | 190 | 195 | - | - | 192 |
| C 16 | 485785 | 329* | 133 | 120 | 113 | 122 |
| C 17 | 495785 | 329 | 311 | - | - | 320 |
| C 18 | 465775 | 290 | 285 | - | - | 288 |
| C 19 | 475775 | 410* | 260 | 232 | 217 | 236 |
| C 20 | 485775 | 320* | 266 | 229 | 238 | 244 |
| C 21 | 495775 | 285* | 235 | 197 | 196 | 209 |
| C 22 | 465765 | 159 | 181 | - | - | 170 |
| C 23 | 475765 | 156 | 158 | - | - | 157 |
| C 24 | 485765 | 349 | 323 | - | - | 336 |
| C 25 | 495765 | 202 | 210 | - | - | 206 |
| D 1 | 325805 | 190 | 183 | - | - | 186 |
| D 2 | 335805 | 455* | 343 | 329 | 330 | 334 |
| D 3 | 345805 | 183 | 184 | - | - | 184 |
| D 4 | 355805 | 306 | 308 | - | - | 307 |
| D 5 | 325795 | 152 | 160 | - | - | 156 |
| D 6 | 335795 | 170 | 160 | - | - | 165 |
| D 7 | 345795 | 270 | 332* | 283 | 253 | 269 |
| D 8 | 355795 | 233 | 245 | 211 | 219 | 227 |
| D 9 | 325785 | 192 | 195 | - | - | 194 |
| D 10 | 335785 | 160 | 152 | - | - | 156 |
| D 11 | 345785 | 192 | 178 | - | - | 185 |
| D 12 | 355785 | 156 | 157 | - | - | 156 |
| D 13 | 325775 | 160 | 186 | - | - | 173 |
| D 14 | 335775 | 100 | 108 | - | - | 104 |
| D 15 | 345775 | 251 | 246 | - | - | 248 |
| D 16 | 355775 | 158 | 169 | - | - | 164 |
| D 17 | 325765 | 124 | 131 | - | - | 128 |
| D 18 | 335765 | 139 | 153 | - | - | 146 |
| D 19 | 345765 | 105 | 113 | - | - | 109 |

APPENDIX 4.b. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| D 20 | 355765 | 156 | 168 | - | - | 162 |
| D 21 | 325755 | 152 | 132 | - | - | 142 |
| D 22 | 335755 | 162 | 163 | - | - | 162 |
| D 23 | 345755 | 137 | 163 | - | - | 150 |
| D 24 | 355765 | 167 | 176 | - | - | 172 |
| E 1 | 265795 | 344 | 295 | - | - | 320 |
| E 2 | 275795 | 116 | 117 | - | - | 116 |
| E 3 | 285795 | 6 | 14 | - | - | 10 |
| E 4 | 295795 | 172 | 196 | - | - | 184 |
| E 5 | 305795 | 425 | 410 | - | - | 418 |
| E 6 | 315795 | 319 | 355 | - | - | 337 |
| E 7 | 265785 | 50 | 61 | - | - | 56 |
| E 8 | 275785 | 47 | 55 | - | - | 51 |
| E 9 | 285785 | 381 | 307 | - | - | 344 |
| E 10 | 295785 | 272.5* | 141 | 151 | 136 | 143 |
| E 11 | 305785 | 187 | 186 | - | - | 186 |
| E 12 | 315785 | 102 | 81 | 90 | - | 91 |
| E 13 | 265775 | 94 | 95 | - | - | 94 |
| E 14 | 275775 | 90* | 159 | 133.5 | 140 | 144 |
| E 15 | 285775 | 150 | 122 | - | - | 136 |
| E 16 | 295775 | 123 | 142 | - | - | 132 |
| E 17 | 305775 | 146* | 301 | 229 | 249.5 | 260 |
| E 18 | 315775 | 308* | 242 | 232 | 254 | 243 |
| E 19 | 265765 | 286* | 178 | 165.5 | 159 | 168 |
| E 20 | 275765 | 206* | 129 | 112 | 114 | 118 |
| E 21 | 285765 | 178 | 177 | - | - | 175 |
| E 22 | 295765 | 98 | 94 | - | - | 94 |
| E 23 | 305765 | 237 | 216 | - | - | 226 |
| E 24 | 315765 | 281 | 271 | - | - | 276 |
| F 1 | 275755 | 50 | 43 | 41 | - | 45 |
| F 2 | 285755 | 441.5* | 241 | 245 | - | 243 |
| F 3 | 295755 | 104 | 78 | 74 | - | 87 |
| F 4 | 305755 | 92.5 | 80 | 81 | - | 84 |
| F 5 | 315755 | 148.5 | ND | - | - | 148 |
| F 6 | 275745 | 308 | 336 | 346 | - | 330 |
| F 7 | 285745 | 48.5 | 46 | - | - | 47 |
| F 8 | 295745 | 320.5* | 109 | 107 | - | 108 |
| F 9 | 305745 | 132.5 | 124 | 122 | - | 126 |
| F 10 | 315745 | 145.5 | 132 | 135 | - | 138 |
| F 11 | 285735 | 174.5 | 177.5 | 173 | - | 175 |
| F 12 | 295735 | 96 | 99 | 92 | - | 96 |
| F 13 | 305735 | 307* | 108 | 106 | - | 107 |
| F 14 | 315735 | 83.5 | 89 | 85 | - | 86 |
| F 15 | 285725 | 42.5* | 27.5 | 23 | - | 25 |
| F 16 | 295725 | 138 | 134 | 149 | 139 | 140 |
| F 17 | 305725 | 116 | 108 | 89 | 92 | 101 |
| F 18 | 315725 | 123.5 | 116 | 108 | - | 116 |
| F 19 | 285715 | 218* | 25 | 27 | - | 26 |
| F 20 | 295715 | 171.5 | 190 | 201 | - | 187 |
| F 21 | 305715 | 199.5 | 160 | 169 | - | 176 |
| F 22 | 315715 | 126.5 | 114 | 111 | - | 117 |
| F 23 | 285705 | 104.5 | 114 | 103 | - | 107 |
| F 24 | 295705 | 284.5 | 302 | 306 | - | 298 |
| F 25 | 305705 | 544* | 266 | 307.5 | - | 287 |
| F 26 | 315705 | 189 | 166 | 156 | - | 170 |
| G 1 | 325745 | 130 | 125 | 120 | - | 125 |
| G 2 | 335745 | 115 | 100 | 105 | - | 107 |
| G 3 | 345745 | 105 | 90 | - | - | 98 |
| G 4 | 355745 | 120 | 105 | - | - | 112 |
| G 5 | 325735 | 170 | 150 | - | - | 160 |
| G 6 | 335735 | 185 | 170 | - | - | 178 |
| G 7 | 345735 | 160 | 135 | 145 | - | 147 |
| G 8 | 355735 | 220 | 205 | - | - | 212 |
| G 9 | 325725 | 140* | 105 | 106 | 116 | 110 |
| G 10 | 335725 | 150 | 155 | - | - | 152 |
| G 11 | 345725 | 140* | 110 | 121 | 109 | 113 |
| G 12 | 355725 | 380 | 355 | - | - | 368 |
| G 13 | 325715 | 170 | 155 | - | - | 162 |
| G 14 | 335715 | 180 | 165 | - | - | 172 |
| G 15 | 345715 | 200 | 195 | - | - | 198 |
| G 16 | 355715 | 235 | 225 | - | - | 230 |
| G 17 | 325705 | 215 | 205 | - | - | 210 |
| G 18 | 335705 | 210 | 205 | - | - | 208 |
| G 19 | 345705 | 300 | 281 | - | - | 290 |
| G 20 | 355705 | 310 | 290 | - | - | 300 |
| G 21 | 325695 | 220 | 225 | - | - | 222 |
| G 22 | 335695 | 210 | 200 | - | - | 205 |
| G 23 | 345695 | 170 | 165 | - | - | 168 |
| G 24 | 355695 | 195 | 215 | - | - | 205 |
| H 1 | 425725 | 129 | 124 | - | - | 126 |
| H 2 | 435725 | 144 | 145 | - | - | 144 |
| H 3 | 405715 | 220 | 200 | - | - | 210 |
| H 4 | 415715 | 219 | 225 | - | - | 222 |
| H 5 | 425715 | 120 | 140 | - | - | 130 |
| H 6 | 435715 | 170 | 150 | - | - | 160 |
| H 7 | 445715 | 145 | 140 | - | - | 142 |
| H 8 | 455715 | 154 | 160 | - | - | 157 |
| H 9 | 405705 | 165 | 155 | - | - | 160 |
| H 10 | 415705 | 160 | 145 | - | - | 152 |
| H 11 | 425705 | 265 | 245 | - | - | 255 |
| H 12 | 435705 | 176 | 145 | - | - | 160 |
| H 13 | 445705 | 124 | 125 | - | - | 124 |
| H 14 | 455705 | 74 | 80 | - | - | 77 |
| H 15 | 405695 | 145 | 135 | - | - | 140 |
| H 16 | 415695 | 164 | 160 | - | - | 162 |
| H 17 | 425695 | 190 | 175 | - | - | 182 |

APPENDIX 4.b. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| H 18 | 435695 | 605 | 576 | - | - | 590 |
| H 19 | 445695 | 109 | 110 | - | - | 110 |
| H 20 | 455695 | 105 | 110 | - | - | 108 |
| H 21 | 405685 | 194 | 200 | - | - | 197 |
| H 22 | 415685 | 280 | 280 | - | - | 280 |
| H 23 | 425685 | 120 | 117 | 111 | - | 116 |
| H 24 | 435685 | 124 | 125 | - | - | 124 |
| H 25 | 445685 | 149 | 145 | - | - | 147 |
| H 26 | 455685 | 110 | 105 | - | - | 108 |
| I 1 | 325685 | 24 | 20 | - | - | 22 |
| I 2 | 335685 | 74 | 70 | - | - | 72 |
| I 3 | 345685 | 233.5 | 230 | - | - | 232 |
| I 4 | 355685 | 229 | 235 | - | - | 232 |
| I 5 | 325675 | 54 | 50 | - | - | 52 |
| I 6 | 335675 | 139 | 135 | - | - | 137 |
| I 7 | 345675 | 104 | 105 | - | - | 104 |
| I 8 | 355675 | 99 | 100 | - | - | 100 |
| I 9 | 325665 | 149 | 150 | - | - | 150 |
| I 10 | 335665 | 896 | 898 | - | - | 897 |
| I 11 | 345665 | 124 | 130 | - | - | 127 |
| I 12 | 355665 | 79 | 85 | - | - | 82 |
| I 13 | 325655 | 154* | 290 | 249 | 286 | 275 |
| I 14 | 335655 | 109 | 105 | - | - | 107 |
| I 15 | 345655 | 293 | 310 | - | - | 302 |
| I 16 | 355655 | 109 | 120 | - | - | 114 |
| I 17 | 325645 | 374 | 345 | - | - | 360 |
| I 18 | 335645 | 194 | 160 | - | - | 177 |
| I 19 | 345645 | 189 | 180 | - | - | 184 |
| I 20 | 355645 | 189 | 169.5 | - | - | 179 |
| I 21 | 325635 | 150 | 125 | - | - | 138 |
| I 22 | 335635 | 164* | 275 | 307 | 288 | 290 |
| I 23 | 345635 | 849 | 799 | 798 | 777 | 806 |
| I 24 | 355635 | 149 | 149 | 165 | 165 | 157 |
| J 1 | 365695 | 167 | 157 | - | - | 162 |
| J 2 | 375695 | 153 | 155 | 152 | - | 153 |
| J 3 | 385695 | 290 | 302 | - | - | 296 |
| J 4 | 395695 | 232 | 233 | - | - | 232 |
| J 5 | 365685 | 140 | 123 | - | - | 132 |
| J 6 | 375685 | 151.5 | 160 | - | - | 156 |
| J 7 | 385685 | 251 | 237.5 | - | - | 244 |
| J 8 | 395685 | 248 | 245 | - | - | 246 |
| J 9 | 365675 | 496 | 491 | 478 | 493 | 490 |
| J 10 | 375675 | 131 | 124 | - | - | 128 |
| J 11 | 385675 | 195 | 196 | - | - | 196 |
| J 12 | 395675 | 228 | 221.5 | - | - | 225 |
| J 13 | 365665 | 156 | 164 | - | - | 160 |
| J 14 | 375665 | 265 | 251 | 253.5 | 254 | 256 |
| J 15 | 385665 | 260 | 247 | - | - | 254 |
| J 16 | 395665 | 312.5 | 325 | - | - | 319 |
| J 17 | 365655 | 86 | 79 | 84 | - | 83 |
| J 18 | 375655 | 137 | 122 | 122 | - | 127 |
| J 19 | 385655 | 115 | 118.5 | 112 | 113.5 | 115 |
| J 20 | 395655 | 194 | 187 | - | - | 190 |
| J 21 | 365645 | 89 | 78 | - | - | 84 |
| J 22 | 375645 | 172.5 | 165 | - | - | 169 |
| J 23 | 385645 | 444 | 436 | 433 | - | 438 |
| J 24 | 395645 | 140 | 134 | - | - | 137 |
| K 1 | 285695 | 157 | 156 | - | - | 156 |
| K 2 | 295695 | 36 | 43.5 | - | - | 40 |
| K 3 | 305695 | 82.5 | 77 | - | - | 80 |
| K 4 | 315695 | 71 | 69 | - | - | 70 |
| K 5 | 285685 | 74 | 65 | 74 | - | 78 |
| K 6 | 295685 | 49 | 50 | 51 | - | 50 |
| K 7 | 305685 | 33 | 36 | - | - | 34 |
| K 8 | 315685 | 43 | 44 | - | - | 44 |
| K 9 | 285675 | 60 | 56 | - | - | 58 |
| K 10 | 295675 | 47 | 50 | - | - | 48 |
| K 11 | 305675 | 86 | 89 | - | - | 88 |
| K 12 | 315675 | 39 | 45 | - | - | 42 |
| K 13 | 285665 | 19 | 26 | - | - | 22 |
| K 14 | 295665 | 30 | 36.5 | - | - | 33 |
| K 15 | 305665 | 67 | 72 | - | - | 70 |
| K 16 | 315665 | 54 | 58 | - | - | 56 |
| K 17 | 285655 | 43 | 54.5 | - | - | 49 |
| K 18 | 295655 | 54 | 57 | - | - | 56 |
| K 19 | 305655 | 88 | 100 | - | - | 94 |
| K 20 | 315655 | 69.5 | 80 | - | - | 75 |
| K 21 | 285645 | 178 | 186 | - | - | 182 |
| K 22 | 295645 | 68 | 77 | - | - | 72 |
| K 23 | 305645 | 57 | 67 | - | - | 62 |
| K 24 | 315645 | 66 | 66 | - | - | 66 |
| L 1 | 405675 | 142 | 141 | - | - | 142 |
| L 2 | 415675 | 239 | 229 | - | - | 234 |
| L 3 | 425675 | 99 | 100 | - | - | 100 |
| L 4 | 435675 | 159 | 166 | - | - | 162 |
| L 5 | 445675 | 122 | 126 | - | - | 124 |
| L 6 | 455675 | 102.5 | 104.5 | - | - | 104 |
| L 7 | 405665 | 178 | 175 | 169.5 | - | 174 |
| L 8 | 415665 | 97 | 92 | 107 | - | 99 |
| L 9 | 425665 | 105 | 110 | 110 | - | 108 |
| L 10 | 435665 | 99.5 | 100.5 | - | - | 100 |
| L 11 | 445665 | 146 | 149 | - | - | 148 |
| L 12 | 455665 | 233 | 236 | - | - | 234 |
| L 13 | 405655 | 207 | 212 | - | - | 210 |
| L 14 | 415655 | 263 | 260.5 | - | - | 262 |
| L 15 | 425655 | 172 | 169.5 | - | - | 171 |

APPENDIX 4.b. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( # = rejected from mean calc.) | | | | |
| L 16 | 435655 | 181 | 177 | - | - | 179 |
| L 17 | 445655 | 81.5 | 88 | - | - | 85 |
| L 18 | 455655 | 112 | 109 | - | - | 110 |
| L 19 | 405645 | 230 | 253 | - | - | 242 |
| L 20 | 415645 | 146.5 | 146 | - | - | 146 |
| L 21 | 425645 | 115 | 119 | - | - | 117 |
| M 1 | 375635 | 231 | 250 | - | - | 240 |
| M 2 | 385635 | 299 | 299 | - | - | 299 |
| M 3 | 395635 | 258 | 264 | - | - | 261 |
| M 4 | 405635 | 122 | 125 | - | - | 124 |
| M 5 | 415635 | 105.5 | 115 | - | - | 110 |
| M 6 | 425635 | 119 | 121 | - | - | 120 |
| M 7 | 435635 | 151 | 156 | - | - | 154 |
| M 8 | 375625 | 124 | 129 | - | - | 126 |
| M 9 | 385625 | 198 | 215 | - | - | 206 |
| M 10 | 395625 | 100 | 102 | - | - | 101 |
| M 11 | 405625 | 149 | 156 | - | - | 152 |
| M 12 | 415625 | 147.5 | 141 | - | - | 144 |
| M 13 | 425625 | 239.5 | 256.5 | - | - | 248 |
| M 14 | 435625 | 116 | 119 | - | - | 118 |
| M 15 | 375615 | 176 | 198 | - | - | 187 |
| M 16 | 385615 | 165 | 153 | - | - | 159 |
| M 17 | 395615 | 199 | 225 | - | - | 212 |
| M 18 | 405615 | 105 | 114 | - | - | 110 |
| M 19 | 415615 | 134 | 150 | - | - | 142 |
| M 20 | 425615 | 171 | 177 | - | - | 174 |
| M 21 | 435615 | 206 | 205 | 199 | - | 203 |
| M 22 | 375605 | 83 | 91 | 84 | - | 86 |
| M 23 | 385605 | 141 | 135 | 133 | - | 136 |
| M 24 | 395605 | 196 | 182 | 183 | - | 187 |
| M 25 | 405605 | 360 | 356 | 350.5 | - | 356 |
| M 26 | 415605 | 152 | 156 | 151 | - | 153 |
| M 27 | 425605 | 156 | 159 | 158.5 | - | 158 |
| N 1 | 315635 | 160 | 173 | - | - | 166 |
| N 2 | 365635 | 132.5 | 123 | - | - | 128 |
| N 3 | 315625 | 92 | 106 | - | - | 101 |
| N 4 | 325625 | 109.5 | 110 | - | - | 110 |
| N 5 | 335625 | 1003 | 999 | - | - | 1001 |
| N 6 | 345625 | 1814 | 2018.5 | - | - | 1916 |
| N 7 | 355625 | 653 | 679.5 | - | - | 666 |
| N 8 | 365625 | 253.5 | 262 | - | - | 260 |
| N 9 | 325615 | 67.5 | 73 | - | - | 70 |
| N 10 | 335615 | 242.5 | 283 | - | - | 263 |
| N 11 | 345615 | 4240 | 4282 | - | - | 4261 |
| N 12 | 355615 | 898.5 | 894 | - | - | 896 |
| N 13 | 365615 | 311 | 283 | - | - | 297 |
| N 14 | 335605 | 110.5 | 128.5 | - | - | 120 |
| N 15 | 354605 | 144 | 152 | - | - | 148 |
| N 16 | 355605 | 523 | 542 | - | - | 532 |
| N 17 | 365605 | 133 | 151 | - | - | 142 |
| O 1 | 335595 | 231.5 | 221 | - | - | 226 |
| O 2 | 345595 | 361 | 374 | - | - | 368 |
| O 3 | 355595 | 129 | 155 | - | - | 142 |
| O 4 | 365595 | 82 | 94 | - | - | 88 |
| O 5 | 375595 | 145 | 158 | - | - | 152 |
| O 6 | 385595 | 245 | 243 | - | - | 244 |
| O 7 | 345585 | 94 | 100 | - | - | 97 |
| O 8 | 355585 | 145.5 | 153 | - | - | 149 |
| O 9 | 365585 | 176 | 182 | - | - | 177 |
| O 10 | 375585 | 169 | 190 | - | - | 180 |
| O 11 | 385585 | 169 | 181 | - | - | 175 |
| O 12 | 355575 | 176 | 183 | - | - | 180 |
| O 13 | 365575 | 159 | 163 | - | - | 161 |
| O 14 | 375575 | 315 | 283 | - | - | 299 |
| O 15 | 385575 | 365 | 364.5 | - | - | 365 |
| O 16 | 365565 | 205 | 230.5 | - | - | 218 |
| O 17 | 375565 | 166 | 156 | - | - | 161 |
| O 18 | 385565 | 225 | 191 | - | - | 208 |
| P 1 | 395595 | 123 | 125 | - | - | 124 |
| P 2 | 405595 | 476 | 464 | - | - | 470 |
| P 3 | 415595 | 290 | 253 | - | - | 272 |
| P 4 | 425595 | 102 | 104 | - | - | 103 |
| P 5 | 395585 | 167 | 170 | - | - | 168 |
| P 6 | 405585 | 138 | 141 | - | - | 140 |
| P 7 | 415585 | 116 | 116 | - | - | 117 |
| P 8 | 425585 | 131 | 126.5 | - | - | 129 |
| P 9 | 395575 | 93.5 | 93 | - | - | 93 |
| P 10 | 405575 | 115 | 107 | - | - | 111 |
| P 11 | 415575 | 110.5 | 105 | - | - | 108 |
| P 12 | 425575 | 302 | 286 | - | - | 294 |
| P 13 | 395565 | 110 | 112.5 | - | - | 111 |
| P 14 | 405565 | 209 | 197 | - | - | 203 |
| P 15 | 415565 | 104 | 113 | - | - | 108 |
| P 16 | 425565 | 265 | 272 | - | - | 278 |

APPENDIX 4.c. Complete data results for total copper in soil for the North East Derbyshire Soil Survey (µg/g).

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| A 1 | 405805 | 20 | 19.5 | - | - | 20 |
| A 2 | 415805 | 46 | 48 | - | - | 47 |
| A 3 | 425805 | 40 | 46 | - | - | 43 |
| A 4 | 435805 | 25 | 26 | - | - | 26 |
| A 5 | 445805 | 65 | 50 | - | - | 58 |
| A 6 | 455805 | 36 | 42 | - | - | 39 |
| A 7 | 405795 | 40 | 41 | - | - | 40 |
| A 8 | 415795 | 34 | 35 | - | - | 34 |
| A 9 | 425795 | 42 | 45 | - | - | 44 |
| A 10 | 435795 | 42 | 220* | 43 | 43 | 43 |
| A 11 | 445795 | 44 | 46 | - | - | 45 |
| A 12 | 455795 | 40 | 42 | - | - | 41 |
| A 13 | 405785 | 37 | 39 | - | - | 38 |
| A 14 | 415785 | 20 | 20 | - | - | 20 |
| A 15 | 425785 | 39 | 42 | - | - | 40 |
| A 16 | 435785 | ND | ND | ND | ND | ND |
| A 17 | 445785 | 37 | 39 | - | - | 38 |
| A 18 | 455785 | 34 | 36 | - | - | 35 |
| A 19 | 405775 | 18 | 16 | - | - | 17 |
| A 20 | 415775 | 23 | 23 | - | - | 23 |
| A 21 | 425775 | 32 | 33 | - | - | 32 |
| A 22 | 435775 | 30 | 32 | - | - | 31 |
| A 23 | 445775 | 41 | 41 | - | - | 41 |
| A 24 | 455775 | 34 | 55 | 22 | - | 37 |
| B 1 | 365825 | 65 | 40 | - | - | 52 |
| B 2 | 375825 | 55 | 35 | - | - | 45 |
| B 3 | 385825 | 45 | 40 | - | - | 42 |
| B 4 | 395825 | 35 | 45 | - | - | 40 |
| B 5 | 405825 | 32 | 32 | - | - | 32 |
| B 6 | 365815 | 32 | 35 | - | - | 34 |
| B 7 | 375815 | 45 | 35 | - | - | 40 |
| B 8 | 385815 | 29 | 28 | - | - | 28 |
| B 9 | 395815 | 39 | 50 | - | - | 44 |
| B 10 | 405815 | 36 | 38 | - | - | 37 |
| B 11 | 365805 | 27 | 27 | - | - | 27 |
| B 12 | 375805 | 27 | 28 | - | - | 28 |
| B 13 | 385805 | 31 | 32 | - | - | 32 |
| B 14 | 395805 | 39 | 38 | - | - | 38 |
| B 15 | 365795 | 39 | 39 | - | - | 39 |
| B 16 | 375795 | 39 | 40 | - | - | 40 |
| B 17 | 385795 | 24 | 25 | - | - | 24 |
| B 18 | 395795 | 51.5 | 52 | - | - | 52 |
| B 19 | 365785 | 29 | 32 | - | - | 30 |
| B 20 | 375785 | 26 | 27 | - | - | 26 |
| B 21 | 385785 | 29 | 32 | - | - | 30 |
| B 22 | 395785 | 46.5 | 42 | - | - | 44 |
| B 23 | 365775 | 61.5 | 57 | - | - | 59 |
| B 24 | 375775 | 42 | 37 | - | - | 40 |
| B 25 | 385775 | 34 | 31 | - | - | 32 |
| B 26 | 395775 | 34 | 31 | - | - | 32 |
| C 1 | 455815 | 61.5 | 59.5 | - | - | 60 |
| C 2 | 465815 | 64 | 62 | - | - | 63 |
| C 3 | 475815 | 50 | 52 | 54 | 54 | 52 |
| C 4 | 485815 | 59 | 54.5 | - | - | 57 |
| C 5 | 495815 | 19 | 47* | 19 | 20.5 | 20 |
| C 6 | 465805 | 74 | 64.5 | - | - | 69 |
| C 7 | 475805 | 46.5 | 44.5 | - | - | 46 |
| C 8 | 485805 | 156.5 | 154.5 | - | - | 156 |
| C 9 | 495805 | 41.5 | 32 | - | - | 37 |
| C 10 | 465795 | 54 | 49.5 | - | - | 52 |
| C 11 | 475795 | 27.5 | 24.5 | - | - | 26 |
| C 12 | 485795 | 24 | 22 | - | - | 23 |
| C 13 | 495795 | 24 | 22 | - | - | 23 |
| C 14 | 465785 | 31 | 27.5 | - | - | 29 |
| C 15 | 475785 | 44 | 37.5 | - | - | 41 |
| C 16 | 485785 | 32 | 28.5 | - | - | 30 |
| C 17 | 495785 | 31.5 | 31.5 | - | - | 32 |
| C 18 | 465775 | 54 | 54.5 | - | - | 54 |
| C 19 | 475775 | 39 | 36.5 | - | - | 38 |
| C 20 | 485775 | 36 | 36 | - | - | 36 |
| C 21 | 495775 | 29.5 | 27 | - | - | 28 |
| C 22 | 465765 | 32 | 33 | - | - | 33 |
| C 23 | 475765 | 27 | 25.5 | - | - | 26 |
| C 24 | 485765 | 69 | 64.5 | - | - | 67 |
| C 25 | 495765 | 31 | 28 | - | - | 30 |
| D 1 | 325805 | 64 | 57 | - | - | 60 |
| D 2 | 335805 | 74 | 72 | - | - | 73 |
| D 3 | 345805 | 44 | 44.5 | - | - | 44 |
| D 4 | 355805 | 65 | 59.5 | - | - | 62 |
| D 5 | 325795 | 39 | 32 | - | - | 36 |
| D 6 | 335795 | 36 | 31.5 | - | - | 34 |
| D 7 | 345795 | 54 | 89.5* | 49 | 49.5 | 51 |
| D 8 | 355795 | 10* | 54 | 55 | 52 | 54 |
| D 9 | 325785 | 30 | 33 | - | - | 32 |
| D 10 | 335785 | 31 | 31 | - | - | 31 |
| D 11 | 345785 | 27 | 26 | - | - | 26 |
| D 12 | 355785 | 37 | 39 | - | - | 38 |
| D 13 | 325775 | 26 | 27 | - | - | 26 |
| D 14 | 335775 | 21 | 22 | - | - | 22 |
| D 15 | 345775 | 47 | 48 | - | - | 48 |
| D 16 | 355775 | 26 | 25 | - | - | 26 |
| D 17 | 325765 | 26 | 27 | - | - | 26 |
| D 18 | 335765 | 31 | 34 | - | - | 32 |
| D 19 | 345765 | 22 | 24 | - | - | 23 |

APPENDIX 4.c. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| D 20 | 355765 | 35 | 38 | - | - | 36 |
| D 21 | 325755 | 27 | 29 | - | - | 28 |
| D 22 | 335755 | 39 | 40 | - | - | 40 |
| D 23 | 345755 | 23 | 24 | - | - | 24 |
| D 24 | 355755 | 27 | 27 | - | - | 27 |
| E 1 | 265795 | 21 | 20 | 19 | 19* | 20 |
| E 2 | 275795 | 14 | 14 | - | - | 14 |
| E 3 | 285795 | 16 | 16 | - | - | 16 |
| E 4 | 295795 | 25 | 29 | - | - | 27 |
| E 5 | 305795 | 43 | 50 | - | - | 46 |
| E 6 | 315795 | 43 | 50 | - | - | 46 |
| E 7 | 265785 | 16 | 18 | - | - | 17 |
| E 8 | 275785 | 22 | 24 | - | - | 23 |
| E 9 | 285785 | 34 | 38 | - | - | 36 |
| E 10 | 295785 | 29 | 24 | 25 | 27 | 26 |
| E 11 | 305785 | 24 | 27 | - | - | 26 |
| E 12 | 315785 | 26 | 27 | 28 | - | 27 |
| E 13 | 265775 | 13 | 13 | - | - | 13 |
| E 14 | 275775 | 14 | 15 | - | - | 14 |
| E 15 | 285775 | 19 | 22 | - | - | 20 |
| E 16 | 295775 | 27 | 26 | - | - | 26 |
| E 17 | 305775 | 39 | 42 | - | - | 40 |
| E 18 | 315775 | 30 | 29 | - | - | 30 |
| E 19 | 265765 | 13 | 13 | - | - | 13 |
| E 20 | 275765 | 8 | 13 | - | - | 10 |
| E 21 | 285765 | 38 | 36 | - | - | 37 |
| E 22 | 295765 | 14 | 13 | - | - | 14 |
| E 23 | 305765 | 32 | 30 | - | - | 31 |
| E 24 | 315765 | 41 | 39 | - | - | 40 |
| F 1 | 275755 | 11 | 19 | - | - | 15 |
| F 2 | 285755 | 29 | 22 | - | - | 26 |
| F 3 | 295755 | 39 | 39 | - | - | 39 |
| F 4 | 305755 | 27 | 28 | - | - | 28 |
| F 5 | 315755 | 49 | 51 | - | - | 50 |
| F 6 | 275745 | 37 | 44 | - | - | 40 |
| F 7 | 285745 | 10 | 10 | - | - | 10 |
| F 8 | 295745 | 23 | 22 | - | - | 22 |
| F 9 | 305745 | 25 | 25 | - | - | 25 |
| F 10 | 315745 | 26 | 25 | - | - | 26 |
| F 11 | 285735 | 22 | 21 | - | - | 22 |
| F 12 | 295735 | 53 | 51 | - | - | 52 |
| F 13 | 305735 | 22 | 21 | - | - | 22 |
| F 14 | 315735 | 14 | 14 | - | - | 14 |
| F 15 | 285725 | 33 | 17* | 30 | 29 | 31 |
| F 16 | 295725 | 20 | 18 | - | - | 19 |
| F 17 | 305725 | 16 | 24 | - | - | 20 |
| F 18 | 315725 | 18 | 31* | 17 | 15 | 17 |
| F 19 | 285715 | 23 | 23 | - | - | 23 |
| F 20 | 295715 | 20* | 31 | 29 | 28 | 29 |
| F 21 | 305715 | 13* | 31 | 35 | 35 | 34 |
| F 22 | 315715 | 17 | 24 | - | - | 20 |
| F 23 | 285705 | 10* | 17 | 15 | 15 | 16 |
| F 24 | 295705 | 21* | 55 | 62 | 61 | 59 |
| F 25 | 305705 | 10* | 27 | 28 | 30.5 | 28 |
| F 26 | 315705 | 15* | 44 | 38 | 44 | 42 |
| G 1 | 325745 | 25 | 26 | 22 | - | 24 |
| G 2 | 335745 | 24 | 22 | 22 | - | 23 |
| G 3 | 345745 | 36 | 35 | - | - | 36 |
| G 4 | 355745 | 29 | 26 | - | - | 28 |
| G 5 | 325735 | 43 | 39 | - | - | 41 |
| G 6 | 335735 | 34.5 | 35.5 | - | - | 35 |
| G 7 | 345735 | 62 | 60.5 | 61 | - | 62 |
| G 8 | 355735 | 71 | 68 | - | - | 70 |
| G 9 | 325725 | 26 | 24 | - | - | 25 |
| G 10 | 335725 | 31 | 31 | - | - | 31 |
| G 11 | 345725 | 40 | 37 | - | - | 38 |
| G 12 | 355725 | 125.5 | 109 | - | - | 117 |
| G 13 | 325715 | 30 | 28 | - | - | 29 |
| G 14 | 335715 | 35 | 33 | - | - | 34 |
| G 15 | 345715 | 38 | 36 | - | - | 37 |
| G 16 | 355715 | 71.5 | 60.5 | - | - | 66 |
| G 17 | 325705 | 45 | 36* | 42 | 43.5 | 44 |
| G 18 | 335705 | 41.5 | 39 | - | - | 40 |
| G 19 | 345705 | 56.5 | 45 | 52 | 50 | 51 |
| G 20 | 355705 | 65.5 | 57 | - | - | 61 |
| G 21 | 325695 | 37 | 35 | - | - | 36 |
| G 22 | 335695 | 26 | 26 | - | - | 26 |
| G 23 | 345695 | 29 | 28 | - | - | 28 |
| G 24 | 355695 | 39 | 36 | - | - | 38 |
| H 1 | 425725 | 29 | 25 | - | - | 27 |
| H 2 | 435725 | 32 | 33 | - | - | 32 |
| H 3 | 405715 | 19* | 37.5 | 36 | - | 37 |
| H 4 | 415715 | 45 | 45 | - | - | 45 |
| H 5 | 425715 | 31* | 47 | 55 | - | 51 |
| H 6 | 435715 | 20* | 45 | 37 | - | 41 |
| H 7 | 445715 | 12* | 29 | 24 | - | 26 |
| H 8 | 455715 | 93 | 95 | - | - | 94 |
| H 9 | 405705 | 22* | 45 | 44 | - | 44 |
| H 10 | 415705 | 19* | 44.5 | 39 | - | 42 |
| H 11 | 425705 | 18* | 53 | 49 | - | 51 |
| H 12 | 435705 | 72 | 61 | 64 | 67 | 66 |
| H 13 | 445705 | 29 | 27 | - | - | 28 |
| H 14 | 455705 | 60.5 | 61 | - | - | 61 |
| H 15 | 405695 | 15* | 38.5 | 33 | - | 36 |
| H 16 | 415695 | 35 | 33 | - | - | 34 |
| H 17 | 425695 | 19* | 44.5 | 35 | - | 40 |

APPENDIX 4.c. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| H 18 | 435695 | 14* | 37 | 30 | - | 34 |
| H 19 | 445695 | 24 | 20 | - | - | 22 |
| H 20 | 455695 | 22 | 22 | - | - | 22 |
| H 21 | 405685 | 43 | 49.5 | - | - | 46 |
| H 22 | 415685 | 26* | 55.5 | 48 | - | 52 |
| H 23 | 425685 | 15* | 36 | 30 | 33 | 33 |
| H 24 | 435685 | 41 | 45 | - | - | 43 |
| H 25 | 445685 | 29 | 29 | - | - | 29 |
| H 26 | 455685 | 11* | 26 | 21.5 | - | 24 |
| I 1 | 325685 | 13 | 13 | - | - | 13 |
| I 2 | 335685 | 9.5 | 10 | - | - | 10 |
| I 3 | 345685 | 31 | 33 | - | - | 32 |
| I 4 | 355685 | 33 | 36 | - | - | 34 |
| I 5 | 325675 | 20 | 19 | - | - | 20 |
| I 6 | 335675 | 18 | 17 | - | - | 18 |
| I 7 | 345675 | 15.5 | 15 | - | - | 15 |
| I 8 | 355675 | 20.5 | 19 | - | - | 20 |
| I 9 | 325665 | 21 | 20 | - | - | 20 |
| I 10 | 335665 | 22 | 20 | - | - | 21 |
| I 11 | 345665 | 13 | 13 | - | - | 13 |
| I 12 | 355665 | 12 | 10 | - | - | 11 |
| I 13 | 325655 | 22.5 | 23 | - | - | 23 |
| I 14 | 335655 | 19 | 18 | - | - | 18 |
| I 15 | 345655 | 28 | 27 | - | - | 28 |
| I 16 | 355655 | 18 | 17 | - | - | 18 |
| I 17 | 325645 | 25 | 20 | - | - | 22 |
| I 18 | 335645 | 14 | 13 | - | - | 14 |
| I 19 | 345645 | 21 | 20 | - | - | 20 |
| I 20 | 355645 | 20 | 17 | - | - | 18 |
| I 21 | 325635 | 16 | 15 | - | - | 16 |
| I 22 | 335635 | 26 | 25 | - | - | 26 |
| I 23 | 345635 | 28 | 27 | 27 | 26 | 27 |
| I 24 | 355635 | 16 | 15 | 17 | 17 | 16 |
| J 1 | 365695 | 47 | 50 | - | - | 48 |
| J 2 | 375695 | 38 | 44 | 44 | - | 42 |
| J 3 | 385695 | 69 | 63 | - | - | 66 |
| J 4 | 395695 | 49 | 50 | - | - | 50 |
| J 5 | 365685 | 39 | 41 | - | - | 40 |
| J 6 | 375685 | 19 | 19 | - | - | 19 |
| J 7 | 385685 | 39 | 60* | 41.5 | - | 40 |
| J 8 | 395685 | 61 | 61 | - | - | 61 |
| J 9 | 365675 | 39 | 37 | 41 | 40 | 39 |
| J 10 | 375675 | 38 | 35 | - | - | 36 |
| J 11 | 385675 | 43 | 47 | - | - | 45 |
| J 12 | 395675 | 15 | 15 | - | - | 15 |
| J 13 | 365665 | 29 | 29 | - | - | 29 |
| J 14 | 375665 | 54 | 54 | 54 | 52 | 54 |
| J 15 | 385665 | 91 | 90 | - | - | 90 |
| J 16 | 395665 | 63 | 63.5 | - | - | 63 |
| J 17 | 365655 | 12 | 17 | 17 | - | 15 |
| J 18 | 375655 | 27 | 31 | 30 | - | 29 |
| J 19 | 385655 | 30 | 30 | 37 | 38 | 34 |
| J 20 | 395655 | 32 | 35 | - | - | 34 |
| J 21 | 365645 | 16 | 19 | - | - | 18 |
| J 22 | 375645 | 30 | 29 | - | - | 30 |
| J 23 | 385645 | 45.5 | 49 | 49 | - | 48 |
| J 24 | 395645 | 21 | 24 | - | - | 22 |
| K 1 | 285695 | 22 | 25 | - | - | 24 |
| K 2 | 295695 | 22 | 22 | - | - | 22 |
| K 3 | 305695 | 53.5 | 51 | - | - | 52 |
| K 4 | 315695 | 14 | 17 | - | - | 16 |
| K 5 | 285685 | 30 | 32 | 29 | - | 30 |
| K 6 | 295685 | 31 | 38 | 37 | - | 35 |
| K 7 | 305685 | 20 | 19 | - | - | 20 |
| K 8 | 315685 | 13 | 17 | - | - | 15 |
| K 9 | 285675 | 32 | 34 | - | - | 33 |
| K 10 | 295675 | 18.5 | 19 | - | - | 19 |
| K 11 | 305675 | 25 | 22 | - | - | 24 |
| K 12 | 315675 | 25 | 23.5 | - | - | 24 |
| K 13 | 285665 | 10 | 11 | - | - | 10 |
| K 14 | 295665 | 5.5 | 5 | - | - | 5 |
| K 15 | 305665 | 11 | 11 | - | - | 11 |
| K 16 | 315665 | 9 | 9 | - | - | 9 |
| K 17 | 285655 | 22 | 19 | - | - | 20 |
| K 18 | 295655 | 11 | 10 | - | - | 10 |
| K 19 | 305655 | 13 | 12 | - | - | 12 |
| K 20 | 315655 | 13.5 | 13 | - | - | 13 |
| K 21 | 285645 | 19 | 17 | - | - | 18 |
| K 22 | 295645 | 9 | 7 | - | - | 8 |
| K 23 | 305645 | 11 | 8 | - | - | 10 |
| K 24 | 315645 | 13 | 11 | - | - | 12 |
| L 1 | 405675 | 49 | 47 | - | - | 48 |
| L 2 | 415675 | 54 | 50 | - | - | 52 |
| L 3 | 425675 | 48 | 47 | - | - | 48 |
| L 4 | 435675 | 48 | 45.5 | - | - | 47 |
| L 5 | 445675 | 34 | 33.5 | - | - | 34 |
| L 6 | 455675 | 25 | 24.5 | - | - | 25 |
| L 7 | 405665 | 48 | 46 | 49 | - | 48 |
| L 8 | 415665 | 13.5 | 14 | 17 | - | 15 |
| L 9 | 425665 | 26 | 26 | 29.5 | - | 27 |
| L 10 | 435665 | 36 | 36 | - | - | 36 |
| L 11 | 445665 | 31.5 | 31 | - | - | 31 |
| L 12 | 455665 | 46 | 41 | - | - | 44 |
| L 13 | 405655 | 65 | 61 | - | - | 63 |
| L 14 | 415655 | 49 | 45 | - | - | 47 |
| L 15 | 425655 | 48 | 42 | - | - | 45 |

APPENDIX 4.c. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| L 16 | 435655 | 55 | 50 | - | - | 52 |
| L 17 | 445655 | 22 | 20 | - | - | 21 |
| L 18 | 455655 | 23 | 23 | - | - | 23 |
| L 19 | 405645 | 33 | 33 | - | - | 33 |
| L 20 | 415645 | 35 | 33 | - | - | 34 |
| L 21 | 425645 | 23 | 22 | - | - | 22 |
| M 1 | 375635 | 34 | 32 | - | - | 33 |
| M 2 | 385635 | 50 | 48 | - | - | 49 |
| M 3 | 395635 | 48.5 | 46 | - | - | 47 |
| M 4 | 405635 | 30 | 30 | - | - | 30 |
| M 5 | 415635 | 37 | 36 | - | - | 36 |
| M 6 | 425635 | 26 | 24.5 | - | - | 25 |
| M 7 | 435635 | 42 | 40 | - | - | 41 |
| M 8 | 375625 | 25 | 24 | - | - | 24 |
| M 9 | 385625 | 42 | 40.5 | - | - | 41 |
| M 10 | 395625 | 17 | 16 | - | - | 16 |
| M 11 | 405625 | 34.5 | 32 | - | - | 33 |
| M 12 | 415625 | 30 | 26 | - | - | 28 |
| M 13 | 425625 | 48 | 42 | - | - | 45 |
| M 14 | 435625 | 25 | 23 | - | - | 24 |
| M 15 | 375615 | 28 | 25 | - | - | 26 |
| M 16 | 385615 | 47 | 41 | - | - | 44 |
| M 17 | 395615 | 32 | 31 | - | - | 32 |
| M 18 | 405615 | 67.5 | 64 | - | - | 66 |
| M 19 | 415615 | 32 | 29.5 | - | - | 31 |
| M 20 | 425615 | 60 | 55 | - | - | 58 |
| M 21 | 435615 | 100 | 101 | 99 | - | 100 |
| M 22 | 375605 | 16 | 20 | 17 | - | 18 |
| M 23 | 385605 | 29 | 28 | 30.5 | - | 29 |
| M 24 | 395605 | 171* | 99.5 | 100 | - | 100 |
| M 25 | 405605 | 46 | 46 | 48 | - | 47 |
| M 26 | 415605 | 50 | 49 | 51 | - | 50 |
| M 27 | 425605 | 54 | 47 | 48 | - | 50 |
| N 1 | 315635 | 28 | 25 | - | - | 26 |
| N 2 | 365635 | 19 | 15 | - | - | 17 |
| N 3 | 315625 | 15 | 13 | - | - | 14 |
| N 4 | 325625 | 14 | 12.5 | - | - | 13 |
| N 5 | 335625 | 24 | 24 | - | - | 24 |
| N 6 | 345625 | 41 | 40 | - | - | 40 |
| N 7 | 355625 | 40 | 50 | 43 | 47 | 45 |
| N 8 | 365625 | 30 | 26 | - | - | 28 |
| N 9 | 325615 | 10 | 9 | - | - | 10 |
| N 10 | 335615 | 12.5 | 11 | - | - | 12 |
| N 11 | 345615 | 78 | 79 | - | - | 78 |
| N 12 | 355615 | 29 | 28 | - | - | 28 |
| N 13 | 365615 | 26 | 25 | - | - | 26 |
| N 14 | 335605 | 10.5 | 10 | - | - | 10 |
| N 15 | 354605 | 13 | 13 | - | - | 13 |
| N 16 | 355605 | 28 | 26 | - | - | 27 |
| N 17 | 365605 | 17 | 17 | - | - | 17 |
| O 1 | 335595 | 24 | 25 | - | - | 24 |
| O 2 | 345595 | 236 | 246 | - | - | 241 |
| O 3 | 355595 | 14 | 13 | - | - | 14 |
| O 4 | 365595 | 17 | 14 | - | - | 16 |
| O 5 | 375595 | 31 | 27 | - | - | 29 |
| O 6 | 385595 | 48 | 41 | - | - | 44 |
| O 7 | 345585 | 15.5 | 12 | - | - | 14 |
| O 8 | 355585 | 25 | 19 | - | - | 22 |
| O 9 | 365585 | 18 | 14 | - | - | 16 |
| O 10 | 375585 | 28 | 24.5 | - | - | 26 |
| O 11 | 385585 | 35 | 31 | - | - | 33 |
| O 12 | 355575 | 23 | 18 | - | - | 20 |
| O 13 | 365575 | 20 | 13 | - | - | 16 |
| O 14 | 375575 | 51 | 43 | - | - | 47 |
| O 15 | 385575 | 48 | 39.5 | - | - | 44 |
| O 16 | 365565 | 29 | 24 | - | - | 26 |
| O 17 | 375565 | 24 | 15 | - | - | 20 |
| O 18 | 385565 | 39 | 33 | - | - | 36 |
| P 1 | 395595 | 29 | 29 | - | - | 29 |
| P 2 | 405595 | 49 | 49.5 | - | - | 49 |
| P 3 | 415595 | 41 | 42 | - | - | 42 |
| P 4 | 425595 | 25 | 26 | - | - | 26 |
| P 5 | 395585 | 48 | 47 | - | - | 48 |
| P 6 | 405585 | 30 | 30 | - | - | 30 |
| P 7 | 415585 | 26 | 26 | - | - | 26 |
| P 8 | 425585 | 31 | 32 | - | - | 32 |
| P 9 | 395575 | 21 | 20 | - | - | 20 |
| P 10 | 405575 | 30.5 | 26 | - | - | 28 |
| P 11 | 415575 | 22 | 22 | - | - | 22 |
| P 12 | 425575 | 120 | 110 | - | - | 115 |
| P 13 | 395565 | 25 | 25 | - | - | 25 |
| P 14 | 405565 | 41 | 35 | - | - | 38 |
| P 15 | 415565 | 43 | 36 | - | - | 40 |
| P 16 | 425565 | 173 | 166.5 | - | - | 170 |

APPENDIX 4.d. Complete data results for total cadmium in soil for the North East Derbyshire Soil Survey (µg/g).

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| A 1 | 405805 | <1 | - | - | - | <1 |
| A 2 | 415805 | <1 | - | - | - | <1 |
| A 3 | 425805 | <1 | - | - | - | <1 |
| A 4 | 435805 | <1 | - | - | - | <1 |
| A 5 | 445805 | <1 | - | - | - | <1 |
| A 6 | 455805 | <1 | - | - | - | <1 |
| A 7 | 405795 | <1 | - | - | - | <1 |
| A 8 | 415795 | <1 | - | - | - | <1 |
| A 9 | 425795 | 1.5 | - | - | - | 1.5 |
| A 10 | 435795 | <1 | - | - | - | <1 |
| A 11 | 445795 | <1 | - | - | - | <1 |
| A 12 | 455795 | <1 | - | - | - | <1 |
| A 13 | 405785 | 4.1 | - | - | - | 4.1 |
| A 14 | 415785 | <1 | - | - | - | <1 |
| A 15 | 425785 | 1.4 | - | - | - | 1.4 |
| A 16 | 435785 | ND | - | - | - | ND |
| A 17 | 445785 | 1.4 | - | - | - | 1.4 |
| A 18 | 455785 | 1.4 | - | - | - | 1.4 |
| A 19 | 405775 | <1 | - | - | - | <1 |
| A 20 | 415775 | <1 | - | - | - | <1 |
| A 21 | 425775 | <1 | - | - | - | <1 |
| A 22 | 435775 | <1 | - | - | - | <1 |
| A 23 | 445775 | <1 | - | - | - | <1 |
| A 24 | 455775 | 1.4 | - | - | - | 1.4 |
| B 1 | 365825 | 1.4 | - | - | - | 1.4 |
| B 2 | 375825 | 1.4 | - | - | - | 1.4 |
| B 3 | 385825 | 1.4 | - | - | - | 1.4 |
| B 4 | 395825 | <1 | - | - | - | <1 |
| B 5 | 405825 | <1 | - | - | - | <1 |
| B 6 | 365815 | <1 | - | - | - | <1 |
| B 7 | 375815 | 1.4 | - | - | - | 1.4 |
| B 8 | 385815 | <1 | - | - | - | <1 |
| B 9 | 395815 | <1 | - | - | - | <1 |
| B 10 | 405815 | 1.3 | - | - | - | 1.3 |
| B 11 | 365805 | <1 | - | - | - | <1 |
| B 12 | 375805 | <1 | - | - | - | <1 |
| B 13 | 385805 | 1.4 | - | - | - | 1.4 |
| B 14 | 395805 | <1 | - | - | - | <1 |
| B 15 | 365795 | <1 | - | - | - | <1 |
| B 16 | 375795 | 1.5 | - | - | - | 1.5 |
| B 17 | 385795 | <1 | - | - | - | <1 |
| B 18 | 395795 | <1 | - | - | - | <1 |
| B 19 | 365785 | <1 | - | - | - | <1 |
| B 20 | 375785 | <1 | - | - | - | <1 |
| B 21 | 385785 | 1.2 | - | - | - | 1.2 |
| B 22 | 395785 | 1.3 | - | - | - | 1.3 |
| B 23 | 365775 | <1 | - | - | - | <1 |
| B 24 | 375775 | <1 | - | - | - | <1 |
| B 25 | 385775 | <1 | - | - | - | <1 |
| B 26 | 395775 | <1 | - | - | - | <1 |
| C 1 | 455815 | 2.2 | - | - | - | 2.2 |
| C 2 | 465815 | <1 | - | - | - | <1 |
| C 3 | 475815 | 1.2 | - | - | - | 1.2 |
| C 4 | 485815 | <1 | - | - | - | <1 |
| C 5 | 495815 | <1 | - | - | - | <1 |
| C 6 | 465805 | <1 | - | - | - | <1 |
| C 7 | 475805 | 1.2 | - | - | - | 1.2 |
| C 8 | 485805 | <1 | - | - | - | <1 |
| C 9 | 495805 | 1.2 | - | - | - | 1.2 |
| C 10 | 465795 | <1 | - | - | - | <1 |
| C 11 | 475795 | <1 | - | - | - | <1 |
| C 12 | 485795 | <1 | - | - | - | <1 |
| C 13 | 495795 | 1.4 | - | - | - | 1.4 |
| C 14 | 465785 | 1.4 | - | - | - | 1.4 |
| C 15 | 475785 | <1 | - | - | - | <1 |
| C 16 | 485785 | <1 | - | - | - | <1 |
| C 17 | 495785 | 1.2 | - | - | - | 1.2 |
| C 18 | 465775 | <1 | - | - | - | <1 |
| C 19 | 475775 | <1 | - | - | - | <1 |
| C 20 | 485775 | <1 | - | - | - | <1 |
| C 21 | 495775 | 1.4 | - | - | - | 1.4 |
| C 22 | 465765 | 1.2 | - | - | - | 1.2 |
| C 23 | 475765 | <1 | - | - | - | <1 |
| C 24 | 485765 | 1.2 | - | - | - | 1.2 |
| C 25 | 495765 | <1 | - | - | - | <1 |
| D 1 | 325805 | <1 | - | - | - | <1 |
| D 2 | 335805 | 2.6 | - | - | - | 2.6 |
| D 3 | 345805 | <1 | - | - | - | <1 |
| D 4 | 355805 | <1 | - | - | - | <1 |
| D 5 | 325795 | 1.2 | - | - | - | 1.2 |
| D 6 | 335795 | 1.3 | - | - | - | 1.3 |
| D 7 | 345795 | <1 | - | - | - | <1 |
| D 8 | 355795 | <1 | - | - | - | <1 |
| D 9 | 325785 | <1 | - | - | - | <1 |
| D 10 | 335785 | <1 | - | - | - | <1 |
| D 11 | 345785 | <1 | - | - | - | <1 |
| D 12 | 355785 | <1 | - | - | - | <1 |
| D 13 | 325775 | <1 | - | - | - | <1 |
| D 14 | 335775 | <1 | - | - | - | <1 |
| D 15 | 345775 | <1 | - | - | - | <1 |
| D 16 | 355775 | <1 | - | - | - | <1 |
| D 17 | 325765 | <1 | - | - | - | <1 |
| D 18 | 335765 | <1 | - | - | - | <1 |
| D 19 | 345765 | <1 | - | - | - | <1 |

APPENDIX 4.d. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( # = rejected from mean calc.) | | | | |
| D 20 | 355765 | 1 | - | - | - | 1 |
| D 21 | 325755 | 1 | - | - | - | 1 |
| D 22 | 335755 | 1 | - | - | - | 1 |
| D 23 | 345755 | 1 | - | - | - | 1 |
| D 24 | 355755 | 1 | - | - | - | 1 |
| E 1 | 265795 | 1 | - | - | - | 1 |
| E 2 | 275795 | 1 | - | - | - | 1 |
| E 3 | 285795 | 1 | - | - | - | 1 |
| E 4 | 295795 | 1 | - | - | - | 1 |
| E 5 | 305795 | 1 | - | - | - | 1 |
| E 6 | 315795 | 1 | - | - | - | 1 |
| E 7 | 265785 | 1 | - | - | - | 1 |
| E 8 | 275785 | 1 | - | - | - | 1 |
| E 9 | 285785 | 1 | - | - | - | 1 |
| E 10 | 295785 | 1 | - | - | - | 1 |
| E 11 | 305785 | 1 | - | - | - | 1 |
| E 12 | 315785 | 1 | - | - | - | 1 |
| E 13 | 265775 | 1 | - | - | - | 1 |
| E 14 | 275775 | 1 | - | - | - | 1 |
| E 15 | 285775 | 1 | - | - | - | 1 |
| E 16 | 295775 | 1 | - | - | - | 1 |
| E 17 | 305775 | 1 | - | - | - | 1 |
| E 18 | 315775 | 1 | - | - | - | 1 |
| E 19 | 265765 | 1 | - | - | - | 1 |
| E 20 | 275765 | 1 | - | - | - | 1 |
| E 21 | 285765 | 1 | - | - | - | 1 |
| E 22 | 295765 | 1 | - | - | - | 1 |
| E 23 | 305765 | 1 | - | - | - | 1 |
| E 24 | 315765 | 1 | - | - | - | 1 |
| F 1 | 275755 | 1 | - | - | - | 1 |
| F 2 | 285755 | 2.0 | - | - | - | 2.0 |
| F 3 | 295755 | 1 | - | - | - | 1 |
| F 4 | 305755 | 1 | - | - | - | 1 |
| F 5 | 315755 | 1 | - | - | - | 1 |
| F 6 | 275745 | 1 | - | - | - | 1 |
| F 7 | 285745 | 1 | - | - | - | 1 |
| F 8 | 295745 | 1 | - | - | - | 1 |
| F 9 | 305745 | 1 | - | - | - | 1 |
| F 10 | 315745 | 1 | - | - | - | 1 |
| F 11 | 285735 | 1 | - | - | - | 1 |
| F 12 | 295735 | 1 | - | - | - | 1 |
| F 13 | 305735 | 1 | - | - | - | 1 |
| F 14 | 315735 | 1 | - | - | - | 1 |
| F 15 | 285725 | 1 | - | - | - | 1 |
| F 16 | 295725 | 1 | - | - | - | 1 |
| F 17 | 305725 | 1 | - | - | - | 1 |
| F 18 | 315725 | 1 | - | - | - | 1 |
| F 19 | 285715 | 1 | - | - | - | 1 |
| F 20 | 295715 | 1 | - | - | - | 1 |
| F 21 | 305715 | 1 | - | - | - | 1 |
| F 22 | 315715 | 1 | - | - | - | 1 |
| F 23 | 285705 | 1 | - | - | - | 1 |
| F 24 | 295705 | (2) 2.0 | - | - | - | (2) 2.0 |
| F 25 | 305705 | (2) 2.0 | - | - | - | (2) 2.0 |
| F 26 | 315705 | (2) 1.0 | - | - | - | (2) 1.0 |
| G 1 | 325745 | 1 | - | - | - | 1 |
| G 2 | 335745 | 1 | - | - | - | 1 |
| G 3 | 345745 | 1 | - | - | - | 1 |
| G 4 | 355745 | 1 | - | - | - | 1 |
| G 5 | 325735 | 1 | - | - | - | 1 |
| G 6 | 335735 | 1 | - | - | - | 1 |
| G 7 | 345735 | 1 | - | - | - | 1 |
| G 8 | 355735 | 1 | - | - | - | 1 |
| G 9 | 325725 | 1 | - | - | - | 1 |
| G 10 | 335725 | 1 | - | - | - | 1 |
| G 11 | 345725 | 1 | - | - | - | 1 |
| G 12 | 355725 | 1 | - | - | - | 1 |
| G 13 | 325715 | 1 | - | - | - | 1 |
| G 14 | 335715 | 1 | - | - | - | 1 |
| G 15 | 345715 | 1 | - | - | - | 1 |
| G 16 | 355715 | 1 | - | - | - | 1 |
| G 17 | 325705 | 1 | - | - | - | 1 |
| G 18 | 335705 | 1 | - | - | - | 1 |
| G 19 | 345705 | 1 | - | - | - | 1 |
| G 20 | 355705 | 1 | - | - | - | 1 |
| G 21 | 325695 | 1 | - | - | - | 1 |
| G 22 | 335695 | 1 | - | - | - | 1 |
| G 23 | 345695 | 1 | - | - | - | 1 |
| G 24 | 355695 | 1 | - | - | - | 1 |
| H 1 | 425725 | 1.1 | 1.1 | - | - | 1.1 |
| H 2 | 435725 | 1 | 1 | - | - | 1 |
| H 3 | 405715 | 1 | - | - | - | 1 |
| H 4 | 415715 | 1 | 1 | - | - | 1 |
| H 5 | 425715 | 1 | - | - | - | 1 |
| H 6 | 435715 | 1 | - | - | - | 1 |
| H 7 | 445715 | 1 | - | - | - | 1 |
| H 8 | 455715 | 1.6 | 1.1 | - | - | 1.3 |
| H 9 | 405705 | 1 | - | - | - | 1 |
| H 10 | 415705 | 1 | - | - | - | 1 |
| H 11 | 425705 | 1.3 | - | - | - | 1.3 |
| H 12 | 435705 | 1 | - | - | - | 1 |
| H 13 | 445705 | 1 | 1 | - | - | 1 |
| H 14 | 455705 | 1 | 1 | - | - | 1 |
| H 15 | 405695 | 1 | - | - | - | 1 |
| H 16 | 415695 | 1 | 1 | - | - | 1 |
| H 17 | 425695 | 1 | - | - | - | 1 |

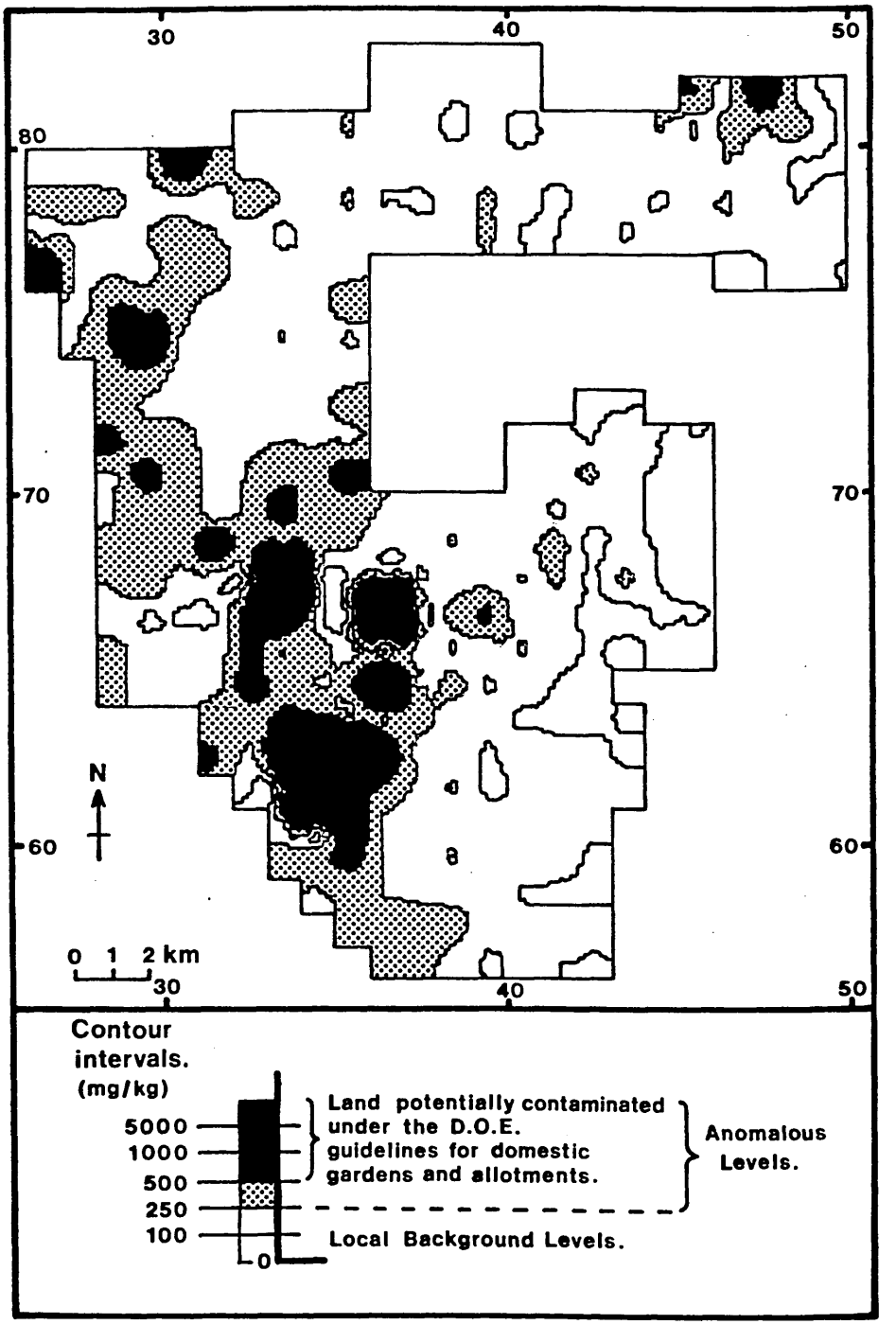
APPENDIX 4.d. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( # = rejected from mean calc.) | | | | |
| H 18 | 435695 | 1 | | | | 1 |
| H 19 | 445695 | 1 | 1 | | | 1 |
| H 20 | 455695 | 1 | 1 | | | 1 |
| H 21 | 405685 | 1 | 1 | | | 1 |
| H 22 | 415685 | 1 | | | | 1 |
| H 23 | 425685 | 1 | | | | 1 |
| H 24 | 435685 | 1 | | | | 1 |
| H 25 | 445685 | 1 | 1 | | | 1 |
| H 26 | 455685 | 1 | 1 | | | 1 |
| I 1 | 325685 | 1 | 1 | | | 1 |
| I 2 | 335685 | 1 | 1 | | | 1 |
| I 3 | 345685 | 1 | 1 | | | 1 |
| I 4 | 355685 | 1.5 | 1.1 | | | 1.3 |
| I 5 | 325675 | 1 | 1 | | | 1 |
| I 6 | 335675 | 1.1 | 1.1 | | | 1.1 |
| I 7 | 345675 | 1 | 1 | | | 1 |
| I 8 | 355675 | 1 | 1 | | | 1 |
| I 9 | 325665 | 1.3 | 1.3 | | | 1.3 |
| I 10 | 335665 | 2.4 | 1.1 | | | 1.7 |
| I 11 | 345665 | 1.1 | 1.1 | | | 1.1 |
| I 12 | 355665 | 1 | 1 | | | 1 |
| I 13 | 325655 | 1.3 | 1.5 | | | 1.4 |
| I 14 | 335655 | 1 | 1 | | | 1 |
| I 15 | 345655 | 1.8 | 1.5 | | | 1.7 |
| I 16 | 355655 | 1 | 1 | | | 1 |
| I 17 | 325645 | 1.3 | 1 | | | 1.2 |
| I 18 | 335645 | 1.5 | 1.4 | | | 1.4 |
| I 19 | 345645 | 1.3 | 2 | | | 2 |
| I 20 | 355645 | 1 | 1 | | | 1 |
| I 21 | 325635 | 1.4 | 2.0 | | | 1.8 |
| I 22 | 335635 | 1.9 | 2.1 | | | 2.5 |
| I 23 | 345635 | 7.0 | 5.5 | 7.0 | 5.5 | 6.3 |
| I 24 | 355635 | 1.3 | 1.6 | 2.0 | 1.9 | 1.7 |
| J 1 | 365695 | 1 | 1 | | | 1 |
| J 2 | 375695 | 1 | 1 | | | 1 |
| J 3 | 385695 | 1 | 1 | | | 1 |
| J 4 | 395695 | 1.3 | 1.1 | | | 1.2 |
| J 5 | 365685 | 1 | 1 | | | 1 |
| J 6 | 375685 | 1.3 | 1.3 | | | 1.3 |
| J 7 | 385685 | 1.6 | 1.9 | | | 1.7 |
| J 8 | 395685 | 1 | 1 | | | 1 |
| J 9 | 365675 | 1.3 | 1.3 | 0.9 | 1.1 | 1.4 |
| J 10 | 375675 | 1 | 1 | | | 1 |
| J 11 | 385675 | 1 | 1 | | | 1 |
| J 12 | 395675 | 1 | 1 | | | 1 |
| J 13 | 365665 | 1.3 | 1.3 | | | 1.3 |
| J 14 | 375665 | 1 | 1 | | | 1 |
| J 15 | 385665 | 1.5 | 1.5 | | | 1.5 |
| J 16 | 395665 | 1.3 | 1.3 | | | 1.3 |
| J 17 | 365655 | 1 | 1 | | | 1 |
| J 18 | 375655 | 1 | 1 | | | 1 |
| J 19 | 385655 | 1.2 | 1.2 | | | 1.2 |
| J 20 | 395655 | 1 | 1 | | | 1 |
| J 21 | 365645 | 1 | 1 | | | 1 |
| J 22 | 375645 | 1.5 | 1.5 | | | 1.5 |
| J 23 | 385645 | 1 | 1 | | | 1 |
| J 24 | 395645 | 1 | 1 | | | 1 |
| K 1 | 285695 | 1 | 1 | | | 1 |
| K 2 | 295695 | 1 | 1 | | | 1 |
| K 3 | 305695 | 1 | 1 | | | 1 |
| K 4 | 315695 | 1 | 1 | | | 1 |
| K 5 | 285685 | 1.1 | 1.1 | | | 1.1 |
| K 6 | 295685 | 1 | 1 | | | 1 |
| K 7 | 305685 | 1 | 1 | | | 1 |
| K 8 | 315685 | 1 | 1 | | | 1 |
| K 9 | 285675 | 1 | 1 | | | 1 |
| K 10 | 295675 | 1 | 1 | | | 1 |
| K 11 | 305675 | 1 | 1 | | | 1 |
| K 12 | 315675 | 1 | 1 | | | 1 |
| K 13 | 285665 | 1 | 1 | | | 1 |
| K 14 | 295665 | 1 | 1 | | | 1 |
| K 15 | 305665 | 1 | 1 | | | 1 |
| K 16 | 315665 | 1 | 1 | | | 1 |
| K 17 | 285655 | 1 | 1 | | | 1 |
| K 18 | 295655 | 1 | 1 | | | 1 |
| K 19 | 305655 | 1 | 1 | | | 1 |
| K 20 | 315655 | 1 | 1 | | | 1 |
| K 21 | 285645 | 1.2 | 1.5 | | | 1.3 |
| K 22 | 295645 | 1 | 1 | | | 1 |
| K 23 | 305645 | 1 | 1 | | | 1 |
| K 24 | 315645 | 1 | 1 | | | 1 |
| L 1 | 405675 | 1 | 1 | | | 1 |
| L 2 | 415675 | 1 | 1 | | | 1 |
| L 3 | 425675 | 1 | 1 | | | 1 |
| L 4 | 435675 | 1 | 1 | | | 1 |
| L 5 | 445675 | 1 | 1 | | | 1 |
| L 6 | 455675 | 1 | 1 | | | 1 |
| L 7 | 405665 | 1 | 1 | | | 1 |
| L 8 | 415665 | 1 | 1 | | | 1 |
| L 9 | 425665 | 1 | 1 | | | 1 |
| L 10 | 435665 | 1 | 1 | | | 1 |
| L 11 | 445665 | 1 | 1 | | | 1 |
| L 12 | 455665 | 1 | 1 | | | 1 |
| L 13 | 405655 | 1 | 1 | | | 1 |
| L 14 | 415655 | 1 | 1 | | | 1 |
| L 15 | 425655 | 1 | 1 | | | 1 |

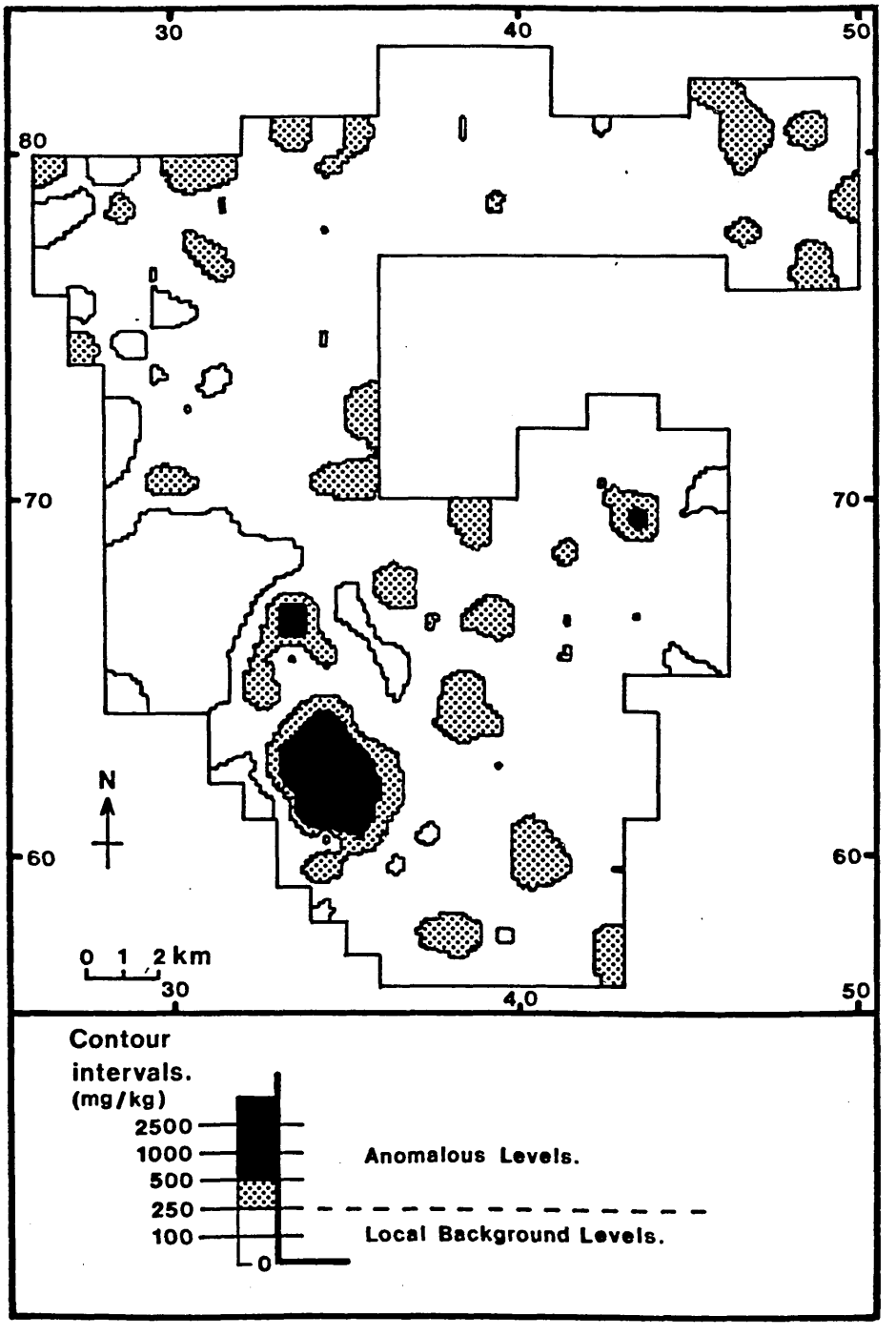
APPENDIX 4.d. Continued

| Study location. | | Results of replicate analyses. | | | | |
|---|---|---|---|---|---|---|
| Site Code. | National Grid Ref. | a. | b. | c. | d. | mean. |
| | | ( * = rejected from mean calc.) | | | | |
| L 16 | 435655 | A1 | A1 | | | A1 |
| L 17 | 445655 | A1 | A1 | | | A1 |
| L 18 | 455655 | A1 | A1 | | | A1 |
| L 19 | 405645 | A1 | A1 | | | A1 |
| L 20 | 415645 | A1 | A1 | | | A1 |
| L 21 | 425645 | A1 | A1 | | | A1 |
| M 1 | 375635 | 1.1 | 1.1 | | | 1.1 |
| M 2 | 385635 | A1 | A1 | | | A1 |
| M 3 | 395635 | A1 | A1 | | | A1 |
| M 4 | 405635 | A1 | A1 | | | A1 |
| M 5 | 415635 | A1 | A1 | | | A1 |
| M 6 | 425635 | A1 | A1 | | | A1 |
| M 7 | 435635 | A1 | A1 | | | A1 |
| M 8 | 375625 | A1 | A1 | | | A1 |
| M 9 | 385625 | 1.5 | 1.1 | | | 1.3 |
| M 10 | 395625 | A1 | A1 | | | A1 |
| M 11 | 405625 | A1 | A1 | | | A1 |
| M 12 | 415625 | A1 | A1 | | | A1 |
| M 13 | 425625 | A1 | A1 | | | A1 |
| M 14 | 435625 | A1 | A1 | | | A1 |
| M 15 | 375615 | A1 | A1 | | | A1 |
| M 16 | 385615 | A1 | A1 | | | A1 |
| M 17 | 395615 | A1 | A1 | | | A1 |
| M 18 | 405615 | A1 | A1 | | | A1 |
| M 19 | 415615 | A1 | A1 | | | A1 |
| M 20 | 425615 | A1 | A1 | | | A1 |
| M 21 | 435615 | 1.1 | 1.3 | 1.2 | | 1.2 |
| M 22 | 375605 | A1 | A1 | | | A1 |
| M 23 | 385605 | 1.1 | 1.1 | | | 1.1 |
| M 24 | 395605 | 1.1 | 1.4 | | | 1.3 |
| M 25 | 405605 | 1.1 | 1.7 | | | 1.4 |
| M 26 | 415605 | A1 | A1 | | | A1 |
| M 27 | 425605 | 1.1 | 1.1 | | | 1.1 |
| N 1 | 315635 | 1.6 | 2.0 | | | 1.8 |
| N 2 | 365635 | A1 | A1 | | | A1 |
| N 3 | 315625 | A1 | A1 | | | A1 |
| N 4 | 325625 | A1 | A1 | | | A1 |
| N 5 | 335625 | 12.1 | 12.0 | | | 12.0 |
| N 6 | 345625 | 18.6 | 19.0 | | | 18.8 |
| N 7 | 355625 | 11.0 | 11.8 | | | 11.4 |
| N 8 | 365625 | 1.5 | 2.0 | | | 1.8 |
| N 9 | 325615 | A1 | A1 | | | A1 |
| N 10 | 335615 | 1.8 | 3.5 | | | 2.6 |
| N 11 | 345615 | 49.0 | 50.3 | | | 49.6 |
| N 12 | 355615 | 8.7 | 8.6 | | | 8.6 |
| N 13 | 365615 | 1.9 | 2.3 | | | 2.1 |
| N 14 | 335605 | A1 | A1 | | | A1 |
| N 15 | 354605 | A1 | A1 | | | A1 |
| N 16 | 355605 | 4.3 | 4.3 | | | 4.3 |
| N 17 | 365605 | A1 | A1 | | | A1 |
| O 1 | 335595 | 1.3 | 1.8 | | | 1.6 |
| O 2 | 345595 | 2.4 | 2.6 | | | 2.5 |
| O 3 | 355595 | A1 | A1 | | | A1 |
| O 4 | 365595 | A1 | A1 | | | A1 |
| O 5 | 375595 | A1 | A1 | | | A1 |
| O 6 | 385595 | 1.6 | 4.0 | | | 2.8 |
| O 7 | 345585 | A1 | A1 | | | A1 |
| O 8 | 355585 | A1 | A1 | | | A1 |
| O 9 | 365585 | 1.9 | 1.0 | | | 1.4 |
| O 10 | 375585 | 1.6 | 2.6 | | | 2.1 |
| O 11 | 385585 | A1 | A1 | | | A1 |
| O 12 | 355575 | A1 | A1 | | | A1 |
| O 13 | 365575 | A1 | A1 | | | A1 |
| O 14 | 375575 | A1 | A1 | | | A1 |
| O 15 | 385575 | 3.2 | 5.0 | | | 4.1 |
| O 16 | 365565 | 1.3 | 4.0 | | | 2.6 |
| O 17 | 375565 | A1 | A1 | | | A1 |
| O 18 | 385565 | A1 | A1 | | | A1 |
| P 1 | 395595 | A1 | A1 | | | A1 |
| P 2 | 405595 | 1.6 | 1.6 | | | 1.6 |
| P 3 | 415595 | A1 | A1 | | | A1 |
| P 4 | 425595 | A1 | A1 | | | A1 |
| P 5 | 395585 | A1 | A1 | | | A1 |
| P 6 | 405585 | A1 | A1 | | | A1 |
| P 7 | 415585 | A1 | A1 | | | A1 |
| P 8 | 425585 | A1 | A1 | | | A1 |
| P 9 | 395575 | A1 | A1 | | | A1 |
| P 10 | 405575 | A1 | A1 | | | A1 |
| P 11 | 415575 | A1 | A1 | | | A1 |
| P 12 | 425575 | 1.9 | 2.6 | | | 2.2 |
| P 13 | 395565 | A1 | A1 | | | A1 |
| P 14 | 405565 | A1 | A1 | | | A1 |
| P 15 | 415565 | A1 | A1 | | | A1 |
| P 16 | 425565 | A1 | A1 | | | A1 |

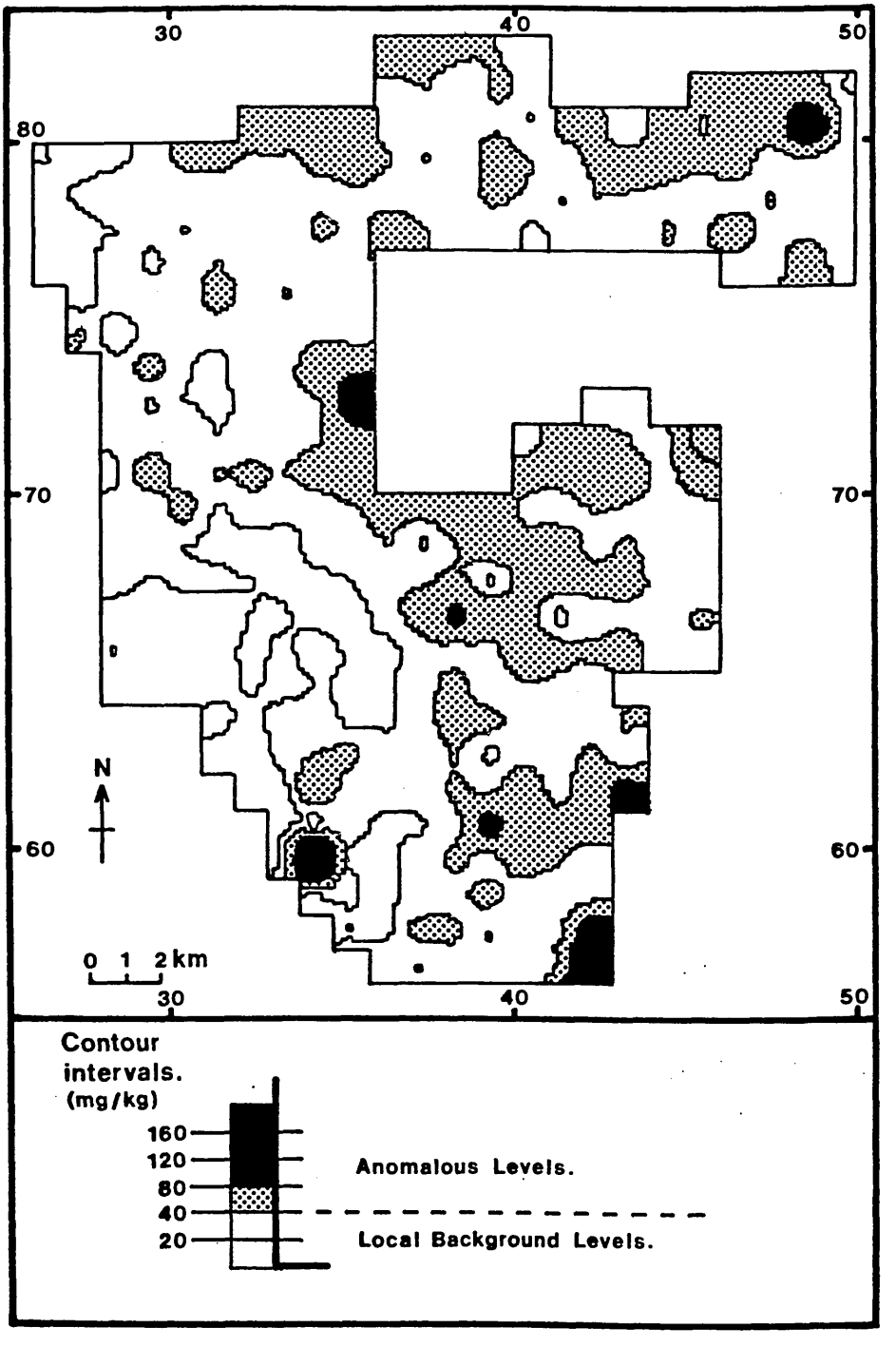
Appendix 4.e. Total lead in soil distribution showing anomalous levels highlighted.



Appendix 4.f. Total zinc in soil distribution, showing anomalous levels highlighted.



Appendix 4.g. Total copper in soil distribution. showing anomalous levels highlighted.



APPENDIX 5.a.

Replicate ashed whole leaf punch results - Dandelion & Broad Dock.

| n | DANDELION LEAF, (conc. µg/g) | BROAD DOCK LEAF, (conc. µg/g) |
|---|---|---|
| 1 | 4,6 | 6,8 |
| 2 | 2,6 | 1,5 |
| 3 | 4,1 | 5,1 |
| 4 | 4,3 | 5,4 |
| 5 | 4,0 | 5,4 |
| 6 | 4,5 | 5,3 |
| 7 | 2,6 | 4,4 |
| 8 | 1,4 | 6,0 |
| 9 | 2,9 | 4,0 |
| 10 | 6,0 | 4,0 |
| 11 | 2,7 | 7,1 |
| 12 | 3,4 | 7,0 |
| 13 | 2,2 | 4,4 |
| 14 | 3,2 | 4,4 |
| 15 | 2,0 | 5,1 |
| 16 | 4,0 | 3,2 |
| 17 | 4,3 | 6,1 |
| 18 | 3,3 | 4,9 |
| 19 | 1,4 | 9,2 |
| 20 | 5,3 | 8,0 |
| 21 | 11,4 | 6,0 |
| 22 | 5,6 | 6,2 |
| 23 | 2,5 | 4,5 |
| 24 | 3,9 | 4,7 |
| Mean - | 3,85 | 5,36 |
| Std Dev - | 2,02 | 1,60 |
| RSD % - | 52,5 | 29,8 |

APPENDIX 5.b.

Replicate ashed whole punch results -
Potato tuber slice A and slice C.

| n | POTATO TUBER SLICE A (conc, µg/g) | | POTATO TUBER SLICE C. (conc, µg/g) |
|---|---|---|---|
| 1 | 0,07 | 0,11 | 0,11 |
| 2 | 0,09 | 0,09 | 0,15 |
| 3 | 0,10 | 0,09 | 0,10 |
| 4 | 0,10 | 0,08 | 0,12 |
| 5 | 0,09 | 0,09 | 0,13 |
| 6 | 0,06 | 0,12 | 0,10 |
| 7 | 0,09 | 0,11 | 0,16 |
| 8 | 0,09 | 0,09 | 0,12 |
| 9 | 0,08 | 0,11 | 0,09 |
| 10 | 0,10 | 0,09 | 0,12 |
| 11 | 0,14 | 0,07 | 0,12 |
| 12 | 0,10 | 0,09 | 0,07 |
| 13 | 0,08 | 0,09 | 0,14 |
| 14 | 0,07 | 0,06 | 0,17 |
| 15 | 0,09 | 0,09 | 0,13 |
| 16 | 0,11 | 0,10 | 0,12 |
| 17 | 0,09 | 0,11 | 0,11 |
| 18 | 0,08 | 0,10 | 0,12 |
| 19 | 0,09 | 0,09 | 0,08 |
| 20 | 0,08 | | 0,12 |
| 21 | | | 0,12 |
| 22 | | | 0,10 |
| 23 | | | 0,12 |
| 24 | | | 0,12 |
| n | 39 | | 24 |
| Mean | 0,092 | | 0,118 |
| Std Dev | 0,016 | | 0,023 |
| RSD % | 17 | | 19 |

Appendix 6.a. Lead in soil results using various extraction procedures (ALL SITES).
(N.B. - Data forms Table 26 in body of text.)

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. | (mg/l) C. | (mg/l) D. |
|---|---|---|---|---|---|
| X 1 | | 70 | 0.5 | 0.6 | 26 |
| X 2 | | 76 | 0.4 | 0.4 | 30 |
| X 3 | | 77 | 0.4 | 0.3 | 31 |
| X 4 | | 66 | 0.4 | 0.3 | 25 |
| X 5 | | 75 | 0.4 | 0.4 | 28 |
| X 6 | | 84 | 0.4 | 0.5 | 31 |
| X 7 | | 54 | 0.4 | 0.4 | 24 |
| X 8 | | 78 | 0.5 | 0.4 | 31 |
| Mean | = | 73 | 0.4 | 0.4 | 28 |
| Std. Dev. | = | 9 | 0.05 | 0.1 | 3 |
| C.V.% | = | 13 | 11 | 24 | 10 |
| Y 1 | | 4194 | 192 | 128 | 2867 |
| Y 2 | | 3990 | 170 | 132 | 2688 |
| Y 3 | | 4329 | 177 | 116 | 2771 |
| Y 4 | | 4327 | 148 | 107 | 2863 |
| Y 5 | | 3738 | 184 | 106 | 2392 |
| Y 6 | | 3901 | 164 | 114 | 2542 |
| Y 7 | | 4075 | 84 | 188 | 2617 |
| Y 8 | | 4407 | 676 | 110 | 2762 |
| Mean | = | 4120 | 224 | 125 | 2690 |
| Std. Dev. | = | 235 | 186 | 27 | 164 |
| C.V.% | = | 6 | 83 | 22 | 6 |
| Z 1 | | 39931 | 3227 | 7708 | 33292 |
| Z 2 | | 39553 | 3476 | 7267 | 33458 |
| Z 3 | | 38661 | 3643 | 7525 | 34708 |
| Z 4 | | 37791 | 3294 | 7242 | 33208 |
| Z 5 | | 36514 | 3598 | 7833 | 33000 |
| Z 6 | | 37127 | 2472 | 7858 | 31708 |
| Z 7 | | 37622 | 2637 | 6800 | 32875 |
| Z 8 | | 37140 | 2306 | 5767 | 25333 |
| Mean | = | 38000 | 3080 | 7250 | 32200 |
| Std. Dev. | = | 1200 | 531 | 697 | 2890 |
| C.V.% | = | 3 | 17 | 10 | 9 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = M Ammonium Nitrate Extraction
(mean result of 3 determinations)
C. = 0.5 M Acetic Acid Extraction
(mean result of 3 determinations).
D. = 0.05 M Ammonium E.D.T.A. Extraction
(mean result of 3 determinations).

Appendix 6.b. Cadmium in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE. (µg/g) A. | (mg/l) B. | (mg/l) C. |
|---|---|---|---|---|
| X 1 | | 1.8 | <0.05 | <0.2 |
| X 2 | | 1.2 | <0.05 | <0.2 |
| X 3 | | 1.5 | <0.05 | <0.2 |
| X 4 | | 1.5 | <0.05 | <0.2 |
| X 5 | | 1.8 | <0.05 | <0.2 |
| X 6 | | 1.8 | <0.05 | <0.2 |
| X 7 | | 1.8 | <0.05 | <0.2 |
| X 8 | | 2.0 | <0.05 | <0.2 |
| Mean | = | 1.7 | - | - |
| Std. Dev. | = | 0.3 | - | - |
| C.V.% | = | 17 | - | - |
| Y 1 | | 2.0 | <0.3 | <0.7 |
| Y 2 | | 1.5 | <0.3 | <0.7 |
| Y 3 | | 1.5 | <0.3 | <0.7 |
| Y 4 | | 1.5 | <0.3 | <0.7 |
| Y 5 | | 1.2 | <0.3 | <0.7 |
| Y 6 | | 1.2 | <0.3 | <0.7 |
| Y 7 | | 1.5 | <0.3 | <0.7 |
| Y 8 | | 1.5 | <0.3 | <0.7 |
| Mean | = | 1.5 | - | - |
| Std. Dev. | = | 0.3 | - | - |
| C.V.% | = | 17 | - | - |
| Z 1 | | 1.5 | <0.2 | <0.5 |
| Z 2 | | 1.5 | <0.2 | <0.5 |
| Z 3 | | 1.2 | <0.2 | <0.5 |
| Z 4 | | 1.2 | <0.2 | <0.5 |
| Z 5 | | 1.8 | <0.2 | <0.5 |
| Z 6 | | 1.8 | <0.2 | <0.5 |
| Z 7 | | 1.2 | <0.2 | <0.5 |
| Z 8 | | 1.2 | <0.2 | <0.5 |
| Mean | = | 1.4 | - | - |
| Std. Dev. | = | 0.3 | - | - |
| C.V.% | = | 19 | - | - |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = 0.5 M Acetic Acid Extraction (mean result of 3 determinations).
C. = 0.05 M Ammonium E.D.T.A. Extraction (meam result of 3 determinations).

Appendix 6.c. Copper in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. | (mg/l) C. |
|---|---|---|---|---|
| X 1 | | 22 | <0.2 | 6.7 |
| X 2 | | 22 | <0.2 | 7.1 |
| X 3 | | 23 | <0.2 | 7.0 |
| X 4 | | 22 | <0.2 | 6.9 |
| X 5 | | 22 | <0.2 | 6.5 |
| X 6 | | 22 | <0.2 | 7.3 |
| X 7 | | 20 | <0.2 | 6.4 |
| X 8 | | 22 | <0.2 | 6.8 |
| Mean | = | 22 | - | 6.8 |
| Std. Dev. | = | 0.8 | - | 0.3 |
| C.V.% | = | 3.8 | - | 4.4 |
| Y 1 | | 34 | <0.2 | 14.6 |
| Y 2 | | 35 | <0.2 | 15.9 |
| Y 3 | | 36 | <0.2 | 16.4 |
| Y 4 | | 36 | <0.2 | 15.5 |
| Y 5 | | 32 | <0.2 | 14.5 |
| Y 6 | | 34 | <0.2 | 14.9 |
| Y 7 | | 33 | <0.2 | 11.6 |
| Y 8 | | 34 | <0.2 | 14.7 |
| Mean | = | 34 | - | 14.8 |
| Std. Dev. | = | 1.4 | - | 1.4 |
| C.V.% | = | 4.1 | - | 9.8 |
| Z 1 | | 38 | 2.0 | 26.5 |
| Z 2 | | 36 | 2.0 | 26.3 |
| Z 3 | | 37 | 2.2 | 26.7 |
| Z 4 | | 40 | 2.5 | 27.3 |
| Z 5 | | 38 | 2.4 | 26.3 |
| Z 6 | | 40 | 2.5 | 26.7 |
| Z 7 | | 38 | 2.2 | 27.0 |
| Z 8 | | 36 | 1.3 | 22.8 |
| Mean | = | 38 | 2.1 | 26.2 |
| Std. Dev. | = | 1.5 | 0.4 | 1.4 |
| C.V.% | = | 4.1 | 18 | 5.4 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = 0.5 M Acetic Acid Extraction (mean result of 3 determinations).
C. = 0.05 M Ammonium E.D.T.A. Extraction (mean result of 3 determinations).

Appendix 6.d. Calcium in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. |
|---|---|---|---|
| X 1 | | 3901 | 1525 |
| X 2 | | 3154 | 1717 |
| X 3 | | 2742 | 1742 |
| X 4 | | 2814 | 1525 |
| X 5 | | 2614 | 1717 |
| X 6 | | 2898 | 1567 |
| X 7 | | 2985 | 1467 |
| X 8 | | 2858 | 1600 |
| Mean | = | 2996 | 1608 |
| Std. Dev. | = | 399 | 105 |
| C.V.% | = | 13 | 6.5 |
| Y 1 | | 6058 | 1483 |
| Y 2 | | 4850 | 1589 |
| Y 3 | | 5214 | 1496 |
| Y 4 | | 6016 | 1460 |
| Y 5 | | 4056 | 1355 |
| Y 6 | | 4276 | 1433 |
| Y 7 | | 8817 | 7081 |
| Y 8 | | 6148 | 1784 |
| Mean | = | 5679 | 2210 |
| Std. Dev. | = | 1504 | 1972 |
| C.V.% | = | 26 | 89 |
| Z 1 | | 239800 | 350 |
| Z 2 | | 259400 | 372 |
| Z 3 | | 250600 | 304 |
| Z 4 | | 253000 | 393 |
| Z 5 | | 259100 | 300 |
| Z 6 | | 256000 | 506 |
| Z 7 | | 253200 | 544 |
| Z 8 | | 253700 | 714 |
| Mean | = | 253100 | 435 |
| Std. Dev. | = | 6182 | 143 |
| C.V.% | = | 2.4 | 33 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = M Ammonium Nitrate Extraction (mean result of 3 determinations).

Appendix 6.e. Chromium in soil results (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. |
|---|---|---|
| X 1 | | 10 |
| X 2 | | 11 |
| X 3 | | 10 |
| X 4 | | 9 |
| X 5 | | 11 |
| X 6 | | 11 |
| X 7 | | 10 |
| X 8 | | 11 |
| Mean | = | 10.4 |
| Std. Dev. | = | 0.7 |
| C.V.% | = | 7.1 |
| Y 1 | | 18 |
| Y 2 | | 18 |
| Y 3 | | 18 |
| Y 4 | | 19 |
| Y 5 | | 17 |
| Y 6 | | 18 |
| Y 7 | | 20 |
| Y 8 | | 20 |
| Mean | = | 18.5 |
| Std. Dev. | = | 1.1 |
| C.V.% | = | 5.8 |
| Z 1 | | 11 |
| Z 2 | | 10 |
| Z 3 | | 11 |
| Z 4 | | 10 |
| Z 5 | | 9 |
| Z 6 | | 10 |
| Z 7 | | 10 |
| Z 8 | | 8 |
| Mean | = | 9.9 |
| Std. Dev. | = | 1.0 |
| C.V.% | = | 10 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).

Appendix 6.f. Iron in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. |
|---|---|---|---|
| X 1 | | 40908 | 0.3 |
| X 2 | | 42858 | 0.3 |
| X 3 | | 42242 | 0.3 |
| X 4 | | 41814 | 0.4 |
| X 5 | | 41404 | 0.4 |
| X 6 | | 39046 | 0.1 |
| X 7 | | 36984 | 0.2 |
| X 8 | | 40411 | 0.3 |
| Mean | = | 40708 | - |
| Std. Dev. | = | 1906 | - |
| C.V.% | = | 4.7 | - |
| Y 1 | | 8286 | 2.3 |
| Y 2 | | 8525 | 1.4 |
| Y 3 | | 8428 | 2.6 |
| Y 4 | | 8688 | 2.2 |
| Y 5 | | 6710 | 1.9 |
| Y 6 | | 7252 | 1.4 |
| Y 7 | | 7718 | 1.1 |
| Y 8 | | 8623 | 2.6 |
| Mean | = | 8029 | - |
| Std. Dev. | = | 727 | - |
| C.V.% | = | 9 | - |
| Z 1 | | 6054 | 102 |
| Z 2 | | 6001 | 102 |
| Z 3 | | 5777 | 108 |
| Z 4 | | 5920 | 101 |
| Z 5 | | 5694 | 104 |
| Z 6 | | 5776 | 121 |
| Z 7 | | 5707 | 116 |
| Z 8 | | 5698 | 111 |
| Mean | = | 5828 | 108 |
| Std. Dev. | = | 144 | 7.4 |
| C.V.% | = | 2.5 | 6.8 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = M Ammonium Nitrate Extraction (mean result of 3 determinations).

Appendix 6.g. Magnesium in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. |
|---|---|---|---|
| X 1 | | 1888 | 317 |
| X 2 | | 1697 | 312 |
| X 3 | | 1690 | 334 |
| X 4 | | 1750 | 292 |
| X 5 | | 1564 | 306 |
| X 6 | | 1737 | 301 |
| X 7 | | 1748 | 297 |
| X 8 | | 1584 | 243 |
| Mean | = | 1707 | 300.2 |
| Std. Dev. | = | 102 | 26.6 |
| C.V.% | = | 6.0 | 8.7 |
| Y 1 | | 1602 | 76 |
| Y 2 | | 1850 | 85 |
| Y 3 | | 1479 | 74 |
| Y 4 | | 1930 | 68 |
| Y 5 | | 1151 | 66 |
| Y 6 | | 1226 | 87 |
| Y 7 | | 1174 | 76 |
| Y 8 | | 1424 | 99 |
| Mean | = | 1480 | 78.9 |
| Std. Dev. | = | 299 | 11 |
| C.V.% | = | 20 | 14 |
| Z 1 | | 355 | 21 |
| Z 2 | | 351 | 18 |
| Z 3 | | 384 | 18 |
| Z 4 | | 414 | 21 |
| Z 5 | | 364 | 18 |
| Z 6 | | 376 | 35 |
| Z 7 | | 366 | 32 |
| Z 8 | | 398 | 38 |
| Mean | = | 376 | 25.1 |
| Std. Dev. | = | 21.7 | 8.4 |
| C.V.% | = | 5.8 | 34 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = M Ammonium Nitrate Extraction (mean result of 3 determinations).

Appendix 6.h. Manganese in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. |
|---|---|---|---|
| X 1 | | 1050 | 2.0 |
| X 2 | | 1113 | 8.4 |
| X 3 | | 1102 | 10.0 |
| X 4 | | 1038 | 5.9 |
| X 5 | | 1038 | 6.9 |
| X 6 | | 1062 | 2.0 |
| X 7 | | 962 | 0.8 |
| X 8 | | 1197 | 3.2 |
| Mean | = | 1070 | 4.9 |
| Std. Dev. | = | 69 | 3.4 |
| C.V.% | = | 6.4 | 69 |
| Y 1 | | 62 | 7.0 |
| Y 2 | | 146 | 9.0 |
| Y 3 | | 76 | 8.3 |
| Y 4 | | 57 | 6.1 |
| Y 5 | | 44 | 5.0 |
| Y 6 | | 66 | 6.4 |
| Y 7 | | 54 | 2.5 |
| Y 8 | | 58 | 4.9 |
| Mean | = | 70 | 6.1 |
| Std. Dev. | = | 32 | 2.1 |
| C.V.% | = | 45 | 34 |
| Z 1 | | 136 | 161 |
| Z 2 | | 118 | 210 |
| Z 3 | | 130 | 202 |
| Z 4 | | 132 | 319 |
| Z 5 | | 126 | 181 |
| Z 6 | | 126 | 213 |
| Z 7 | | 117 | 220 |
| Z 8 | | 120 | 141 |
| Mean | = | 126 | 206 |
| Std. Dev. | = | 6.9 | 53 |
| C.V.% | = | 5.5 | 26 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = M Ammonium Nitrate Extraction (mean result of 3 determinations).

Appendix 6.i. Nickel in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. | (mg/l) C. |
|---|---|---|---|
| X 1 | 18 | 0.4 | 2.5 |
| X 2 | 16 | 0.5 | 2.9 |
| X 3 | 17 | 0.5 | 3.3 |
| X 4 | 18 | 0.4 | 2.6 |
| X 5 | 17 | 0.4 | 2.6 |
| X 6 | 16 | 0.6 | 2.6 |
| X 7 | 17 | 0.4 | 2.2 |
| X 8 | 18 | 0.5 | 3.0 |
| Mean = | 17 | - | 2.7 |
| Std. Dev. = | 0.8 | - | 0.3 |
| C.V.% = | 4.8 | - | 13 |
| Y 1 | 30 | 1.3 | 6.0 |
| Y 2 | 26 | 1.2 | 5.7 |
| Y 3 | 27 | 1.3 | 5.8 |
| Y 4 | 29 | 1.2 | 6.0 |
| Y 5 | 24 | 1.1 | 5.0 |
| Y 6 | 24 | 1.1 | 5.2 |
| Y 7 | 27 | 1.2 | 5.1 |
| Y 8 | 30 | 1.2 | 5.8 |
| Mean = | 27 | - | 5.6 |
| Std. Dev. = | 2.4 | - | 0.4 |
| C.V.% = | 8.9 | - | 7.3 |
| Z 1 | 41 | 0.8 | 2.0 |
| Z 2 | 38 | 0.8 | 1.9 |
| Z 3 | 40 | 0.8 | 1.9 |
| Z 4 | 38 | 0.9 | 2.1 |
| Z 5 | 36 | 0.9 | 1.9 |
| Z 6 | 38 | 1.0 | 2.2 |
| Z 7 | 36 | 1.0 | 2.0 |
| Z 8 | 36 | 0.9 | 2.1 |
| Mean = | 38 | - | 2.0 |
| Std. Dev. = | 1.9 | - | 0.1 |
| C.V.% = | 5.0 | - | 5.6 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = 0.5 M Acetic Acid Extraction (mean result of 3 determinations).
C. = 0.05 M Ammonium E.D.T.A. Extraction (mean result of 3 determinations).

Appendix 6.j. Zinc in soil results using various extraction procedures (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION. | | EXTRACTION PROCEDURE (µg/g) A. | (mg/l) B. | (mg/l) C. |
|---|---|---|---|---|
| X 1 | | 112 | 2.8 | 8 |
| X 2 | | 110 | 3.1 | 8 |
| X 3 | | 111 | 3.1 | 9 |
| X 4 | | 107 | 2.8 | 7 |
| X 5 | | 111 | 3.0 | 8 |
| X 6 | | 113 | 3.2 | 9 |
| X 7 | | 95 | 3.0 | 7 |
| X 8 | | 109 | 2.9 | 9 |
| Mean | = | 108 | 3.0 | 8.1 |
| Std. Dev. | = | 5.8 | 0.2 | 0.8 |
| C.V.% | = | 5.3 | 5.0 | 10 |
| Y 1 | | 172 | 16 | 42 |
| Y 2 | | 151 | 15 | 40 |
| Y 3 | | 159 | 14 | 41 |
| Y 4 | | 184 | 16 | 42 |
| Y 5 | | 140 | 13 | 39 |
| Y 6 | | 140 | 14 | 39 |
| Y 7 | | 157 | 16 | 40 |
| Y 8 | | 176 | 14 | 40 |
| Mean | = | 160 | 14.8 | 40.4 |
| Std. Dev. | = | 16.3 | 1.2 | 1.2 |
| C.V.% | = | 10.2 | 7.8 | 2.9 |
| Z 1 | | 302 | 9 | 50 |
| Z 2 | | 350 | 11 | 47 |
| Z 3 | | 325 | 9 | 50 |
| Z 4 | | 325 | 10 | 50 |
| Z 5 | | 300 | 9 | 50 |
| Z 6 | | 350 | 11 | 51 |
| Z 7 | | 300 | 10 | 47 |
| Z 8 | | 300 | 9 | 32 |
| Mean | = | 319 | 9.8 | 47.1 |
| Std. Dev. | = | 21.9 | 0.9 | 6.3 |
| C.V.% | = | 6.9 | 9.1 | 13 |

A. = 1+1 Nitric Acid Extraction (mean result of 2 determinations).
B. = 0.5 M Acetic Acid Extraction (mean result of 3 determinations).
C. = 0.05 M Ammonium E.D.T.A. Extraction (mean result of 3 determinations).

Appendix 6.k. Soil results on harvesting for nitrate/nitrogen, phosphorus, potassium, organic content indicator and acidity (ALL SITES).

| SOIL MEDIUM/ SITE LOCATION | NITRATE/ NITROGEN. (N) (mg/l) ** | PHOSPHORUS. (P) (mg/l) ** | POTASSIUM. (K) (mg/l) *** | % LOSS ON IGNITION. * | ACIDITY (pH) ** |
|---|---|---|---|---|---|
| X 1 | 7.7 | 17.5 | 127 | 14.4 | 5.7 |
| X 2 | 44.7 | 20.6 | 202 | 13.7 | 5.1 |
| X 3 | 32.0 | 22.3 | 196 | 12.4 | 5.2 |
| X 4 | 31.2 | 18.2 | 198 | 11.1 | 5.3 |
| X 5 | 58.5 | 19.4 | 232 | 13.2 | 5.1 |
| X 6 | 7.5 | 18.8 | 194 | 14.1 | 5.7 |
| X 7 | 8.2 | 16.8 | 203 | 12.6 | 5.9 |
| X 8 | 4.7 | 29.8 | 183 | 12.4 | 5.4 |
| Mean = | 24.3 | 20.4 | 192 | 13 | 5.4 |
| Std. Dev. = | 20.3 | 4.2 | 29.7 | 1.08 | 0.3 |
| C.V.% = | 83.5 | 20.6 | 15.5 | 8.3 | 5.7 |
| Y 1 | 24.2 | 13.8 | 168 | 16.6 | 4.6 |
| Y 2 | 29.2 | 14.6 | 142 | 15.4 | 4.5 |
| Y 3 | 14.8 | 18.8 | 207 | 16.9 | 4.4 |
| Y 4 | 13.5 | 18.7 | 202 | 17.1 | 4.5 |
| Y 5 | 25.5 | 16.3 | 161 | 17.1 | 4.4 |
| Y 6 | 4.8 | 16.5 | 168 | 15.8 | 4.6 |
| Y 7 | 5.0 | 15.4 | 148 | 16.3 | 5.7 |
| Y 8 | 4.0 | 21.4 | 141 | 16.2 | 4.6 |
| Mean = | 15.1 | 16.9 | 167 | 16.4 | 4.7 |
| Std. Dev. = | 10.2 | 2.5 | 25.4 | 0.6 | 0.4 |
| C.V.% = | 67.5 | 15.0 | 15.2 | 3.8 | 9.2 |
| Z 1 | 23.2 | 45.0 | 58 | 3.1 | 5.5 |
| Z 2 | 53.5 | 50.0 | 60 | 4.4 | 5.4 |
| Z 3 | 48.0 | 48.0 | 72 | 4.6 | 5.3 |
| Z 4 | 54.5 | 45.6 | 74 | 4.1 | 5.4 |
| Z 5 | 31.8 | 47.5 | 78 | 4.0 | 5.4 |
| Z 6 | 4.5 | 49.4 | 57 | 4.0 | 5.9 |
| Z 7 | 23.5 | 49.4 | 94 | 4.4 | 5.7 |
| Z 8 | 1.2 | 41.2 | 52 | 4.7 | 5.9 |
| Mean = | 30.0 | 47.0 | 68 | 4.2 | 5.6 |
| Std. Dev. = | 20.9 | 3.0 | 14.0 | 0.5 | 0.2 |
| C.V.% = | 69.6 | 6.3 | 20.5 | 12.0 | 4.3 |

* = Result reported based on 1 determination only.
** = Result reported is mean of 2 analytical determinations.
*** = Result reported is mean of 3 analytical determinations.

Appendix 6.1. Stem and tuber yield (ALL SITES)
(N. B. - Data forms Tables 30 and 31 in the text)

| SOIL MEDIUM/ SITE LOCATION. | TUBER YIELD. (g. wet Wt. per row) | STEM YIELD. (Washed stems per row) (g. dry Wt.) | (Mean stem height) (cm.) | (Washed stem ÷ mean stem hight) (g/cm x $10^{-3}$) |
|---|---|---|---|---|
| X 1 | 538 | 1.7 | 22 | 77 |
| X 2 | 364 | 0.6 | 19 | 32 |
| X 3 | 442 | 1.7 | 18 | 94 |
| X 4 | 528 | 1.1 | 14 | 78 |
| X 5 | 584 | 2.0 | 26 | 77 |
| X 6 | 666 | 0.8 | 8 | 100 |
| X 7 | 410 | 0.7 | 10 | 70 |
| X 8 | 472 | 5.3 | 46 | 115 |
| Mean = | 501 | 1.7 | 20.4 | 80.4 |
| Std. Dev. = | 98 | 1.5 | 12 | 25 |
| C.V.% = | 20 | 89 | 59 | 31 |
| Y 1 | 506 | 2.1 | 23 | 91 |
| Y 2 | 445 | 1.4 | 23 | 61 |
| Y 3 | 542 | 3.0 | 29 | 104 |
| Y 4 | 628 | 1.1 | 16 | 69 |
| Y 5 | 700 | 2.0 | 27 | 74 |
| Y 6 | 757 | 0.7 | 9 | 78 |
| Y 7 | 540 | 1.7 | 15 | 113 |
| Y 8 | 567 | 3.8 | 43 | 88 |
| Mean = | 586 | 1.98 | 23.1 | 84.6 |
| Std. Dev. = | 103 | 1 | 10 | 18 |
| C.V.% = | 18 | 51 | 43 | 21 |
| Z 1 | 195 | 0.6 | 20 | 30 |
| Z 2 | 141 | 0.6 | 14 | 43 |
| Z 3 | 197 | 0.2 | 8 | 25 |
| Z 4 | 191 | 0.5 | 10 | 50 |
| Z 5 | 203 | 0.5 | 10 | 50 |
| Z 6 | 185 | 0.1 | 2 | 50 |
| Z 7 | 123 | 0.3 | 5 | 60 |
| Z 8 | 142 | 0.9 | 18 | 50 |
| Mean = | 173 | 0.46 | 10.9 | 44.8 |
| Std. Dev. = | 30 | 0.26 | 6.2 | 12 |
| C.V.% = | 17 | 56 | 57 | 27 |

Appendix 6.m. Lead in potato plants by acid digestion procedure. Results for leaves (ALL SITES) (µg/g dwt)
(N. B. - data forms Table 33 in the text).

| SOIL MEDIUM/ SITE LOCATION. | | LEAF UNWASHED. (A)* | LEAF WASHED. (B)* | LEAF SURFACE. CONTAMINATION. (A-B)* |
|---|---|---|---|---|
| X 1 | | 140 | 23 | 117 |
| X 2 | | 110 | 8 | 102 |
| X 3 | | 48 | 9 | 39 |
| X 4 | | 26 | 8 | 18 |
| X 5 | | 34 | 8 | 26 |
| X 6 | | 65 | 30 | 35 |
| X 7 | | 51 | 9 | 42 |
| X 8 | | 12 | 5 | 7 |
| Mean | = | 60.8 | 12.5 | 48.3 |
| Std. Dev. | = | 44 | 8.9 | 40 |
| C.V.% | = | 72 | 71 | 82 |
| Y 1 | | 175 | 69 | 106 |
| Y 2 | | 141 | 51 | 90 |
| Y 3 | | 95 | 48 | 47 |
| Y 4 | | 75 | 60 | 15 |
| Y 5 | | 70 | 43 | 27 |
| Y 6 | | 190 | 133 | 57 |
| Y 7 | | 102 | 51 | 51 |
| Y 8 | | 32 | 26 | 6 |
| Mean | = | 110 | 60 | 49.9 |
| Std. Dev. | = | 55 | 32 | 35 |
| C.V.% | = | 50 | 53 | 70 |
| Z 1 | | 1236 | 67 | 1169 |
| Z 2 | | 765 | 54 | 711 |
| Z 3 | | 1142 | 78 | 1064 |
| Z 4 | | 1150 | 280 | 870 |
| Z 5 | | 2057 | 142 | 1915 |
| Z 6 | | 4110 | 302 | 3808 |
| Z 7 | | 1591 | 92 | 1499 |
| Z 8 | | 651 | 19 | 632 |
| Mean | = | 1588 | 129 | 1458 |
| Std. Dev. | = | 1112 | 106 | 1039 |
| C.V.% | = | 70 | 82 | 71 |

(* = Results based on 1 analytical determination.)

Appendix 6.n. Lead in potato plants by acid digestion procedure. Results for stems (ALL SITES) (µg/g dwt)
(N.B. - data forms Table 34 in the text)

| SOIL MEDIUM/ SITE LOCATION. | | STEM UNWASHED. (A)* | STEM WASHED. (B)* | STEM SURFACE CONTAMINATION. (A-B)* |
|---|---|---|---|---|
| X 1 | | 26 | 4 | 22 |
| X 2 | | 24 | 9 | 15 |
| X 3 | | 15 | 3 | 12 |
| X 4 | | 18 | 4 | 14 |
| X 5 | | 15 | 4 | 11 |
| X 6 | | 33 | 8 | 25 |
| X 7 | | 17 | 3 | 14 |
| X 8 | | 9 | 5 | 4 |
| Mean | = | 19.6 | 5.0 | 14.6 |
| Std. Dev. | = | 7.6 | 2.3 | 6.5 |
| C.V.% | = | 39 | 45 | 45 |
| Y 1 | | 300 | 300 | 0 |
| Y 2 | | 358 | 364 | -6 |
| Y 3 | | 312 | 349 | -37 |
| Y 4 | | 476 | 518 | -42 |
| Y 5 | | 313 | 322 | -9 |
| Y 6 | | 512 | 431 | 81 |
| Y 7 | | 338 | 390 | -52 |
| Y 8 | | 250 | 250 | 0 |
| Mean | = | 357 | 366 | -8.1 |
| Std. Dev. | = | 91 | 83 | - |
| C.V.% | = | 25 | 23 | - |
| Z 1 | | 1447 | 131 | 1316 |
| Z 2 | | 1110 | 225 | 885 |
| Z 3 | | 1235 | 132 | 1103 |
| Z 4 | | 807 | 227 | 580 |
| Z 5 | | 1254 | 212 | 1042 |
| Z 6 | | 3108 | 396 | 2712 |
| Z 7 | | 1927 | 390 | 1537 |
| Z 8 | | 212 | 304 | -92 |
| Mean | = | 1388 | 252 | 1135 |
| Std. Dev. | = | 853 | 103 | 808 |
| C.V.% | = | 62 | 41 | 71 |

(* = Results based on 1 analytical determination)

Appendix 6.o. Lead in potato plants by acid digestion procedure. Results for roots, tuber peel and tuber (peeled) (ALL SITES)(µg/g dwt)
(N. B. - data forms Table 35 in the text)

| SOIL MEDIUM/ SITE LOCATION. | | ROOTS. (Washed) ** | TUBER PEEL. (washed) ** | TUBER. (peeled) ** |
|---|---|---|---|---|
| X 1 | | 18 | 6.0 | 1.4 |
| X 2 | | 32 | 3.1 | 1.2 |
| X 3 | | 28 | 2.7 | 1.1 |
| X 4 | | 21 | 2.4 | 1.4 |
| X 5 | | 23 | 3.7 | 1.0 |
| X 6 | | 45 | 3.8 | 3.0 |
| X 7 | | 21 | 2.6 | 1.2 |
| X 8 | | 15 | 2.2 | 1.0 |
| Mean | = | 25.4 | 3.31 | 1.41 |
| Std. Dev. | = | 9.6 | 1.2 | 0.7 |
| C.V.% | = | 38 | 37 | 47 |
| Y 1 | | 835 | 19.4 | 5.8 |
| Y 2 | | 761 | 15.1 | 5.7 |
| Y 3 | | 762 | 15.8 | 5.2 |
| Y 4 | | 718 | 27.8 | 5.2 |
| Y 5 | | 630 | 26.6 | 4.8 |
| Y 6 | | 865 | 21.6 | 4.0 |
| Y 7 | | 714 | 17.5 | 5.2 |
| Y 8 | | 1416 | 23.4 | 7.5 |
| Mean | = | 837.6 | 20.9 | 5.42 |
| Std. Dev. | = | 245 | 4.8 | 1 |
| C.V.% | = | 29 | 23 | 19 |
| Z 1 | | 8321 | 164 | 6.2 |
| Z 2 | | 8086 | 199 | 4.1 |
| Z 3 | | 8618 | 216 | 4.2 |
| Z 4 | | 10979 | 235 | 4.6 |
| Z 5 | | 10751 | 503 | 7.7 |
| Z 6 | | 9628 | 378 | 7.6 |
| Z 7 | | 6451 | 233 | 5.0 |
| Z 8 | | 5138 | 437 | 7.6 |
| Mean | = | 8496 | 296 | 5.88 |
| Std. Dev. | = | 2007 | 126 | 1.6 |
| C.V.% | = | 24 | 42 | 27 |

(** = Results based on mean of 2 analytical determinations.)

Appendix 6.p. Lead in potato plant sections by solid sample micro-sampling cup procedure - results for soil medium X (ALL SITES) (ug/g dwt)

| PLANT PART. | | SITE LOCATION. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | X1 | X2 | X3 | X4 | X5 | X6 | X7 | X8 |
| Leaf | -a. | 4,94 | 1,57 | 3,44 | 1,19 | 3,15 | 4,87 | 1,07 | 0,28 |
| section | b. | 9,01 | 1,39 | 3,15 | 1,91 | 3,37 | 6,69 | 1,34 | 1,44 |
| | c. | 8,75 | 1,84 | 3,37 | 2,02 | 5,01 | 5,45 | 1,51 | 1,19 |
| | d. | 3,15 | 1,87 | 4,05 | 1,51 | 4,05 | 5,55 | 1,60 | 1,48 |
| Leaf | -a. | 9,27 | 1,94 | 10,73 | 0,78 | 2,02 | 2,89 | 4,04 | 0,46 |
| petiole | b. | 2,19 | 3,39 | 2,45 | 0,72 | 1,67 | 2,13 | 2,95 | 0,87 |
| section | c. | 24,85 | 2,08 | 2,84 | 2,52 | 1,97 | 3,79 | 1,49 | 1,82 |
| | d. | 1,70 | 1,03 | 1,21 | 0,32 | 5,46 | 1,45 | 3,40 | 0,51 |
| Stem | -a. | 5,00 | 1,65 | 7,70 | 2,08 | 2,26 | 2,82 | 12,86 | 0,82 |
| section | b. | 4,88 | 3,49 | 3,47 | 1,97 | 3,62 | 1,88 | 3,67 | 0,53 |
| | c. | 33,90 | 1,70 | 2,12 | 1,25 | 2,14 | 3,00 | 1,83 | 0,74 |
| | d. | 2,37 | 6,41 | 6,54 | 6,05 | 3,38 | 3,55 | 3,37 | 3,15 |
| Tuber peel. | -a. | 2,35 | 0,84 | 1,20 | 0,51 | 0,60 | 0,83 | 0,34 | 0,94 |
| Tuber | -a. | 0,10 | 0,05 | 0,12 | 0,04 | 0,04 | 0,06 | 0,05 | 0,07 |
| section | b. | 0,13 | 0,03 | 0,10 | 0,03 | 0,19 | 0,03 | 0,02 | 0,05 |
| | c. | 0,16 | 0,06 | 0,12 | 0,10 | 0,11 | 0,06 | 0,03 | 0,08 |
| | d. | 0,41 | 0,11 | 0,05 | 0,06 | 0,06 | 0,09 | 0,05 | 0,06 |
| | e. | 0,11 | 0,13 | 0,04 | 0,05 | 0,09 | 0,16 | 0,04 | 0,06 |
| Tuber peel. | -b. | 3,07 | 1,27 | ND | 0,76 | 0,78 | 0,81 | 0,70 | 0,88 |
| Root | -a. | 7,9 | 27,5 | 71,4 | 46,6 | 26,4 | 49,2 | 24,9 | 8,0 |
| section | b. | 9,5 | 32,5 | 65,5 | 14,6 | 21,8 | 44,5 | 18,8 | 7,4 |
| | c. | 16,3 | 33,7 | 113,4 | 37,1 | 7,4 | 73,4 | 26,9 | 17,5 |
| | d. | 28,8 | 31,9 | 141,3 | 37,0 | 14,2 | 87,6 | 13,1 | 32,7 |

---

| | X1 | X2 | X3 | X4 | X5 | X6 | X7 | X8 |
|---|---|---|---|---|---|---|---|---|
| Surface leaf contamination, - - - - - | 117 | 102 | 39 | 18 | 26 | 35 | 42 | 7 |
| Total lead in soil, - - - - - - - - | 70 | 76 | 77 | 66 | 75 | 84 | 54 | 78 |
| Available lead in soil, - - - - - - - - (EDTA extraction) | 26 | 30 | 31 | 25 | 28 | 31 | 24 | 31 |

Appendix 6.q. Lead in potato plant sections by solid sample micro-sampling cup procedure - results for soil medium Y (ALL SITES) (µg/g dwt)

| PLANT PART | | SITE LOCATION, | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Y1 | Y2 | Y3 | Y4 | Y5 | Y6 | Y7 | Y8 |
| Leaf section | -a, | 50,3 | 24,7 | 73,0 | 190,2 | 65,8 | 121,8 | 43,6 | 84,1 |
| | b, | 50,8 | 19,2 | 81,7 | 198,7 | 52,3 | 164,6 | 29,3 | 73,0 |
| | c, | 59,6 | 29,6 | 79,8 | 178,6 | 57,2 | 119,1 | 32,6 | 75,1 |
| | d, | 44,3 | 26,9 | 75,7 | 175,7 | 48,3 | 123,6 | 31,0 | 77,4 |
| Leaf petiole section | -a, | 161,1 | 65,0 | 18,8 | 293,3 | 64,2 | 328,7 | 235,6 | 20,0 |
| | b, | 93,8 | 55,6 | 21,9 | 246,9 | 96,9 | 189,6 | 178,2 | 17,7 |
| | c, | 169,0 | 51,2 | 186,8 | 163,5 | 57,2 | 236,4 | 91,1 | 26,1 |
| | d, | 217,5 | 64,5 | 186,9 | 171,4 | 173,4 | 162,3 | 298,1 | 24,7 |
| Stem section | -a, | 59,4 | 24,9 | 135,6 | >390 | 129,8 | 150,8 | 186,4 | 16,1 |
| | b, | 99,6 | 70,9 | 233,3 | >910 | 236,0 | 470,1 | 206,0 | 21,6 |
| | c, | >549 | 178,9 | >437 | >679 | 799,1 | >625 | >602 | 114,3 |
| | d, | >369 | >340 | 377,9 | >510 | >493 | >436 | >601 | 139,1 |
| Tuber peel | -a, | 18,8 | 109,0 | 38,4 | 19,3 | 78,6 | 89,5 | 28,1 | 86,6 |
| Tuber section | -a, | 0,56 | 1,02 | 1,96 | 4,27 | 1,44 | 1,39 | 1,17 | 2,94 |
| | b, | 2,14 | 1,00 | 1,85 | 1,62 | 2,62 | 1,12 | 2,50 | 3,21 |
| | c, | 3,77 | 1,30 | 3,48 | 0,61 | 2,64 | 2,25 | 2,59 | 2,23 |
| | d, | 2,65 | 2,08 | 1,64 | 2,28 | 2,61 | 0,58 | 3,26 | 7,13 |
| | e, | 1,21 | 2,12 | 1,82 | 0,54 | 1,08 | 0,77 | 2,58 | 2,28 |
| Tuber peel | -b, | 44,0 | 25,2 | 55,4 | 16,1 | 59,2 | 31,8 | 13,6 | 65,0 |
| Root section | -a, | 1415,0 | 1395,8 | 150,9 | >1558 | 265,8 | 434,5 | 1711,0 | >1715 |
| | b, | >962 | 862,5 | 160,0 | 400,0 | 222,2 | ND | 1442,9 | >2127 |
| | c, | 2284,8 | 166,7 | 278,6 | 1040,5 | 403,5 | 250,0 | 1620,4 | >2305 |
| | d, | 1798,8 | 172,1 | 5170,4 | 603,8 | 130,8 | 347,2 | >958 | >1279 |

---

| | Y1 | Y2 | Y3 | Y4 | Y5 | Y6 | Y7 | Y8 |
|---|---|---|---|---|---|---|---|---|
| Surface leaf contamination, - - | 106 | 90 | 47 | 15 | 27 | 57 | 51 | 6 |
| Total lead in soil, - - - - - | 4194 | 3990 | 4329 | 4327 | 3738 | 3901 | 4075 | 4407 |
| Available lead in soil, - - - - - (EDTA extraction) | 2867 | 2688 | 2771 | 2863 | 2392 | 2542 | 2617 | 2762 |

Appendix 6.r. Lead in potato plant sections by solid sample micro-sampling cup procedure - results for soil medium Z (ALL SITES) (µg/g dwt)

| PLANT PART | | SITE LOCATION. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Z1 | Z2 | Z3 | Z4 | Z5 | Z6 | Z7 | Z8 |
| Leaf section | -a. | 60,2 | 16,4 | 37,2 | 32,4 | 20,2 | 58,4 | 18,6 | 5,3 |
| | b. | 47,8 | 17,1 | 30,9 | 38,5 | 23,6 | 91,7 | 27,0 | 20,1 |
| | c. | 46,4 | 28,3 | 40,1 | 24,3 | 25,2 | 33,4 | 17,0 | 8,3 |
| | d. | 203,6 | 21,7 | 26,7 | 27,8 | 49,1 | 37,5 | 24,3 | 8,5 |
| Leaf petiole section | -a. | 45,2 | 31,6 | 39,5 | 161,4 | 240,1 | 220,2 | 105,6 | 19,0 |
| | b. | 74,2 | 24,8 | 39,5 | 200,9 | 116,2 | 137,9 | 184,5 | 28,0 |
| | c. | 63,5 | 17,1 | 43,2 | 160,1 | 162,2 | 144,3 | 128,8 | 9,4 |
| | d. | 27,6 | 14,6 | 330,2 | 364,4 | 103,8 | 148,0 | 334,8 | 22,8 |
| Stem section | -a. | 65,6 | 53,0 | 61,9 | 326,2 | 73,7 | 518,9 | 545,7 | 26,1 |
| | b. | 31,6 | 86,7 | 105,9 | 518,5 | 90,0 | 202,3 | 770,5 | 27,1 |
| | c. | 79,1 | 166,7 | 368,5 | 469,0 | 214,3 | 605,7 | >1044 | 79,8 |
| | d. | 261,1 | 462,1 | >1229 | 1243,3 | 350,0 | >324 | >826 | 101,7 |
| Tuber peel | -a. | >383 | >294 | >202 | >242 | >386 | >170 | >192 | >261 |
| Tuber section | -a. | 1,29 | 1,24 | 3,27 | 0,80 | 0,97 | 1,83 | 2,31 | 3,13 |
| | b. | 1,68 | 1,86 | 0,73 | 1,18 | 1,49 | 2,43 | 2,28 | 4,07 |
| | c. | 2,78 | 0,68 | 0,70 | 0,83 | 1,20 | 2,84 | 1,48 | 3,58 |
| | d. | 1,13 | 1,76 | 0,70 | 0,86 | 1,60 | 0,81 | 2,44 | 2,86 |
| | e. | 1,46 | 2,26 | 2,43 | 1,25 | 1,58 | 2,46 | 1,83 | 0,89 |
| Tuber peel | -b. | >178 | >300 | >210 | >72 | >274 | >175 | >268 | >178 |
| Root section | -a. | >1676 | >1164 | >2801 | >1400 | >1958 | >3457 | >1010 | >992 |
| | b. | >1158 | >1558 | >2127 | >1689 | >2107 | >2049 | >1333 | >1286 |
| | c. | >1702 | >1216 | >2169 | >653 | >1975 | >3073 | >1325 | >1676 |
| | d. | >1333 | >2990 | >2087 | >1034 | >1146 | >1770 | >2573 | >2127 |

---

| | Z1 | Z2 | Z3 | Z4 | Z5 | Z6 | Z7 | Z8 |
|---|---|---|---|---|---|---|---|---|
| Surface leaf contamination, - - | 1169 | 711 | 1064 | 870 | 1915 | 3808 | 1499 | 632 |
| Total lead in soil, - - - - - | 39931 | 39553 | 38661 | 37791 | 36514 | 37127 | 37622 | 37140 |
| Available lead in soil, - - - - - (EDTA extraction) | 33292 | 33458 | 34708 | 33208 | 33000 | 31708 | 32875 | 25333 |