

The Camborne Mining District in 1904

A view taken from the Engine House of Dolcoath Mine, looking eastwards along the strike of the lodes. Mines in the picture include South Crofty, East Pool and Agar, Cooks Kitchen, Carn Brea and Tincroft (Geological Survey Photograph No. A.37).

DISTRIBUTION, DISPERSION AND AGRICULTURAL SIGNIFICANCE OF METALS IN SOILS OF THE MINING REGIONS OF SOUTH WEST ENGLAND

by

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A thesis submitted for the degree of Doctor of Philosophy of the University of London and for the Diploma of Membership of the Imperial College.

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This thesis is dedicated to Mum, Dad and the many friends I have met over the last few years; without them, all this would not be worthwhile.

"you may say I'm a dreamer
but I'm not the only one
i hope someday you'll join us
and the world will be as one."

John Lennon (1940-1980)

ABSTRACT

Previous stream sediment sampling within the Hayle/Camborne-Redruth area of South-west England revealed extensive trace-element contamination which was related to areas of mineralisation and historic metalliferous mining activity. A soil reconnaissance survey confirmed these initial observations, and indicated the order of soil trace-element contamination as Sn> As> Cu> Zn> Pb. Whilst the highest trace-element concentrations occur generally within the topsoils (0-15cm), elevated concentrations are also found within the subsoils (30-45cm). The topsoil As, Cu, Pb and Zn concentrations are significantly correlated with the distribution of these trace-elements in the stream sediments. On the basis of these statistical correlations, the stream sediment data comprising the Wolfson Geochemical Atlas of England and Wales was used to delineate the areas of soil contamination throughout South-west England. In all, a total of 1,092km^2 of land, equivalent to 11.9% of the total area studied, is believed to be highly or moderately contaminated by one or more of the elements As, Cu, Pb and Zn.

Elevated concentrations of several trace-elements occur in the slate, granite and greenstone parent materials of the Hayle/Camborne-Redruth study area. Any natural soil enrichment is largely masked by trace-element contamination derived from sources associated with the mining industry : the contamination from mine spoil, a former tin smelter and a former arsenic calcining works is described.

The uptake and translocation of As, Cu, Fe, Mn and Zn in pasture herbage varies according to the trace-element concerned. The factors

influencing the trace-element content of herbage has been studied by ridge regression analysis. In addition, the relative accumulation of As, Cu, Fe, Mn and Zn by herbage suggests that the pasture species also control the rate of trace-element uptake and translocation within the plant.

The involuntary ingestion of soil by cattle is seasonal and may account for up to 18% of the ruminant dry matter intake. Pasture herbage is particularly susceptible to As and Fe soil contamination. Thus soil is a major source of both elements to cattle, accounting for up to 97% and 95% of the As and Fe intake respectively. It is proposed in this study that cattle may ingest up to 31 times the amount of As compared to areas of normal soil As content.

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CHAPTER 1

GEOCHEMISTRY AND THE ENVIRONMENT

(I) INTRODUCTION AND OUTLINE OF THESIS

Hunger is not new to the world. It has always been a threat to man's survival. At some place on earth, through the centuries, scarcity of food has brought misery, disease, and even death to man. But never in recorded history has the threat of starvation been greater than it is today. This threat is not due to the reduced capacity of the world to supply food. Indeed, this capacity is greater today than it has ever been and is continuing to grow at a reasonable rate. The problem lies in the even more rapid rate at which world population is increasing. Experts predict the world's population will be between 6 and 7 billion by the year 2000 - double that of today. It is no wonder that the world food supply is considered by some to be mankind's most serious problem. World food production per person is at best holding its own. In selected areas it is declining.

In order to survive, therefore, man must intensify and increase his food production. Such a feat can only be achieved by long, detailed research. Widespread field and laboratory investigation has revealed that a large number of elements are essential to both plant and animal life. Some (i.e. N, Cl, Ca, K, Mg, Na, P and S) are required in relatively large amounts; these are the major or macro-elements. Of increasing interest over the past 15 years, however,

are those elements needed in only small quantities as minor or trace-elements.

Fifteen trace elements are known to be essential for plant and animal nutrition. Of these, B, Cu, Fe, Mn, Mo, Si, V and Zn are required by plants, whilst Cu, Co, F, I, Fe, Mn, Mo, Se and Zn are required by animals. In addition, essential roles for As, Ni, Si, Sn(?) and V in animal nutrition have recently been established, the list growing each year as a result of intensive research (Davies, 1981). It is likely that most, if not all, of the elements found to be essential in animals will be shown to be so for man - the last link in a dynamic and complicated food chain.

The soil is the main source of most biologically active trace-elements. The optimum range of these elements in the soil is narrow since both deficiencies and excesses can occur giving rise to serious clinical and sub-clinical problems. The concepts of deficiency, adequacy and toxicity are illustrated in Figure 1 for several micro-nutrients.

Of the elements listed as essential to animals, F, Ni, Si, Sn and V are usually present in plants at well above deficiency concentrations so that absolute deficiencies of these elements in grazing livestock are unlikely. However, in the UK, deficiencies of Cu, Co, I, Fe, Mn and Se have been reported in grazing livestock, and of B, Cu, Fe, Mn, Mo and Zn in crops (Thornton and Webb, 1979). Multi-element deficiencies are also possible as the sandy drift and sandstone derived soils of England and Wales are low in a number of essential elements (Wood, 1975).

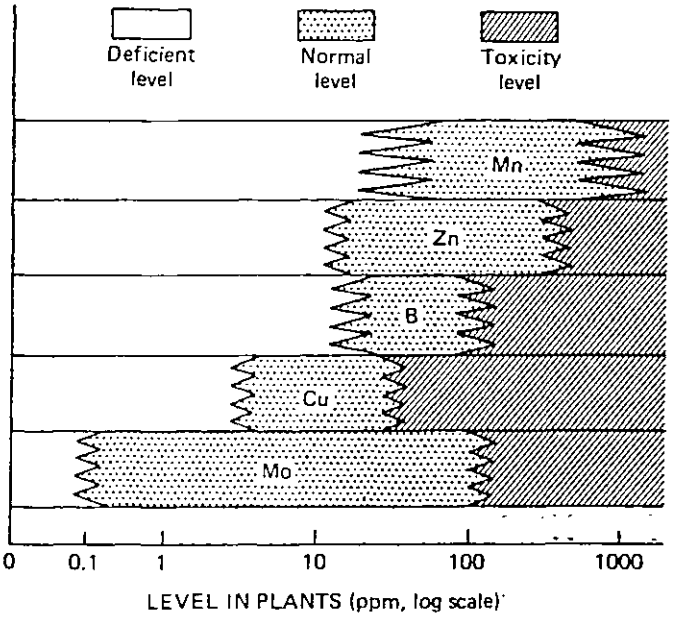


Figure 1. Deficient, normal and toxic concentrations in plants for five essential micronutrients (reproduced from Brady, 1974).

Excessive amounts of all trace-elements may be toxic to plants and/or animals and may affect the quality of foodstuffs and water for human consumption. Also of importance here are other elements which, although not biologically essential to life, are distributed throughout the biosphere. Such metals like Cd, Hg and Pb have no known metabolic significance and yet are highly toxic if present in sufficient amounts in the soil. Thus a large number of elements including As, B, Cd, Cu, Fe, Pb, Hg, Mo, Ni, Se and Zn can occur in deleterious toxic amounts either singly or, as often found, as multi-element suites.

Although the link between geochemistry and the environment is now well established, man's first major practical use of geochemical techniques was in the field of mineral exploration (Hawkes and Webb, 1962). Before the 1960's, comparisons between the distribution of trace elements in the environment and agricultural and human disorders in the UK were primarily confined to ad hoc studies in areas associated with particular agricultural disorders or with unusual human mortality or morbidity records. A growing awareness of the importance of environmental geochemistry in the 1960's (Webb, 1964) created a need for more systematic geochemical data in order to produce trace-element maps for focussing attention on possible suspect areas.

Ideally, trace-element maps for agricultural use should be based on the analysis of soil or vegetation sampled at a density sufficiently intensive enough to account for differences in parent material or soil type. In Britain, however, such an approach has proved impractical because of the cost and time required in taking

the numerous closely spaced samples needed to represent the many units related to complex geology, topography and soil type. Thus, although some recent work on soil geochemistry has been initiated by the Soil Survey of England and Wales and by the Macaulay Institute in Scotland, the regional mapping of trace-element distribution in Great Britain has so far been mostly limited to multi-element geochemical reconnaissance surveys based on stream sediment sampling conducted by the Applied Geochemistry Research Group (AGRG) at Imperial College, and by the Institute of Geological Sciences.

These surveys have been conducted on both a local (Webb et al., 1973; Nichol et al., 1971) and regional scale (Webb et al., 1978; Plant and Moore, 1979), and are based on the premise that stream sediment sampling is a cost-effective technique with the sediments being readily obtained, well mixed, composite samples which chemically reflect the composition of the local rocks and soils. Despite problems of interpretation in some moorland areas - where Fe and Mn oxides act as scavenging agents for various trace metals in the stream environment (Nichol et al., 1967) - and in areas of calcareous rocks where a massive precipitation of $CaCO_3$ in the surface drainage system can seriously dilute the content of other metals, good correlations often exist between the metal content of the stream sediments and the surrounding soils (e.g. Bradley et al., 1978). Because of such valid correlations, stream sediment sampling is widely used in the study of environmental geochemistry, focussing attention on suspect areas wherein to concentrate more detailed and costly surveys for interpreting agricultural disorders (Webb and Atkinson, 1965; Thornton et al., 1972; Jordan et al., 1975), soil

contamination problems (Thornton, 1975; Thornton and Webb, 1975; Colbourn et al., 1975), water monitoring and estuarine studies (Thornton et al., 1975; Aston and Thornton, 1975), and epidemiological research (Thornton and Webb, 1979; Thornton and Plant, 1980).

The objective of this thesis was to interpret the large scale geochemical anomalies in south-west England disclosed by stream sediment sampling, the results of which were incorporated in the Wolfson Geochemical Atlas of England and Wales (Webb et al., 1978). Further detailed stream sediment sampling had been undertaken in the Hayle/Camborne-Redruth district by members of the Applied Geochemistry Research Group in 1974. In this present research, soil reconnaissance sampling was concentrated within the Hayle/Camborne-Redruth district in order to observe to what extent the soil trace-element concentrations reflected those of the stream sediments. This part of the research is outlined in Chapter 4 of the thesis. Further soil and rock samples were collected from the study area in order to investigate the sources of trace-elements to the soils; this work is presented in Chapter 5. Considerable importance was attached to the agricultural significance of the soil trace-element contamination, and research within the Hayle/Camborne-Redruth study area involved an investigation into the uptake of trace-elements by pasture herbage, and also a study into the intake of trace-elements by grazing cattle. This research is outlined in Chapters 6 and 7.

(II) THE PATHWAYS OF TRACE-ELEMENTS IN ROCK-SOIL-HERBAGE-ANIMAL-HUMAN SYSTEMS AND THEIR ENVIRONMENTAL SIGNIFICANCE

Trace-elements, including those that are known to be essential for plant and animal growth, move from geochemical sources to plants and then to animals and man; they are then returned to the soil in various forms to complete the cycle. Although there are a number of pathways that individual trace-elements may follow, in most circumstances that from soil through plant roots to their shoots and then to animals and man is the main one. In any study relating to trace-elements in soil, therefore, an understanding of the complex, dynamic cycling that exists within the immediate environment is vital.

a) Trace-Elements in Rocks

The main sources of trace-elements in soils are the underlying parent materials from which they are derived. These may be weathered bedrock or overburden which have been transported by wind, water or glacial action and which may be of local or exotic origin. Such materials contribute both the primary source and potential reserve of trace-elements to soils.

The earth's crust is composed of 95% igneous rocks and 5% sedimentary rocks; of the latter about 80% are shales, 15% sandstones and 5% limestones (Mitchell, 1955). However, the surface distribution of the earth shows a somewhat greater proportion of sedimentary rocks, which tend to form a relatively thin skin overlying the igneous rocks from which they were derived. The crustal abundance of those elements which are of relevance to this thesis are outlined in Table 1.

	Element										
	Al	As	Ca	Cd	Co	Cu	Fe	Mn	Pb	Sn	Zn
Goldschmidt (1954)	8.13%	5	3.63%	0.18	40	70	5.00%	1000	16	40	80
Taylor (1964)	8.23%	1.8	4.15%	0.2	25	55	5.63%	950	12.5	2	70
Fyfe (1974)	8.36%	1.8	4.66%	0.16	29	68	6.22%	1060	13	2.1	76

All values in μg/g unless stated

Table 1. The abundance of selected elements in the earth's crust.

Typically, the trace-elements found in igneous rocks are geochemically related, with ultrabasic and basic rocks being enriched in, amongst others, Co, Cr, Cu, Mg, Ni and V and containing relatively little Li, Rb, Cs, Ba and Sr. Acidic rocks are rich in alkaline and alkaline earth elements, B and Sn, but have relatively low amounts of Cr, Co, Cu and Ni (Aubert and Pinta, 1977).

The degree to which trace-elements become incorporated in sedimentary rocks depends on the type of minerals present in the rocks from which they are formed and their rate of weathering. Dissolution, precipitation, oxidation, reduction, hydrolysis and carbonation processes are, therefore, all important. The interaction of these may be complicated, but generally the ionic potentials of ions are of importance in guiding their distribution. Large ions with small charges are found in evaporites, whilst elements like Ni occur in hydrolysates such as clays and shales (Mitchell, 1947). Some of the geochemical associations which exist in igneous rocks do not, therefore, persist in the sedimentary cycle. Magnesium and Ni are good examples.

The biologically important trace elements occur mainly in the more easily weathered constituents of basic igneous rocks such as biotite, augite, hornblende and olivine (Table 2). Thus, soils derived from sandstones are often deficient in these elements, since the parent material is composed of minerals that weather with difficulty (e.g. quartz and zircon). Shales on the other hand are often enhanced in trace metals, especially if they contain a great amount of organic matter. Other organic parent materials (e.g. coal) may be similarly enriched (Davies, 1975).

Increasing Stability ↓

Mineral	Major Constituents	Trace Constituents
Olivine	Mg, Fe, Si	Ni, Co, Mn, Li, Zn, Cu, Mo
Hornblende	Mg, Fe, Ca, Al, Si	Ni, Co, Mn, Sc, Li, V, Zn, Cu, Ga
Augite	Ca, Mg, Al, Si	Ni, Co, Mn, Sc, Li, V, Zn, Pb, Cu, Ga
Biotite	K, Mg, Fe, Al, Si	Rb, Ba, Ni, Co, Sc, Li, Mn, V, Zn, Cu, Ga
Apatite	Ca, P, F	Rare earths, Pb, Sr
Anorthite	Ca, Al, Si	Sr, Cu, Ga, Mn
Andesine	Ca, Na, Al, Si	Sr, Cu, Ga, Mn
Oligoclase	Na, Ca, Al, Si	Cu, Ga
Albite	Na, Al, Si	Cu, Ga
Garnet	Ca, Mg, Fe, Al, Si	Mn, Cr, Ga
Orthoclase	K, Al, Si	Rb, Ba, Sr, Cu, Ga
Muscovite	K, Al, Si	F, Rb, Ba, Sr, Ga, V
Titanite	Ca, Ti, Si	Rare earths, V, Sn
Ilmenite	Fe, Ti	Co, Ni, Cr, V
Magnetite	Fe	Zn, Co, Ni, Cr, V
Tourmaline	Ca, Mg, Fe, B, Al, Si	Li, F, Ga
Zircon	Zr, Si	Hf
Quartz	Si	

Table 2. The trace-elements associated with some common minerals of igneous rocks. The minerals are arranged approximately in the order of increasing stability (From Mitchell, 1971).

Metamorphic rocks can usually be expected to contain the trace constituents which were present in the original parent rocks. However, according to Mitchell (1947), concentrations of volatile elements like B or Li may occur in metamorphic aureoles. Arsenic was found to be similarly enhanced in the aureoles around the granites of south-west England (Aguilar Ravello, 1974), although Onishi and Sandell (1955) noted that a loss of As occurs through high grade regional metamorphism. The application of heat and pressure to argillaceous sediments may result in a recrystallisation of clay minerals, thus transforming their potential availability to plants. Boron, for example, may be incorporated in the very resistant mineral tourmaline.

Appreciable geochemical variation may occur in rocks even when the lithology is uniform. Thus sedimentary rocks may differ in composition within the same lithological unit owing to variations in the source of material and/or to selective mobilization and redeposition of certain elements during the course of compaction and diagenesis. Le Riche (1959) commented on the difference in molybdenum status between the Lower Lias 'teart' shales of Somerset and those of Glamorgan. Similarly, geochemical differences may be apparent within individual igneous or metamorphic rock assemblages. Floyd (1972) related differences in the geochemistry of the Cornubrian granites of England to differential development.

b) Trace-Elements in Soils: Their Concentration, Distribution and Fractionation within Soils and their Profiles

A knowledge of the distribution of trace-elements in rocks is important since residual soils, formed in situ from the underlying bedrock, tend to reflect their chemical composition. Archer (1979) reports that many of the sandy soils found in England and Wales contain lower concentrations of Co, Cu and B than the soils derived from other parent materials. In north-west Pembrokeshire, the soils have developed characteristic geochemical suites of metals from the differing rock types (Bradley et al., 1978). Ultrabasic and basic rocks can weather and release high amounts of some metals including Mn, Ni, Cr and Co into the overlying soil - this phenomena may even reach a point where the soils are transformed into veritable ores leading to their industrial exploitation. Mineralisation may also lead to high concentrations of certain metals in the overlying soils (Davies, 1968). The consequences of such enhancement is discussed in Chapter 2.

Normal amounts of metals found in agricultural soils have been reported by a number of workers; these concentrations are given in Table 3. For some elements (e.g. Ag, Mo, Se and Hg) the total concentration encountered in soils fall within a relatively narrow range of values. The range of some metals such as Pb and Zn is much wider, whilst due to the extreme geochemical differences which may be encountered between different rock types, very large ranges are found in soils for trace-elements such as Cr (Figure 2).

	Element									
	Al	As	Cd	Co	Cu	Fe	Mn	Pb	Sn	Zn
Swaine (1955)	-	1-600	1	1-40	2-100	-	200-3000	2-200	Up to 10	10-300
Archer (1979)	-	-	1	8	17	-	-	42	-	77
Berrow and Burridge (1979b)										
i) Normal range	10000-300000	0.1-40	0.01-1.0	1-40	2-100	10000-200000	100-4000	2-200	1-10	10-300
ii) Typical concentration	70000	6	0.5	15	20	40000	800	20	3	50
Woolson (1969)	-	5	-	-	-	-	-	-	-	-

All values in µg/g

Table 3. Typical contents of selected trace-elements in uncontaminated soils.

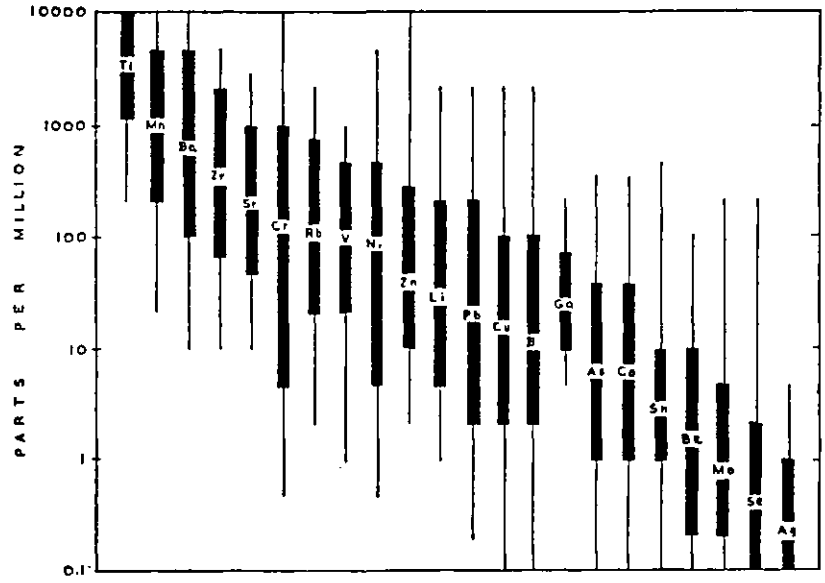


Figure 2. Range of contents of some trace elements commonly found in mineral soils. Thin lines indicate more unusual values; certain extremely high contents reported from abnormal localities influenced, for instance, by ore deposits have been ignored (from Mitchell, 1955).

The influence of the underlying solid geology on the metal content of soil can be modified to varying degrees by:

i) Alluvium and drift deposits: Alluvium, loess or glacial drift deposits may partially or completely mask the underlying bedrock. At times, the effect of bedrock composition on that of the soil may be smeared in the direction of water flow or ice movement.

ii) Man: Although the effects of human interference are generally of secondary importance (Mitchell, 1955) they may be of great significance on a local scale. The trace-element content of a soil may be modified via agricultural or horticultural additives such as lime, fertilizers, manures, irrigation waters, sewage sludges (Berrow and Burridge, 1979b) or inorganic sprays used as herbicides or fungicides (Jones and Hatch, 1945). Most of the materials added to improve cultivated soils have low trace-element contents and when used at normal rates are unlikely to seriously affect trace-element levels in soils and crops, although serious contamination can occur occasionally (Berrow and Burridge, 1979a).

Metals may also enter a soil through municipal waste disposal or through vehicle and industrial contamination which, like the agricultural sources, may prove potentially deleterious to plant, animal or human health if present in sufficient amounts. A full appraisal of these anthropogenic sources is discussed by Jarvis (1976) and by Berrow and Burridge (1979a).

Contrary to adding metals to soils, man may also remove them by depletion caused by crop removal. According to Mitchell (1955) these effects are just as significant as the addition of metals caused by soil treatments and atmospheric pollution.

iii) Pedogenetic processes: The pedogenetic processes which occur within a soil lead to the mobilisation and redistribution of trace-elements both within the soil profile and between neighbouring soil types. As a result of these processes, metals in soils can occur in a number of forms:

a) as ionic, chelated or colloidal forms in the soil solution,

b) as readily exchangeable ions in inorganic and organic exchange active materials,

c) as more firmly bound ions in the exchange complexes,

d) as chelated ions in an organic or organo-mineral complex,

e) incorporated in precipitated sesquioxides or insoluble salts,

f) fixed in the crystal lattice of primary and secondary minerals.

These divisions are not precise, however, since the relative amount of each form depends on the element in question and on the prevailing but constantly changing soil conditions. The nature and intensity of weathering is of prime importance. In the United Kingdom and similar temperate areas, most soils are relatively young with the parent material remaining the dominant factor in determining the metal

content of the soil. In tropical climates - where pedological weathering is enhanced - and on mature land surfaces, weathering processes have been more vigorous and/or of much greater duration meaning that the relationships between the chemical composition of the original parent materials and the soil are modified by the mobilisation and redistribution of chemical elements and the formation of secondary minerals.

The relative mobilities of trace-elements through soils are quite variable. Of 11 elements studied, Korte et al. (1976) found Hg to be the most mobile and Cu and Pb the least mobile elements. The mobility of an element in soils is no more than a reflection of its solution concentration as it is affected by the movement of H_2O through the profile. As such, any factor that affects the solubility of an element must in some way affect its movement. As mineral decomposition occurs, the primary minerals are changed to oxides, carbonates, sulphates and secondary silicates. The micro-nutrients released by these processes are subjected to adsorption by inorganic and organic colloids. These minute silicate-clay and organic colloid particles, referred to as miscelles, ordinarily carry negative charges which attract positive cations, thus protecting the latter from leaching down the soil profile and away from the plant roots. Hydrous oxide clays possess similar properties of cation adsorption. As such, their occurrence and distribution is of prime importance to the soil-plant-animal system.

An interchange between cations on the surface of these active materials and the soil solution occurs by the process of cation exchange. The sum total of exchangeable cations that a soil can adsorb is referred to as the cation exchange capacity (CEC). Soil colloids differ in their CEC - humus, vermiculite, montmorillinite, hydrous mica and chlorite,

kaolinite and hydrous oxides are more or less in the order of 200, 150, 100, 30, 8 and 4 meq per 100 gms respectively (Brady, 1974). Although humus colloids have the greatest nutrient holding capacity, because the clays are generally present in larger amounts in a soil, the contribution of the latter to chemical properties within a soil will usually equal that of humus. Hydrous oxide clays have a weak CEC due to the smaller numbers of negative charges per micelle than the other colloids. However, since hydrous oxides can have positive charges on their crystal surfaces, they are important for anion adsorption. Korte et al. (1976) noted the important role of free iron oxides in the anionic fixation of As, Cr, Se and V.

Cations differ in their affinity for adsorption. Beckwith (1955) noted the strong attraction of Cu ions in organic soils as compared to other divalent cations. Taylor and McKenzie (1966) found a specific scavenging effect between manganese oxides and cobalt. This relationship was not found, however, by Mitchell (1972) when investigating a number of Scottish soils.

The continuous weathering, redistribution and adsorption processes which take place within a single soil unit explain why metals occur in a number of forms. Studies by McLaren and Crawford (1973a, 1973b) revealed that organic matter and free manganese oxides were the dominant constituents in specifically adsorbing Cu; clay minerals and free iron oxides showed only weak specific adsorption but may, nonetheless, be important if they are abundant in the soil. Of the 24 soil types examined, isotopically exchangeable Cu represented between 2 and 21% of the total concentration of this metal (McLaren and Crawford, 1974). It was concluded that copper in soil solution

is in equilibrium with specifically adsorbed forms, predominantly associated with the organic fraction:

(Equation 1)

Cu (soil solution) $\rightleftarrows$ inorganically bound Cu $\rightleftarrows$ organically bound Cu
(acetic acid extractable) (pyrophosphate extractable)

In comparison, arsenic sorption seems to be relatively independent of organic matter (Presant and Tupper, 1966; Wauchope, 1975; Jacobs et al., 1970b). Instead, negatively charged arsenate ions are strongly attracted to positively charged Fe colloids resulting, frequently, in an enrichment of As in the B horizon of soils (Boyle and Jonasson, 1973). The adsorption of As is further influenced by the presence of aluminium oxides and clay minerals (Holobrady and Galba, 1971; Boyle and Jonasson, 1973; Jacobs et al., 1970). However, due to its similar chemistry, phosphorus may compete with As fixation (Woolson et al., 1973). Similarly, arsenite adsorption is influenced by the presence of AsO_4^{3+} (arsenate) ions since the latter have a greater affinity for sorption (Misra and Tiwari, 1963). In any soil, therefore, the partition and redistribution of an element is a complex subject to study.

Transformation of metals from one soil form to another depends upon changes in soil temperature, drainage, texture, pH, the redox potential (Eh), the concentration of other elements present, organic matter status and the activity of plants and micro-organisms. Soil pH, for example, is very important in moderating the adsorption or precipitation of micro-nutrients in soils, determining both the solubility and potential availability of metals to plants (Figure 3). For Cu, as the pH is decreased the equilibrium shown by equation 1 above shifts to the left leading to a replenishment of Cu in the soil

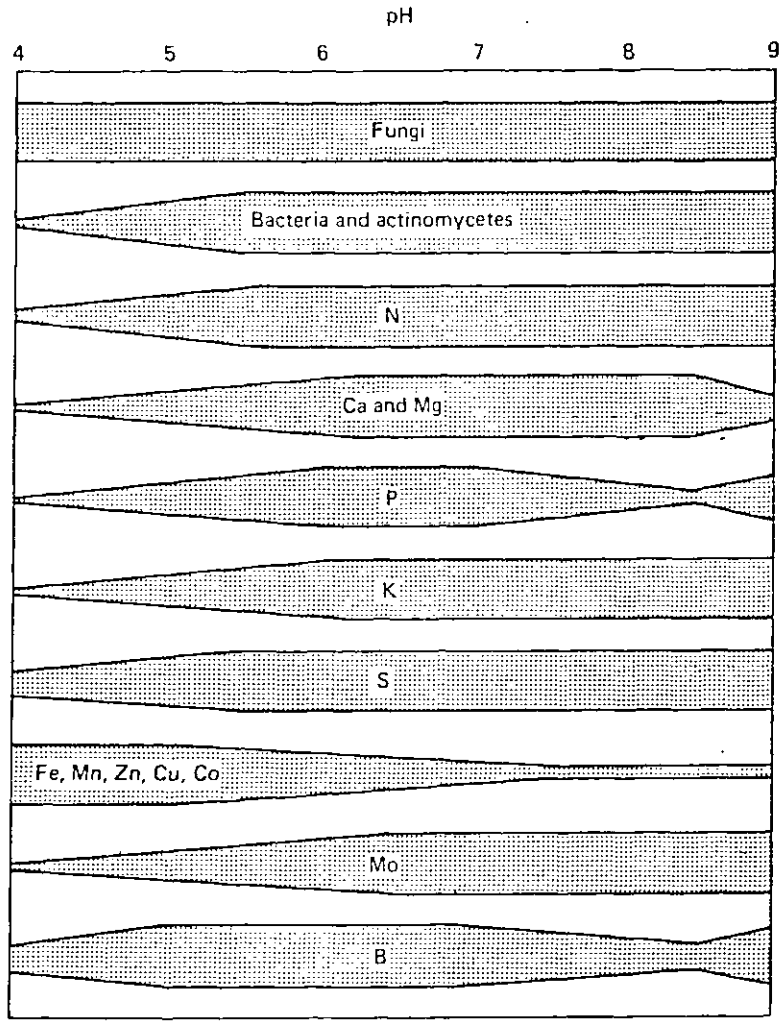


Figure 3. Relationships existing in mineral soils between pH, the activity of microorganisms and the availability of plant nutrients. The wide portions of the bands indicate the zones of greatest microbial activity and the most ready availability of nutrients. Considering the correlations as a whole, a pH range of approximately 6 to 7 seems to promote the most ready availability of plant nutrients (from Brady, 1974).

solution. On the contrary, sorption of As seems to decrease as alkalinity is approached (Gulledge and O'Conner, 1973).

The various forms of metals which are found in soils are of vital importance in determining the distribution within the soil profile. As rocks weather into soils, the elemental constituents within a profile are subjected to leaching waters. Plant roots, adsorbing surfaces and co-precipitating ions compete with the leaching soil solution with the result that each element, responding to these forces in a different way, is distributed throughout the soil, often in a characteristic manner. For example, in podzols a classical distribution of trace elements can occur through two processes:

i) enrichment of the surface layers caused by organic complexing, and

ii) enrichment at depth caused by acidic leaching waters or by organic complexes. The latter are especially important and can complex metals under both anaerobic and aerobic conditions (Ng and Bloomfield, 1962; Bloomfield et al., 1971).

However, although the 'classic' podzolic distribution of metals within a soil has been described by Wright et al. (1955), frequently this pattern has not been observed by other workers. Swaine and Mitchell (1960) after an extensive study of Scottish soils found a uniform distribution of the trace elements from horizon to horizon, thus promoting the idea that a very high degree of profile development caused by an advanced state of weathering is necessary before marked variations in trace-element distributions are clearly observed. Surface enhancement is often evident, however, due to the adsorption

of a wide number of metals by the organic rich topsoil (Beckwith, 1955; Mortensen, 1963; Jenkins and Davies, 1966). Agricultural treatments and contamination may further enhance this surface accumulation of metals (John, 1971; Jenkins and Davies, 1966).

With regard to the mobilisation of trace-elements, drainage is an important soil variable since reduced forms of metals tend to be more soluble than their oxidised states over the pH range found commonly in soils. In Scotland, mobilisation and redistribution of Ag, Co, Cu, Fe, Mn, Mo, Ni, Pb, Zn and V (but not Al) occurred under reducing conditions in poorly drained soils (Mitchell, 1955; Swaine and Mitchell, 1960). In extreme instances, up to 50% of the total element in question was mobilised.

c) The Availability of Trace-Elements and their Uptake by Plants

The partition of trace-elements between the different forms in the soil determines not only the distribution of elements within the soil profile, but also the availability to plants and higher organisms (Figure 4). It is generally agreed that ions reach the root surface from the soil by way of the soil solution. The possibility of there being a direct transfer of cations from negative sites on the soil colloids to the Donnan free space of the root cell wall, as postulated by Jenny and Overstreet (1939), has now been discounted through lack of positive evidence. Instead, it is now known that ions move to the root surface in the soil water in two ways, by mass flow or diffusion (Sutcliffe, 1971; Bowling, 1976). Mass

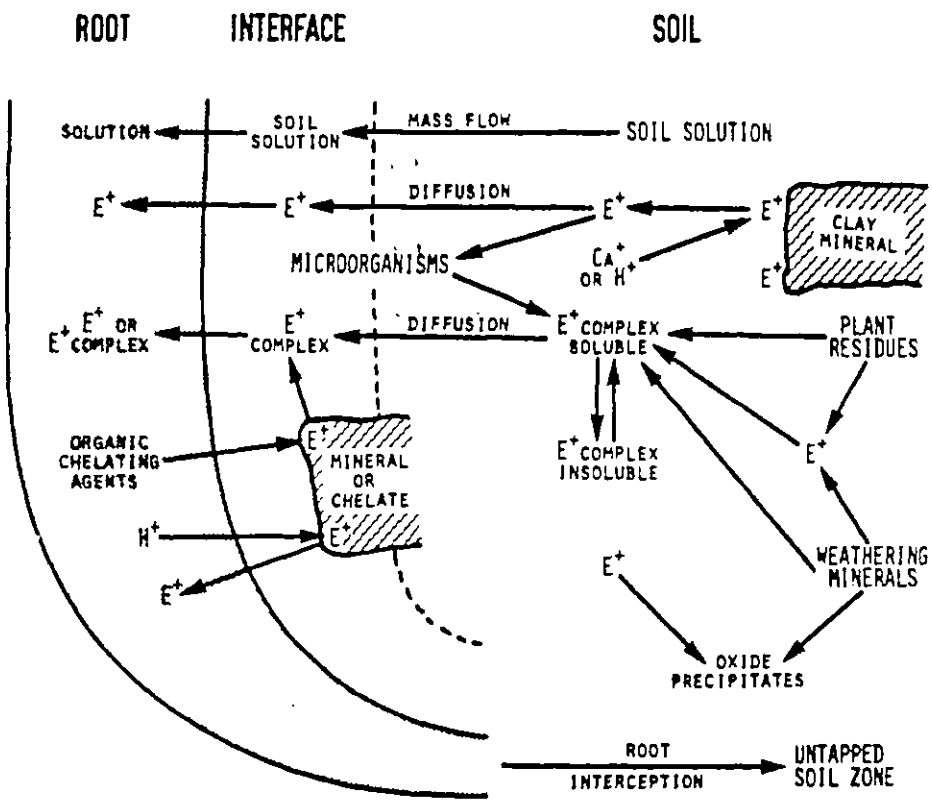


Figure 4. Processes involved in the mobilisation of cationic trace elements in soil and their transfer to the plant root. E^+ signifies a cation of any charge; a complementary diagram could be prepared for anions (adapted from Berrow and Burridge, 1979b).

flow is the passive movement of nutrients to the root surface by the transpiration-induced flow of water to the root. Diffusion is the 'active' movement of ions along a concentration gradient, and occurs when ions are taken up faster than they are being carried to the root surface by mass flow.

A number of soil parameters determine the solubility and availability of an element:

i) Drainage status.

ii) Pedological weathering: which influences the general trend in soils; that of releasing complex, unavailable metals to simple, more soluble forms.

iii) Organic matter, clay minerals and hydrous oxides: can all adsorb and release trace-elements by cation exchange. At times the degree of binding may be so great so as to render the metal unavailable. The strong affinity of organic matter for Cu often leads to crop deficiencies in areas of peat (Davies, 1975). However, organic matter may also promote the availability of certain elements by supplying soluble cation-chelate combinations which are capable of being absorbed by plants.

iv) pH: soil pH has an important influence on the availability of trace metals since it moderates adsorption and precipitation reactions. In very acidic soils, a relative abundance of available ions occur which may lead to toxicity problems. As the pH is increased, the ionic forms of cations are changed to insoluble oxides or hydroxides which are precipitated and then become unavailable:

e.g. $Fe^{++} + 2OH^{-} \longrightarrow Fe(OH)_2$
(soluble) (insoluble)

v) Soil micro-organisms: as yet the influence of soil micro-organisms on trace-element distribution and availability has received little attention. However, it is known that micro-organisms affect the availability by:

a) The release of inorganic ions during the decomposition of organic materials.

b) Immobilisation of ions by incorporation into microbial tissue.

c) Biological oxidation or reduction.

d) Indirect transformation - e.g. changes in soil pH, etc.

Plant roots are known to have an effect on availability since they can exude a great variety of compounds in quantities sufficient to alter markedly the availability of nutrients in their immediate environment. Similarly, the earthworm Dendrobaena rubida has been found to increase the amounts of available Pb, Zn and Ca in soils (Ireland, 1975).

The trace-element content of a plant is further related to:

i) The total amount present in the soil and the proportion of the exchange complex of the soil occupied by the cation in question.

ii) The influence of associated ions, e.g. Fe uptake by Soybeans is reduced by the antagonistic action of Ni, Co, Cu and, especially, Zn ions (Lingle et al., 1963). Similarly, when Zn and Cd are both abundant in soils, Zn has been found to be preferentially absorbed by plants (Jarvis et al., 1976).

iii) The effect of soil colloids: the colloidal micelles differ in the tenacity with which they hold specific cations.

Since the main source of metals in soils are the underlying parent materials, it follows that the trace-element contents of plants are usually related to the geology. Thus, many of the trace element problems encountered in Scotland can be related to the underlying rock type (Mitchell, 1974). Every plant probably contains traces of all the elements present in the immediate environment of its rooting zone. Despite this, the extent to which elements are found in plant tissues varies considerably. According to Lisk (1972), Cd is very readily absorbed by plants (plant/soil ratio $\approx$ 10) when compared to As (ratio $\approx$ 0.12) or Cr (0.02). It seems, however, that uptake is not entirely dependent upon the availability of trace-elements within a soil since plants can regulate the uptake of essential elements like Cu and Zn (Timperley et al., 1970). Indeed, a number of parameters within the plant itself operate to determine the trace-element concentration. These include:

i) the transpiration rate,

ii) the extent and depth of rooting,

iii) the stage and rate of growth: these factors govern the physiological development of a plant. Concentrations of metals vary according to plant part. For example, stems and inflorescences of metal tolerant Agrostis tenuis contain less As than leaves or, especially, seeds (Porter and Peterson, 1975). Leaves of different ages exhibited a ten-fold range from 100 µg As/g in the youngest to 1340 µg As/g in the oldest.

For some species the translocation of certain metals from the root to the shoot is limited. This has been observed in some species for As (Jones and Hatch, 1945), Cd (John et al., 1972; Jarvis et al., 1976), Cu (Jarvis, 1978) and Pb (Jones and Hatch, 1945; John, 1971; Hepple, 1972).

iv) Plant species: clovers and grasses, when growing together under pasture conditions, often provide a good illustration of species-dependent differences in trace-element content (Fleming, 1965; Berrow and Burridge, 1979a). Trace-element variations of 5 to 10 fold or even greater may be apparent between species grown on the same soil (Mitchell, 1947).

v) Seasonal variation: enhanced Pb concentrations in the shoots of pasture herbage during the winter period have been observed by Mitchell and Reith (1966) and attributed to transport from the roots to the shoots during senescence, (although such an explanation is not so readily accepted today). According to Hodgson (1963), the availability of an element within a soil can be seasonal due to changes in soil temperature, moisture or microbial activity. These changes in the availability of an element are commonly reflected in plant response - especially for Mn.

vi) Foliar absorption: Bukovac and Wittwer (1957) found that foliar absorption of Fe, Mn, Zn, Cu, Mo and Co occurs in plants, with young leaves especially being susceptible. Rapid accumulation and limited mobility within the leaves, however, prevents prolonged absorption.

d) Trace-elements in Animals and Man

Both deficiencies and excesses of major and trace-elements in the diet of animals can give rise to clinical or sub-clinical conditions (Underwood, 1971). The grazing requirements of animals differ according to species, age, condition of the animal and feed digestibility. For Co and Cu, the amount needed for maintaining the healthy nutrition of stock is well known; for other essential elements such as Zn, Mn and Se, the requirement needed is less precisely recorded. Despite this lack of information, however, the amounts of trace-elements in pasture required to meet the dietary needs of livestock have been published by ADAS (1975) and Alderman (1968) whilst concentrations of Pb in feedstuffs that are potentially toxic are reported by Tunney et al. (1972).

Since plants reflect their immediate geochemical environment, it follows that the nutritional status of animals also show the same general relationship. The trace-element deficiencies and excess in the UK have been related to specific geological areas (Thornton and Alloway, 1974; Thornton and Webb, 1980). However, the exact relationship between the soil-plant-animal system is dependent upon a number of variables:

i) The dry matter intake of the animal.

ii) The species of forage grown and the selectivity of grazing.

iii) The dependence of grass as a source of trace-element dietary intake.

iv) The form, digestibility and availability of the ingested trace-elements.

v) Soil ingestion: soil can be an important source of trace-elements in the ruminant diet since appreciable amounts may be involuntarily ingested by grazing animals (Healy, 1968a; 1968b). For sheep, ingested soil can account for as much as 14 to 40% of the total dry matter intake (Field and Purves, 1964; Suttle et al., 1975). Thornton (1974) reported soil ingestion in cattle of south-west England as ranging from 1 to 10% during the winter months. Under such conditions, cattle were ingesting up to 10 times the amount of Cu and Pb (and possibly As) in the form of soil as compared to that in herbage. This direct soil-animal pathway may well override the soil-plant-animal system and may have important consequences on the animals.nutrition (Healy, 1972; Suttle et al., 1975), although even now the absorption and utilisation of trace-elements from ingested soil has, with the exception of Cu, received little study. Even so, the total trace-element concentration of a soil can be just as important as the plant available content.

The link between a given element in the soil and man however, is far less direct and, except in isolated primitive communities, much more complex than that of the grazing animal. With the exception of F and I (and Mo in Russia), slow progress has been made with respect to the link between geochemistry and man due to the wide variety of dietary sources from which his supply of trace-elements originates.

Vegetables, like pasture herbage, vary in their metal content both within the individual plants and between species (Warren and Delavault, 1971). Their importance to the diet of any population must also be considered. The direct ingestion of soil, especially by children, can also be important. This can occur either involuntarily or by deliberate ingestion attributable to pica* (Barltrop et al., 1975; Moynahan, 1979).

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* Pica or geophagia is the habitual, purposeful and compulsive search for, and ingestion of, unusual food substances - including soil.

CHAPTER 2

MINERALISATION AND MINING: CONSEQUENCES TO THE SOIL-PLANT-ANIMAL SYSTEM

(I) INTRODUCTION

Natural enhancement of trace-elements in soils can occur by the weathering of mineralised rocks. This enrichment is often complemented and modified by man, whose mining activities release trace-elements to the environment at a greater rate than the natural weathering processes. All trace-elements so released are potentially toxic to life forms if present in the environment in sufficient amounts.

In the United Kingdom, the most extensive areas of metal-rich soils reflect mining and smelting activities complemented by the natural input from geochemically distinct source ore materials (Thornton, 1979). Britain has had a long history of mining which is reflected in the contamination of the environment (Lee and Tallis, 1973). Non-ferrous mining production reached a peak in the mid nineteenth century when Britain produced, from a number of mineralised areas, some 75% of the world's Cu, 60% of the world's Sn, and 50% of the world's Pb (Figure 5). The metalliferous mining industry declined rapidly some 70 years ago, but has left large areas of land contaminated with high concentrations of a number of trace-elements due to the ineffective methods of mining and smelting processes employed. Table 4 shows the calculated amounts of Pb lost to the environment by such methods.

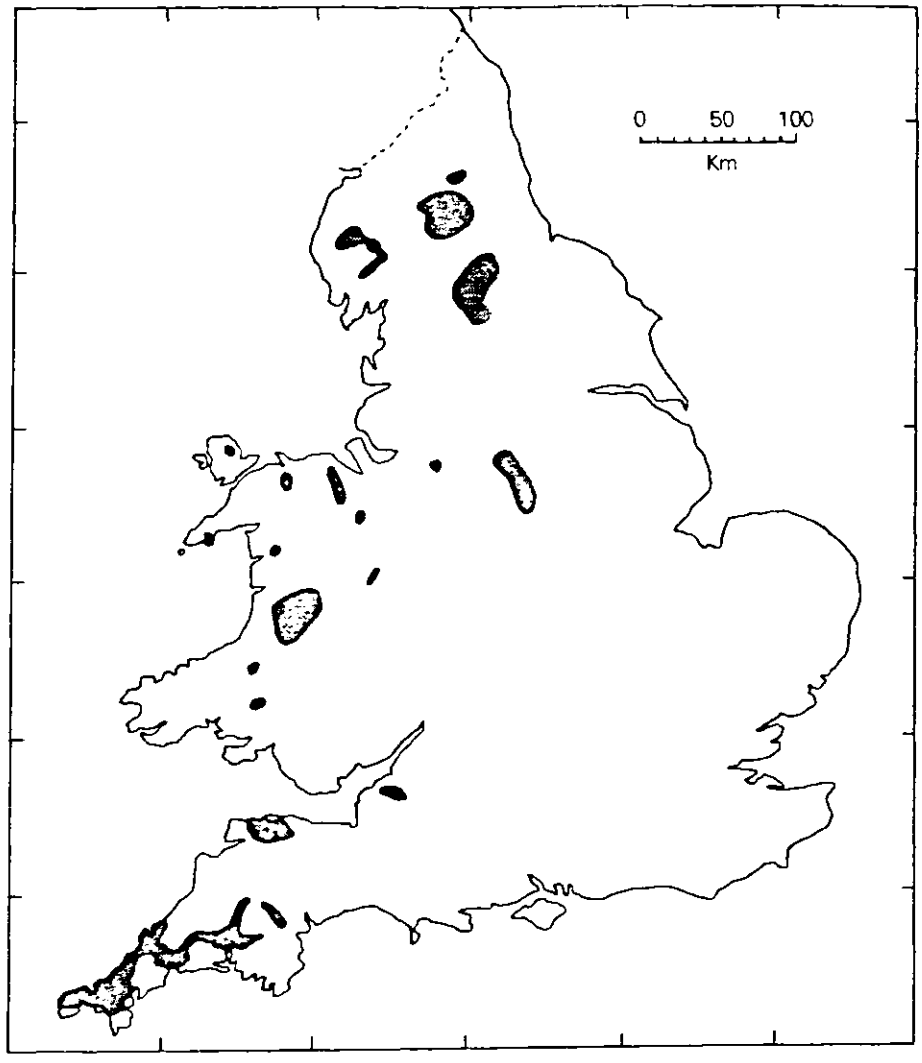


Figure 5. Generalised locations of the non-ferrous mining fields in England and Wales (from Davies, 1979).

MINING DISTRICT	Pb LOST TO ENVIRONMENT (TONNES)			APPROX. AREA OF DISTRICT (Km^2)
	At Concentration	At Smelting	Total	
N. Pennines	1590000	640000	2230000	2850
Lake District	91850	36740	128590	1500
Derbyshire	1000000	640000	1420000	300
Shropshire	80169	32067	112236	290
Clwyd	224000	89600	313600	260
Pumlumon	173820	69528	243348	1040
Mendips	68000	27200	95200	135
Cornwall & Devon	115000	46000	161000	2240000

Table 4. Lead contamination due to mining in England and Wales (from Davies, 1979).

Geochemical reconnaissance surveys based on the analysis of active stream sediments delineate the occurrence and intensity of the metal anomalies caused by the contamination, and indicate that some 4000 km^2 of land is affected (Webb et al., 1978). Concentrations of metals in soils within these areas are greatly enhanced over background values found in uncontaminated areas. Up to 7% Pb has been found in alluvial soils of Derbyshire (Colbourn and Thornton, 1978) and 800 µg/g Cd in agricultural soils of the Mendips (Marples and Thornton, 1980). Thus despite the fact that mining is now largely a part of the country's past history, serious 'fossil' contamination of soils still persists (Thornton, 1975; Thornton and Webb, 1975; Davies, 1979).

(II) SOURCES OF METALS IN MINERALISED AND MINED AREAS

Natural enrichment of soils by mineralisation has been recorded by Hawkes and Webb (1962), Presant (1966) and Riddel (1966). According to Fleisher (1973) concentrations of As may exceed 8000 ug/g in areas of sulphide mineralisation, these concentrations far exceeding those derived from more normal parent materials (Table 3). Enhanced amounts of Pb, Zn, Ni and Cu have been reported in Scandinavia resulting in areas of natural heavy metal poisoning (Bølviken and Lag, 1977; Lag and Bølviken, 1974). Since metallic ores are frequently 'contaminated' with a large number of 'guest' elements (El Shazley et al., 1957), the enhancement of soils is often reflected for several trace-elements. Thus, Cd anomalies occur in areas of sphalerite (ZnS) or smithsonite ($ZnCO_3$) mineralisation (Marples and Thornton, 1980), whilst As anomalies may occur through the element being a common constituent of many sulphide minerals (Fleisher, 1973).

Mining contamination, especially that derived from historical processes, complements the natural geochemical enhancement of trace-elements by providing a number of possible sources from which the elements can be dispersed throughout the environment. Potential sources of contamination include:

a) Contamination of water: The use of water for mining processes, the collapse of mine waste into rivers, and the input of trace-element enriched waters from adits can all lead to the contamination of drainage systems and, consequently, pollution of alluvial soils (Alloway and Davies, 1971; Davies and Lewin, 1974; Johnson and Eaton, 1980) and river estuaries (Thornton, Watling and Darracott, 1975). Historical mining activities have especially led to such contamination; it was not until 1876 that an Act of Parliament forbade the direct input of toxic effluent into river systems, although according to Lucus (1978), the first relevant act on the prevention of river pollution did not become law until 1951. However, the input of mine waste into river systems can still occur today (Plate 1), whilst the redistribution of old contaminated river banks in times of heavy rainfall and flooding, results in 'pollution pulses' and the continued contamination of river systems and alluvial soils (Davies and Lewin, 1974).

b) Blown dust and leaching from mine spoil: Mine spoil tends to be considerably enhanced in metals due to the inefficiencies of separating the metallic ore from the gangue. Surrounding agricultural land may be contaminated by the dispersing action of water and wind on the spoil. Johnson and others reported in 1978 that water redistribution resulted in severe but localised contamination, whilst wind blown dusts from the spoil produced broad but low level haloes of metal



PLATE 1. The present day release of mine waste into the Red River from South Crofty Mine, Camborne.

enhancement. The nature and amount of contamination is, however, dependent upon many factors (Hosking, 1970). Furthermore, the use of mine spoil for levelling fields and for the construction of roads, paths and hedge banks can also lead to the contamination of agricultural land.

c) Smelting and calcining processes: The loss, dispersion and deposition of metal enriched dusts from smelting processes has been discussed in detail by Thomas (1964), Adams (1968), Goodman and Roberts (1971), Lagerwerff et al. (1972), John et al. (1972), Little and Martin (1972), Hutchinson and Whitby (1974) and Hemphill and Clevenger (1979). The contamination of soils in the vicinity of a smelter is dependent upon wind direction, topography and distance, with topsoils being especially enhanced as a result of the atmospheric fall-out. Although the severest contamination of soils can be expected in the immediate vicinity of a smelter, contamination may persist over a considerable area. For example, heavy metal contamination from the ASARCO smelter, Missouri, extends beyond 12 miles (19.3 km) (Hemphill and Clevenger, 1979), whilst Ni contamination around the Sudbury complex in Canada persists up to distances of 31 miles (49.8 km) (Hutchinson and Whitby, 1974).

The sources of contamination described above, coupled with the long complicated histories of many mining districts and the heterogeneous mine wastes produced results in considerably polluted agricultural soils with highly variable metal concentrations (Table 5). The consequences of such contamination to the soil-plant-animal (man) system is considered in the remaining part of this Chapter.

Sites		As	Cu	Zn	n
Hayle district, west Cornwall	Mean	1.0	22.5	13.4	18
	SD	±1.3	±22.1	±15.8	
South Devon (control site)	Mean	0.15	3.60	12.16	28
	SD	0.09	2.16	4.93	

Table 5. Available As, Cu and Zn concentrations in a survey of agricultural soils from south-west England. The raised and variable levels of metals from soils of the contaminated west Cornwall district are clearly seen (data from Hughes, 1979).

(III) MINING CONTAMINATION AND ITS IMPLICATIONS TO THE SOIL-PLANT-ANIMAL SYSTEM

The use of contaminated land for agriculture is a controversial topic requiring detailed assessment dependent upon factors such as the form and distribution of the trace-elements concerned, their solubility, availability and potential toxicity. Local factors such as soil type, pH, drainage and farm management must also be considered. Anomalous concentrations of trace-elements in an agricultural soil does not necessarily imply that toxicity symptoms in plants and animals will be found. Whilst in the past deaths of livestock have been reported (Farey, 1811), today these are the exception rather than the rule. The occurrence of sub-clinical conditions induced by the high concentrations of trace-elements are, however, to a large extent unknown and still require careful evaluation.

The amounts at which trace-elements in the soil become phytotoxic are difficult to categorise since the total concentrations are not a sure guide to toxicity thresholds, although such concentrations have been reported (e.g. Davies, 1968). The fraction available to plants is variable and is highly dependent upon the prevailing soil conditions (Chapter 1). The presence of sulphides in the mine spoil, complemented by SO_2 contamination from smelting processes, can increase availability by lowering the soil pH. Solubility of trace-elements in the various mine wastes can also vary. The work undertaken by Aston and others (1975) indicates that the dissolution of As from spoil tip material may be much less significant than that from condensed smelter fumes and arsenical ores. Similarly, PbO derived from smelters is more soluble than the forms of Pb associated with mine spoil (Colbourn and Thornton, 1978).

Despite the observed reports that trace-elements persist in contaminated soils, there is evidence to suggest that with time such trace-elements may reach some degree of equilibrium with the local environment (Thornton and Webb, 1975). After the closure of a smelter in South Wales, Roberts and Goodman (1973) recorded a slow decrease of exchangeable amounts of metals throughout their sampling period. As the depletion of available metal could not be attributable to leaching, the recorded losses were probably associated with wind erosion and surface run-off. It was estimated that half-lives of the exchangeable metals within the soils varied from 2 to 30 years according to the vegetation cover.

As on uncontaminated sites, plant uptake on metal enriched soils varies according to the plant species. On the heavily contaminated alluvial soils of North Cardiganshire, the order of uptake of heavy metals by plants was of the order radish > lettuce > legumes > grasses (Rudeforth, 1970). Davies and Roberts (1975) similarly noted the ability of radish to concentrate metals. The limited translocation processes which operate within many species, however, has important consequences to the soil-plant-animal system, with plant shoots often having low concentrations of metals, even on the most severely contaminated land (e.g. Thoresby and Thornton, 1979).

Despite these barriers involving uptake and translocation, high concentrations of trace-elements in soils can be phytotoxic to plants as shown by poor seed germination, crytobiosis and chlorosis and necrosis on roots and leaves. Root growth appears to be especially affected (Nichols and McNeilly, 1979). For example, an examination of root condition in high As soils indicates that a brown rot sets in at

the root tips and frequently along the whole length of the root (Thomas, 1979). Toxicity and its manifestation in the plant is dependent upon the trace-element concerned. According to Jowett (1958) the order of toxicity in normal plants is Cu > Ni > Zn > Pb. In severe cases, trace-element toxicity will result in barren ground as no plants can tolerate such extreme conditions. Populations of certain species can, however, become tolerant to metal-rich soils by rendering the trace-elements innocuous within the plant (Gregory and Bradshaw, 1965; Smith and Bradshaw, 1972; Oxbrow and Moffat, 1979; Nicholls and McNeilly, 1979; Wigham et al., 1980). This tolerance may be reflected by the development of indicator plant species and anomalous plant communities which grow 'out of text' with the natural environment (Bølviken and Lag, 1977; Cole, 1980).

The work by Porter (1976) on As tolerant species in south-west England indicates quite clearly that the mechanism of tolerance is not due to the exclusion or restricted uptake of this particular element by the tolerant plants. Accumulations up to 10000 μg As/g in Agrostis canina were recorded in species growing on metal enriched mine spoil. The non-tolerant pasture species growing adjacent to the spoil heaps, however, contained much lower concentrations of As (up to 40 μg/g), despite the undoubted contaminated nature of the soil. Thus, with regard to animal nutrition, unless the soil-plant-animal pathway is by-passed, the restricting processes of uptake and translocation within non-tolerant plants provide an effective barrier which protects the health of grazing livestock.

The direct soil-animal system due to the ingestion of soil is thus of considerable importance, and trace-element toxicity problems caused by the ingestion of soil have been recorded. For example, elevated amounts of Pb contaminated herbage in Swaledale, Yorkshire, has led to blindness and the death of young calves (Harbourne and Watkinson, 1968). Contaminated herbage, due to soil adherence or the deposition of mine waste onto forage has also been reported by Tunney et al. (1972) and Johnson et al. (1978), with both research groups finding concentrations of Pb in excess of the recognised toxicity thresholds. However, the effect of ingestion of trace-element enriched soil on the grazing ruminant remains to a large extent unknown. Research by Suttle et al. (1975) indicates that soil ingestion may actually reduce Cu availability within the animal. Frequently, however, the elevated content of trace-elements present in the mining environment are reflected in the blood, tissue and faeces of the animal (Harbourne and Watkinson, 1968; Lagerwerff and Brower, 1974; Thornton and Kinniburgh, 1978; Marples and Thornton, 1980).

(IV) THE ENVIRONMENTAL IMPACT OF MINING ON MAN

In areas contaminated by metalliferous mining and smelting, the low availability of trace-element contaminants to pasture herbage is on the whole mirrored by the low uptake and translocation of metals to the edible parts of crops (e.g. Jones and Hatch, 1945; Thoresby and Thornton, 1979). Concentrations of trace-elements within any vegetable plant will vary widely according to the season, site of growth, the species concerned and the ability of that species to

incorporate specific elements. Thus when investigating the uptake of metals by radish, Davies and Roberts (1975) noted only a comparatively small increase in the uptake of Pb from contaminated soils as compared to the controls; Zn and Cd were more readily accumulated, rendering some of the crop unfit for human consumption. On As contaminated soils, however, Jacobs et al. (1970a) saw no danger to human health from a variety of vegetable crops.

Animal produce can be elevated in trace-element content in areas of high exposure (Lagerwerff and Brower, 1974), although a number of barriers within the animal will prevent any large-scale accumulation of Pb by man (Hepple, 1972). The concentrations of other metals found in both crop and animal produce will probably be well below any recognised danger level. According to Hughes (1979), in the As and Cu contaminated province of south-west England, an 80 kg person could only achieve the maximum acceptable daily load* of As by eating 5.9 kg of the most heavily contaminated brocolli from a 'mine spoil' area. Approximately 10 times these quantities would have to be eaten to exceed the FAO/WHO threshold level for Cu (0.5 µg/kg body weight). However, people living in a contaminated area can reflect the enhanced concentrations of metals which are present in their immediate environment. For example, Djuric and others (1971) recorded elevated amounts of Pb in urine of people living in a mining area of Yugoslavia, whilst evidence accumulated by Lagerwerff and Brower (1974) indicated that people living in an area of high exposure around a smelter ingested metal at rates >50% above the normal dietary intake. The work

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* As defined by the Joint FAO/WHO Expert Committee on Food Additives (1976).

of Barltrop and others (1974, 1975) suggested that in Derbyshire the major pathway of Pb into humans, especially children, is through the inhalation and involuntary ingestion of dust particles. Voluntary ingestion due to pica may also occur in children (Chisholm, 1968). The medical effects of these elevated metal concentrations on populations are, however, speculative and to a large extent unknown despite the fact that provisional tolerable intake concentrations have been suggested by the World Health Organisation (1976).

Geographical associations between disease and areas of metal enrichment have also been recorded (Howe, 1963), and elevated concentrations of metals in the environment, most notably Pb, have been associated with the abnormal prevalence of dental caries (Anderson et al., 1976; Anderson and Davies, 1980), multiple sclerosis and cancer (Pinsent, 1968; Warren, 1959, 1972). It has been suggested that Cu, Zn, Pb and Mn are worthy of study in the investigation of the relationship between water quality and cardiovascular disease (Wilson, 1979). Whilst the total concentrations of metals may be important in disease mortality, Stocks and Davies (1964) suggest that the ratio between Zn and Cu may be related to the incidence of cancer. However, relationships between the distribution of metals and the incidence of disease are still, in most cases, empirical and in general less well founded than those with agricultural disorders.

O Cornwall I happy blessed spot of ground
Where richest ores of every kind abound
Thy very hills are brass, thy rocks are tin
Thy wealth is not exposed without, but hid within.

Anon

CHAPTER 3

SOUTH-WEST ENGLAND

Reference Sources: Dines, 1956

Rottenbury, 1974

Barton, 1967, 1968a, 1968b

(I) INTRODUCTION

Historically, south-west England was the premier metalliferous mining centre of the World. In Cornwall, more than 600 underground mines have operated in the past, being confined mainly to a belt of mineralised ground some 75 miles long and 10 miles wide. Although Sn and Cu were the main metals extracted, As, W, Pb, Zn, U, Fe, Sb, Ag and Mn were also economically recovered together with occasional amounts of Bi, Ni and Co. Figure 6 indicates the areas of mineralisation within the province.

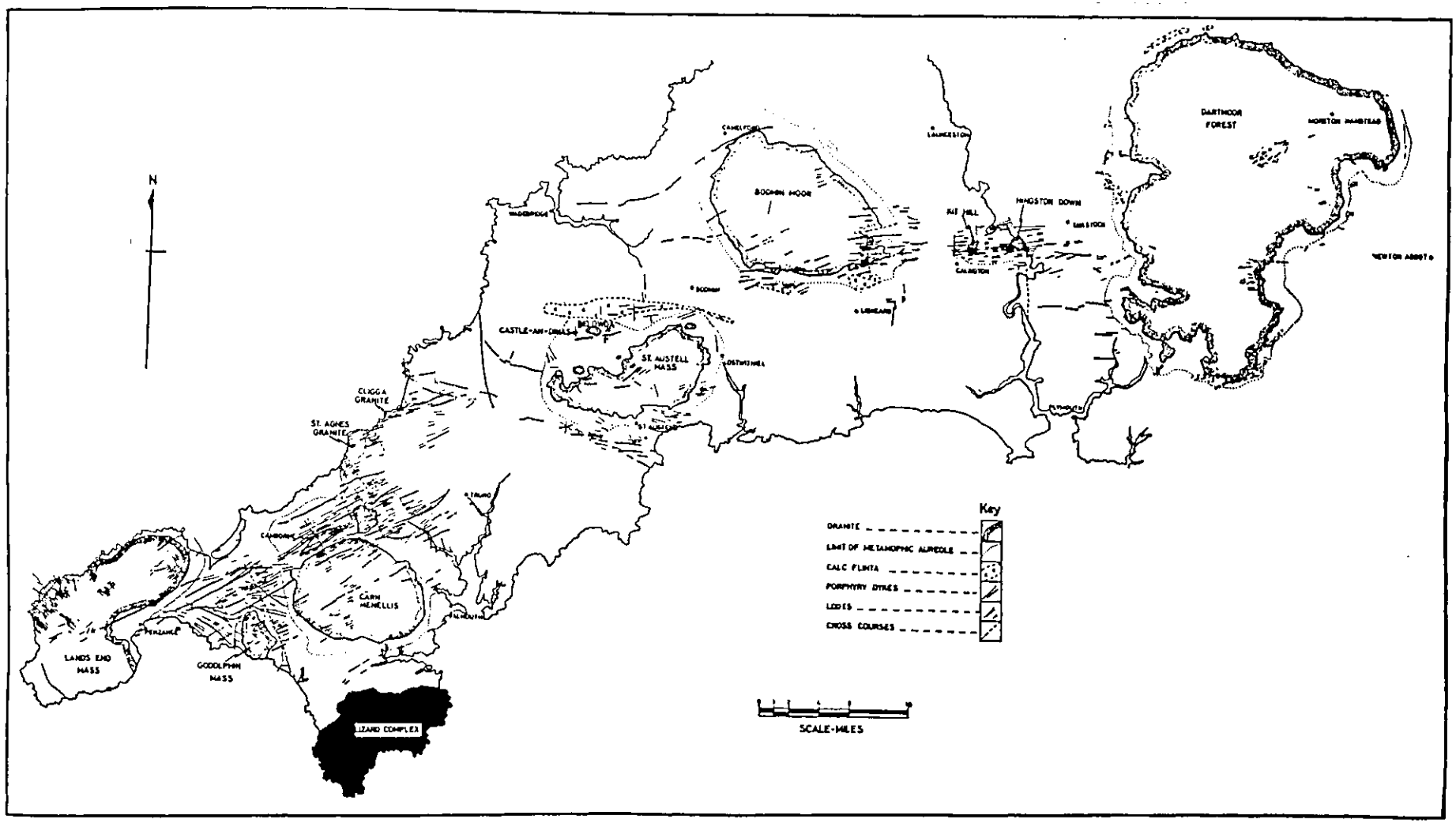


Figure 6. The mineralised districts of south-west England. (from Hosking, 1969).

The beginning of Cornish tin mining occurred in Pre-Christian times although details of these early years are largely a matter of historical speculation. Up to the 18th century, output was relatively small and static despite the fact that the industry was important both locally and as a primary world source of metals. Copper production increased dramatically from the 1720s, reaching a peak in production in 1855-56. By 1867, however, Sn had exceeded Cu to become the premier ore with output peaking in the 1870s (Figure 7). As the lodes were exhausted and overseas competition increased, a dramatic collapse in the mining industry occurred and by 1897 only 9 mines were still active. Today in 1982, 5 underground and 2 alluvial Sn works are still operating (Thorne, 1981).

Total output from the province is large and reflects the former importance of the mining industry to the area. In all, approximately 2 million tons of metallic Sn and 920,000 tons of metallic Cu have been extracted from the vast tonnages of ore material raised from the ground. In the Callington and Tavistock district some half a dozen mines were producing, during the latter part of the 19th century, approximately half of the world's As output. This production has left a legacy of dereliction (Plate 2) and innumerable potential sources of contamination to the surrounding agricultural land.

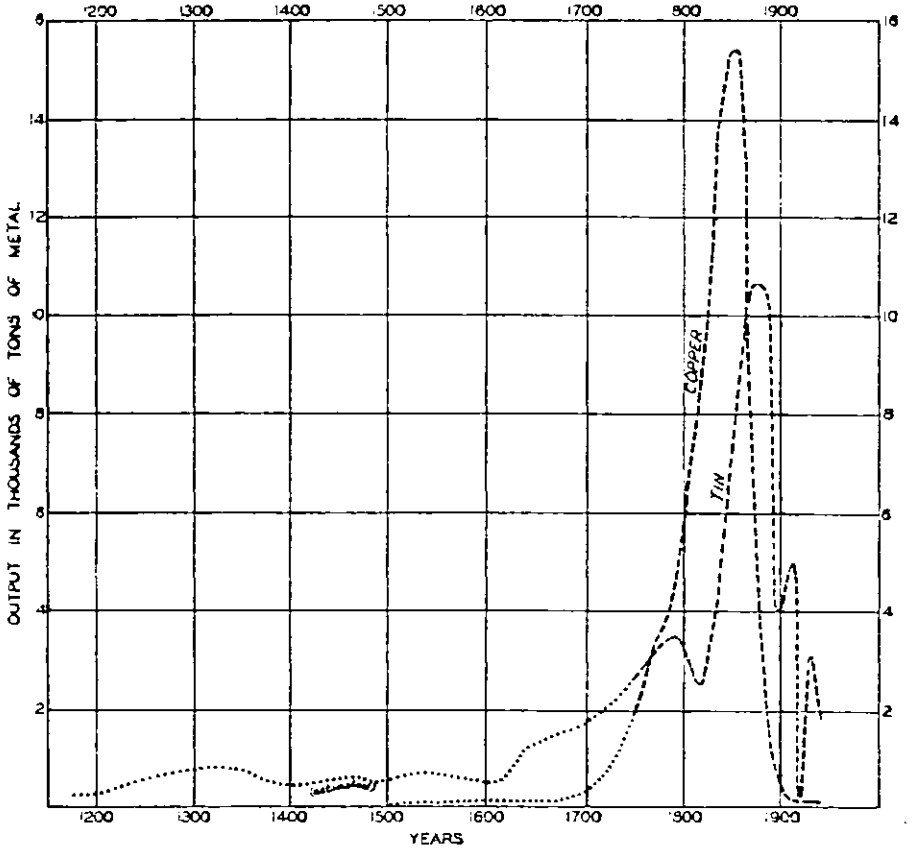


Figure 7. The output of copper and tin from Cornwall and Devon (from Dines, 1956).



PLATE 2. Dereliction in the Red River Valley south of Camborne.

(II) PREVIOUS ENVIRONMENTAL GEOCHEMICAL RESEARCH IN SOUTH-WEST ENGLAND

Early stream sediment reconnaissance work in south-west England was undertaken by Hosking and co-workers in the early and mid-1960s (Hosking et al., 1963; 1965; Hosking and Obial, 1966). The geochemical patterns disclosed were related to areas of mineralisation, mining contamination, human settlement and specific parent materials.

Initial detailed reconnaissance work by the Applied Geochemistry Research Group was completed and published in 1971 (Nichol et al.), although earlier sampling in south-west England had been undertaken for the Wolfson Geochemical Atlas of England and Wales (Webb et al., 1978). This geochemical atlas reveals that the concentrations of As, Cu, Cd, Pb, Sn and Zn in stream sediments of the province are elevated and are amongst the highest concentrations recorded in the England and Wales survey. The anomalies can be related to areas of past metalliferous mining. However, the country rocks of the province are, in certain localities, saturated with certain elements such as As, W and U which may also contribute to the stream sediment composition (Keith Beer, personal communication). For example, a broad zone of As enrichment has been discovered in the stream sediments of the metamorphic aureole surrounding the Dartmoor and Bodmin granite intrusions (Aguilar Ravello, 1974). This is related to the introduction of As bearing fluids derived from the granites into the surrounding metamorphic rocks.

The enhanced concentrations of elements encountered in the stream sediments of south-west England is reflected in the chemistry of the river waters (Thornton et al., 1975; Metcalfe, 1983).

Concentrations up to 3000 µg As/l have been recorded in unfiltered water (Aston and Thornton, 1975; Aston et al., 1975). Old drainage adits, in particular, can lead to severe contamination problems (Plates 3 and 4; Table 6) with resulting toxicity to marine life (Cronwall River Authority Report, 1970).

Research into metal contamination of soils in south-west England has been centred mainly on the metalliferous province of the Tamar Valley, where elevated concentrations up to 960 µg Cu/g and 1200 µg As/g have been found in pasture soils, and 180 µg Cu/g and 335 µg As/g in soils supporting barley (Thoresby and Thornton, 1979). Higher values have been recorded around the Kit Hill and Gunnislake granites, where peak concentrations of 2500 µg As/g and 2000 µg Cu/g reflect the Cu-Sn-As mineralisation (Colbourn et al., 1975). Alluvial soils downstream of the Devon Great Consuls mine near Gunnislake contain large amounts of As, Cu, Pb and Zn compared to those upstream of the mining area (Table 7). This is due to down-wash of metal rich mine waste, run-off from contaminated soils, and suspended solids in adit waters. Alluvium sampled at a site several miles downstream from Devon Great Consuls mine contained in excess of 300 µg As/g, 1000 µg Cu/g, 700 µg Pb/g and 700 µg Zn/g throughout the profile to a depth of 75 cm (the maximum depth sampled), indicating the accumulation of contaminated material over a considerable period of time, no doubt coincident with the mining history of the area (Colbourn, 1976).



PLATE 3. The discharge of contaminated water from Binner adit into the River Hayle. The trace-element concentrations associated with the adit water are presented in Table 6.

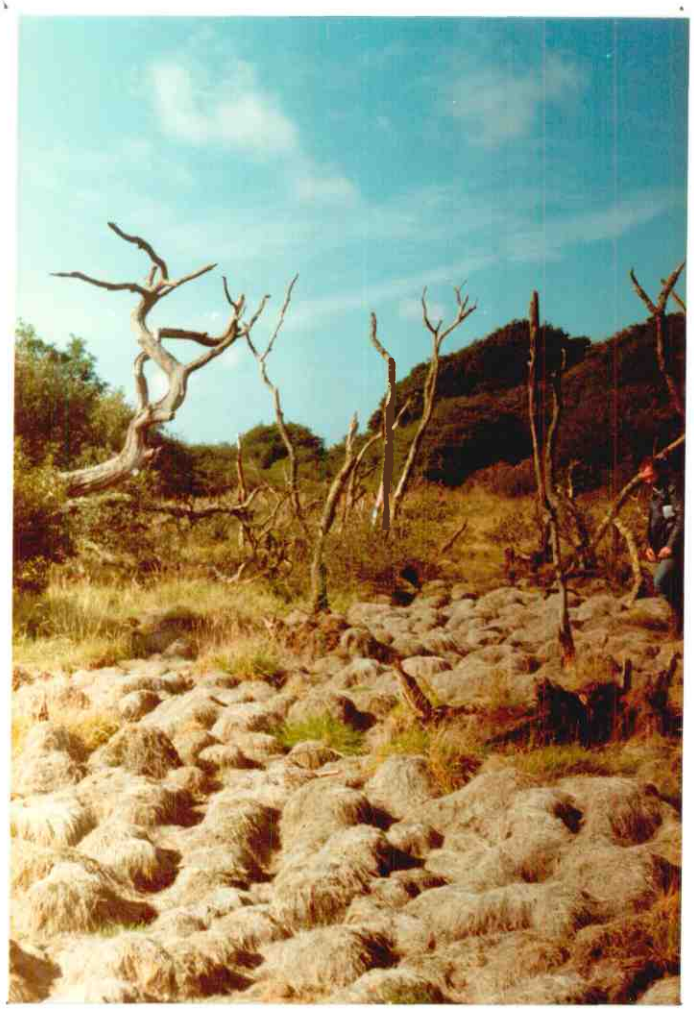


PLATE 4. Metal toxicity symptoms in trees downstream from Binner adit.

	Upstream from Binner adit	Input of water from Binner adit
Cu	18	173
Pb	n.d.	2.3
Zn	127	1250
Cd	0.6	3.1
Fe	99	380
Mn	19	313

n.d. = not detected (detection limit for Pb = 0·5 µg/l)

All values in µg/l

Table 6. The input of dissolved metals (<45µm) in contaminated water from Binner adit into the River Hayle, Cornwall. No downstream information exists, although Binner adit provides approximately 10% of the flow downstream of the confluence (data from Metcalfe, 1983).

	n	As	Cu	Pb	Zn
Tamar Valley area					
Contaminated alluvium	12	309	620	435	368
		90-900	35-2000	60-1008	114-1020
Adjacent slopes	5	110	71	370	217
		90-180	35-76	101-520	140-290
Alluvium control	5	25	44	85	121
		20-30	36-40	72-96	67-180
Upland mining areas	28	385	314	215	207
		60-2500	29-2000	62-850	58-380
Upland control areas:					
a) Devonian slates	8	27	62	121	139
		4-95	42-120	91-144	92-166
b) Carboniferous shales	13	26	43	77	92
		10-40	16-55	48-120	42-149
Dartmoor area					
Metamorphic aureole	17	88	76	98	133
		24-250	20-213	58-168	40-220
Control areas: Devonian, Carboniferous and Permian rocks	21	18	24	59	95
		4-80	7-47	34-144	51-220

All values are in µg/g

Table 7. Ranges and mean total concentrations of arsenic and selected heavy metals in agricultural soils (0-15 cm) from the Tamar Valley and Dartmoor areas of Cornwall. (data from Colbourn et al., 1975).

This work in the Tamar Valley confirms earlier research carried out by Davies (1971) who found that over 40% of the pasture soils examined in the Tamar district are abnormally high in one or more contaminant*. All studies in the province reveal that As and Cu concentrations in the soil are especially elevated, although elements such as Hg which are associated with the main minerals may also be enhanced (Warren and Delevault, 1969; Davies, 1976). Derelict mine sites are especially contaminated with a number of elements (Table 8). However, the underlying parent materials may also exert a strong influence on the geochemistry of the soils of the region. Thus the natural enrichment of the metamorphic aureole surrounding the Dartmoor granite is reflected in the As and Cu concentrations of the overlying soils when compared to those soils developed from unmetamorphosed Devonian, Carboniferous and Permian rocks (Aguilar Ravello, 1974; Colbourn et al., 1975 - Table 7).

Elevated concentrations of metals in forms available to plants are usually found in the contaminated soils (Davies, 1971). Vegetation growing within the metal enriched areas may thus reflect these anomalous concentrations in their trace-element composition. Millman (1957) in a biogeochemical study of Hingston Down, near Gunnislake, showed clear relationships between trace-element concentrations in tissues from tree species and the occurrence of mineralised ground. Similarly, the contaminated nature of the soils within the Tamar district is reflected in the arsenic and metal composition of barley seedlings and pasture herbage (Thoresby and

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* This toxic complex is commonly known as 'mundic', a Cornish or Celtic term which was formerly used to describe the mineral arsenopyrite.

		Cu	Pb	Zn
Control		30	30	30
Whole area (n=29)	Average	1042	3387	2422
	Enrichment Factor	35	113	81
Dressing floor (n=14)	Average	1053	5001	2885
	Enrichment Factor	35	167	96

All values in µg/g

Table 8. Contamination of soils at the South Molton Consols mine. At this particular site, galena (PbS) was the dominant mineral mined; most mines of the province, however, were important for As, Cu and Sn. (Adapted from Badham et al., 1979).

Thornton, 1979). Due to limited uptake and translocation, however, the trace-element concentrations reflect, to only a small degree, the large amounts present in the soil (Table 9).

In the old mine areas, tolerant ecotypes of certain grass species have been recorded; these are genetically adapted to the high soil metal concentrations (Badham et al., 1979). Mine spoil areas may support grass species which are tolerant to high amounts of As (Porter, 1976; Porter and Peterson, 1975, 1977), whilst more recent research has indicated that Cu tolerance mechanisms within the plants are also likely in such adverse environments (Leslie Benson, personal communication).

In areas subjected to agricultural practices, toxicity symptoms, although rare, have been reported and seem to be confined mainly to areas of 'silted-up' settling ponds, leats and drainage adits (Plate 5). Occasional crop failure can occur in areas high in As and Cu. Such failures are not normally considered to be due to phytotoxic effects, however, since extreme chemical pollution of agricultural land is nearly always accompanied by a large dilution of topsoil with waste material whose physical composition is not conductive to crop growth. It seems that the greatest danger of the elevated concentrations of elements found in the soils of the south-west is to the grazing animals through the ingestion of contaminated herbage and mundic soil. Arsenic toxicity has been reported on the 'Bastard Red Soils' of Whiddon Down to the north-east of Dartmoor (Nichol et al., 1971). Similarly, an anomalous lead zone in the Teign Valley is consistent with the tradition that chickens cannot be kept in part of the valley due to the high Pb content of soils and vegetation.

	n	As		Cu		Pb		Zn	
		soil	herbage	soil	herbage	soil	herbage	soil	herbage
Tamar Valley	34	28-1200	0.26-9.60	28-980	8.1-34.0	50-900	6-40	55-670	23-150
		206	2.69	124	13.3	206	12	169	53
Southend (control)	12	7-12	0.25-0.67	16-92	9.6-18.2	30-385	5-20	58-280	36-59
		9	0.43	31	12.2	89	14	103	42
Midhurst (control)	13	9-33	0.20-1.86	7-36	6.0-11.8	15-225	5-14	24-107	26-50
		16	0.50	12	8.6	51	9	56	34

All values in µg/g.

Table 9. Range and mean concentrations of heavy metals and arsenic in topsoil (0-15 cm) and pasture herbage (µg/g dry material) from the Tamar Valley and two control areas (adapted from Thoresby and Thornton, 1979).



PLATE 5. Chlorosis of grass established in a 'silted-up' mine adit near Camborne. The trace-element concentrations recorded from the silt are 336µg As/g, 1179µg Cu/g and 186µg Zn/g; those recorded from the grass samples are 3.06µg As/g, 38µg Cu/g and 312µg Zn/g. Using the linear regression equations calculated in this present research (Chapter 6), the herbage should contain 0.79µg As/g, 21.9µg Cu/g and 47.5µg Zn/g. Under the conditions of growth at this site (i.e. a waterlogged silt) the factors governing the uptake and translocation of these trace-elements have been overcome. This particular example of trace-element toxicity, however, is situated in a derelict area which is of little use to agriculture.

According to Thomas (1979), however, areas of potential danger to grazing animals are limited. Indeed, there is evidence to suggest that enhanced intake of As is beneficial to the ruminant since a healthy appearance of cattle grazing on contaminated land is apparent. Excessive intake of any element may be prevented by a 'dilution' caused through grazing uncontaminated pasture. Furthermore, animals are protected from ingesting large quantities of herbage containing excessive amounts of potentially dangerous elements since normal pasture species will not grow in severely contaminated areas. On less severely contaminated land, the limited translocation of certain elements from the roots to the shoots (Chapter 2) is also of extreme importance to the nutrition of the grazing ruminant. Hughes (1979) concludes that the agricultural consequences of abandoned mine workings are as follows:

1. The presence of spoil heaps and areas of general dereliction reduce the amount of land available for agriculture.
2. Abandoned mine shafts are a potential hazard to both personnel and livestock.
3. Stock may suffer poisoning following ingestion of heavily contaminated soils.
4. Although there are no records of stock suffering from eating herbage growing on contaminated ground, cattle are thought to lose condition if reared in a contaminated locality and subsequently moved to an arsenic-free environment.
5. Occasionally abnormally high soil contamination may effect the desirability of embarking on capital intensive enterprises involving crops thought to be sensitive to As or heavy metals.

(III) GEOCHEMISTRY AND HUMAN DISEASE IN SOUTH-WEST ENGLAND

There has always been a large number of traditions and "old wives' tales" in south-west England associating a number of localities with various forms of illness caused by the adverse effects of the mineralised ground and the mining industry. Although such ideas were to some extent rejected when the germ theory was evolved during the 19th century, in the last 60 years they have revived because of the realisation of the influence of micro-quantities of chemicals in relation to human health requirements.

Accordingly, a higher than average mortality rate or an elevated prevalence of certain diseases including cancer, multiple sclerosis and tooth decay, has been observed in the mineralised areas of Camborne (Hargreaves, 1966), Helston (Warren et al., 1967), Wadebridge (Hargreaves, 1960; Warren et al., 1967) and the Tamar Valley (Allen-Price, 1960; Hargreaves, 1966; Pinsent, 1968; Anderson et al., 1976 and Anderson and Davies, 1980), although much of this work remains to be geochemically, statistically or medically proved. There is some evidence to suggest that local inhabitants may develop a natural tolerance to the high trace-element concentrations encountered in their environment. Non-local people who have moved to Blackwater in Cornwall, for example, have supposedly suffered from As poisoning caused by the consumption of home produced brussel sprouts grown in gardens reclaimed from old metal enriched mine dumps (Thomas, 1979).

Although the effects of the enhanced trace-element concentrations found within south-west England still remain largely unknown, it is possible that any diseases related to the local geochemical conditions are more difficult to distinguish than in the past. Today there is very little reliance on food grown in the immediate locality, whilst local milk supplies are now mainly sent to the nearest dairy. These factors, together with a greater population movement caused by way of employment and change of residence greatly reduces the risk of illness arising from possible toxicities in locally grown food. Another mitigating factor today is the increased surveillance by Public Health Authorites on water quality for human consumption, coupled with the switch from wells to mains water supplies which are carefully monitored. Such supplies may even originate from outside the contaminated areas of the province.

(IV) THE HAYLE/CAMBORNE-REDRUTH DISTRICT

In 1972-73, geochemical maps for 15 of the 21 elements included in the Wolfson Geochemical Atlas were distributed to Geochemical Liaison Committees set up by the Agricultural Development Advisory Service (ADAS) with a view to assessing the practical application of the data to local advisory problems. In 1974, a 310 km^2 section of the Cornish Peninsula centred on Hayle/Camborne-Redruth (Figure 8) was selected by the Geochemical Committee of the South-west Region for a geochemical stream sediment follow-up survey in a region defined by the Atlas as being anomalous for a number of elements. This survey was undertaken by members of the Applied Geochemistry Research Group, and the results of the survey are outlined in Section IVc of this Chapter.

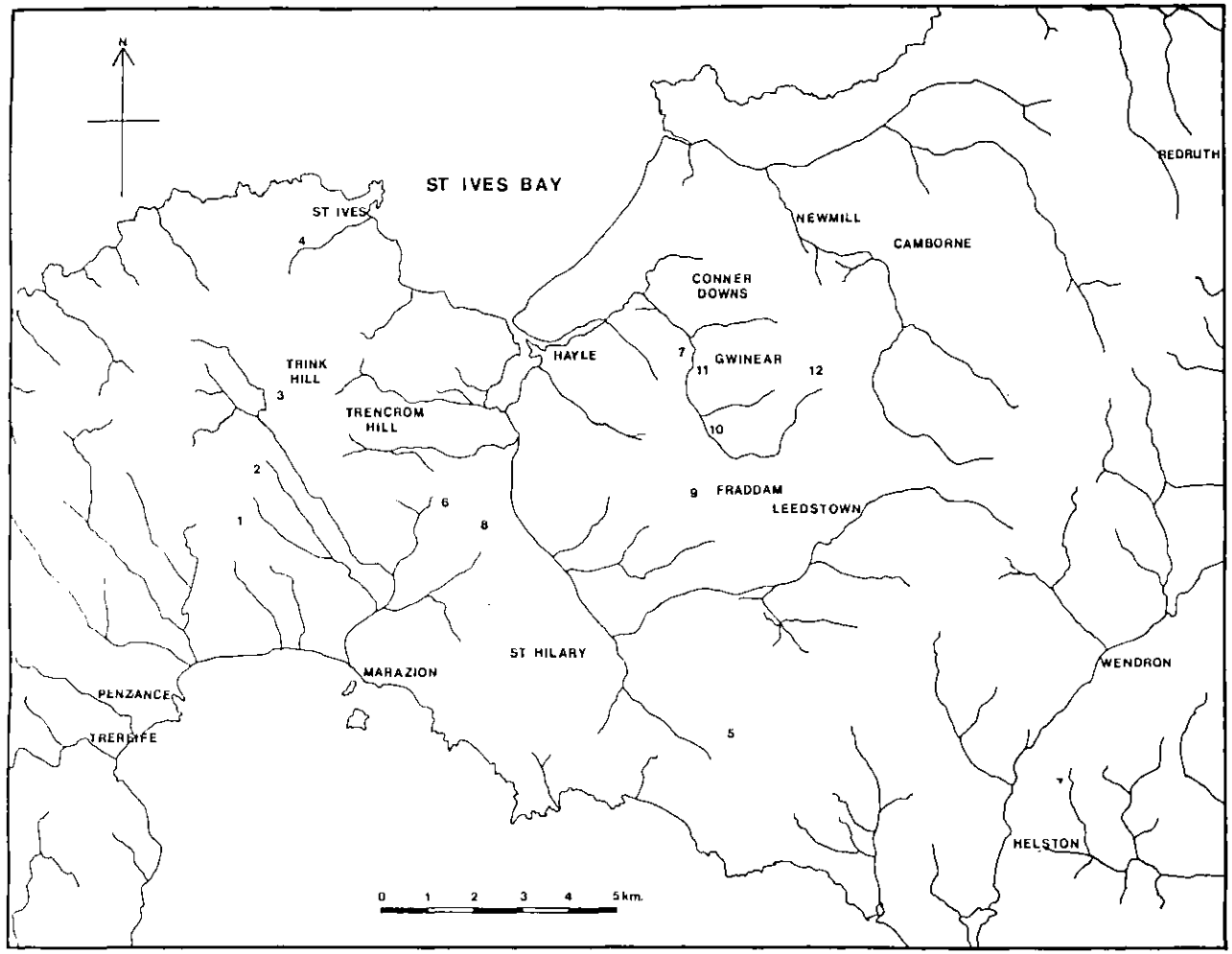


FIGURE 8. The Hayle/Camborne-Redruth district (numbers refer to the farm sites studied in Chapters 6 and 7).

a) Geology and geomorphology

The geological succession found in the Hayle/Camborne-Redruth district is listed in Table 10. Three rock types - the Mylor Slates, greenstones and granites - constitute the dominant parent materials within the area (Figure 9): the other lithological units are of limited occurrence and hence are of little consequence to this thesis.

The Mylor Slates are non-calcareous intensely folded and faulted sediments, known locally as the 'Killas'. The formation consists of a pale and dark grey sediment and a blue-black shale interbedded with narrow, fine, sandy beds, the latter being seldom greater than ½" thick. The stratigraphical position of the slate has long been the subject of conjecture. Whilst Dearman (1971) indicates that the rocks are Lower Devonian in age, Edmonds and others (1969) gives a probable age of Middle Devonian. Recent palynological evidence, however, suggests that sedimentation occurred during the Upper Devonian (Turner et al., 1979).

Of a near contemporaneous age to the slates are basic and ultrabasic rocks known collectively as 'greenstones'. The outcrop of these rocks within the study area is shown in Figure 9, although a recent survey by the Institute of Geological Sciences (as yet unpublished) has much extended their distribution (Roger Taylor, personnal communication). The main outcrop within the study area is now thought to run in a belt trending north-eastwards from Marazion. These rocks consist in the main of fine grained pillow lavas. Other outcrops on the south coast and to the north and west of St. Ives, however, appear to be intrusive (Staines, 1979). Recent evidence has

Period	Formation	Geological Description
Holocene/Pleistocene		Dune sands Peat Alluvium Head (drift) and valley gravel
Pliocene	St. Erth Beds	Marine sands, gravels and clays
Devonian	Mylor Series	Slate
Igneous		Greenstones, Felsite Granite

Table 10. The geological succession found in the Hayle/Camborne-Redruth district.

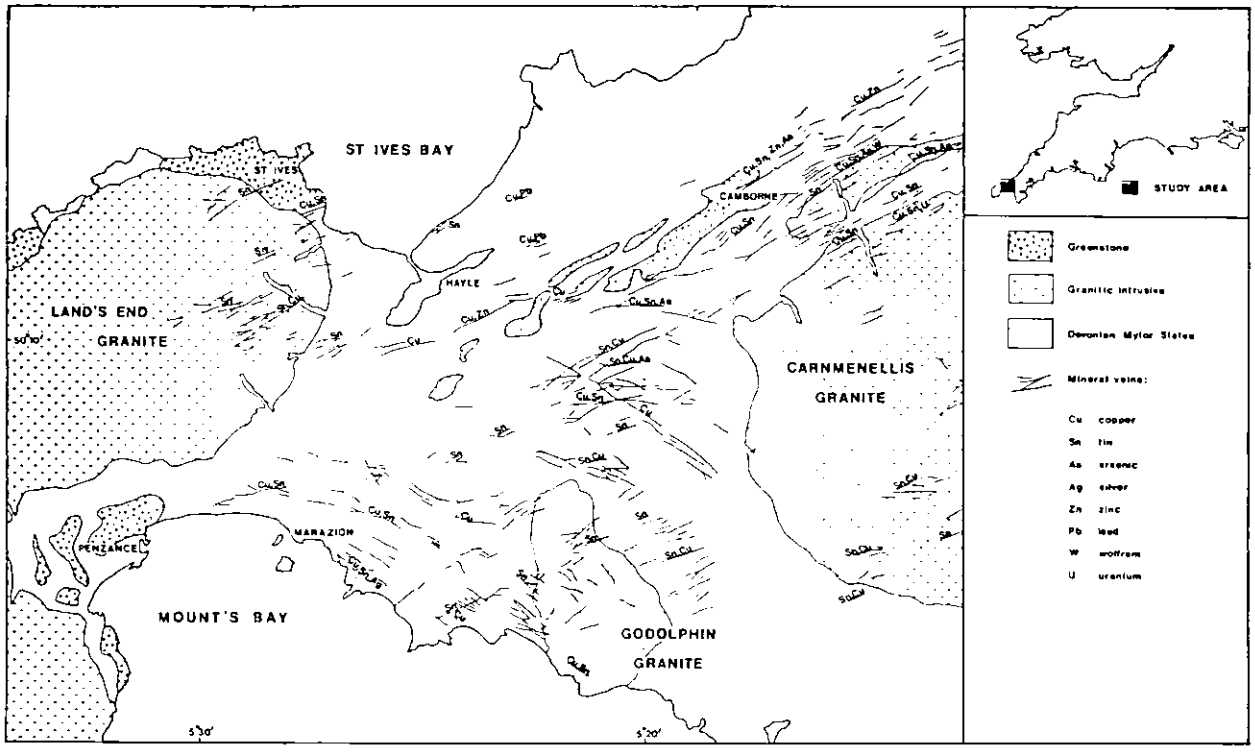


FIGURE 9. Geology of the Hayle/Camborne-Redruth district.

indicated that the greenstones of the study region are predominantly tholeiitic basalts that have suffered chemical and mineralogical change during subsequent regional and contact metamorphism (Floyd and Al-Samman, 1980).

Faulting has divided the central greenstone outcrop into a few large and many smaller fragmentary blocks. Whilst the former outcrops may form prominent features topographically, the latter are difficult to distinguish from the surrounding slate countryside which seldom exceeds 90m (300 ft) above O.D. (Plate 6). The land rises sharply, however, over the Godolphin, Carnmenellis and Lands End granite masses. These are intruded rocks which are linked at depth and which form part of the large granite batholith extending from Dartmoor in the east to the Scilly Isles in the west. Intrusion occured towards the close of the Carboniferous period when pre-existing sediments, including those of the study area, were folded, faulted and metamorphosed by movement of the Armorican orogeny. The heat generated by the intruded granite further metamorphosed the country rocks by contact metamorphism. Evidence by Moore (1977) indicates that most, if not all, of the study area has been affected by this process.

The invaded sedimentary rocks acted as moulds for the ascending magma and impressed a series of approximately north-east and east to west ridges in the granites. A granite cusp developed where the invaded rocks were domed as a result of the two fold systems intersecting. Metal enriched residual fluids derived from the granite were concentrated in these cusps to form emanative centres of mineralisation (Dines, 1934). From these centres, the fluids penetrated fracture systems in the metasedimentary and cooled granite rocks to form mineral veins or



PLATE 6. Aerial view of part of the study area. This photograph shows the subdued relief characteristic of the slate districts. Hayle is the major town in the foreground. Cambridge University Collection copyright reserved.

lodes. Due to the geothermal gradients which were operative during their emplacement (Dewey, 1925; Davison, 1927; Dines, 1934), both metallic and gangue minerals are distributed laterally and vertically in a series of concentric belts around the emanative centres (Figure 10).

The study area itself lies within a region dominated by high temperature (hypothermal) mineralisation (Figure 11). Accordingly, the area was principally important for the mining of Sn, Cu and As ores (Table 11). Due to the mineral zoning, lower temperature (mesothermal) mineralisation - for instance Pb ores - occurs mainly outside the study area. Zinc ores, however, can be found within both hypothermal and mesothermal mineralised zones.

A lithological control on the mineralisation type may occur whereby the ore content of lodes changes when rocks of differing characters are traversed. Henwood (1843) records that the principal variation of this kind is where a lode bears cassiterite (Sn) whilst in the granite, and Cu ores when it enters slate or greenstones. Similarly, Pb lodes within the killas sediments have been proved in several mines to have been preferentially deposited in the shaly rocks; any interbedded siliceous or more sandy beds being barren (Edmonds et al., 1969). Such lithological controls complement the mineral zoning and determines the mining history and development - and hence the nature of any contamination - of the study area.

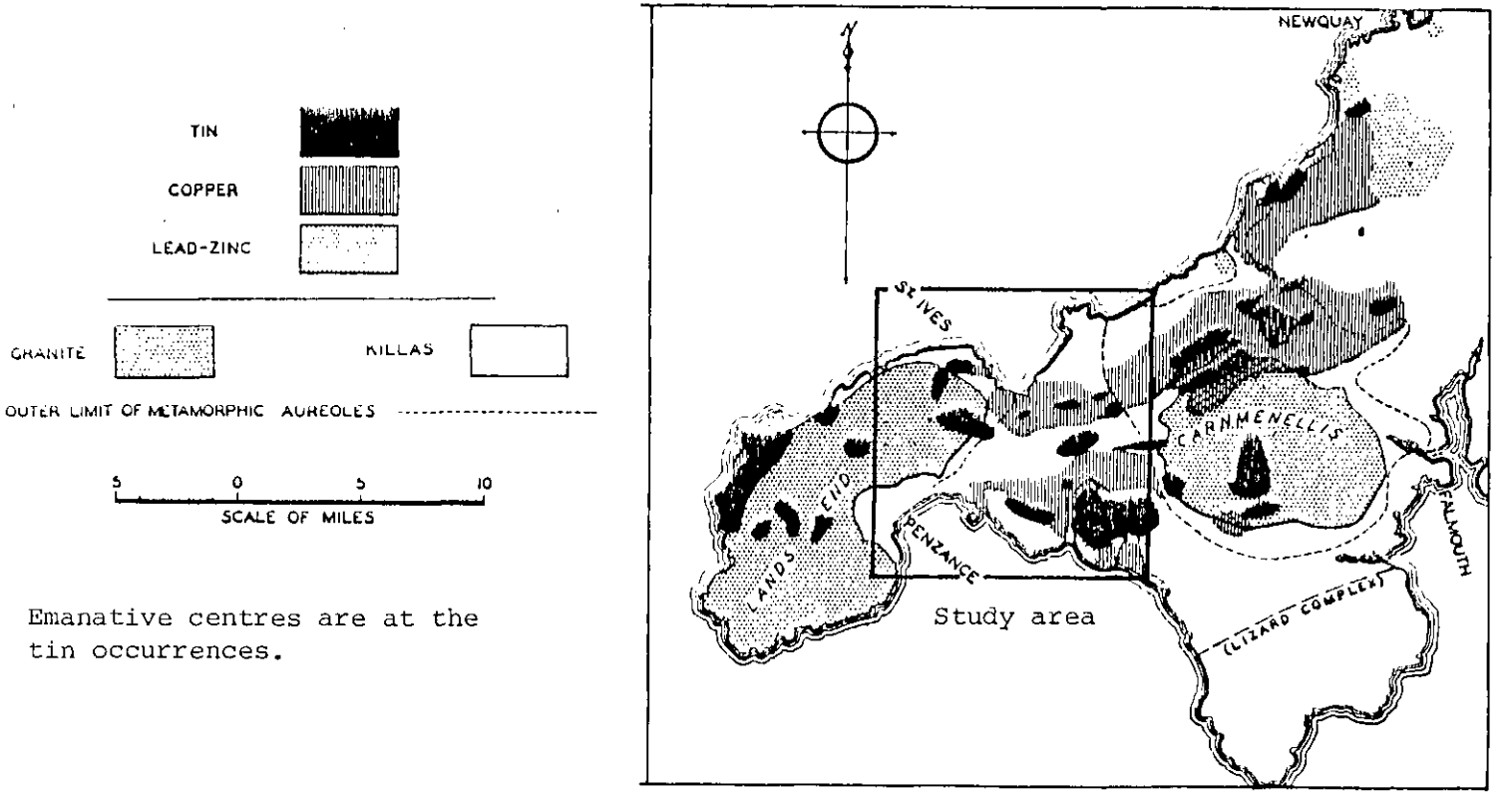


Figure 10. The distribution of tin, copper and lead-zinc ores in west Cornwall (from Dines, 1956).

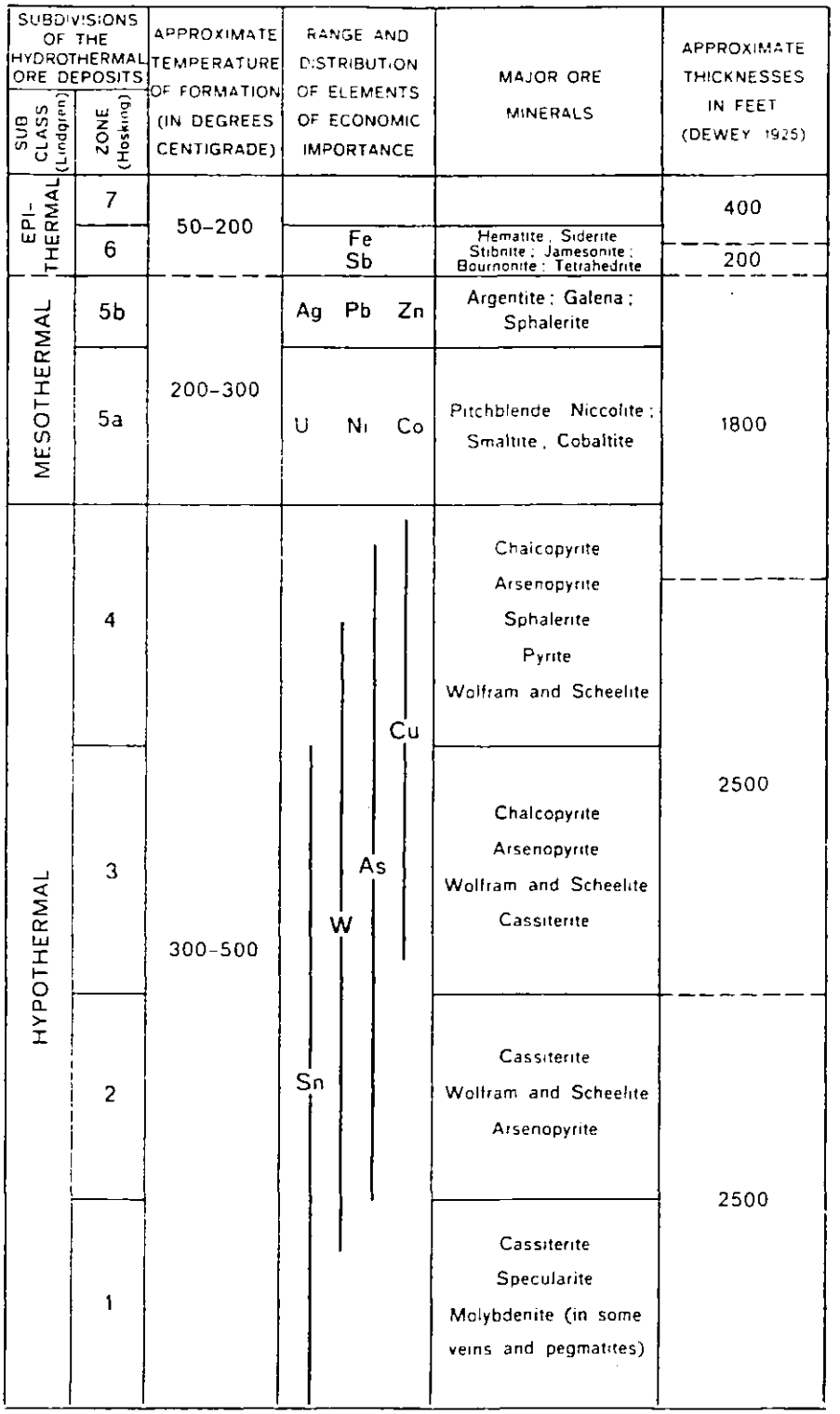


Figure 11. A schematic relationship of the ore-mineral zones found commonly in south-west England. The study area itself is dominated by hypothermal mineralisation (from Edmonds et al., 1969).

District	Tin	Copper	Arsenic	Sulphur (Pyrite)	Lead	Iron
1. Study area						
a) St Ives	4.9	*	-	*	-	-
b) Gwinear	0.9	5.2	0.1	0.3	0.1	*
c) Mounts Bay	6.7	4.5	0.7	*	*	0.1
d) Wendron and Falmouth	3.3	0.1	-	-	*	-
e) Camborne, Redruth and St. Day	53.2	52.6	39.8	42.2	1.8	1.3
Total	69.0	62.4	40.6	42.5	1.9	1.4
2. Other areas						
a) St. Just	12.7	2.2	1.0	-	*	*
b) St. Agnes	5.6	3.8	*	2.8	25.4	9.0
c) St. Austell	6.8	10.0	*	4.1	0.2	27.8
d) Wadebridge	-	*	-	1.8	0.9	*
e) Liskeard	3.3	7.9	0.2	0.5	25.1	4.0
f) Callington and Tavistock	2.2	12.8	57.5	47.6	38.3	1.4
g) Dartmoor and Teign Valley	0.5	*	0.4	0.4	7.1	6.4
h) Okehampton	*	*	*	*	-	-
i) North Devon and West Somerset	-	*	-	-	*	50.0

* = less than 0.1 per cent.

Table 11. The output of minerals from each of the mineralised districts within south-west England. The values are expressed as a percentage of the total recorded production of the whole region (adapted from Dines, 1956).

b) Soils and Land Use

Reference: Staines, 1979*

The distribution of soils within the study area is shown in Figure 12. The region was never glaciated although Head deposits were formed under periglacial conditions. These drift deposits cover much of the district, and since there appears to have been little lateral solifluction, there is a strong relationship between the distribution patterns of the soils and the underlying rocks.

On the slates, the Head is usually 2 m thick and is rarely absent except on convex slopes. The Head generally consists of a stony material in a fine loamy matrix which often shows some evidence of frost heaving. Perhaps surprisingly, the Devonian slates yield a fairly free draining soil since the underlying rocks do not impede drainage as much as the Carboniferous shales found elsewhere in South-west England. Thus although wet, gleyed, soils occur in the valley bottoms, much of the slate outcrop is dominated by fine loamy brown earths of the Highweek series which have been mapped over a wide variety of landscape facets. However, where metamorphism has been most intense along the granite-slate contact in the western half of the district, brown podzolic soils of the Dartington series can be found. These soils also occur in the centre and to the east of the study region, with Staines recording a crude relationship between increasing rainfall amounts across the map area and the proportion of brown podzolic soils.

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* nb. Some of the soil series names recorded by Staines have now been replaced. The original names are used in this thesis; however, the equivalent new names are recorded in Appendix 3.

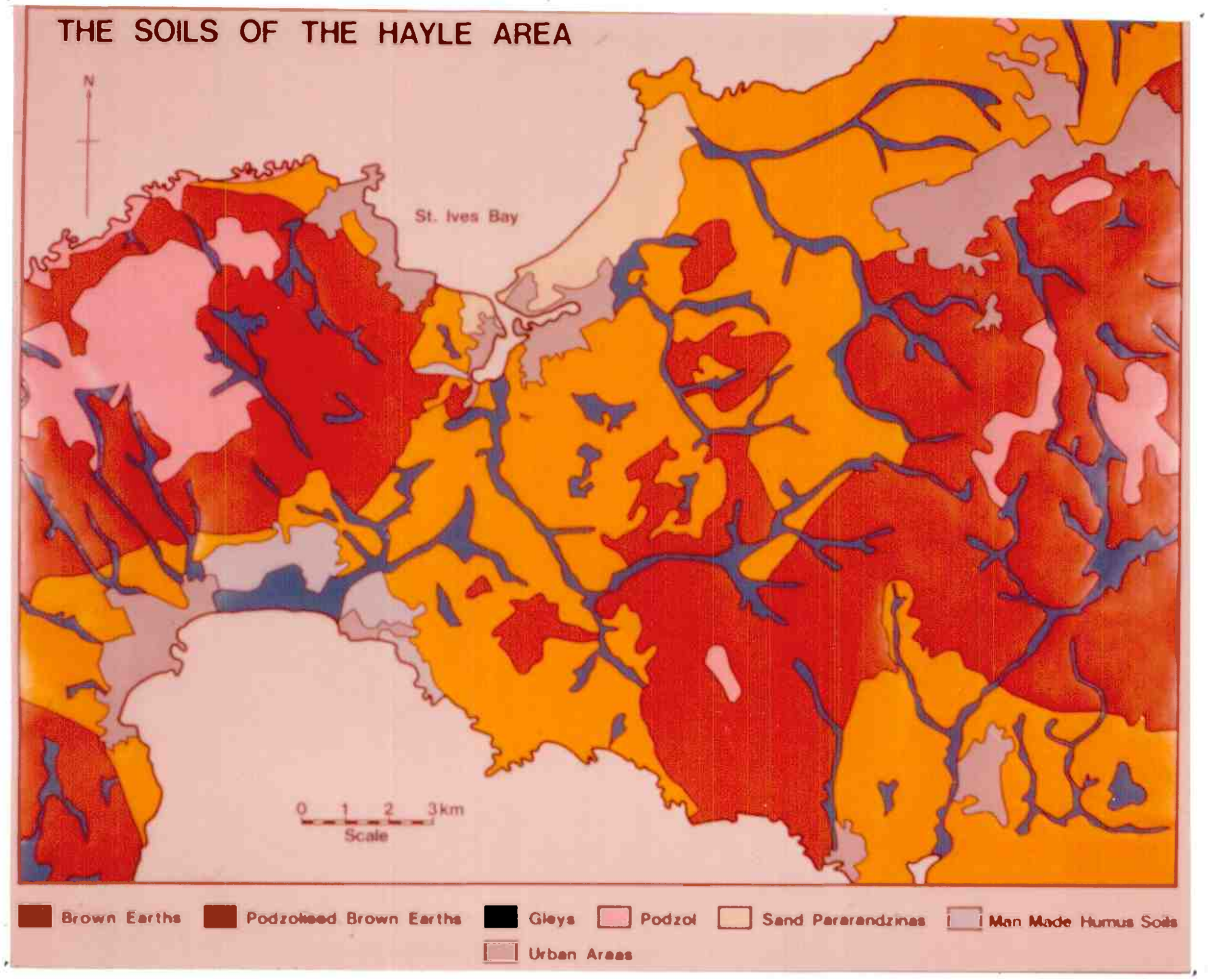


FIGURE 12. The soils of the Hayle area.

Man-made (Plaggen) soils occur on sheltered sites of the south coast where man has, over a considerable period of time, added seaweed, beach sand, animal manures and town refuse to the pre-existing soils, thus completely modifying the natural profile by creating a thick coarse loamy topsoil (Table 12). The application of highly calcareous dune sand from Hayle has, in some cases, considerably affected the pH of these soils. Similarly, coarse loamy calcareous soils may be found to the north-east of Hayle. These soils have been formed naturally by sand which has been blown inland from the nearby dunes.

Elsewhere on the slate lowlands, liming of the soils has been widespread. This agricultural practice has also been carried out extensively on the greenstone outcrops which support deep and shallow brown earths of the Trusham series. Staines records that most of the slate and greenstone derived soils have pH values ranging from 6.0 to as high as 8.2, thus reflecting the application of local calcareous sand or agricultural lime.

In sharp contrast, the soils of the granite hills are more acidic, especially where developed under areas of semi-natural vegetation (Table 13). Coarse, gravelly, often compact, Head mantles much of the granite outcrop which is reflected in the texture of the overlying soils. Soils developed on slate xenoliths incorporated within the Godolphin granite have a less gritty feel and larger silt contents than soils developed on the more normal granite Head. The solid granite itself is only exposed as a few upstanding tors (e.g. Rosewall Hill, Plate 7), whilst most of the lower, gently undulating granite country is occupied by brown podzolic soils of the Moretonhampsted and, to a lesser extent, by the Moor Gate series. Stagnopodzols of the Trink series

Soil Type	Soil Series	pH		Texture (%)		
		in water	in 0.01 M $CaCl_2$	Sand	Silt	Clay
Brown earth	Highweek deep phase	7.0*	6.9*	27	46	27
Brown earth	Highweek calcareous phase	7.5	7.4	49	33	18
Brown earth	Highweek man-made phase	6.0	5.6	51	34	15

* high pH due to agricultural liming.

Table 12. Topsoil pH and texture values obtained from normal deep phase, naturally enriched calcareous phase and man-made phase of the Highweek series (data obtained from Staines, 1979).

Soil Type	Soil Series	pH		Texture (%)		
		in water	in 0.01 M $CaCl_2$	Sand	Silt	Clay
Brown Podzolic	Moretonhampstead	5.2	4.9	47	37	16
Brown Podzolic	Moor Gate	4.0*	3.5*	31	52	17
Podzol	Cucurrian	4.3*	3.4*	56	37	7
Stagnopodzol	Trink	4.3*	3.3*	54	38	8

* Acidity reflects the semi-natural vegetation of the sample site.

Table 13. Soils developed on the granite hills of the Hayle/Camborne-Redruth district (data obtained from Staines, 1979).



PLATE 7. Granite tor on Rosewall Hill (Grid Ref. SW 494392). Stagnopodzols of the Trink series occupy the surrounding areas. The flat lowland in the background is a wave-cut platform of Pliocene age; the soils are brown earths (Trusham series) developed on greenstone rocks.

occur on higher ground, whilst a few slopes are dominated by typical podzols of the Cucurrian series. Humic gley soils occupy the broader valleys and valley heads.

A high incidence of sunshine and the low frequency of frosts during the winter ensures that the growing season lasts for all of the year. With the decline of metalliferous mining, therefore, the local economy is now dominated by agricultural activities. Dairying is by far the most important enterprise financially; beef is not very important and is usually a secondary enterprise on dairy farms. Agriculture and horticulture is closely integrated in the region with farms growing crops - principally broccoli, potatoes or flowers - and keeping a dairy herd. The best land for this practice lies in a central belt from Marazion in the south-west to Connor Downs in the north-east, with the man-made soils being especially important (Figure 13). The granite areas, however, are not so suitable for horticultural production, and are mainly down to grass for beef or dairy (Table 14).

c) Results of the Geochemical Stream Sediment Follow-up Survey

The objective of the stream sediment follow-up survey was firstly to check and confirm the original geochemical Atlas patterns and secondly to accurately define the areas of contamination derived from the mining of a zone of intense mineralisation and those of low cobalt status associated with granitic parent material. Analyses were performed on the samples for total As, Cd, Co, Cu, Pb and Zn*; Sn was not determined in the follow-up survey being, at the time of sampling, of no known agricultural significance.

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* The total Cu, Pb, Zn, Cd and Co content of the samples was determined by atomic absorption spectroscopy following HNO_3 digestion; the total As content was determined by the colorimetric Gutzeit process.

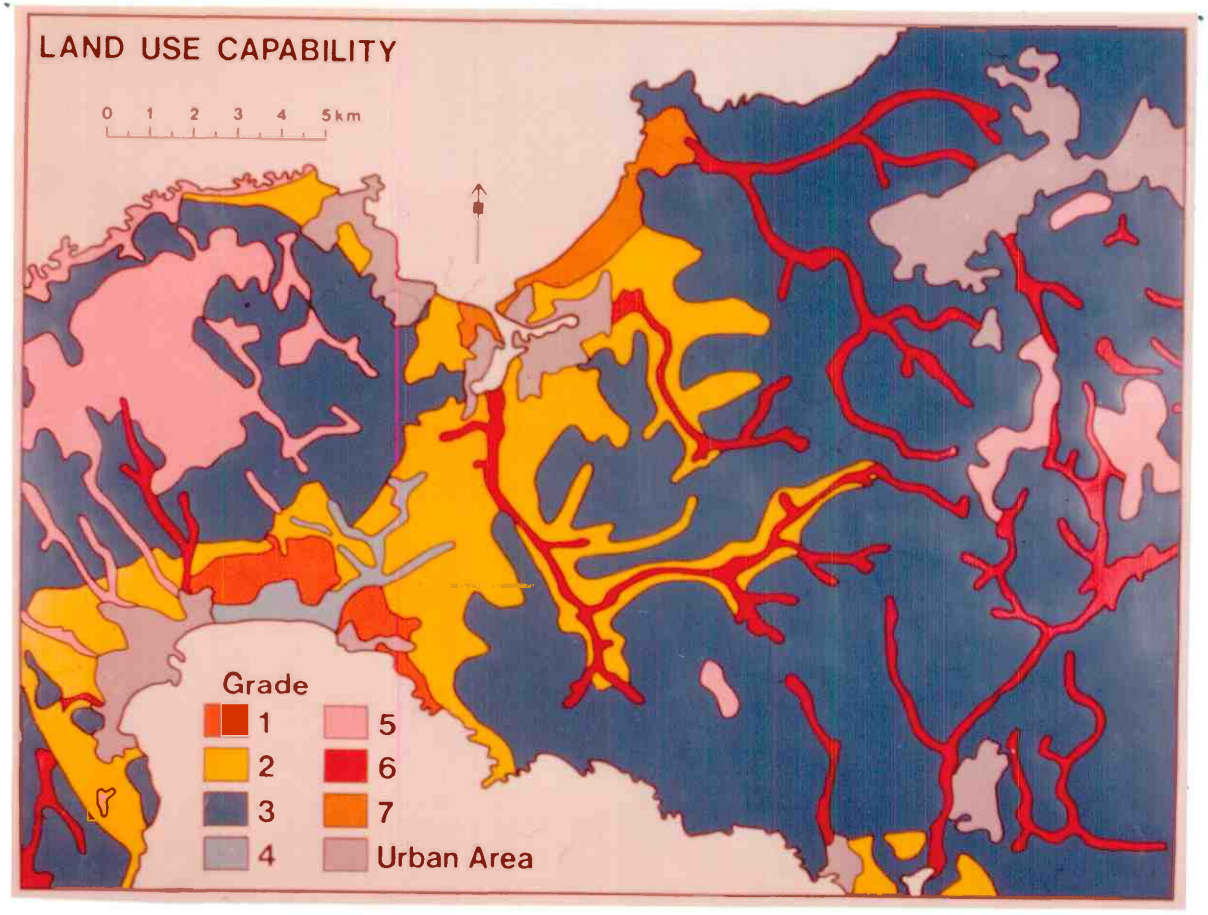


FIGURE 13. Land use capability in the Hayle/Camborne-Redruth district.

Parish	Crops					Livestock		
	% total average of crops and grass					No. per 40 ha (100 acres) crops and gras		
	Cereals	Fodder Crops	Temp. Grass	Perm. Grass	Hort	Dairy cows	Total cows	Total sheep
Marazion (coastal hort. belt)	14	7	10	34	35	15	41	-
St. Erth (inland slate country)	22	4	34	26	15	25	39	12
Towednack (granite hills)	11	4	44	41	1	42	61	3

Table 14. Crops and livestock of three representative Parishes within the Hayle/Camborne-Redruth district. (from Staines, 1979).

A total of 178 samples had been taken within the survey area for the Wolfson Geochemical Atlas (average density 0.6 samples/km^2). In the follow-up survey, duplicate analyses were performed on 124 of these samples as part of the pattern checking programme. One hundred additional stream sediments were collected from sites selected to define more accurately the boundaries of contaminated areas, together with 38 sediments from re-sampled Atlas sites. The final sample density was around 0.9/km^2 (Figure 14).

The results of the follow-up programme showed that virtually the whole of the study area is contaminated by one or more element. The concentrations recorded in Figures 15-19 can be compared to the percentile concentrations obtained from the Wolfson Geochemical Atlas survey (Table 15). Copper and As are the most widespread and elevated contaminants reflecting the hypothermal mineralisation; Pb, Zn and Cd enriched sites are less widespread and, although elevated, are of lesser importance in this particular region of the south-west. The most severe contamination is found in a zone trending to the north-east, from the north of Marazion, and extending between the Lands End, Godolphin and Carnmenellis granites. This zone concides with the most heavily mineralised ground found within the study area (Figure 9). To the east of Hayle, and extending to the Camborne district, As and Cu values in stream sediments exceed 1000 µg/g, with maxima of 14000 µg As/g and 8000 µg Cu/g. Zinc and Pb enriched sites are less widespread than those high in Cu and As, but again the maximum concentrations occur in the Hayle/Camborne areas where maxima of 3900 µg Zn/g and 1160 µg Pb/g are found. Cadmium contamination is widespread, but not severe, and an arbitrary value of 4 µg Cd/g was

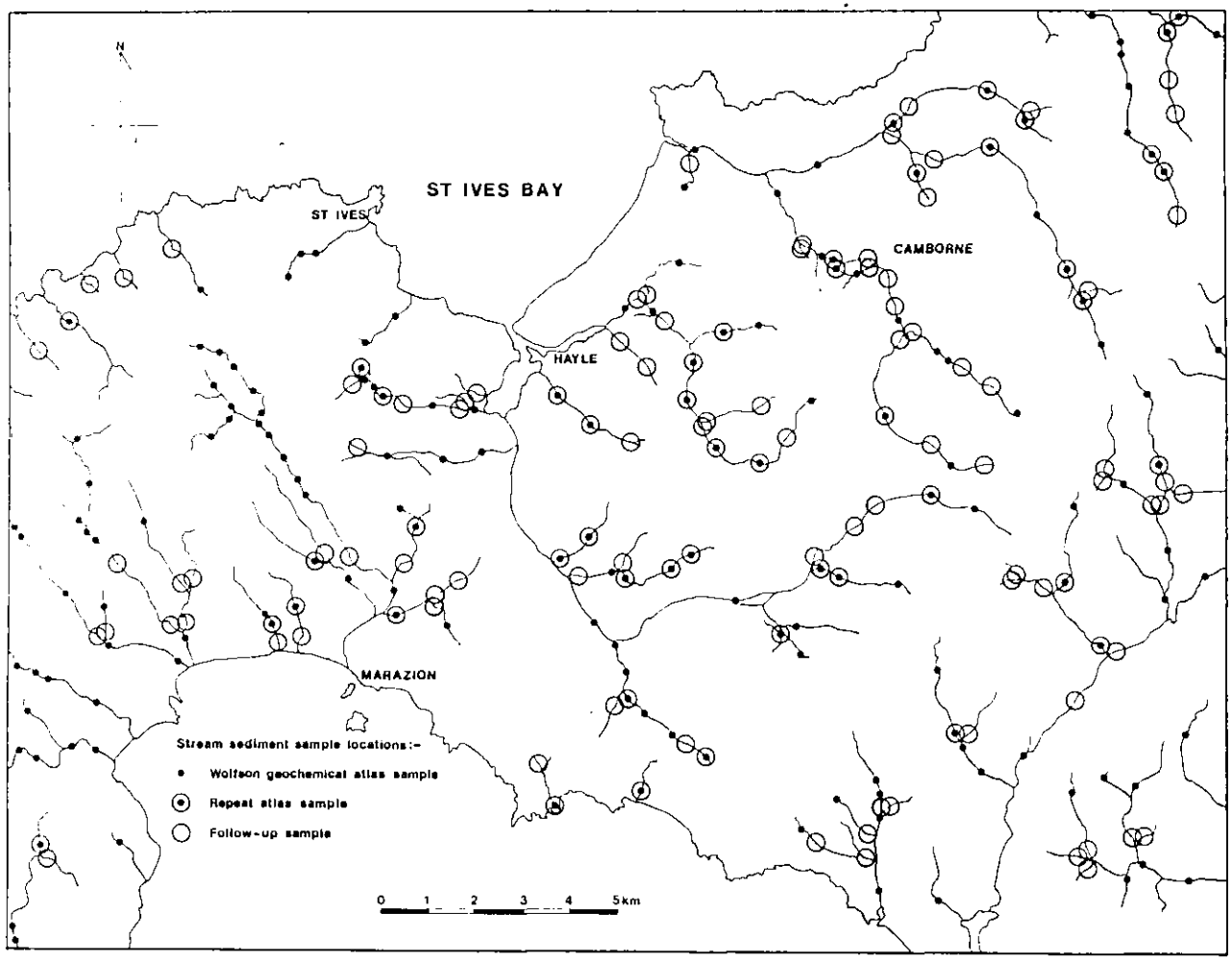


FIGURE 14. Stream sediment locations used in the geochemical follow-up survey of the Hayle/ Camborne-Redruth district.

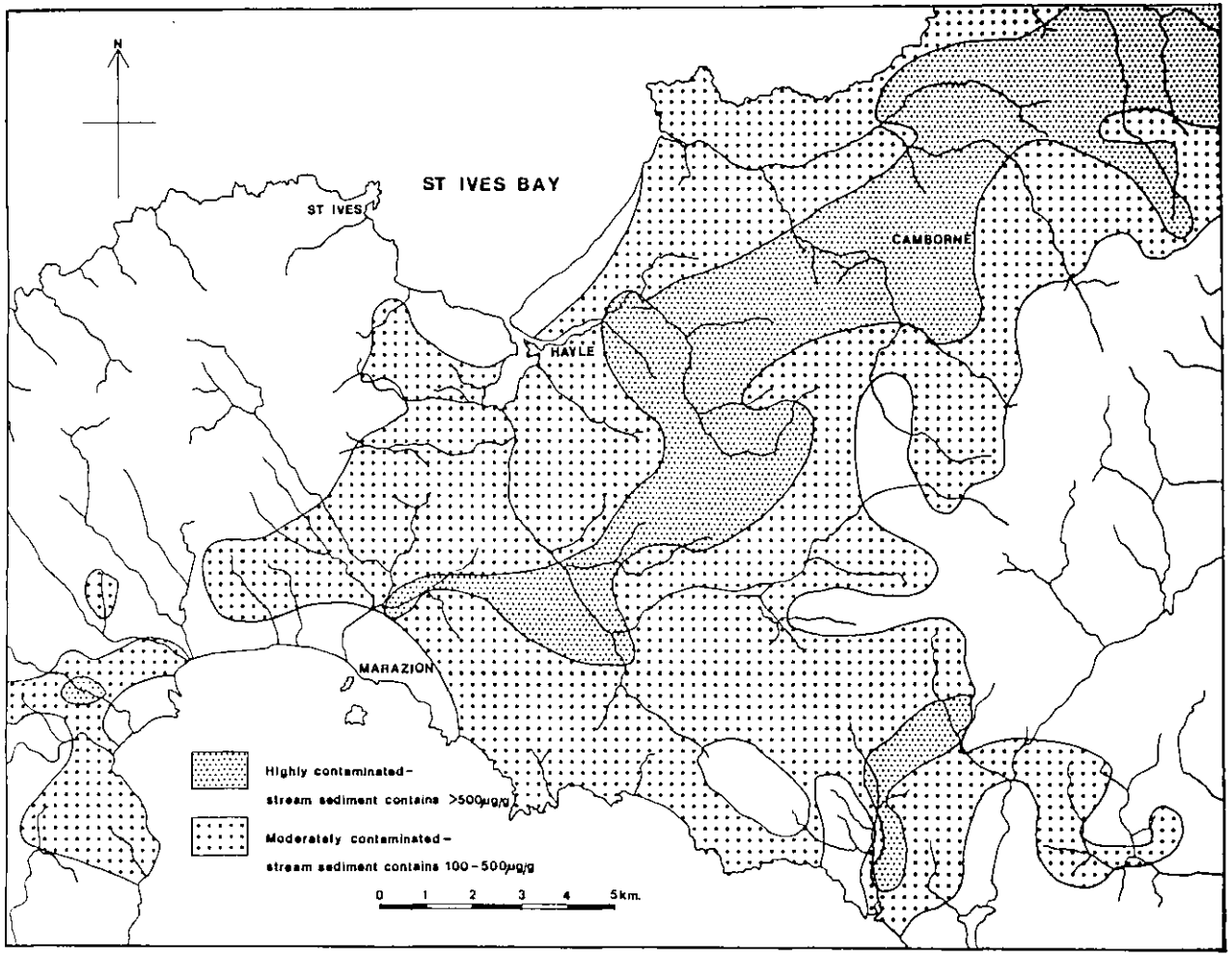


FIGURE 15. The distribution of arsenic in stream sediments of the Hayle/Camborne-Redruth district.

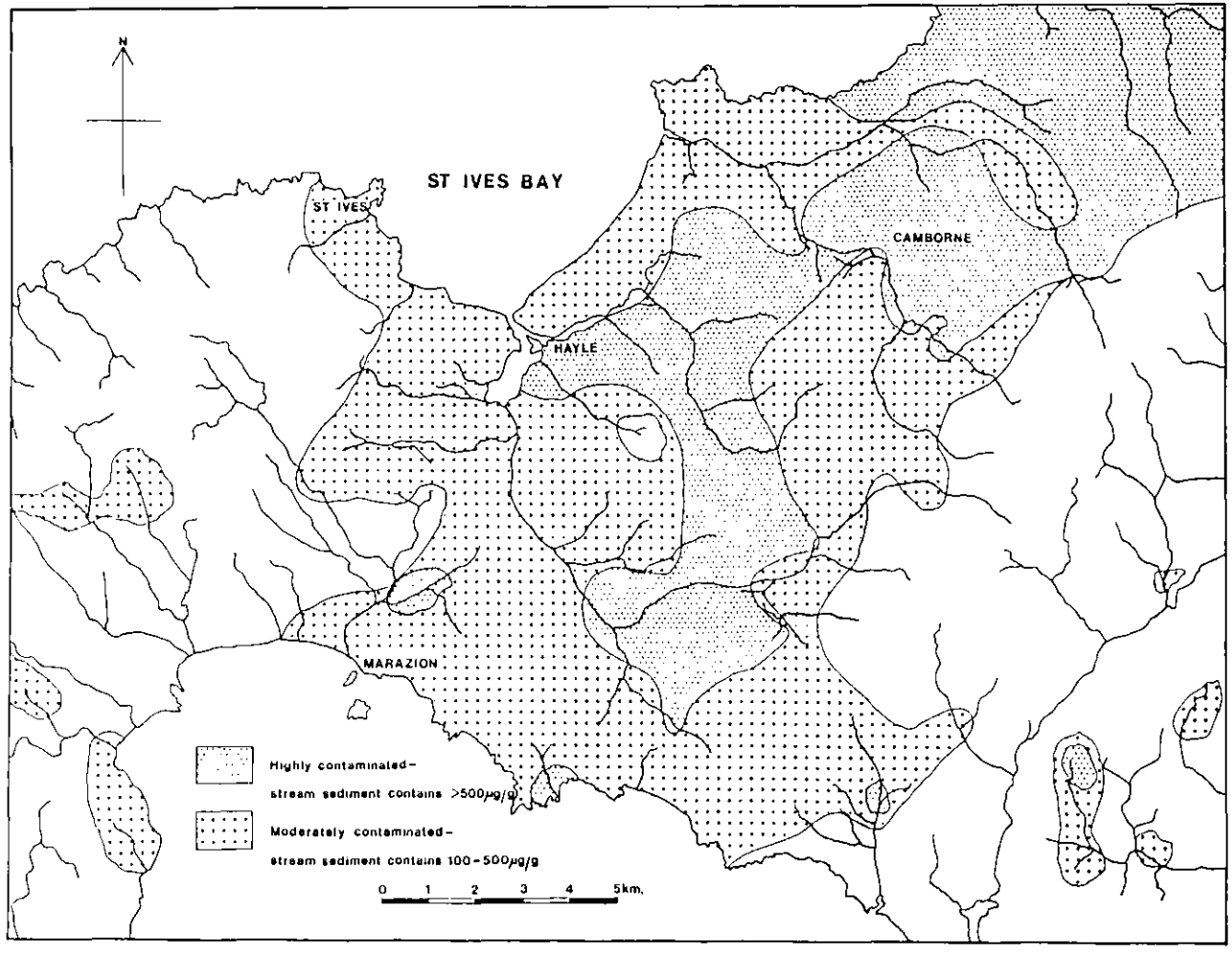


FIGURE 16. The distribution of copper in stream sediments of the Hayle/Camborne-Redruth district.

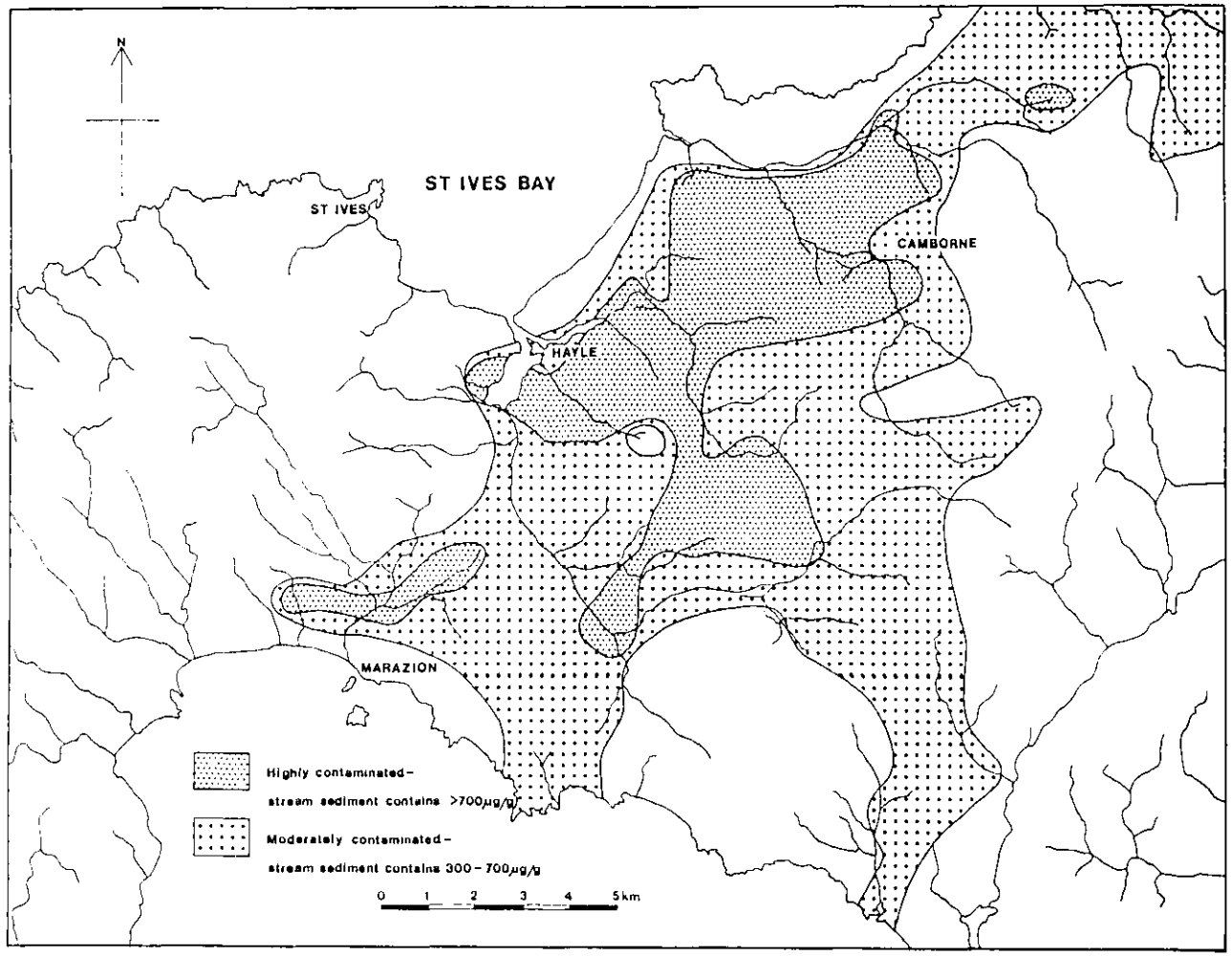


FIGURE 17. The distribution of zinc in stream sediments of the Hayle/Camborne-Redruth district.

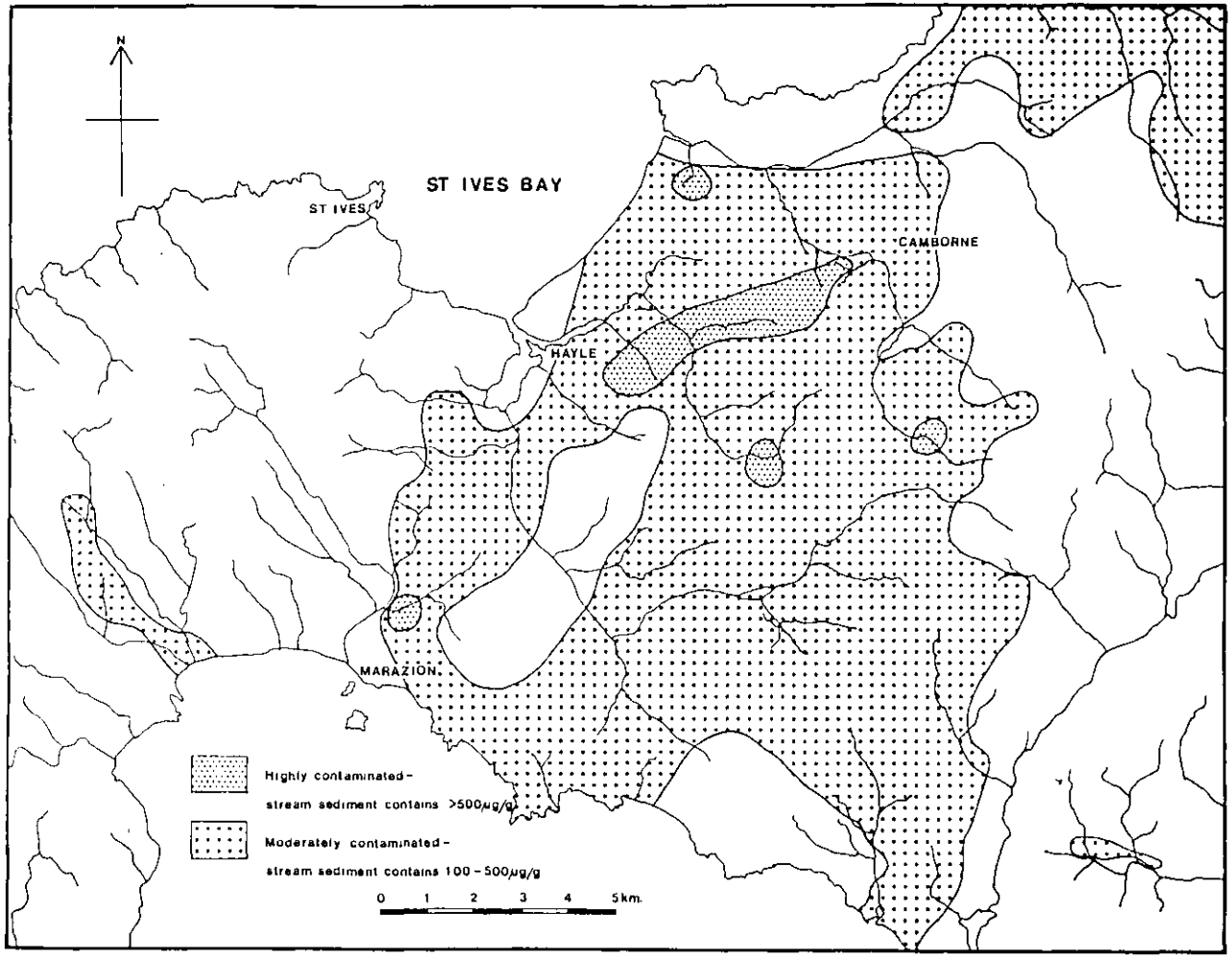


FIGURE 18. The distribution of lead in stream sediments of the Hayle/Camborne-Redruth district.

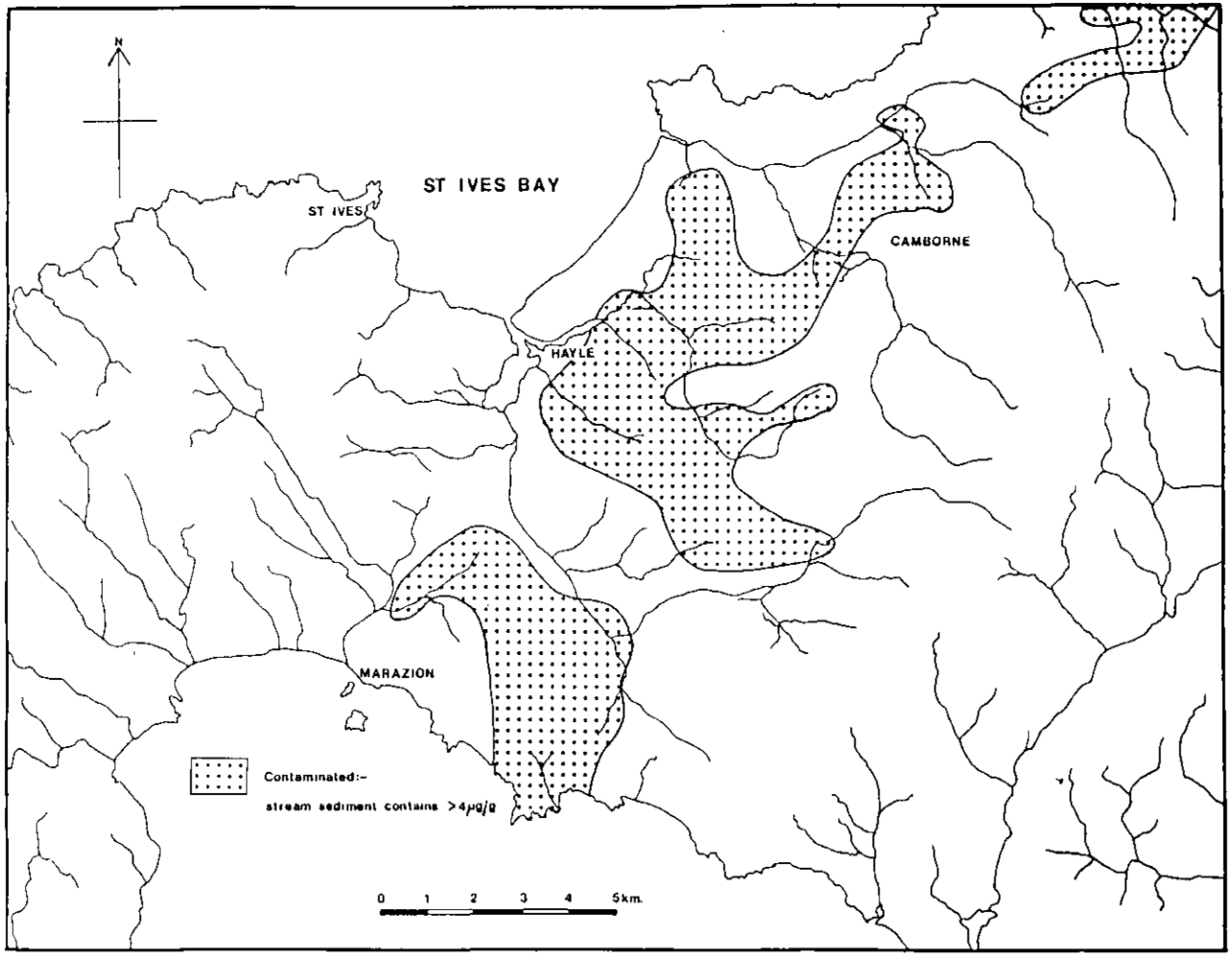


FIGURE 19. The distribution of cadmium in stream sediments of the Hayle/Camborne-Redruth district.

Element	Percentile											
	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	99%
As	2	3	4	6	8	9	10	12	15	20	27	66
Cu	5	6	9	12	14	17	19	22	25	31	40	72
Pb	10	13	17	20	23	26	30	36	46	66	99	259
Sn			1		2	3		4	5	9	22	1059
Zn	41	49	59	79	80	91	104	118	141	182	228	419

All values in μg/g

Table 15. Percentile concentrations of selected elements in stream sediments from data obtained from the Wolfson Geochemical Atlas of England and Wales (Webb et al., 1978).

selected in the survey as indicating contamination. The highest recorded Cd concentration is 18 μg/g located to the east of Hayle.

The continuity of the stream sediment values within the contaminated areas demonstrates considerable downstream movement of contaminated material, and also suggests that pollution may occur far beyond the immediate vicinity of the mining activity caused as a result of secondary redistribution. In addition, some elements occurred in minerals accessory to the main mine products and were released to the environment even though they may not have been economically exploited. Arsenic is a particularly good example of this latter point, being widely associated with Cu throughout the study area, although it was only mined extensively in the Camborne district (Table 11).

Whilst contamination can occur on the granites (e.g. Carn Brea, parts of the Godolphin granite, and the Lands End granite margin immediately south-west of St. Ives), this parent material is more usually associated with stream sediments which are lower in their As and metal content than the rest of the study area. This demonstrates the lesser importance of the granites in the production of Cu, Pb, Zn and As ores caused as a result of the mineral zoning (Figure 10). The mining districts of Trencrom Hill and Wendron which are both situated on the granite were thus worked mainly for Sn (Dines, 1956). A close examination of the granitic stream sediments located outside the designated moderate and highly contaminated areas of Figures 15-19, however, shows that the sediments are elevated in their trace-element composition when compared to the average values associated with granite rock samples (e.g. compare Tables 16 and 30). This may

	Element				
	As	Cd	Cu	Pb	Zn
n	56	67	52	61	72
Mean ($\bar{x}$)	34	1.2	48	41	89
Standard deviation (σ)	17.7	0.72	27.3	19.1	47.3
Median ($\bar{x}m$)	32	1	42	40	80.5
Range	8-80	nd-3	9-95	16-94	25-250

n.d. = not detected

All values in µg/g

Table 16. The trace-element composition of stream sediments draining the granites outside the designated moderate and highly contaminated areas.

indicate minor enrichment of the granite stream sediments by mineralisation and/or by a trace-element enriched parent material. The occurrence of such parent materials within south-west England has already been discussed in this Chapter.

Low concentrations of Co (<10 μg/g) were found in the follow-up survey in three areas extending over 47, 10 and 39 km^2, which correspond to the Lands End, Godolphin and Carnmenellis granite respectively. These low concentrations may be of agricultural significance since Co deficiency in sheep has long been recognised.on soils derived on the Dartmoor and Bodmin Moor granite located to the east of the study area (Patterson, 1938). Cobalt mineralisation itself was not widespread in south-west England since Dines (1956) records that only about 6 mines raised Co ores. To the north of Camborne, however, 2 samples (1160 and 857 μg Co/g) probably indicate the presence of mineralisation and/or contamination.

d) Conclusions of the Stream Sediment Follow-up Survey

A detailed stream sediment survey within the Hayle/Camborne-Redruth area has revealed widespread geochemical anomalies which are related to areas of mineralisation and mining contamination. In terms of area and the concentrations recorded, the anomaly for Cu and As is greater than for the metals Zn, Pb and, particularly, Cd. The extent of the anomaly for each metal is determined by the original mineral zoning within the lodes. This in its turn is an expression of the temperature of deposition and hence the distance of the deposit from the parent granite. Such granites are thus characterised by (usually) low concentrations when compared to the rest of the study area. However, even these concentrations may be slightly

elevated due to mineralisation and/or a trace-element enriched parent material.

Although the severest contamination coincides with the major mineralised and mined areas, the survey has shown that the contamination has spread to cover an area much larger than that occupied by the original workings. Furthermore, within the anomalous areas both metal and As values are consistently high. This suggests that soils may be severely affected well beyond the immediate vicinity of workings and associated dumps.

Low Co patterns define those areas underlain by granitic rocks where soils and herbage may well contain Co at concentrations associated with dietary deficiency in grazing sheep.

CHAPTER 4

THE DISTRIBUTION OF METAL CONTAMINANTS IN THE SOILS OF SOUTH-WEST ENGLAND

(I) INTRODUCTION

During the winter of 1977/78, four reconnaissance soil traverses were selected in the follow-up stream sediment survey area described in Chapter 3, with soil samples taken **systematically*** at approximately 1 km intervals (Figure 20). Soil samples were collected with a 2.5 cm diameter hand screw-auger, with each topsoil (0-15 cm) comprising six bulked sub-samples, and each subsoil (30-45 cm) comprising three bulked sub-samples. The samples were taken at points within a 40 m x 20 m rectangle sited in the centre of each field investigated. In the laboratory, each sample was analysed for Al, As, Ca, Cd, Co, Cu, Fe, Mn, Pb, Sn and Zn. Methods of sample preparation and analysis are outlined in detail in Appendix 1.

(II) THE TRACE-ELEMENT CONTENT OF SOILS IN THE HAYLE/CAMBORNE-REDRUTH AREA

a) Details of the soil traverses

The four traverses were selected according to the geochemical patterns defined by the follow-up stream sediment survey maps. Details relating to the four traverses are outlined below:

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* i.e. wherever the Ordnance Survey grid line bisected the line of the traverse.

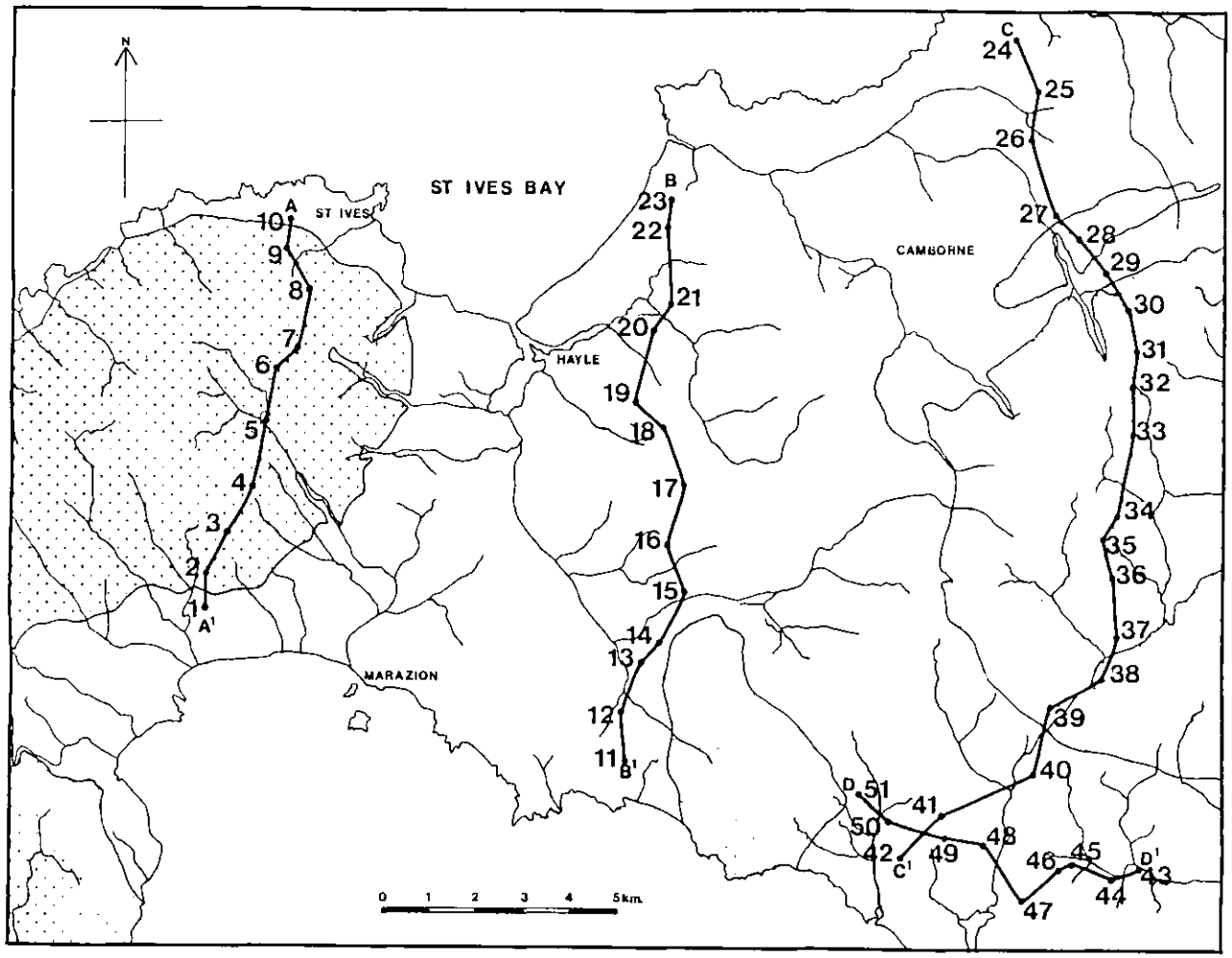


Figure 20. Location of sample sites on the four reconnaissance soil traverses. (Numbers refer to site location).

i) Traverse A/A': Soils on this north-south trending traverse were taken on granitic parent material apart from site 1 (slate) and site 10 (greenstone). All the soils were typical of their respective parent materials except that of site 1. Here, the soil was of a man-made or plaggen type belonging to the Ludgvan ungleyed soil phase (Staines, 1979). These soils are typified by their sandy loam topsoils which are greater than 40 cm in thickness. Accordingly, the 30-45 cm sample taken at this location does not represent a true subsoil.

The stream sediment maps compiled from the follow-up survey show that the traverse does not cross any moderately or highly contaminated areas. Apart from sites 6 and 9, all the soil samples of the traverse lie outside any known mineralised districts. Site 6 was sampled in a field adjacent to the now abandoned Giew mine which was once important for the production of Sn (Dines, 1956). Site 9 is located close to the former workings of St. Ives Wheal Allen, a relatively small Sn mine.

ii) Traverse B/B': This traverse cuts across the strike of the contamination as defined by the stream sediment follow-up survey maps. All samples were taken from locations on the Devonian slates apart from those of site 23 where wind blown calcareous sand provided the parent material. Many samples were taken within mineralised and mined areas; only sites 20-23 are outside the main mineralised ground.

iii) Traverse C/C': The northern extension of traverse C/C' surveys a heavily contaminated area, with soils sampled at sites developed on both mineralised slates and on the granite mass of Carn Brea. South of site 30 the mineralisation is not so widespread, although samples taken on the southern part of the Carnmenellis granite are within the mineralised district of Wendron where Sn was once important (Dines, 1956). South of the Wendron district, sample sites 40, 41 and 42 are all located on the Devonian slate parent material. These three sample sites are all situated within the area of traverse D/D'.

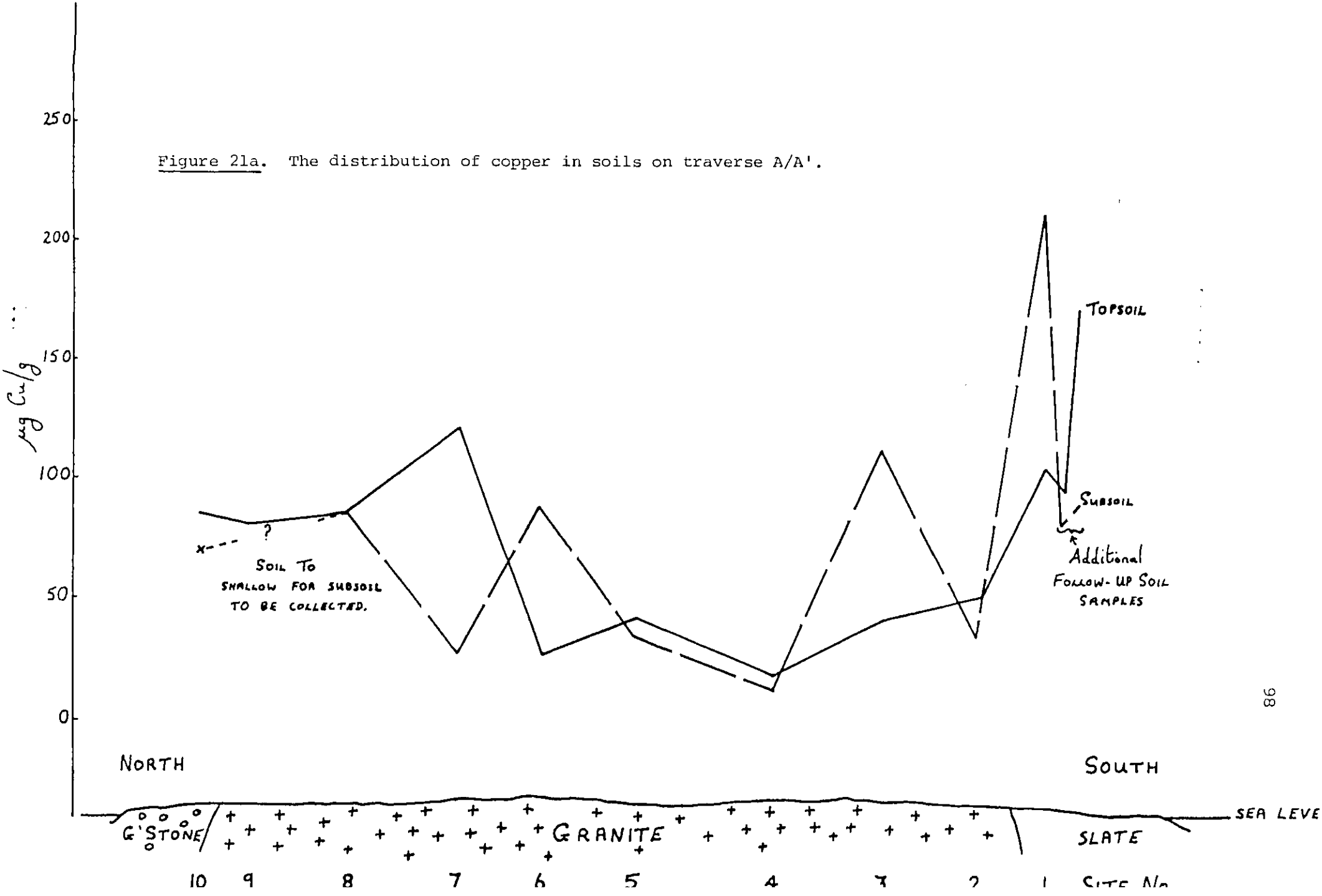
iv) Traverse D/D': Apart from site 48 (greenstone) all soils on this traverse have been formed from the underlying killas (slate) country rock. Although mineralised ground is situated immediately to the north of site 51, no signs of mining was observed at any of the other sample locations. Mineralisation is limited, and only a few small mines have operated within this area. Thus, stream sediment contamination is sporadic, with the concentrations being less enhanced than in the more severely contaminated and mineralised districts such as Camborne (Figures 15-19). According to Dines (1956), Pb appears to be the major metal extracted from mines of this area.

b) The trace-element content of soils on the traverses

i) Traverse A/A'

A number of trends in the metal distribution along traverse A/A' can be observed (Figures 21a-21k). Tin is of particular interest, since the concentrations of this element found along this apparently uncontaminated and, comparatively, unmineralised traverse exceeds those concentrations quoted as being normal for soils (Table). On

Figure 2la. The distribution of copper in soils on traverse A/A'.



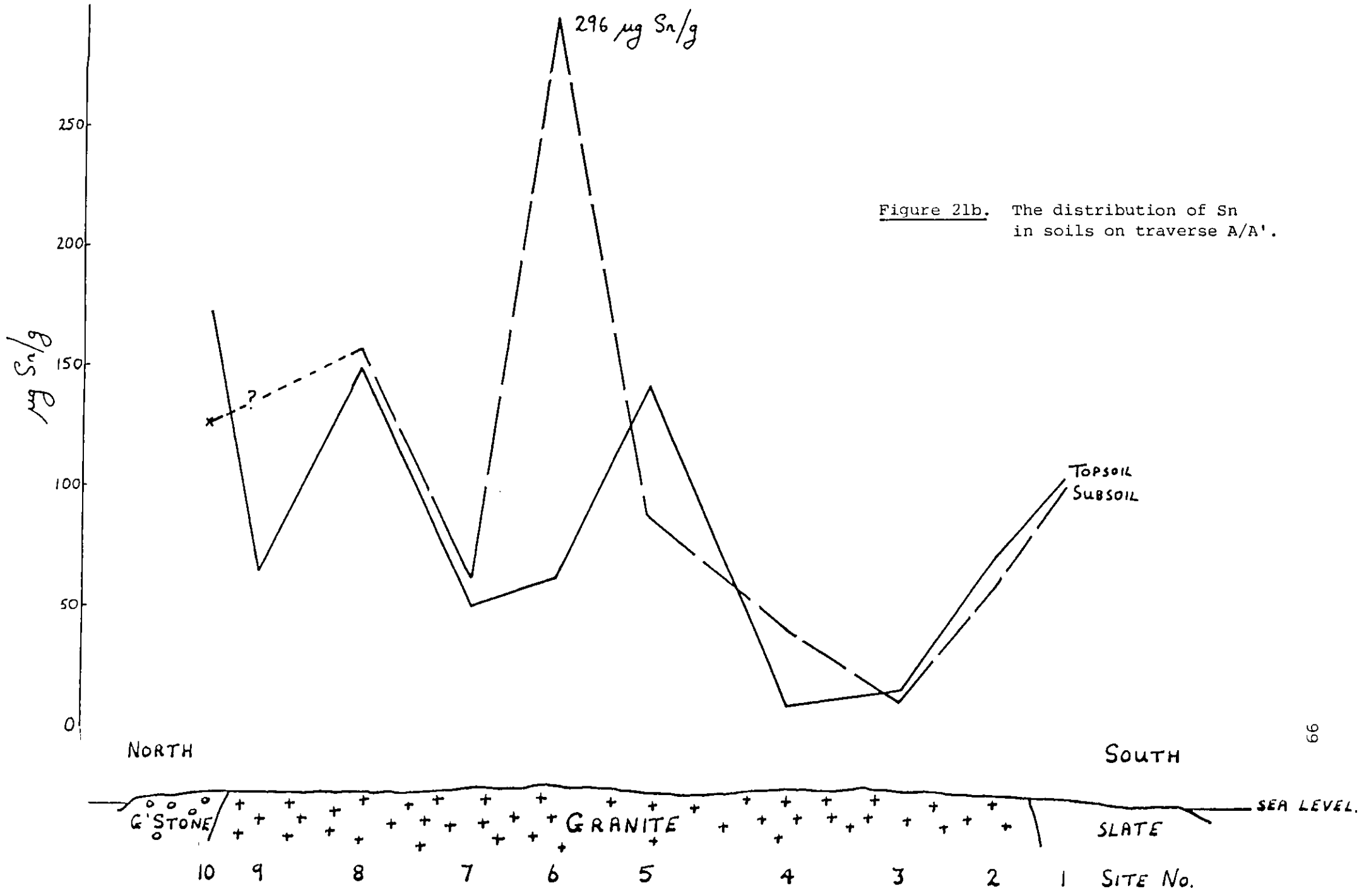
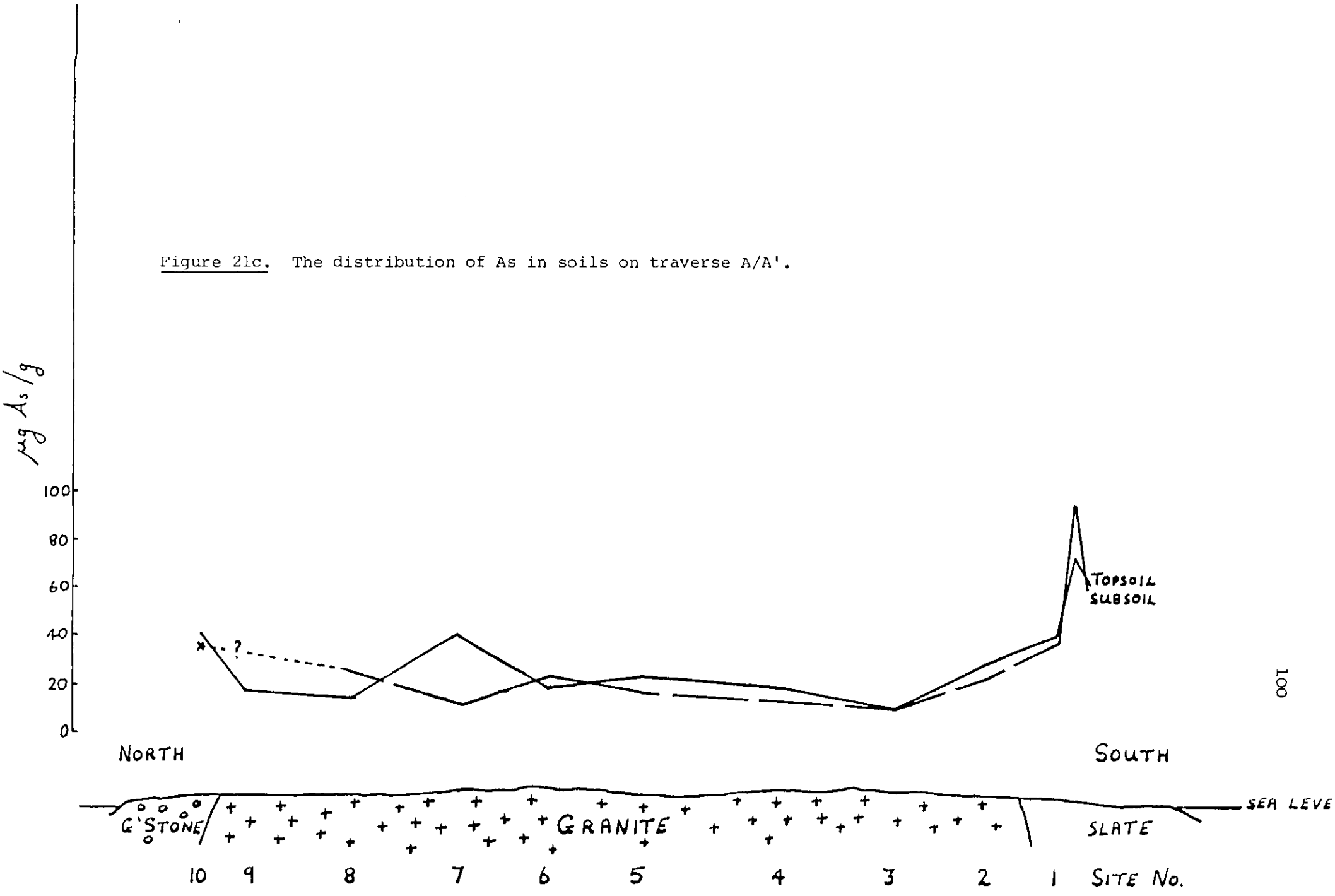


Figure 21b. The distribution of Sn in soils on traverse A/A'.

Figure 21c. The distribution of As in soils on traverse A/A'.



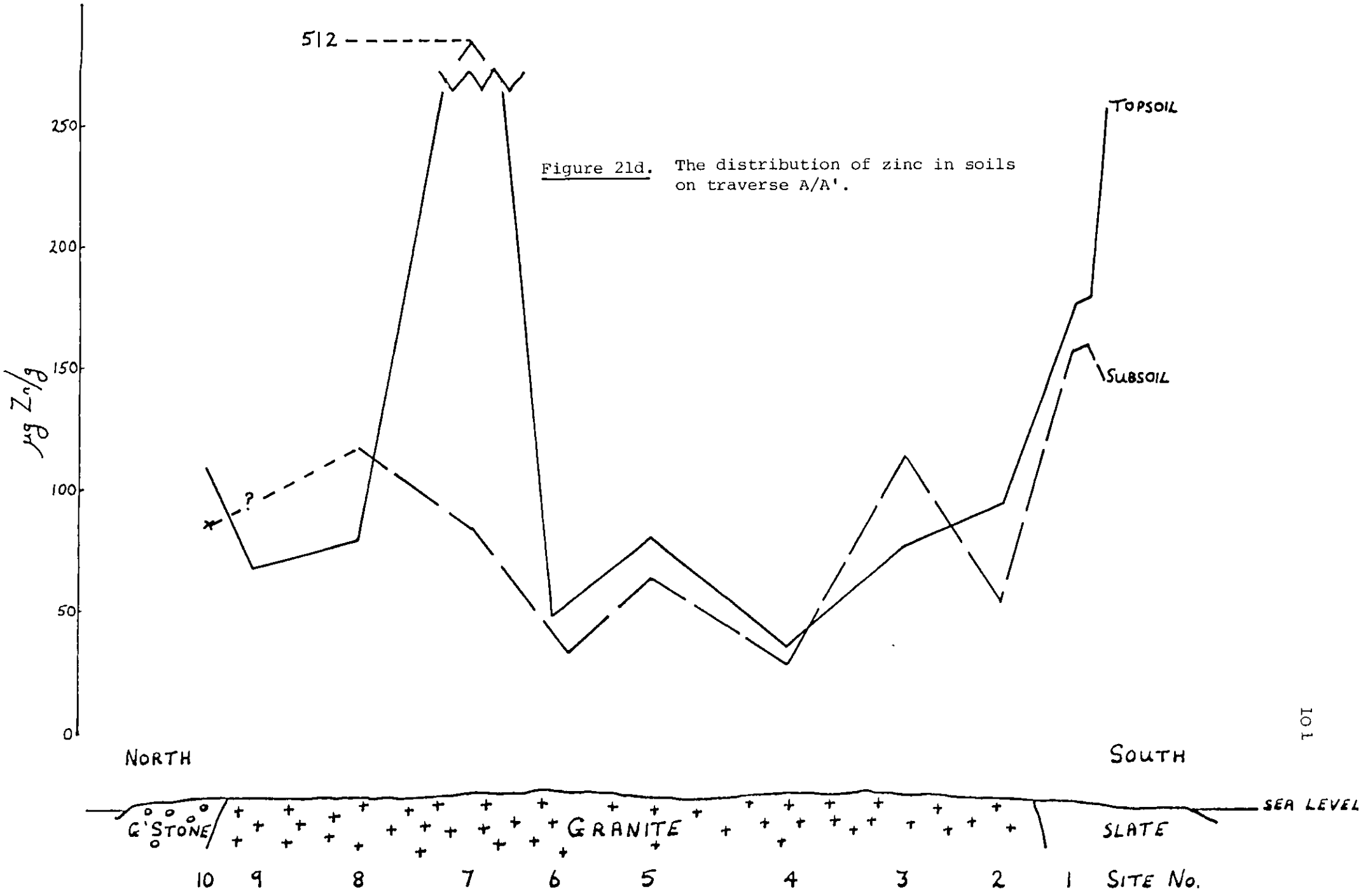


Figure 21d. The distribution of zinc in soils on traverse A/A'.

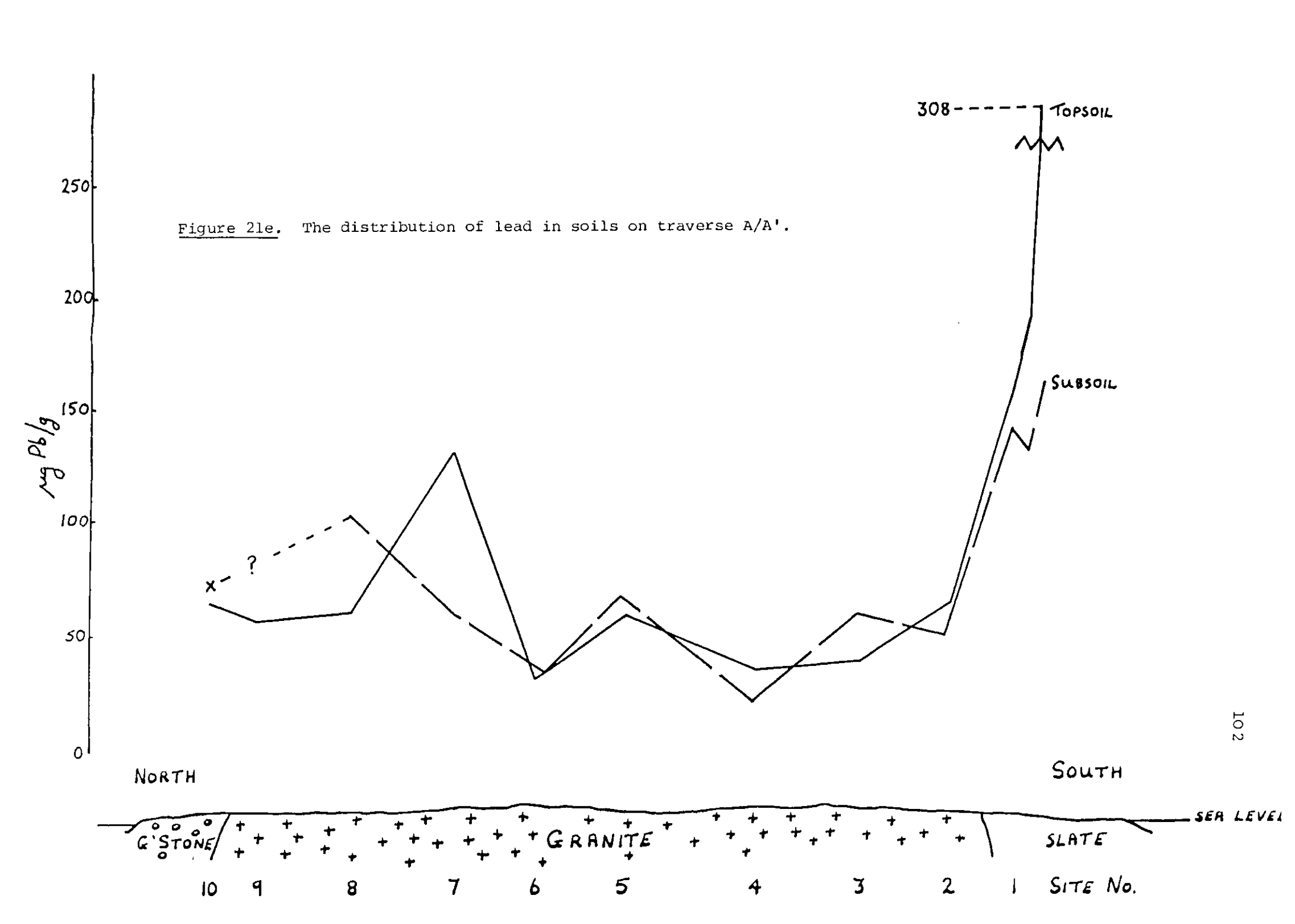


Figure 21e. The distribution of lead in soils on traverse A/A'.

Figure 21g. The distribution of Co in soils on traverse A/A'.

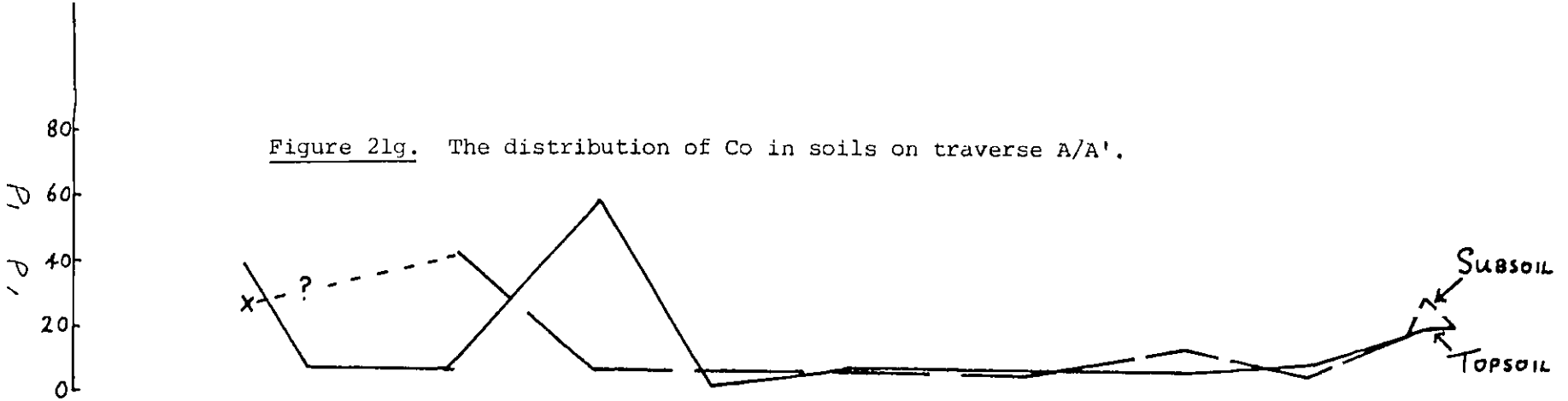
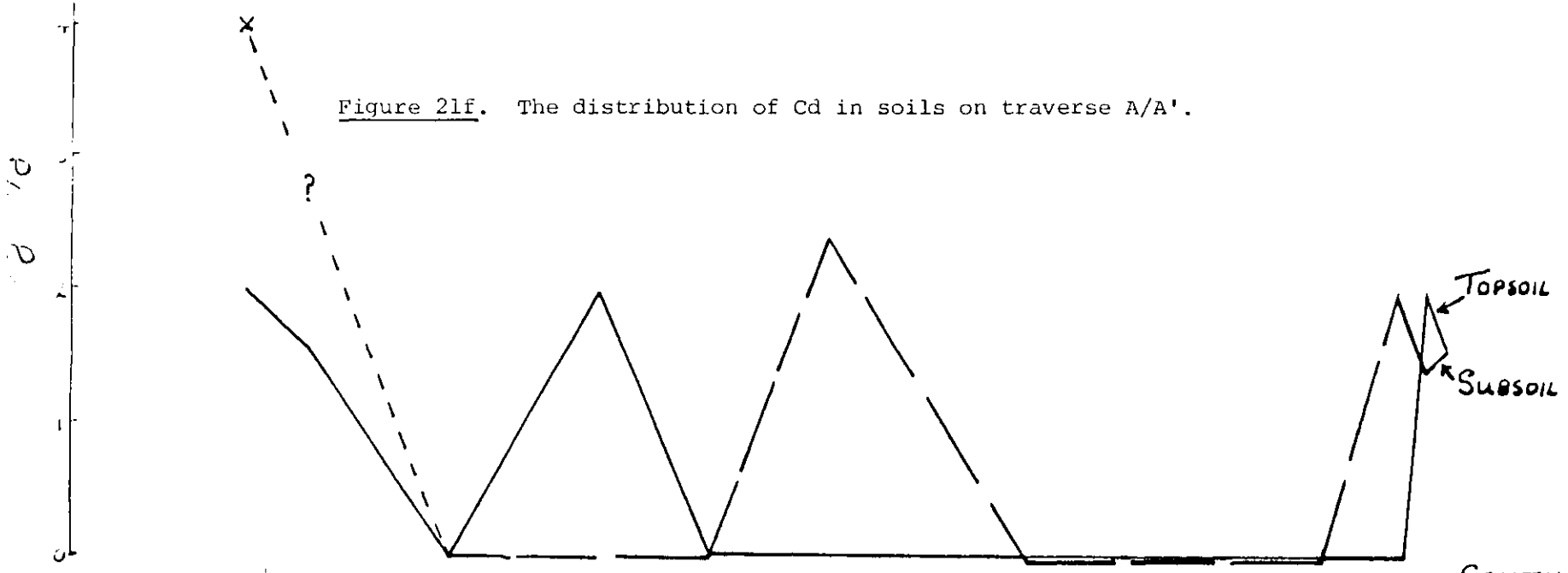
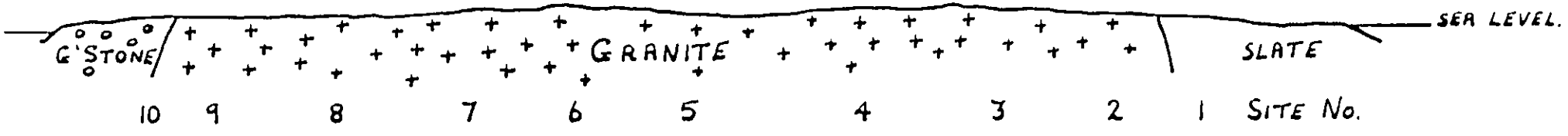


Figure 21f. The distribution of Cd in soils on traverse A/A'.





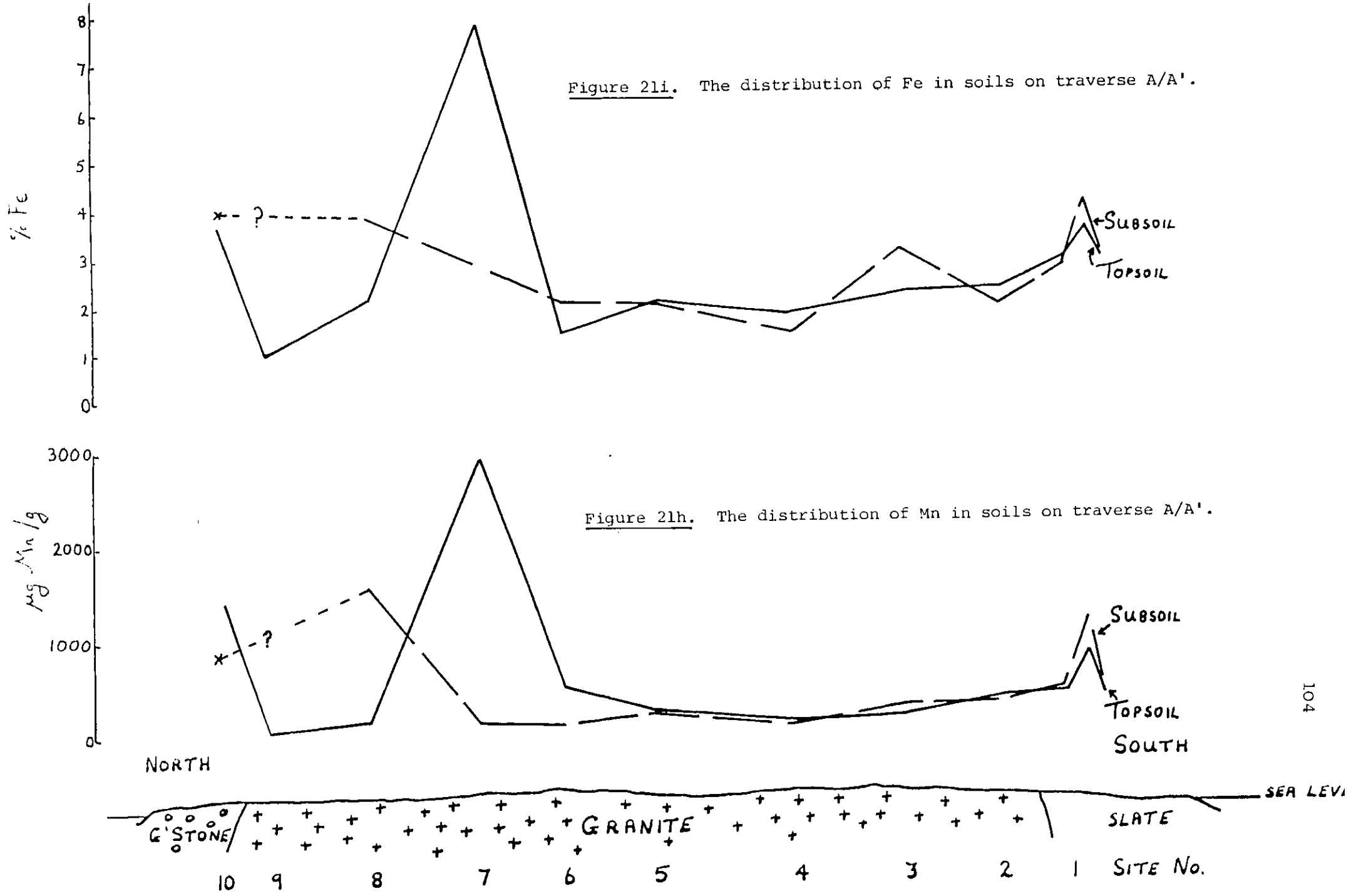


Figure 21i. The distribution of Fe in soils on traverse A/A'.

Figure 21h. The distribution of Mn in soils on traverse A/A'.

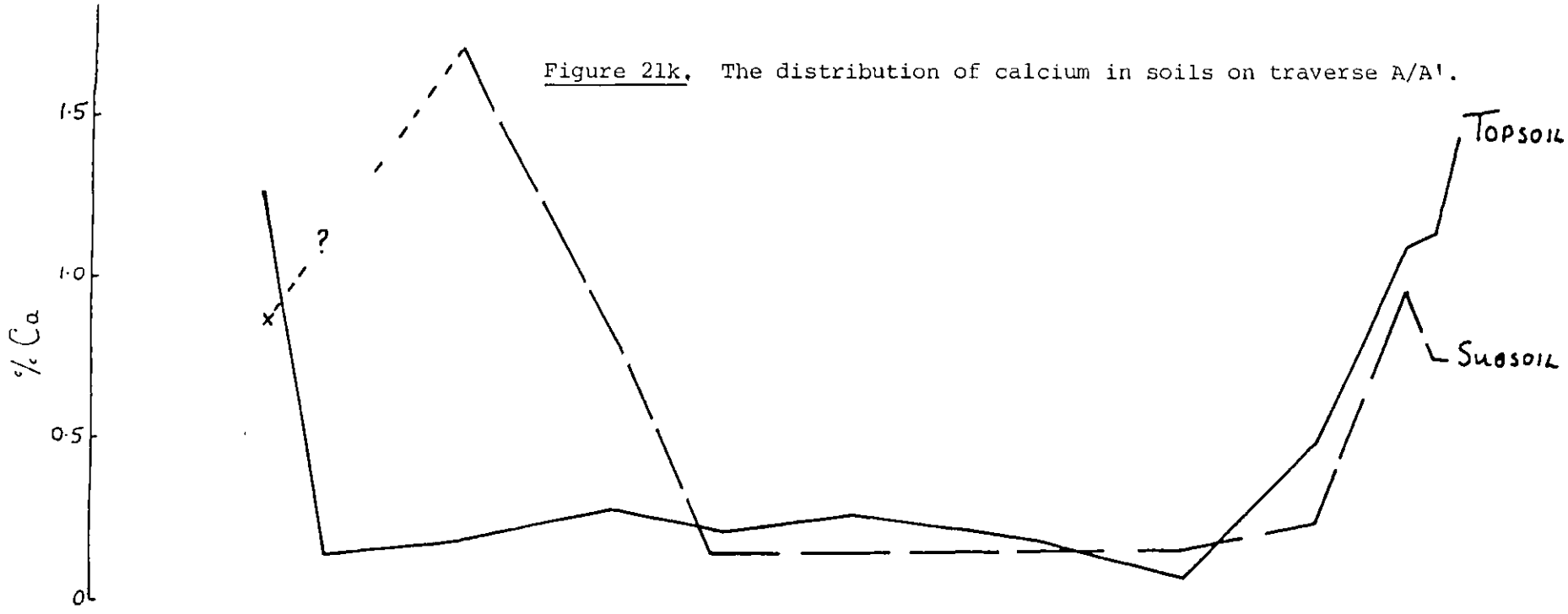


Figure 21k. The distribution of calcium in soils on traverse A/A'.

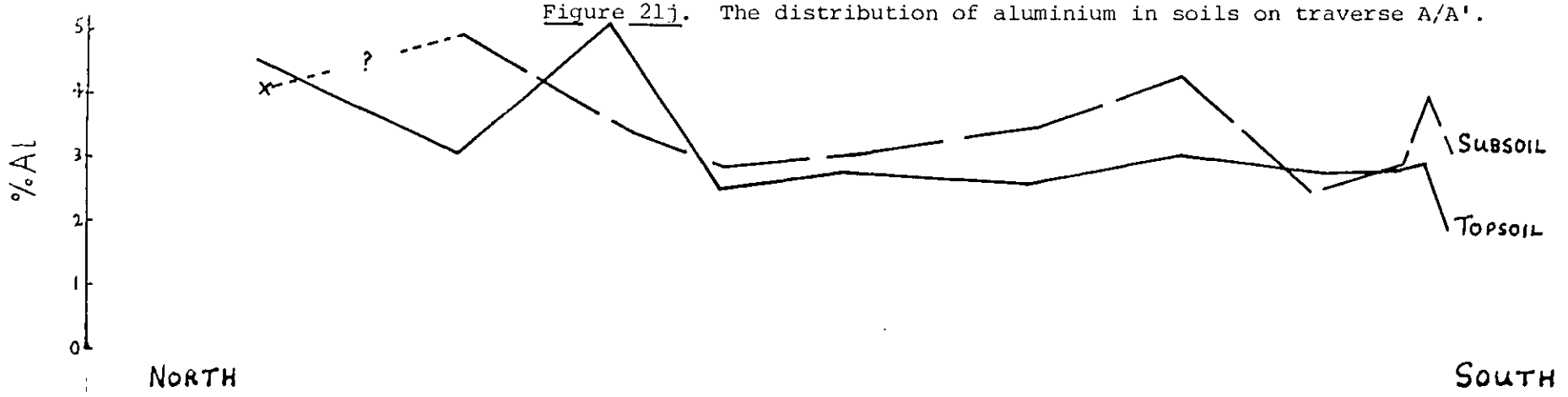
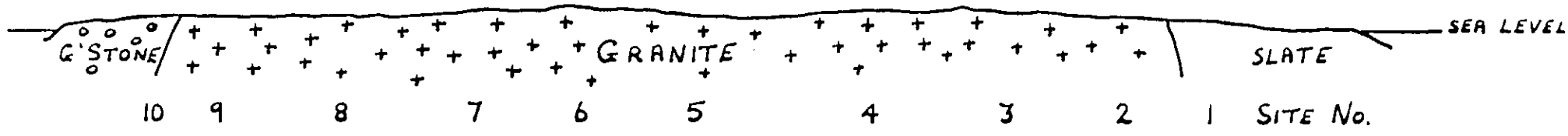


Figure 21j. The distribution of aluminium in soils on traverse A/A'.



the granite, the subsoil at site 6 is particularly enriched (296 μg Sn/g) and reflects the mineralisation at this location, although no corresponding large anomaly is observed in the topsoil sample (63 μg Sn/g). Furthermore, with the exception of Cu in the subsoil at this site (88 μg Cu/g), no other element appears to be associated with the mineralisation. Tin concentrations elsewhere in the granite soils are still elevated despite being significantly lower than the subsoil concentration recorded at site 6. Table 17 records the range and median concentrations of all the elements analysed from the granite soils of traverse A/A'. The median concentration of Sn in both the topsoils and subsoils is 64 μg/g. This concentration exceeds the amounts of Sn which are associated with uncontaminated soils (Table 3). Arsenic appears to be similarly enhanced, with the topsoil median concentration of 20 μg/g and the subsoil median concentration of 18 μg/g being approximately 3 times greater than the average soil. As concentrations presented in Table 3. Further comparisons between Table 3 and Table 17 indicate that the granite soils have median concentrations of Cu and Pb which exceed typically normal amounts. Concentrations of Zn and Co, however, appear normal, whilst Al, Fe and Mn concentrations are well below average.

Figure 21 reveals that the top 15 cm of the granite soils usually contain higher concentrations of As, Co, Cu, Pb and Zn than the underlying subsoils. Topsoil enrichment of these and other elements (Mn, Fe, Cd and Al) is only substantial, however, at site 7. Patches of disturbed and bare ground together with traces of mineralisation on stones found within the soil indicate that the

		Al(%)	As	Ca(%)	Cd	Co	Cu	Fe(%)	Mn	Sn	Pb	Zn
Median ($\bar{x}m$)	Topsoil (n=8)	3.02	20	0.25	-	8	46	2.12	320	64	58	72
	Subsoil (n=7)	3.60	18	0.21	-	8	34	2.12	280	64	60	58
Range	Topsoil	2.60-5.20	12-41	0.14-0.56	N.D.-2.0	4-60	19-121	1.44-7.88	120-2960	12-150	32-132	31-505
	Subsoil	2.68-5.00	13-26	0.17-1.72	N.D.-2.4	8-44	13-113	1.48-3.84	160-1560	14-296	24-160	23-116

All values in µg/g unless specified.
N.D. = Not detected. Detection limit for Cd = 0·24 µg/g.
Median concentrations for Cd could not be determined.

Table 17. The range and median concentrations of elements analysed from the granite soils of Traverse A/A'.

anomaly at this site may be due to contamination. First edition Ordnance Survey maps published in 1888 show the presence of a mine shaft at this location. However, it is surprising that no topsoil enrichment of Sn is observed at this site. Furthermore, the analysis of soils sampled in three fields immediately surrounding site 7 indicates the isolated nature of the anomaly (Table 18). Trace-element concentrations at all three sites approximate to, or are even lower than, the median granite soil concentrations of traverse A/A' presented in Table 17.

The median concentrations of Ca recorded from the granite sites ($\bar{x}m$ = 0.25% in topsoil and 0.2.% in subsoil) reflect the low Ca status of these soils. However, enhanced Ca subsoil concentrations were recorded at sites 7 (8,400 µg/g) and 8 (17,200 µg/g). The cause of this enrichment has not been determined.

In comparison to the granite soils, elevated As and metal concentrations occur within the plaggen soil at site 1 and the brown earth at site 10. Further sampling of the plaggen soil was additionally undertaken to confirm the anomaly at site 1; the locations of these 2 additional sites are noted on Figure 21a. Comparing the man-made soils to those of the granite hills, the plaggen soils contain elevated concentrations of As, Cu, Pb, Zn, Ca and, to a lesser extent, Fe, Co, Cd and Mn. Tin concentrations are also elevated compared to the amounts considered normal in agricultural soils (Table 3), although the concentrations—like the amounts of Al found in these soils—are similar to those found within the soils of the granites.

		Al(%)	As	Ca(%)	Cd	Co	Cu	Fe(%)	Mn	Pb	Zn
Field A	Topsoil	3.00	24	0.296	1.2	N.D.	24	1.52	200	48	31
	Subsoil	4.00	61	0.292	2.0	8	18	2.44	140	36	27
Field B	Topsoil	2.36	13	0.228	1.6	N.D.	19	1.60	160	32	24
	Subsoil	2.86	17	0.146	2.0	8	27	2.24	180	22	24
Field C	Topsoil	2.16	14	0.480	1.6	N.D.	11	1.36	80	24	21
	Subsoil	3.92	19	0.244	1.6	8	12	2.64	168	36	30

N.D. = Not detected. Detection limit for Co = 1·2 µg/g
All values in µg/g unless specified. No analysis was undertaken for Sn.

Table 18. Analytical results of soils sampled from three fields adjacent to the anomaly disclosed at site 7.

A comparison of the trace-element content of the soil developed on greenstone at site 10 to those of the granite hills shows that elevated amounts of As, Al, Ca, Cd, Co, Fe and Mn occur in the former, whilst concentrations of Cu, Pb, Sn and Zn approximate to the highest concentrations found within the granite soils. Comparisons between acidic and basic igneous rocks have demonstrated a considerable difference between the trace-element content of both rock types (Chapter 1). This partially explains the disparity observed in the trace-element content of the greenstone and granite soils. The high concentrations of Sn observed at site 10 (173 µg/g in the topsoil; 126 µg/g in the subsoil), however, also indicates that this site has been affected by contamination or mineralisation.

ii) Traverse B/B'

Concentrations of the trace-elements found within the soils of traverse B/B' are, in general, higher than those of traverse A/A', and thus reflect the mineralisation and contamination of this district (Figures 22a-22k). The order of enrichment based on a comparison between the concentrations found within the soils of traverse B/B' and the average soil concentrations as presented in Table 3 is Sn > As > Cu > Zn > Pb; the main anomalies for Pb are limited to only two locations, site 13 (topsoil concentration = 268 µg/g) and site 19 (subsoil concentration = 376 µg/g). This order of enrichment reflects, in turn, the abundance of each element in the mineral ores of this particular area. Cadmium concentrations in soils of this traverse are also elevated. A maximum concentration of 3.6 µg Cd/g is recorded at sites 16 and 21 (Figure 22f). Such enrichment can be attributed to the close association of Cd with

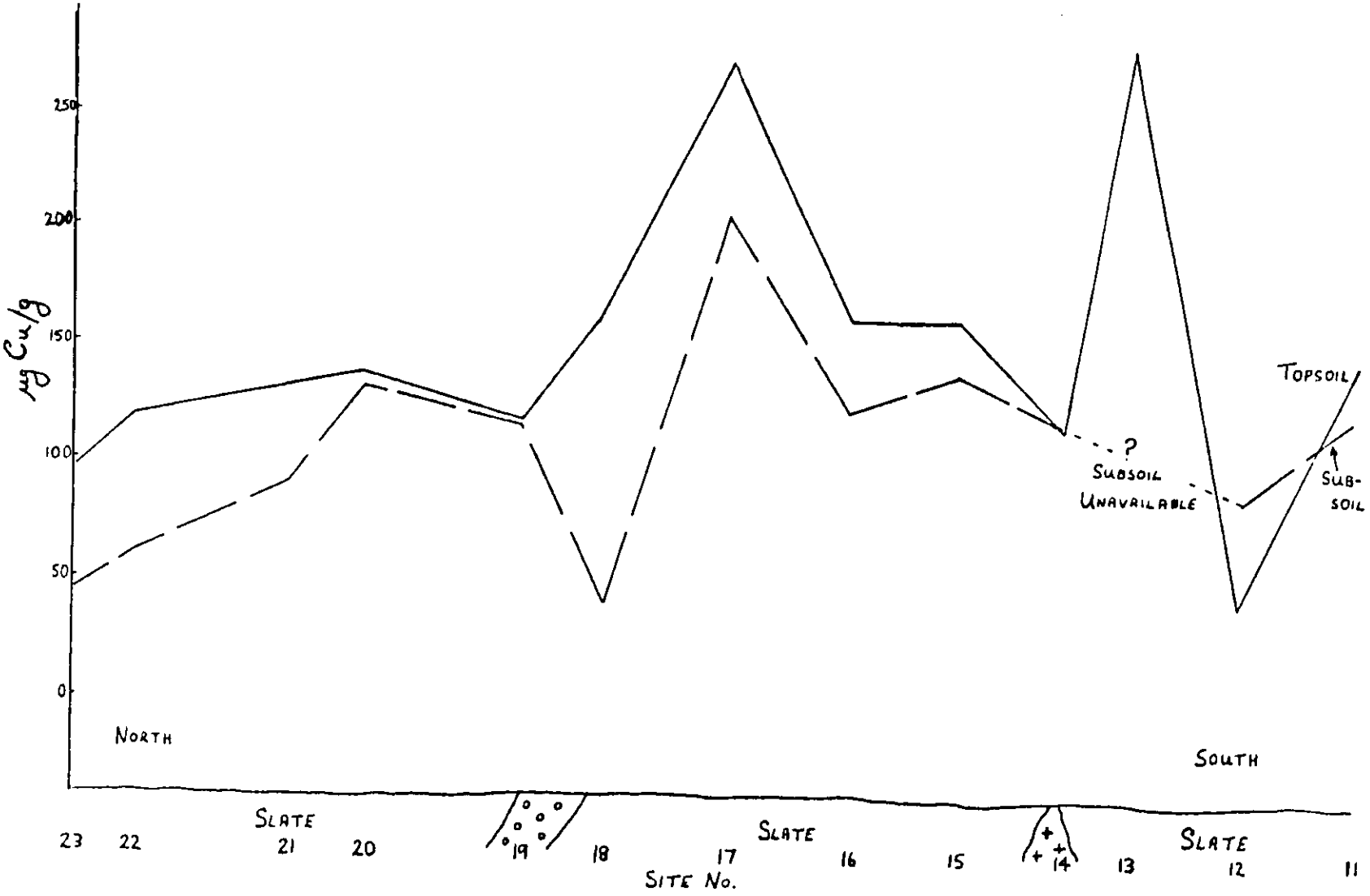


Figure 22a. The distribution of copper in soils on traverse B/B'.

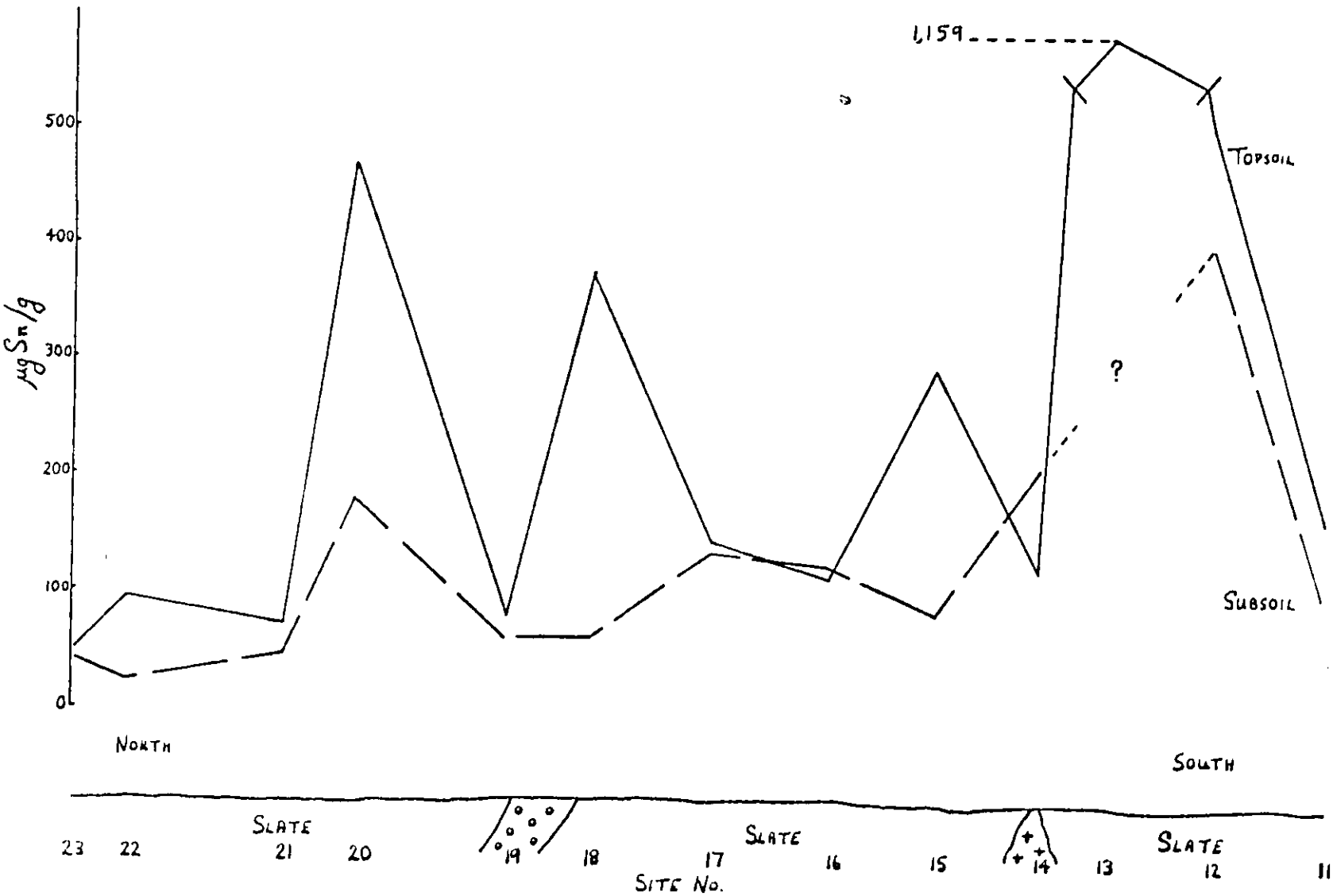


Figure 22b. The distribution of tin in soils on traverse B/B'.

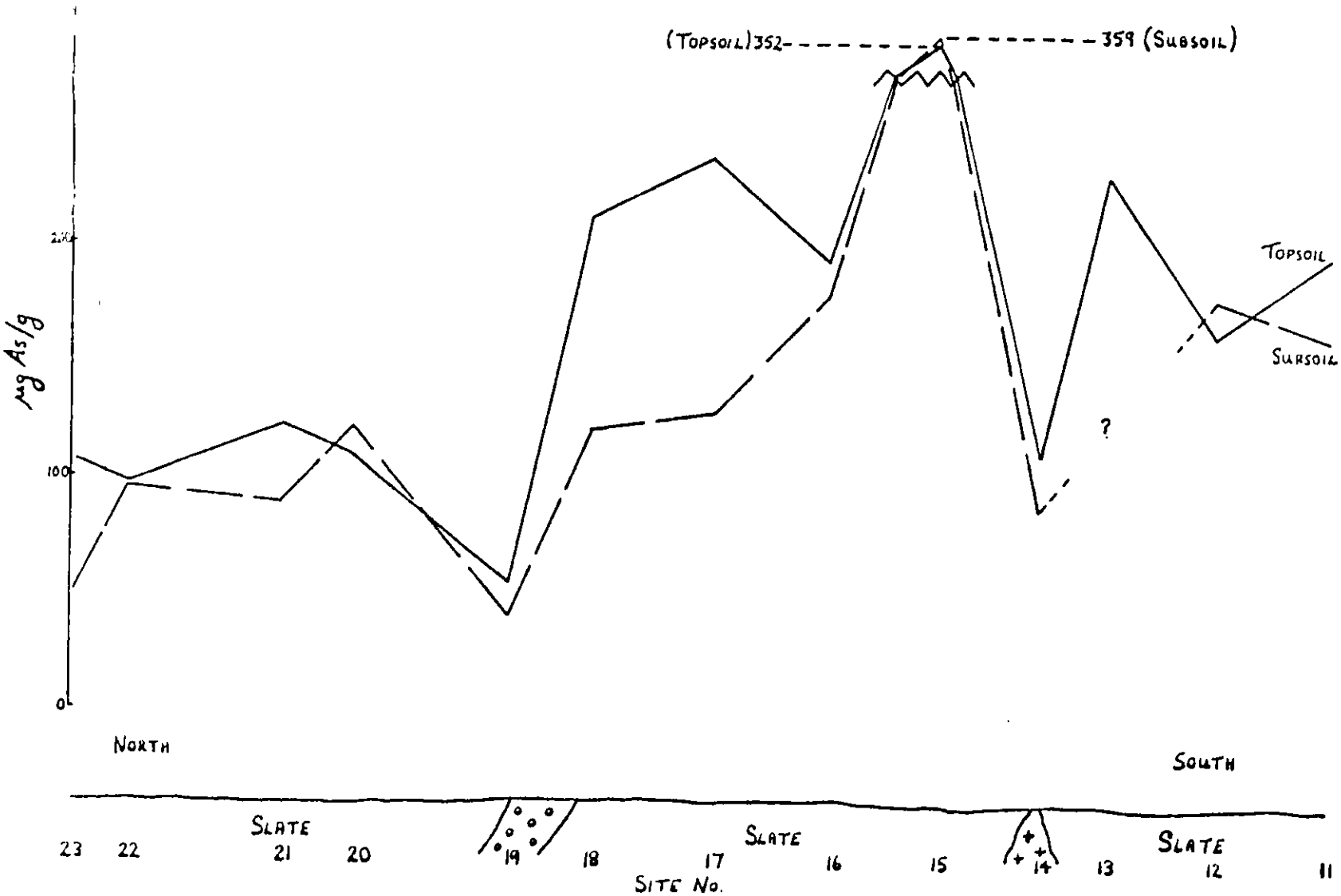


Figure 22c. The distribution of arsenic in soils on traverse B/B'.

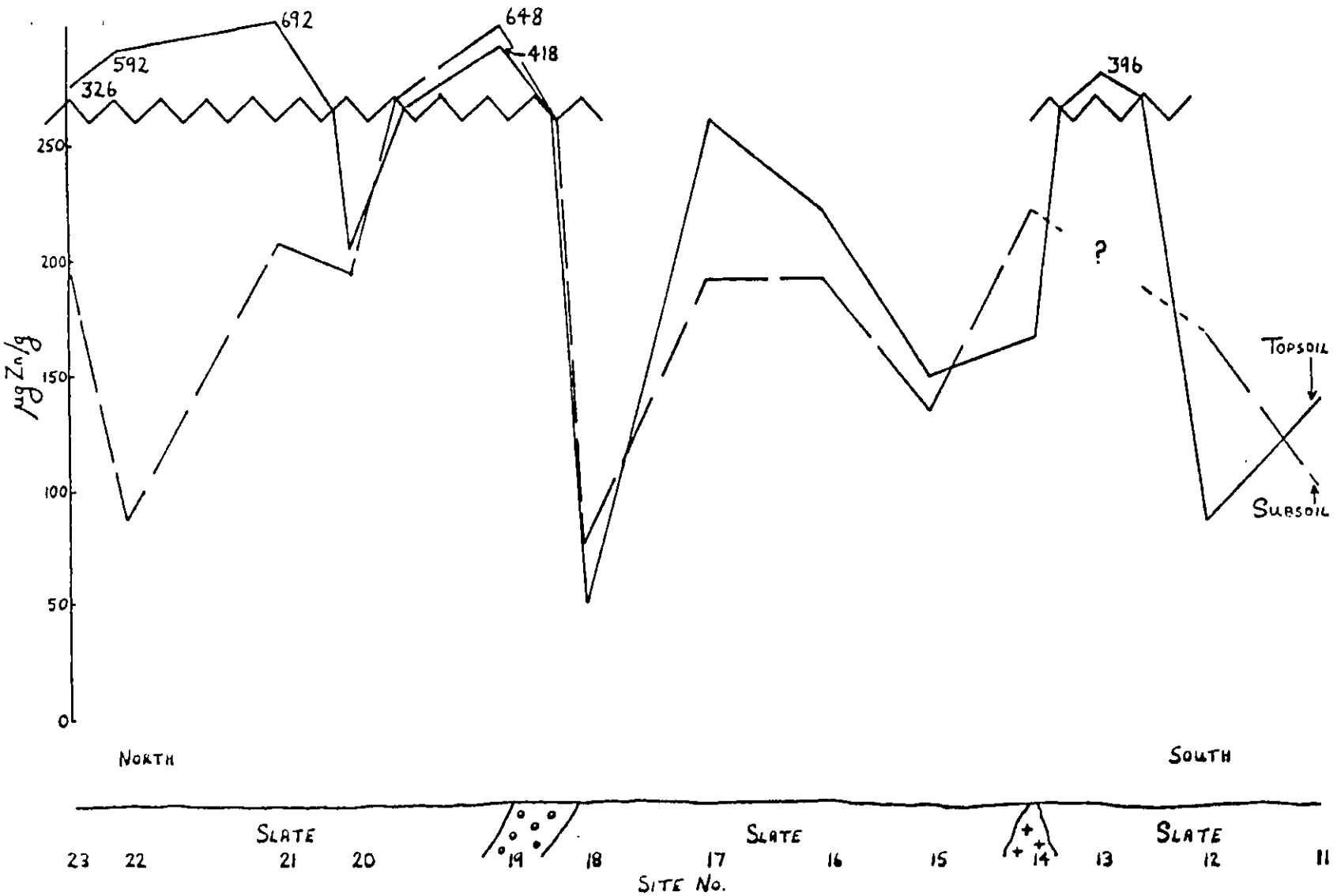


Figure 22d. The distribution of zinc in soils on traverse B/B'.

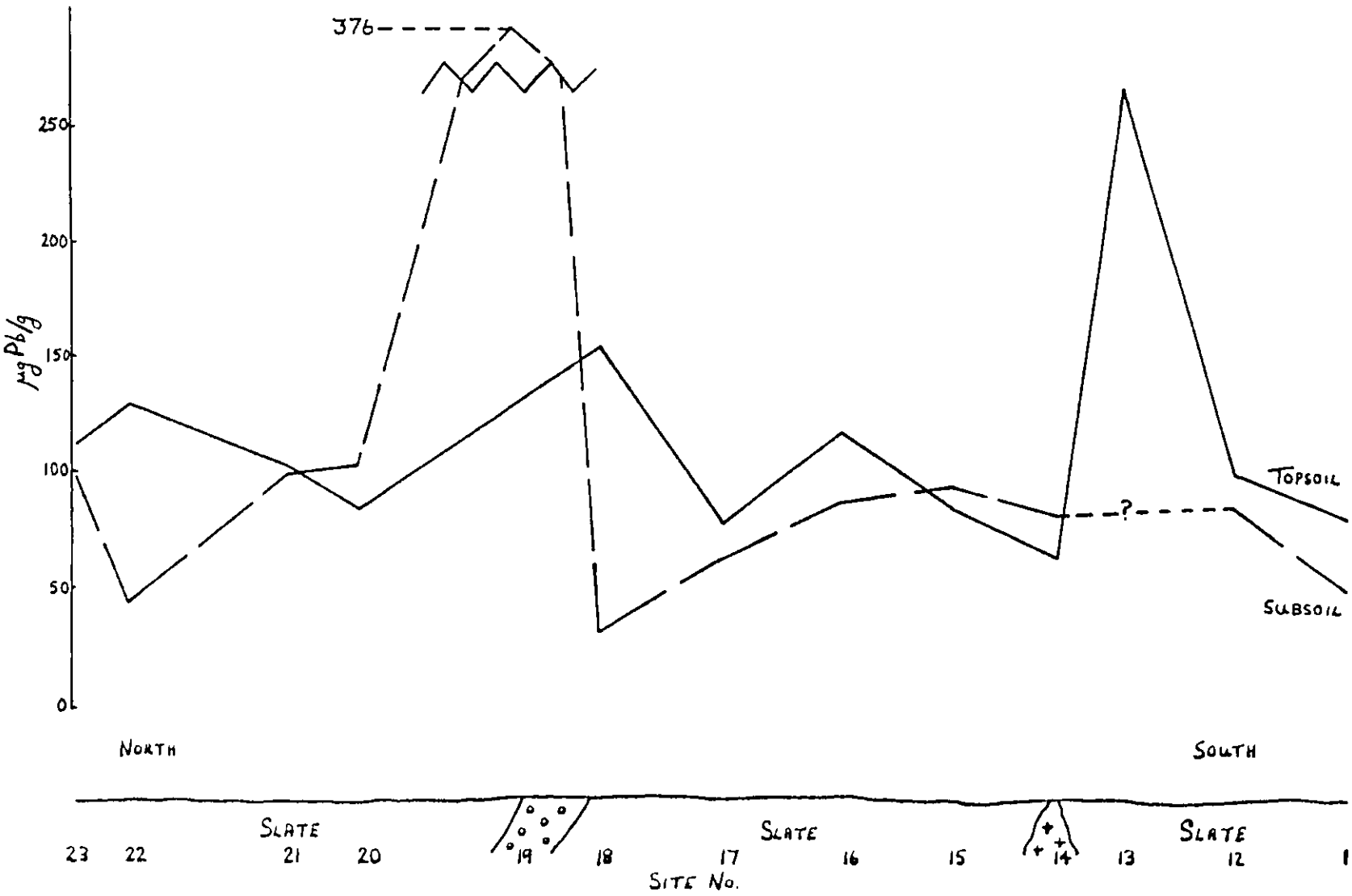


Figure 22e. The distribution of lead in soils on traverse B/B'.

Figure 22g. The distribution of cobalt in soils on traverse B/B'.

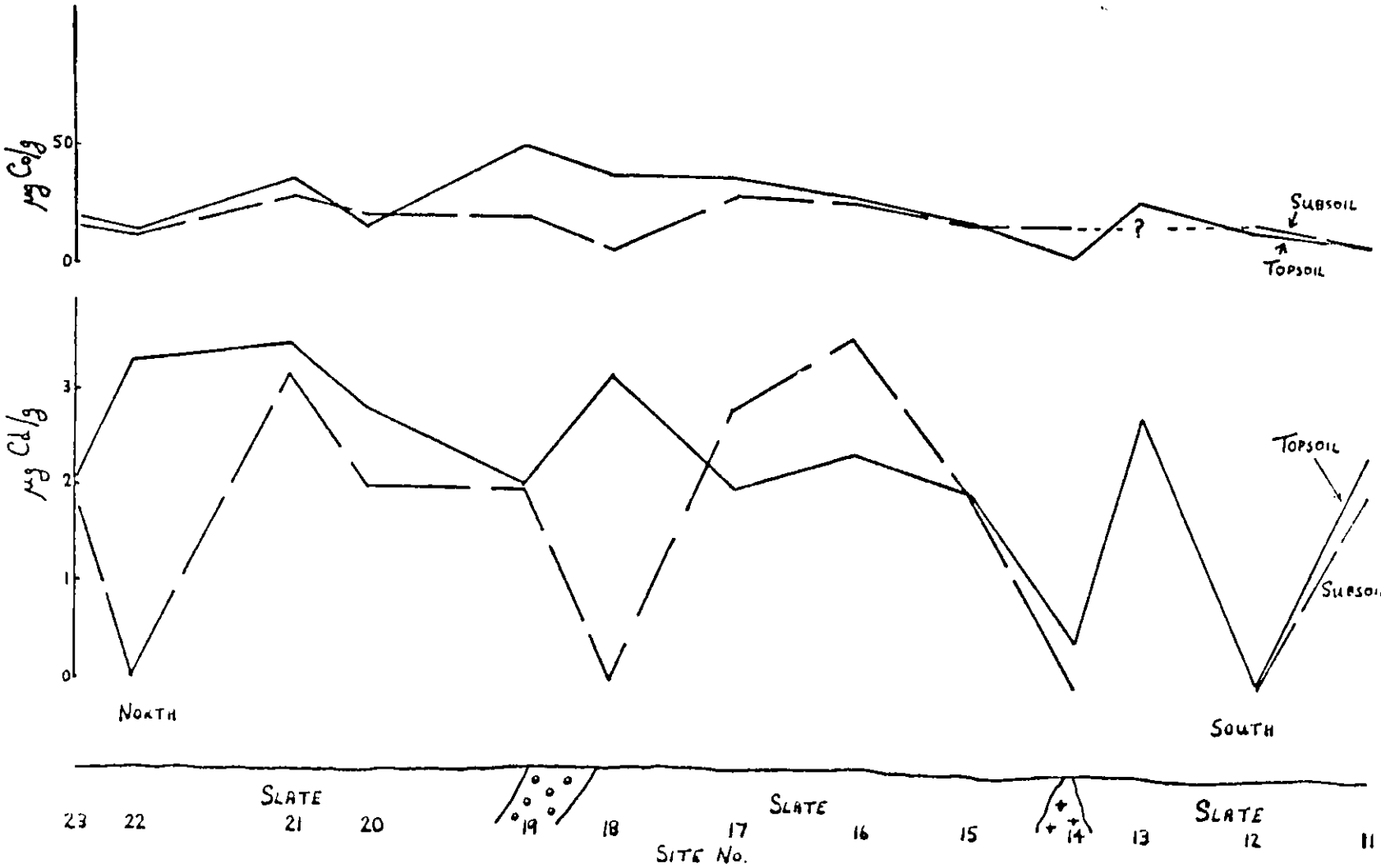


Figure 22f. The distribution of cadmium in soils on traverse B/B'.

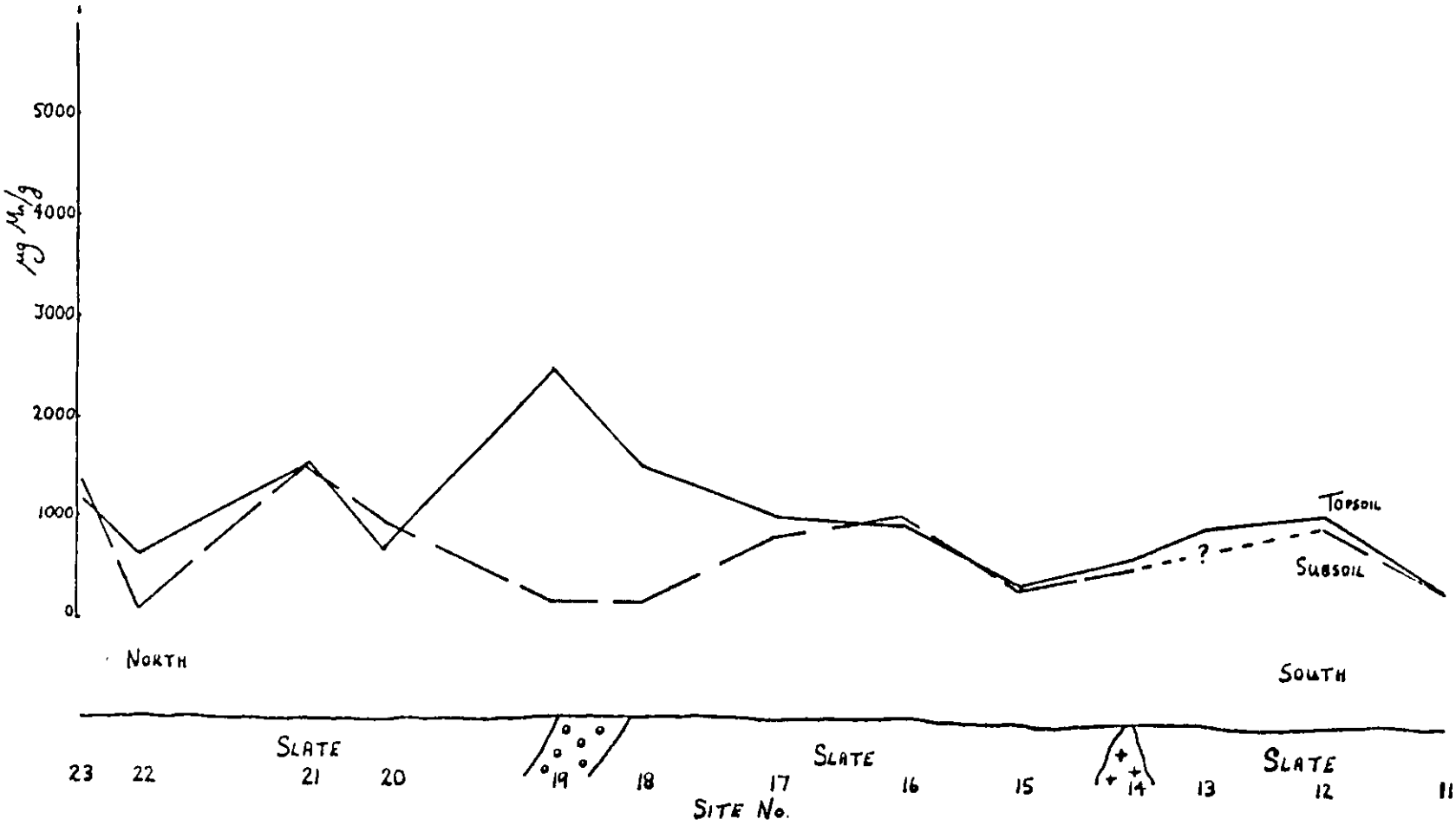


Figure 22h. The distribution of manganese in soils on traverse B/B'.

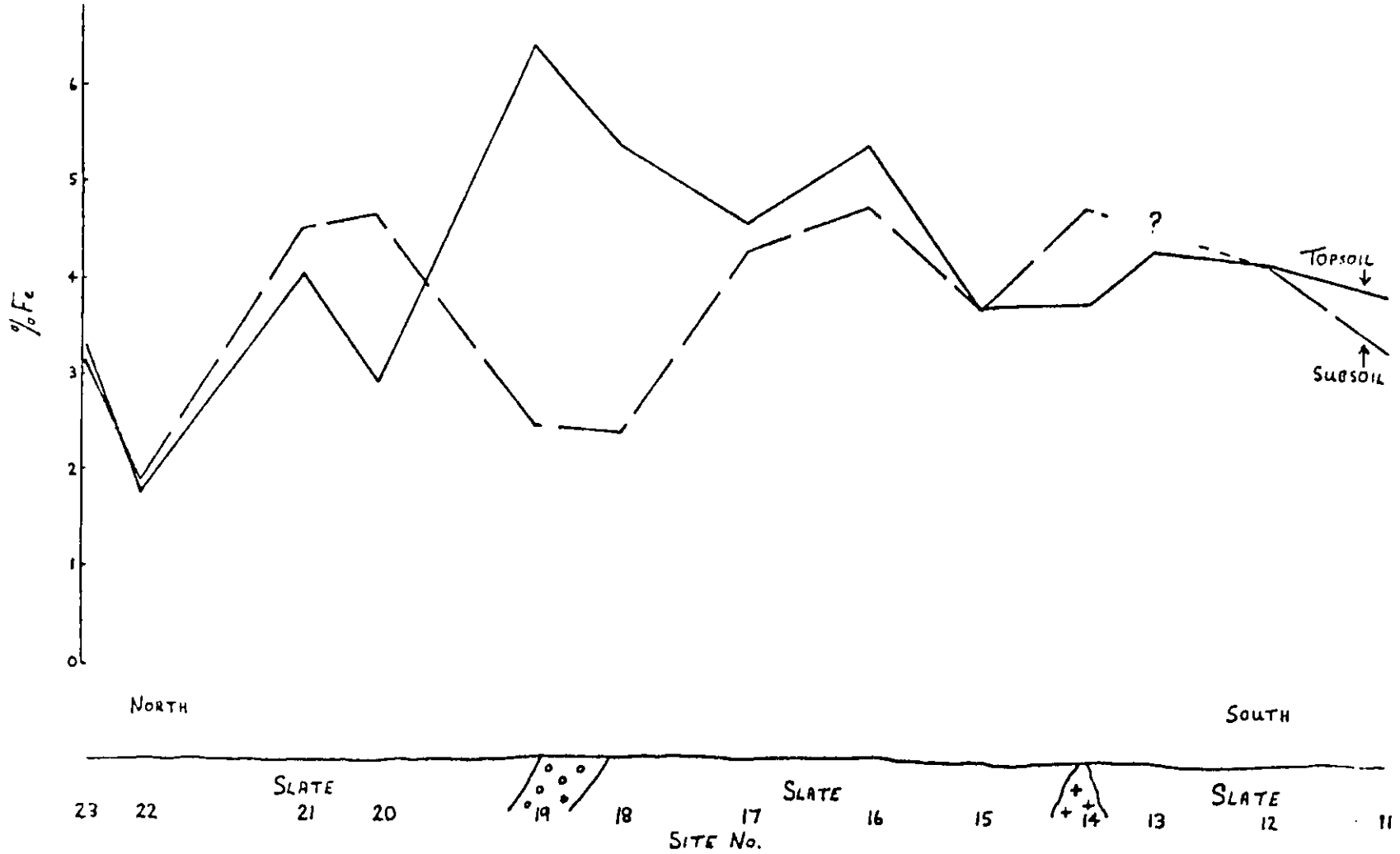


Figure 22i. The distribution of iron in soils on traverse B/B'.

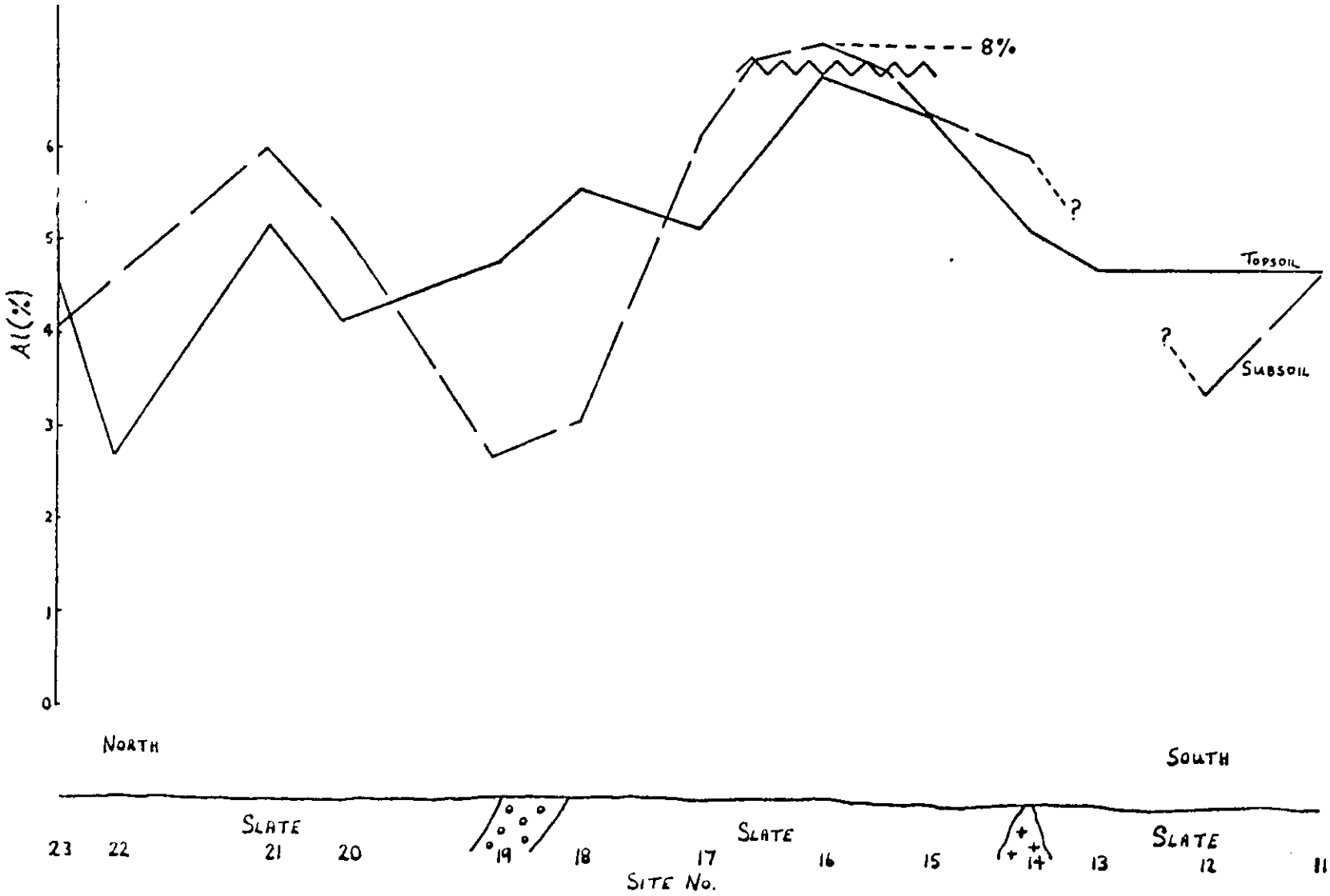


Figure 22j. The distribution of aluminium in soils on traverse B/B'.

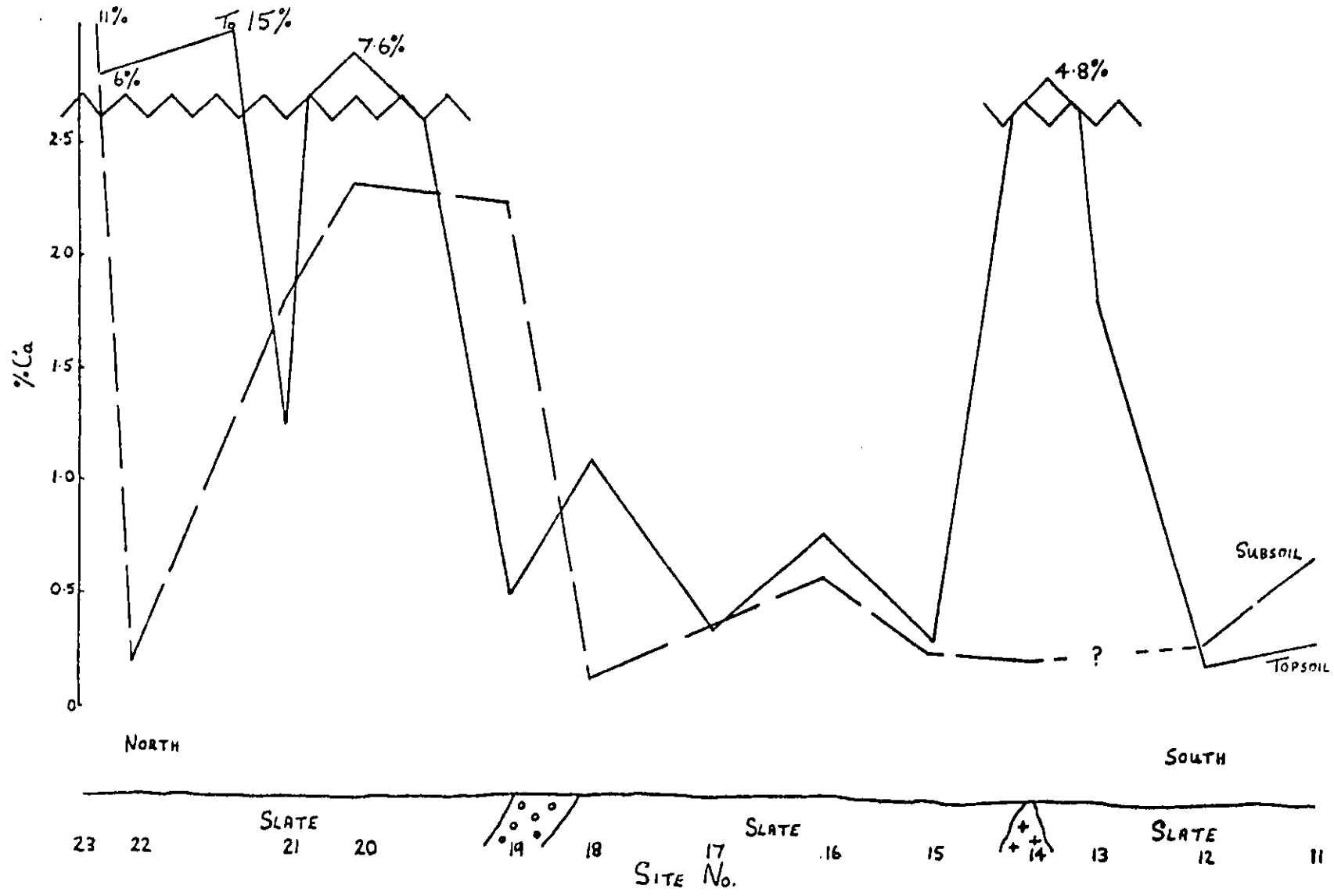


Figure 22k. The distribution of calcium in soils on traverse B/B'.

the metallic ores of the district. Research undertaken by Bird (1981) has revealed a particularly close association between sphalerite (ZnS) and Cd (Table 19).

When examined in detail, each element on the traverse appears to have its own characteristic pattern of dispersion or source, since peaks in concentration of the various elements do not necessarily coincide. However, when the general patterns are examined, some similarities in distribution are found. The highest soil concentrations of Sn (1159 µg/g at site 13), As (359 µg/g at site 15) and Cu (280 µg/g at site 13) occur within the main belt of mineralised ground (Figures 22a, b and c). Both the topsoil and subsoil concentrations of these 3 elements, however, clearly decrease to the north of the traverse which lies outside the major mineralised area. In contrast, whilst elevated Zn concentrations are found within the mineralised district - with a maximum concentration of 396 µg Zn/g occurring at site 13 - the highest concentrations of this element occur in the topsoils north of site 19. A maximum concentration of 692 µg Zn/g was recorded from this traverse at site 21 (Figure 22d).

Despite the close geochemical association between Zn and Cd observed earlier in this section, no corresponding large increase in Cd content is observed in the topsoils at these northern locations on traverse B/B'. However, both topsoils and subsoils at these sites contain extremely high amounts of Ca (Figure 22k). The elevated concentrations of this element (maximum 15% at site 22) are attributed by Staines (1979) to the influx of wind blown calcareous dune sand which borders the coastline of St. Ives Bay. Research, described in detail in section IIc of this chapter, has

Sample Location	Sample Type	As	Cu	Pb	Zn	Cd	Fe(%)	Ca(%)	Al(%)
Wheal Jane	Sphalerite (ZnS)	61	2,283	180	426,000	1,174	10.3	0.02	0.1
"	Chalcopyrite ($CuFeS_2$)	887	118,648	76	53,600	208	11.8	5.60	1.2
"	Arsenopyrite (FeAsS)	32,710	12,100	293	76,800	191	9.5	6.40	0.6
"	Sphalerite and pyrite ($ZnS + FeS_2$)	116	8,600	644	218,000	504	19.0	0.01	N.D.
Geevor	Arsenopyrite (FeAsS)	15,028	6,336	41	1,272	2	10.2	4.00	0.8
"	Galena (PbS)	171	85,240	27,040	190,400	476	3.7	0.38	0.1
"	Chalcopyrite and pyrite ($CuFeS_2 + FeS_2$)	2,460	138,980	274	3,418	11	22.1	0.18	3.0

N.D. = Not determined
All values in μg/g except where indicated.

Table 19. Total metal and arsenic concentrations in ore samples obtained from mines operating in South-west England (data from Bird, 1981).

confirmed the Ca status of the dune sand, but has also indicated the comparatively low amounts of Zn associated with the sand (Table 22). The Zn anomalies found within these soils, therefore, cannot be attributed to this source. The soils at sites 20, 21 and 22 are mapped by Staines (1979) as calcareous brown earths of the Highweek calcareous topsoil phase. The wind blown sand particularly affects the upper Ap horizons of these soils, and considerably influences their pH and texture (Table 12). Calcium is leached from the topsoil, however, to geochemically influence the underlying subsoils (Figure 22k). Staines (op. cit.) records that these soils are consequently calcareous throughout the entire profile. The soil at site 23 is a typical sand pararendzina belonging to the Towans reclaimed phase map unit. Here, the 30-45 cm sample consists of the calcareous shell sand belonging to the C horizon. This explains the very high concentration of Ca (11%) found at this site at depth.

The Ca status of these soils contrast distinctly with those south of site 19 where Ca concentrations rarely exceed 1%. A Ca anomaly, however, is evident at site 13. Analysis of the ores from the province of South-west England has indicated the presence of Ca associated with the lode-stuff (Table 19). The Ca anomaly of 4.8% at site 13, therefore may be caused by mining contamination or mineralisation. Alternatively, the high concentration of Ca recorded at this site may be attributable to agricultural management.

The highest concentrations of Al recorded in the traverse survey occur in the subsoils of the brown podzolic soils (Dartington series) at sites 14-17 (Figure 22j). A maxima of 8% Al was recorded from site 16. The distribution of Al within these soils contrast with the brown earths (Highweek series) at sites 11, 12, 18 and 19 which all have greater concentrations of the element in the topsoils. The Fe distribution within soils of the traverse does not exactly correspond to that of Al, since higher Fe concentrations in the topsoils compared to the 30-45 cm samples are observed in the brown podzolic soils (Figure 22i). A slight topsoil enrichment of Fe is also evident in the brown earth soils. It is possible that the distribution and concentrations of Fe observed in these soils are affected by the mineralisation and contamination. Concentrations of Fe in ores from South-west England may exceed 22% (Table 19).

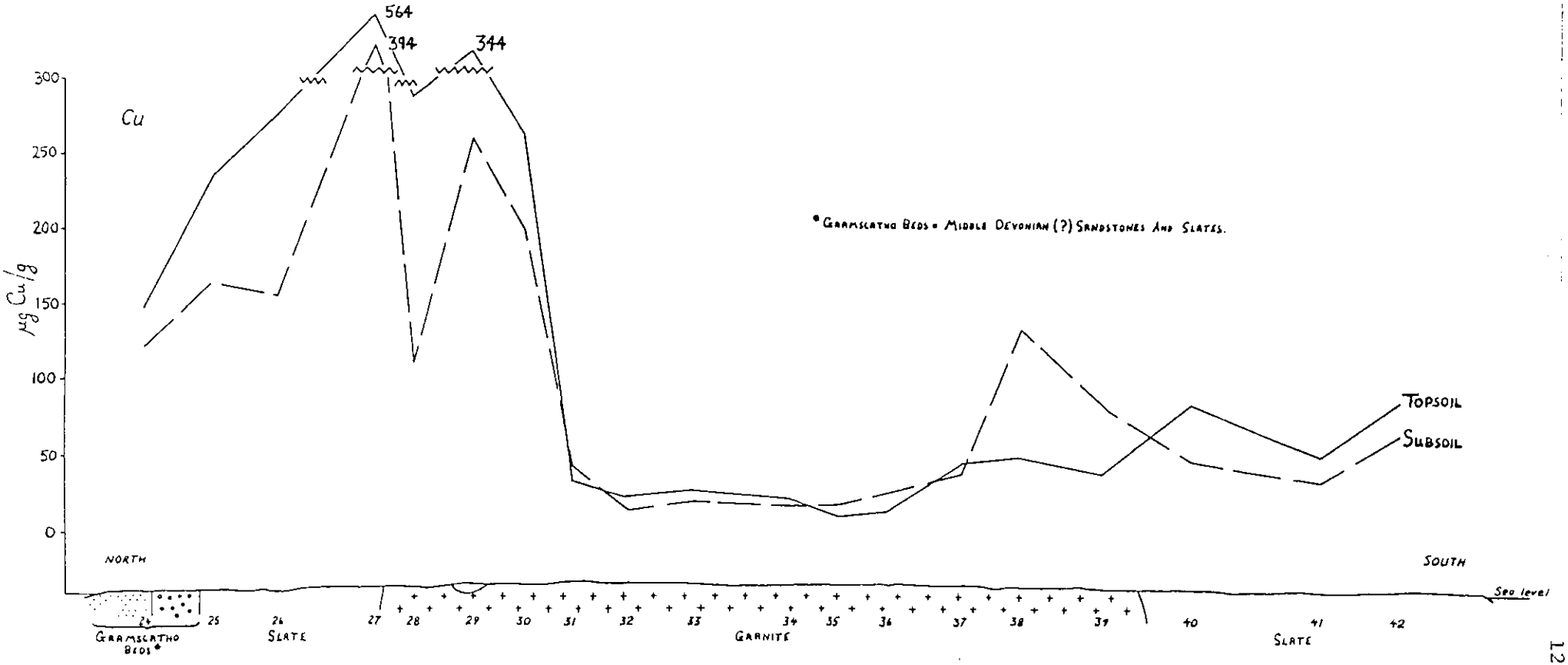
Evidence of Co and Mn enrichment in these soils is also suggested from the data recorded from this traverse. The highest concentrations of both elements (52 μg Co/g and 2520 μg Mn/g) occur in the topsoil at site 19 which also appears to be enriched in Fe (6.44%). Berrow and Burridge (1979b) record the normal soil concentrations of the former elements as being 15 μg Co/g and 800 μg Mn/g (Table 3). However, in terms of both the concentrations recorded and the extent, in area, of the anomalies disclosed, the contamination of soils with Co and Mn appears to be comparable in scale to the Pb anomalies.

iii) Traverse C/C'

The distribution of many of the elements analysed in soils from this traverse are similar. The mineralised ground of the Camborne district is marked by the enrichment of a number of elements, especially between sites 26 to 30 (Figure 23a-23k). The importance of hypothermal mineralisation in the area is reflected by enhanced values of Sn, As and Cu, with the order of enrichment the same as in the contaminated soils of traverse B/B'. Topsoils are especially contaminated, and maximum values of 1088 µg Sn/g, 727 µg As/g and 564 µg Cu/g were recorded at site 27, a location situated in the centre of the mineralised district immediately adjacent to the present workings of South Crofty Mine. Subsoil concentrations of 377 µg Sn/g, 500 µg As/g and 394 µg Cu/g reveal the elevated amounts of these elements which occur also at depth (Figure 23a, b and c).

Anomalies of other trace-elements are associated with the mineralisation and mining activities within the Camborne area. Maximum concentrations of 218 µg Zn/g in the topsoil at site 25 and 200 µg Pb/g in the subsoil at sites 29 and 30 demonstrate a 4-fold and 10-fold enrichment compared to the normal average uncontaminated soil concentrations of these elements disclosed by Berrow and Burridge (1979b) in Table 3. Cadmium concentrations are also elevated throughout the district, with soil values commonly exceeding 1 µg/g (Figure 23f). The peaks in concentration of Co and Mn at site 29 may also reflect contamination and mineralisation (Figure 23g and h). Subsoils at this site are especially elevated in both of these trace-elements, containing 66 µg Co/g and 1720 µg Mn/g. However, these isolated anomalies indicate the lesser importance of these two elements to the mineralisation of the area compared to the other elements discussed above.

Figure 23a. The distribution of copper in soils on traverse C/C¹.



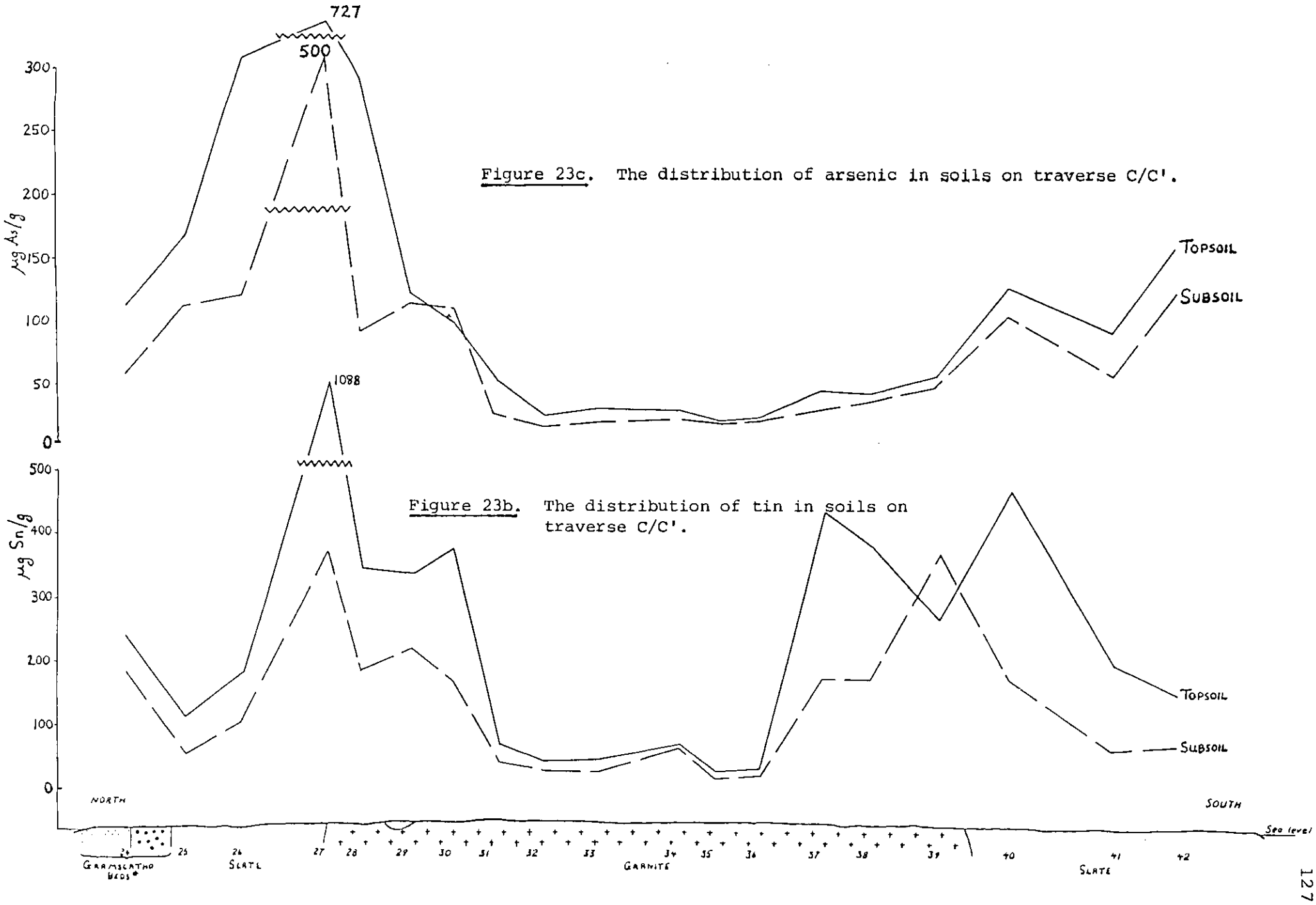


Figure 23c. The distribution of arsenic in soils on traverse C/C'.

Figure 23b. The distribution of tin in soils on traverse C/C'.

Figure 23e. The distribution of lead in soils on traverse C/C'.

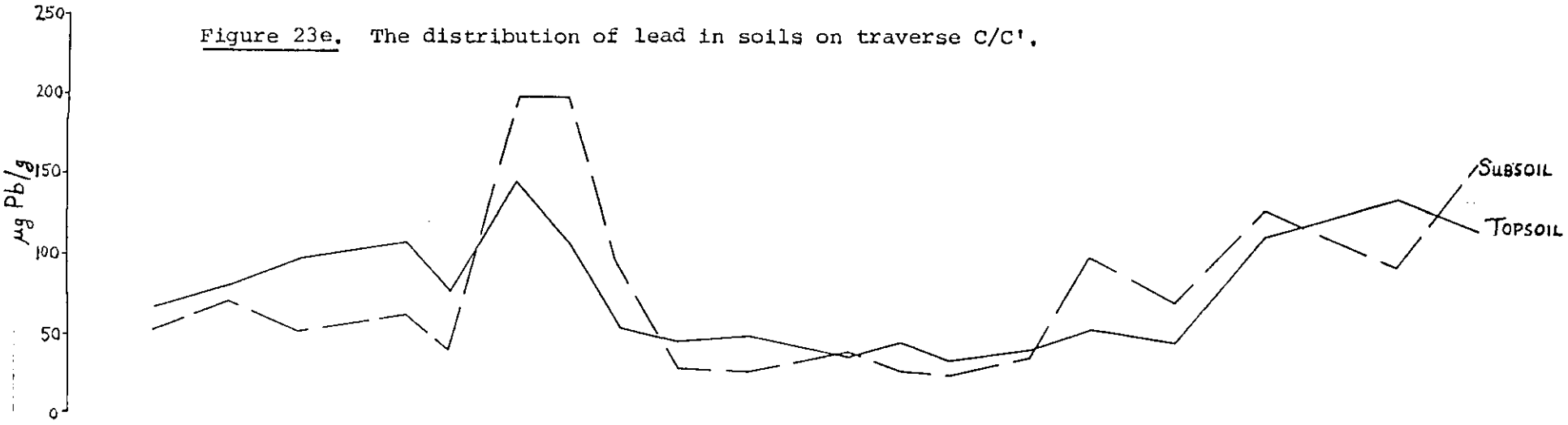


Figure 23d. The distribution of zinc in soils on traverse C/C'.

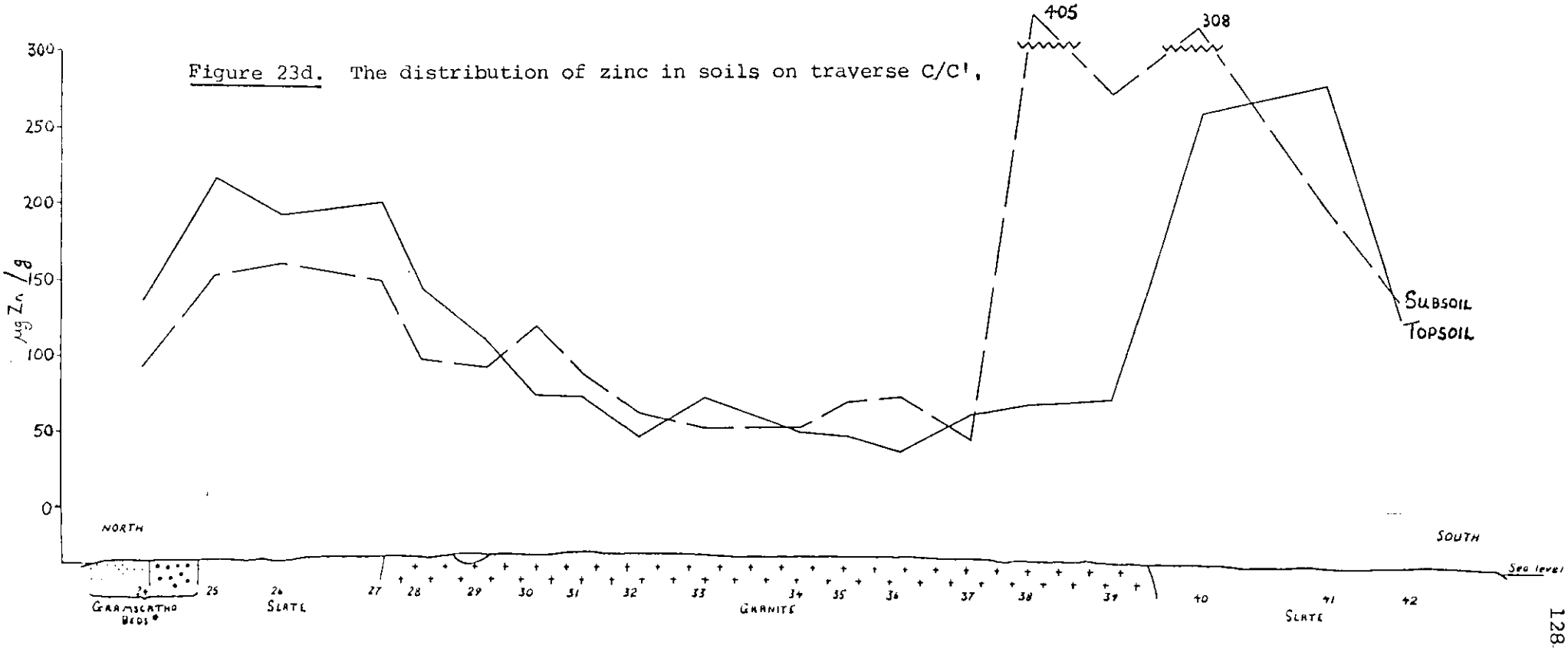


Figure 23f-i. The distributions of cadmium, cobalt, manganese and iron in soils on traverse C/C'.

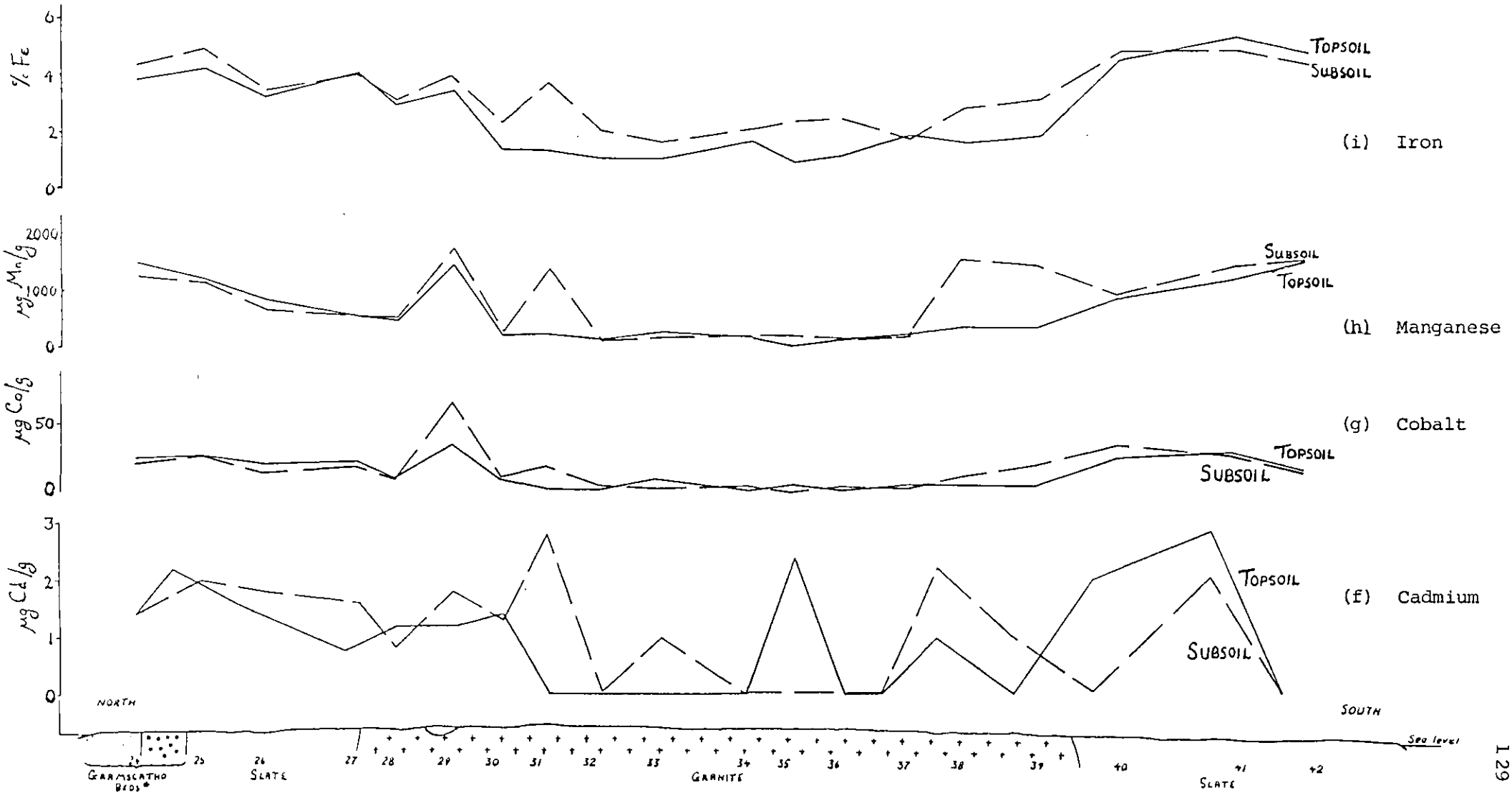


Figure 23k. The distribution of calcium in soils on traverse C/C'.

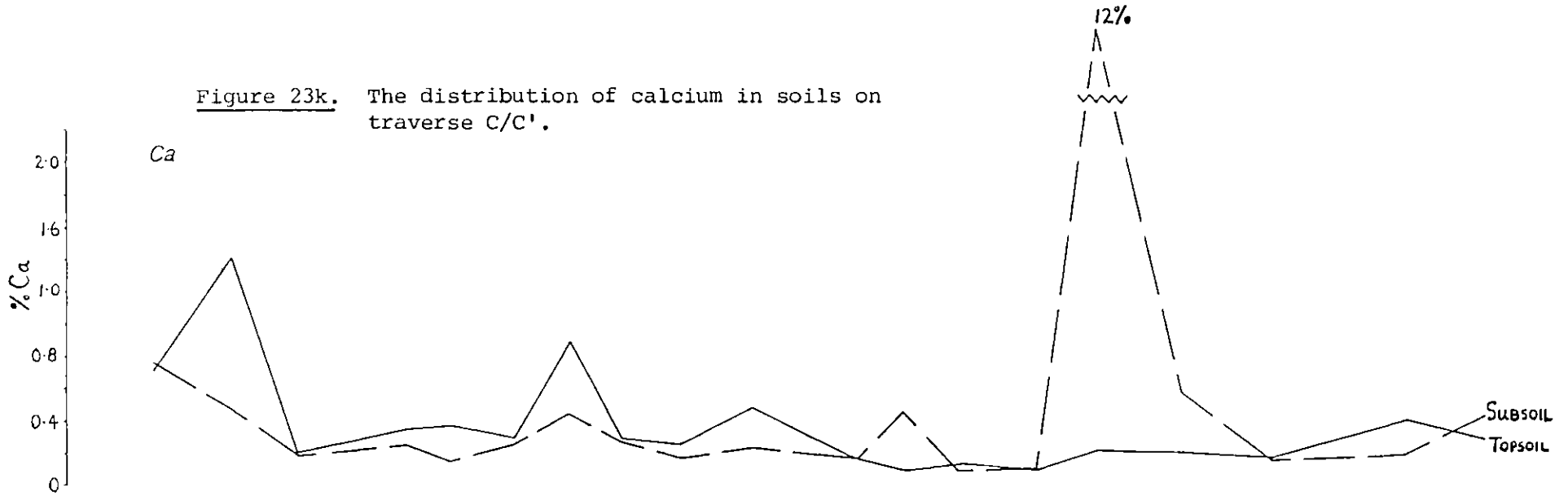
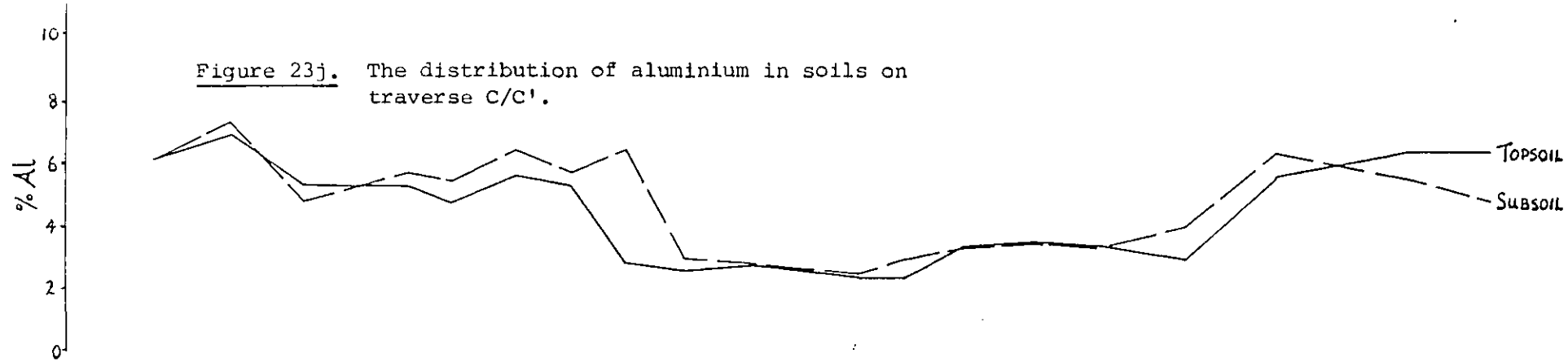
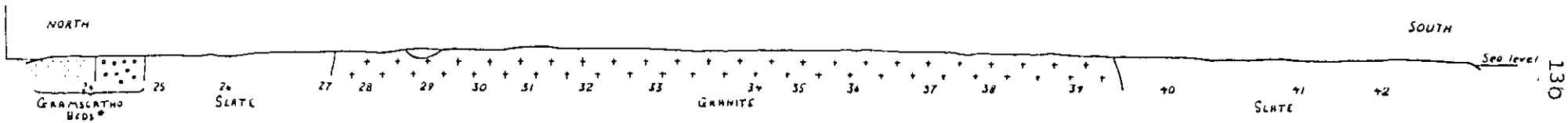


Figure 23j. The distribution of aluminium in soils on traverse C/C'.





Further anomalies for a number of elements are also disclosed by the soils sampled elsewhere along traverse C/C'. Raised concentrations of Sn occur in the soils of sites 37, 38, 39 and 40 (Figure 23b). These sites are all situated within the Sn mining district of Wendron which delineates the location of an emanative centre of mineralisation. However, despite the importance of Sn in the ores of the Wendron region, raised concentrations of As, Cu, Mn, Pb and Zn additionally occur in these soils. Elevated concentrations of the latter four elements in the subsoil strongly suggest an association with the mineralisation. Zinc subsoil concentrations are particularly elevated, with a maximum concentration of 405 µg Zn/g occurring at site 38. No corresponding large increase in Cd concentration is observed at this site (Figure 31f).

The granite soils between sites 30 and 37 lie outside the mineralised districts of Camborne and Wendron. Compared to the soils of these latter regions, therefore, trace-element concentrations are significantly lower. Table 20 records the range and median concentrations of all the elements analysed at these six sites. Compared to the highly variable soil concentrations observed in the mineralised Camborne and Wendron areas, the concentrations of each element in Table 20 reveal little variation between sites. This may indicate that these soils within the centre of the Carnmenellis granite are not affected by contamination. The concentrations of a number of elements including Sn and Cu (but not As) are lower than those encountered within soils of the Lands End granite mass (compare Tables 17 and 20). The median concentrations of Sn calculated from the six locations on the Carnmenellis granite (49 µg/g in the topsoil, 33 µg/g in the subsoil), however, are still considerably elevated compared to the normal uncontaminated soil values of this element quoted in Table 3.

		Al(%)	As	Ca(%)	Cd	Co	Cu	Fe(%)	Mn	Sn	Pb	Zn
Median ($\bar{x}$m)	Topsoil	2.74	26	0.26	-	4	23	1.22	140	49	48	48
	Subsoil	3.11	18	0.21	-	8	19	2.20	160	33	38	61
Range	Topsoil	2.24-3.48	21-29	0.12-0.48	N.D.-2.4	4-12	12-35	1.04-1.72	32-240	32-76	36-56	33-67
	Subsoil	2.68-6.40	15-25	0.10-0.26	N.D.-2.8	4-20	15-43	1.60-3.68	120-1360	22-67	28-96	48-83

n=6
All values in µg/g unless specified.
N.D. = Not detected. Detection limit for Cd = 0.24 µg/g.
Median concentrations for Cd could not be determined.

Table 20. The range and median concentrations of trace-elements recorded from the granite soils of sites 31 to 36.

Calcium concentrations recorded from soils of the traverse reflect the low amounts of this element which are associated with both the granite and slate derived soils. Concentrations of Ca rarely exceed 0.5%, although isolated anomalies indicate areas affected by mineralisation or agricultural liming. The greatest concentration recorded (12% Ca at site 38 within the Wendron district) may reflect mineralisation.

Podzolised soils at sites 28 to 39 contain greater amounts of Fe and Al within the subsoils than the topsoils. Whilst this may be reflecting the podzolisation process with subsequent enrichment of both elements at depth, a similar enrichment of both elements in the subsoils compared to the topsoils can be seen in some of the brown earths of sites 24 to 26 and 40 to 42 (Figure 23i and j). Both elements also appear to be related in distribution to mineralised areas since greater concentrations of both elements occur in the mineralised granite soils south of Camborne compared to the unmineralised granite soils at sites 31 to 36. However, whilst Fe has been shown to be associated with ores of the province, no association of Al with the mineralisation has been demonstrated (Table 19).

iv) Traverse D/D'

The major purpose in collecting the samples along this traverse was to try and obtain geochemical information which would represent background concentrations of the various elements within the slate derived brown earth soils. Although enhanced amounts of various elements - especially Sn - had been disclosed by the Wolfson Geochemical Atlas and the stream sediment follow-up survey (Figures 14-19), it was thought at the time of sampling that these elevated values were due mainly to the downstream transportation of mineralised

and contaminated material derived from the mining fields north of the traverse. As such, the soils of the traverse would not reflect the elevated trace-element content of the stream sediments, especially as mineral veins within the area covered by the traverse are both limited in number and small in recorded output (Dines, 1956). First edition 6" to 1 mile Ordnance Survey maps published in 1888 have proved useful in delineating the sites of old mines and possible contamination sources such as tin smelters and arsenic calciners. An examination of the maps for the area covered by Traverse D/D' confirms the very limited amount of mining activity which occurred within the region.

However, despite these observations and assumptions, analysis of the soils from this traverse indicates that this region is not uncontaminated since elevated amounts of several elements are found associated with these soils (Figure 24a to k). Tin is a particularly useful element in determining if a soil has been contaminated or affected by mineralisation, since low concentrations of this element are associated with uncontaminated soils (Table 3). The concentrations of this element in soils of the traverse attain a maximum of 268 µg Sn/g (Figure 24b), whilst calculated average concentrations exceed 100 µg/g (Table 21). These elevated concentrations are clearly influenced by either contamination or mineralisation and cannot, therefore, be used as a reference value representing the natural (i.e. uncontaminated or unmineralised) Sn content of the slate soils. Similarly, enrichment of the soils is also apparent at some sites for the elements As and Cu, although the high concentrations of both elements recorded are not as elevated or widespread as found in the more heavily mineralised and mined areas such as Camborne. Maximum concentrations of 200 µg Cu/g and 99 µg As/g occur in the topsoils of

Figure 24a. The distribution of copper in soils on traverse D/D'.

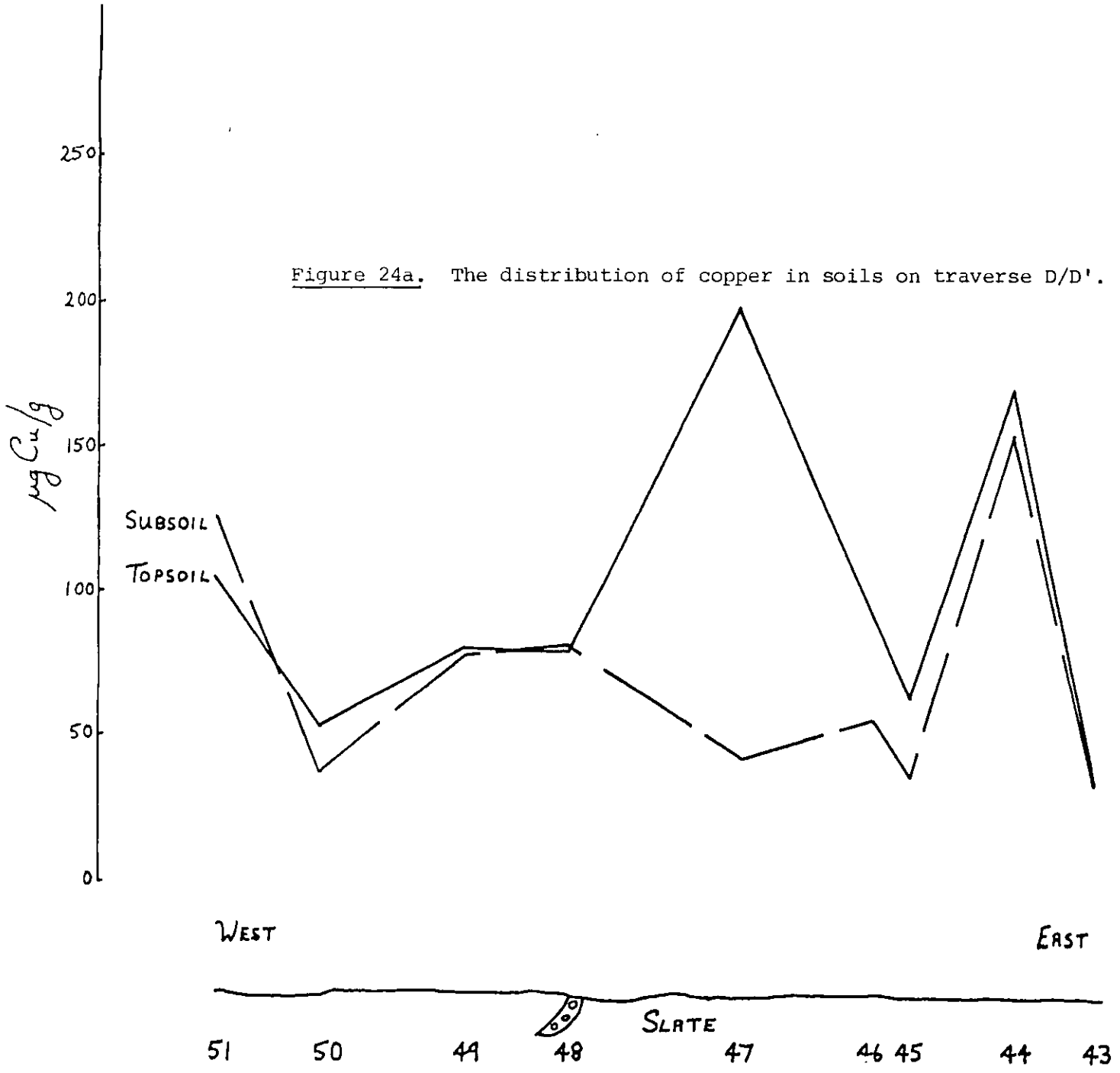
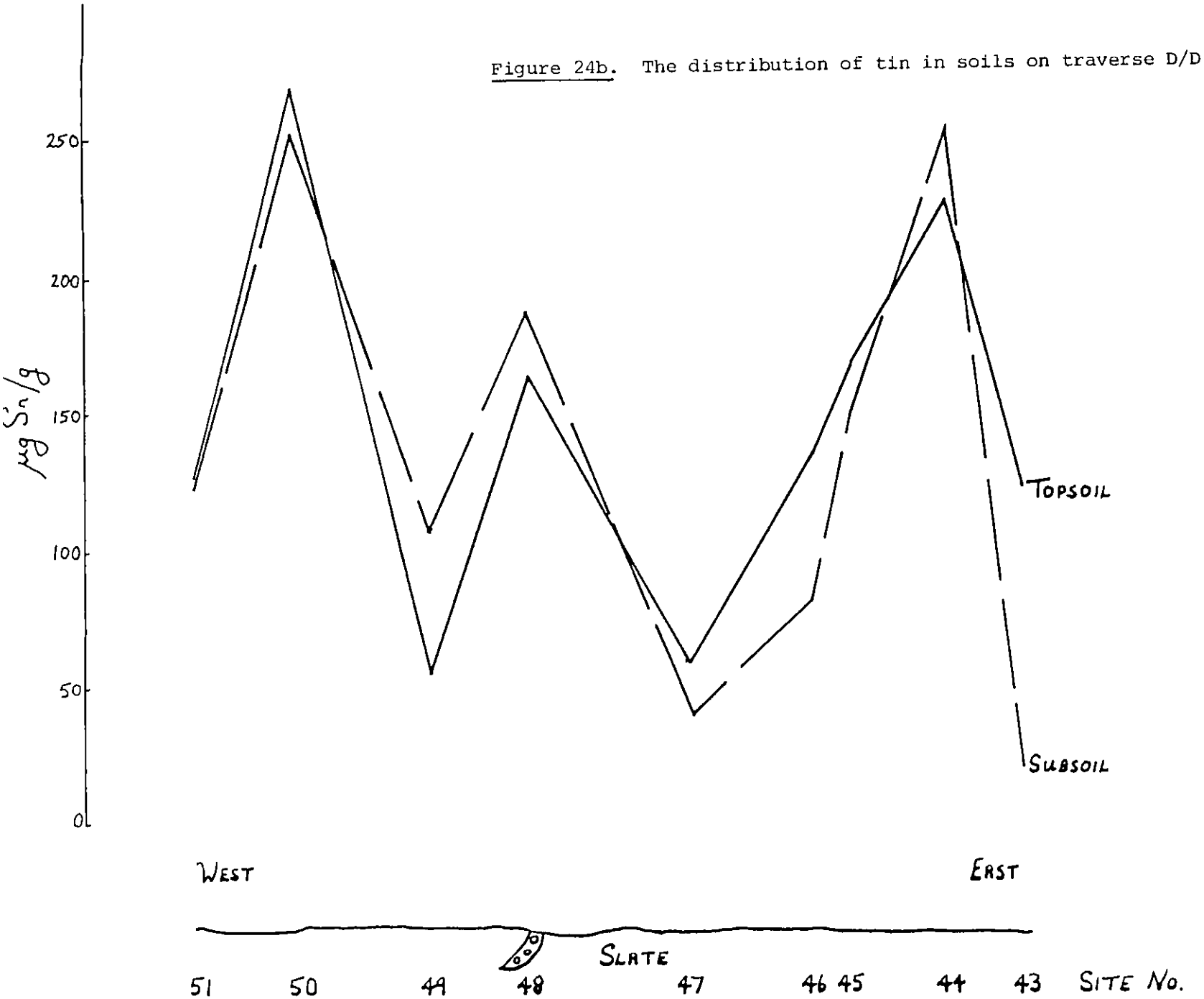


Figure 24b. The distribution of tin in soils on traverse D/D'.



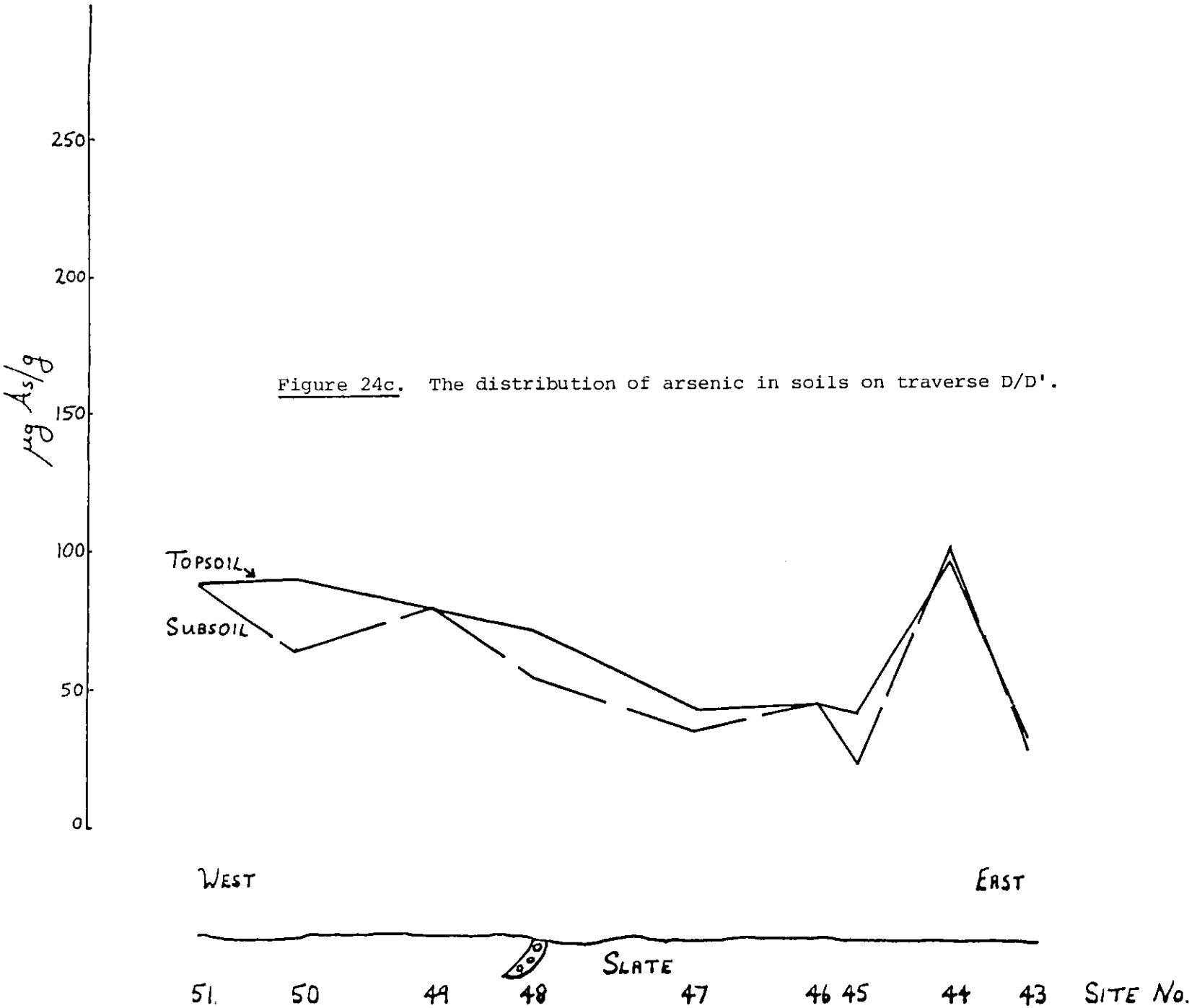


Figure 24c. The distribution of arsenic in soils on traverse D/D'.

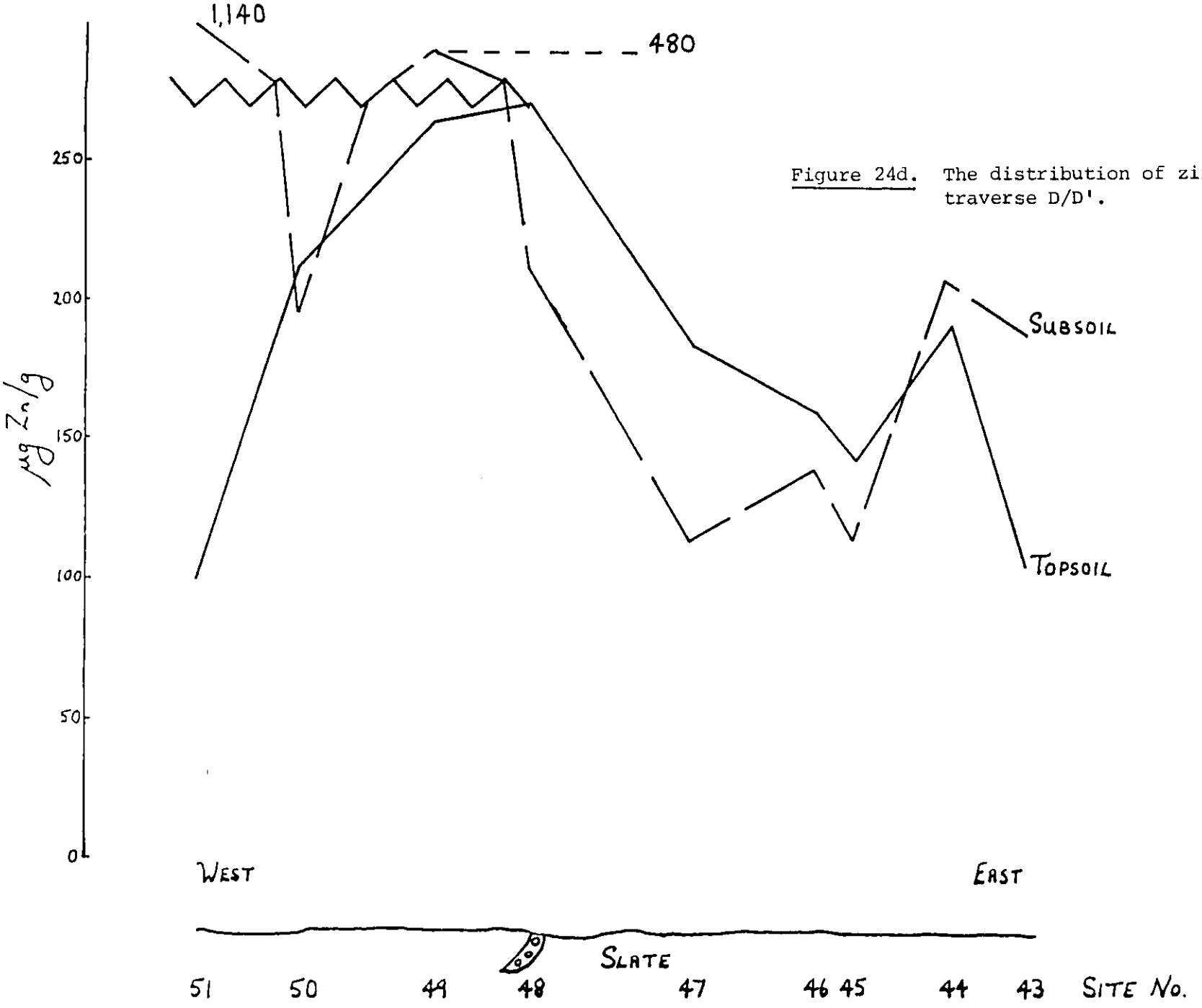


Figure 24d. The distribution of zinc in soils on traverse D/D'.

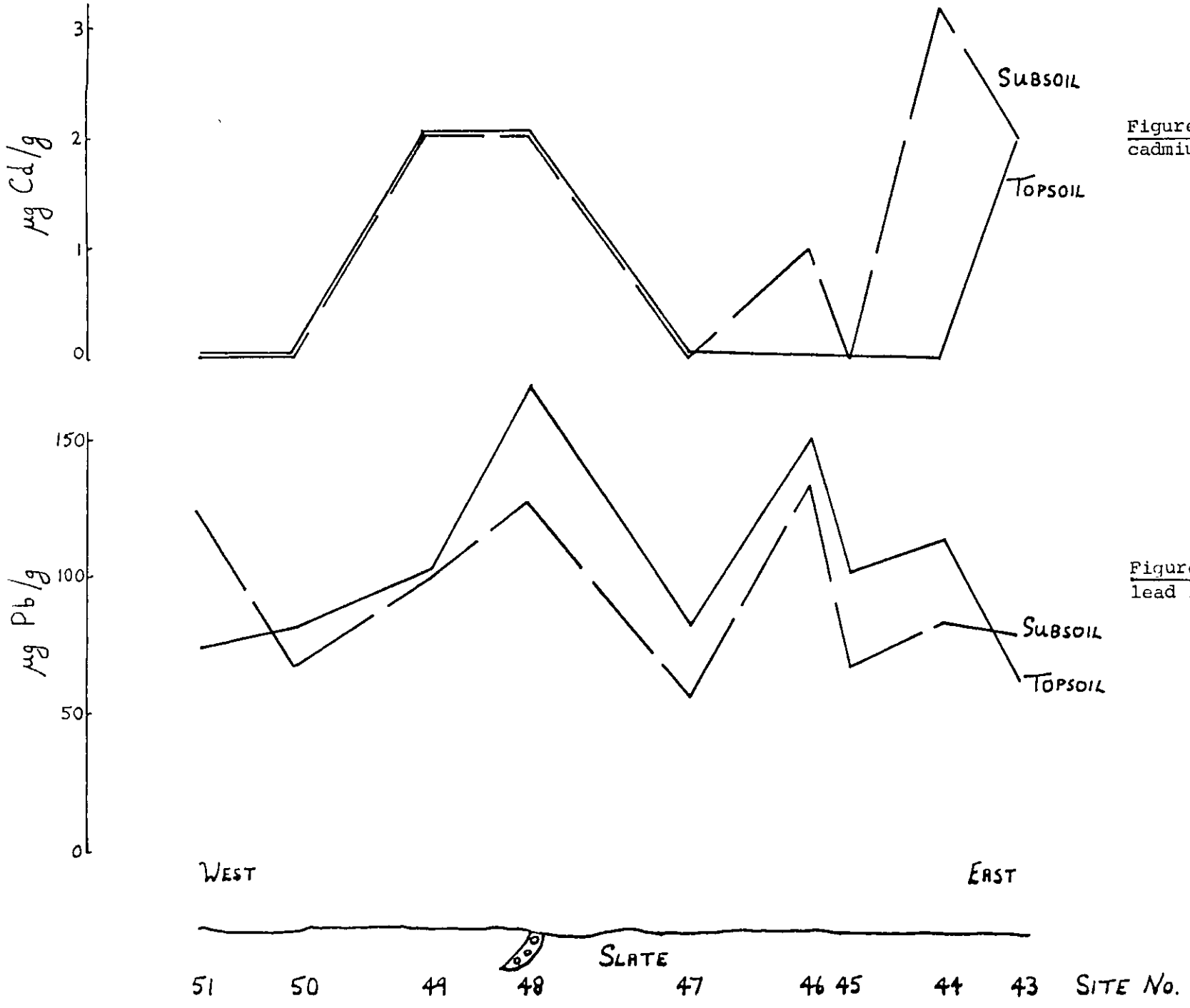


Figure 24f. The distribution of cadmium in soils on traverse D/D'.

Figure 24e. The distribution of lead in soils on traverse D/D'.

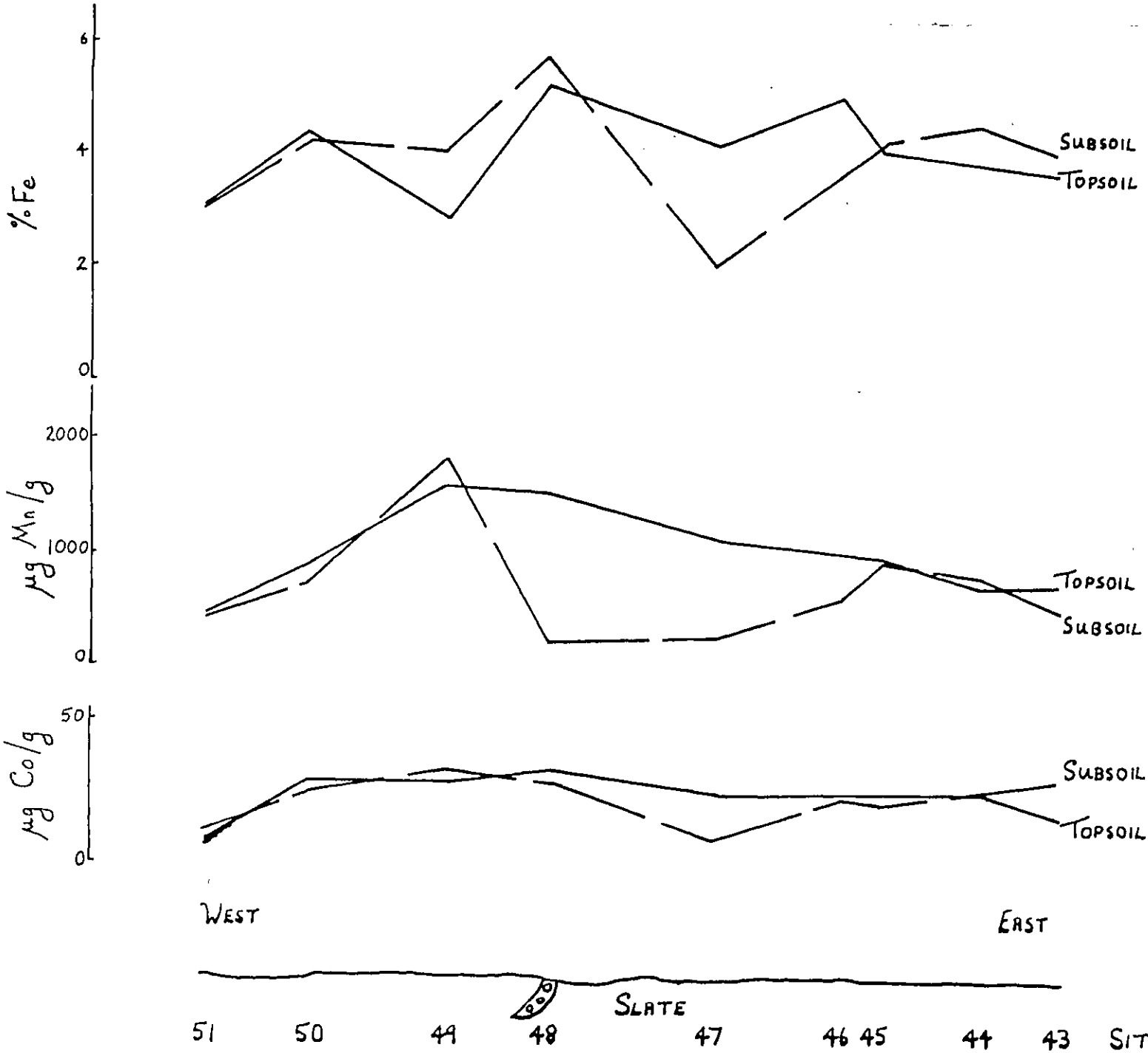


Figure 24i. The distribution of iron in soils on traverse D/D'.

Figure 24h. The distribution of manganese in soils on traverse D/D'.

Figure 24g. The distribution of cobalt in soils on traverse D/

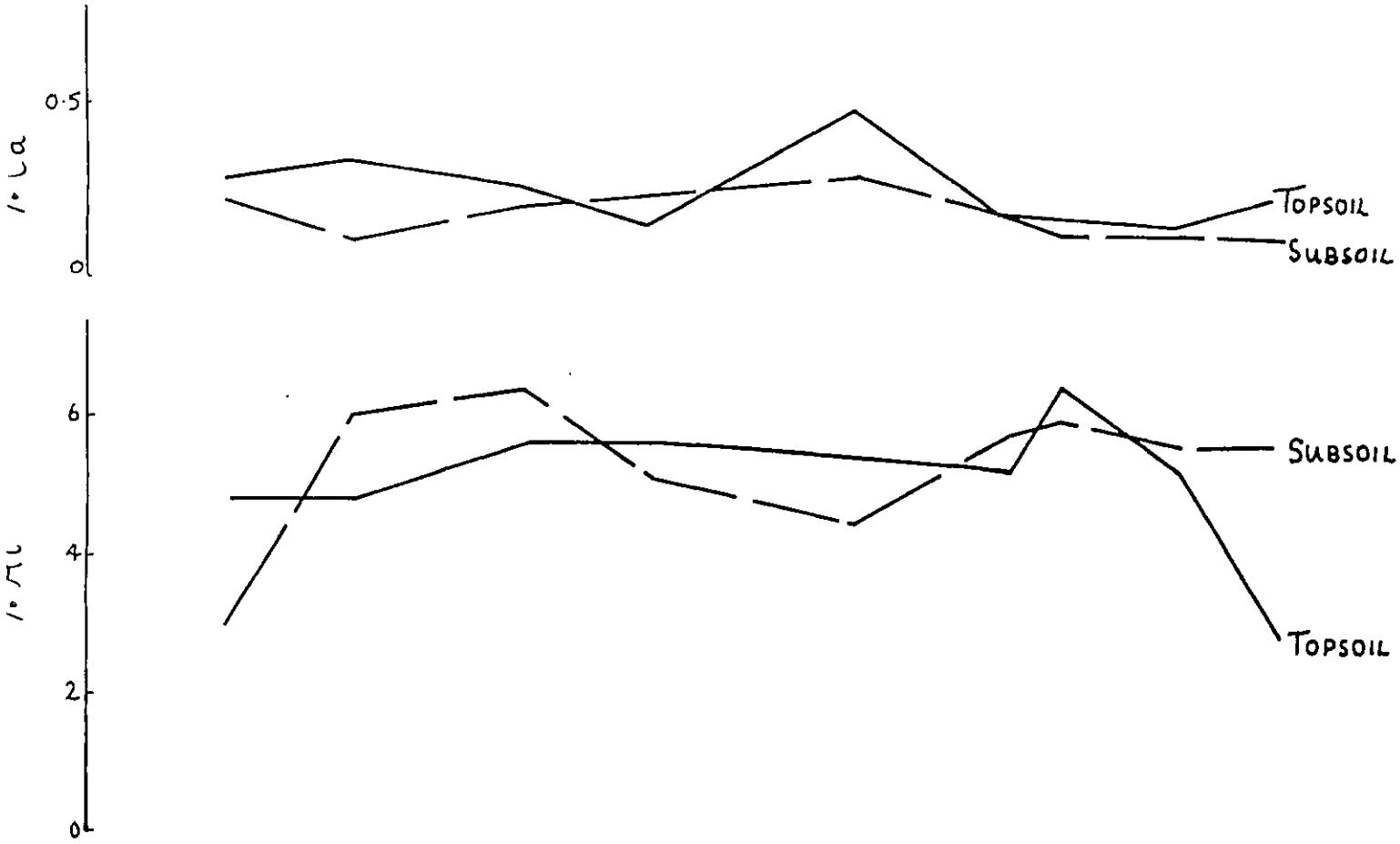
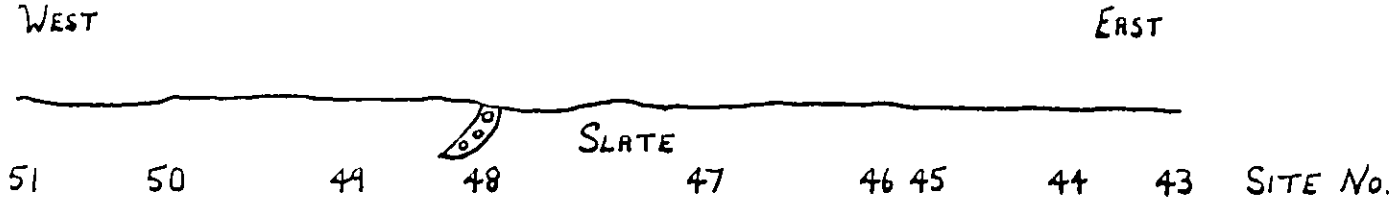


Figure 24k. The distribution of calcium in soils on traverse D/D'.

Figure 24j. The distribution of aluminium in soils on traverse D/D'.



		Al(%)	As	Ca(%)	Cd	Co	Cu	Fe(%)	Mn	Pb	Sn	Zn
Median ($\bar{x}m$)	Topsoil	5.2	72	0.236	-	24	81	4.08	920	104	136	177
	Subsoil	5.6	56	0.196	-	24	56	4.08	580	84	123	189
Mean ($\bar{x}$)	Topsoil	5.1	66	0.250	-	23	99	4.04	920	106	147	175
	Subsoil	5.3	59	0.190	-	22	72	3.95	678	94	136	381
Range	Topsoil	2.8-6.4	35-99	0.160-0.480	N.D.-2.0	8-32	35-200	2.88-5.24	480-1560	64-172	55-268	93-265
	Subsoil	2.96-6.4	25-104	0.112-0.300	N.D.-3.2	8-32	34-156	2.04-5.76	200-1800	56-134	23-253	106-1833

n=9
All values in µg/g unless specified.
N.D. = Not detected. Detection limit for Cd = 0.24 µg/g.
Median and mean concentrations for Cd are not calculated

Table 21. Median, mean and range of trace-element concentrations recorded from the soils of traverse D/D'.

this traverse (Figure 24a and c). Such elevated values raise the median and mean concentrations of both elements presented in Table 21 above the true background values. This is also apparent for Zn due to the high concentrations of this element which occur to the west of the traverse (Figure 24d). A maximum concentration of 1833 µg Zn/g occurs at sample site 51. Such concentrations particularly enhance the mean content of Zn in the subsoils of this traverse to a value (381 µg/g) which cannot be representative of background (Table 21). The minimum concentration of Zn in subsoils of the traverse is 106 µg/g.

Contamination or mineralisation, however, does not appear to have significantly influenced the Pb, Mn and Co concentrations found in the soils of this traverse. Compared to Sn, As, Cu and Zn, enrichment of these three elements through mineralisation or contamination appears to be limited in the slate soils sampled on the other reconnaissance traverses. The mean and median concentrations of the three elements presented in Table 21 are similar to most of the Pb, Co and Mn concentrations recorded in the slate soils of traverses B/B' and C/C' and suggest, therefore, that they may be representative of true background values. The average concentrations of Al, Fe and Ca outlined in Table 21 may also be taken to represent a background situation. This was expected for Al, since its association with the mineralisation of the province is limited (Table 19).

c) Discussion

The results and observations arising from studies on the four reconnaissance traverses indicates that substantially elevated concentrations of a number of elements occur in soils of the study

area. For the main elements of interest to this thesis, the order of trace-element enrichment caused by a combination of mining contamination and mineralisation is Sn > As > Cu > Zn > Pb; anomalies for the latter element appear to be localised in extent. This order of soil enrichment reflects, in turn, the abundance of the trace-elements in the mineral ores within this region of South-west England

The maximum concentrations of the five elements recorded from topsoils of the four soil traverses are 1088 µg Sn/g, 727 µg As/g, 564 µg Cu/g, 685 µg Zn/g and 268 µg Pb/g. Subsoil concentrations, however, are also elevated in these five elements. Maximum concentrations of 400 µg Sn/g, 500 µg As/g, 394 µg Cu/g, 1833 µg Zn/g and 379 µg Pb/g were recorded from the 30-45 cm deep samples taken in this reconnaissance work. Colbourn (1976), working in the mineralised district of Derbyshire, used topsoil/subsoil ratios in determining which soils were affected by surface contamination or underlying mineralisation; such values were called Relative Topsoil Enhancement (R.T.E.) ratios. Colbourn found that soils outside the mineralised area of Derbyshire had R.T.E. (Pb) values of up to 20, and thus showed the regional atmospheric lead pollution caused by smelting processes. In contrast, R.T.E. (Pb) values of less than unity were not uncommon on the Derbyshire limestone dome where mineralisation had raised the subsoil Pb concentrations. These R.T.E. ratios have been calculated in this research, and are presented graphically in Figures 25 to 28. Although topsoils of the study area are highly contaminated in elements such as Sn and As, the elevated subsoil concentrations result in R.T.E. ratios which are generally close to unity. The source of this underlying enrichment can be attributed to mineralisation, although leaching and podzolisation processes operating within the soil profile

Figure 25

R.T.E. VALUES FOR TRAVERSE A/A'

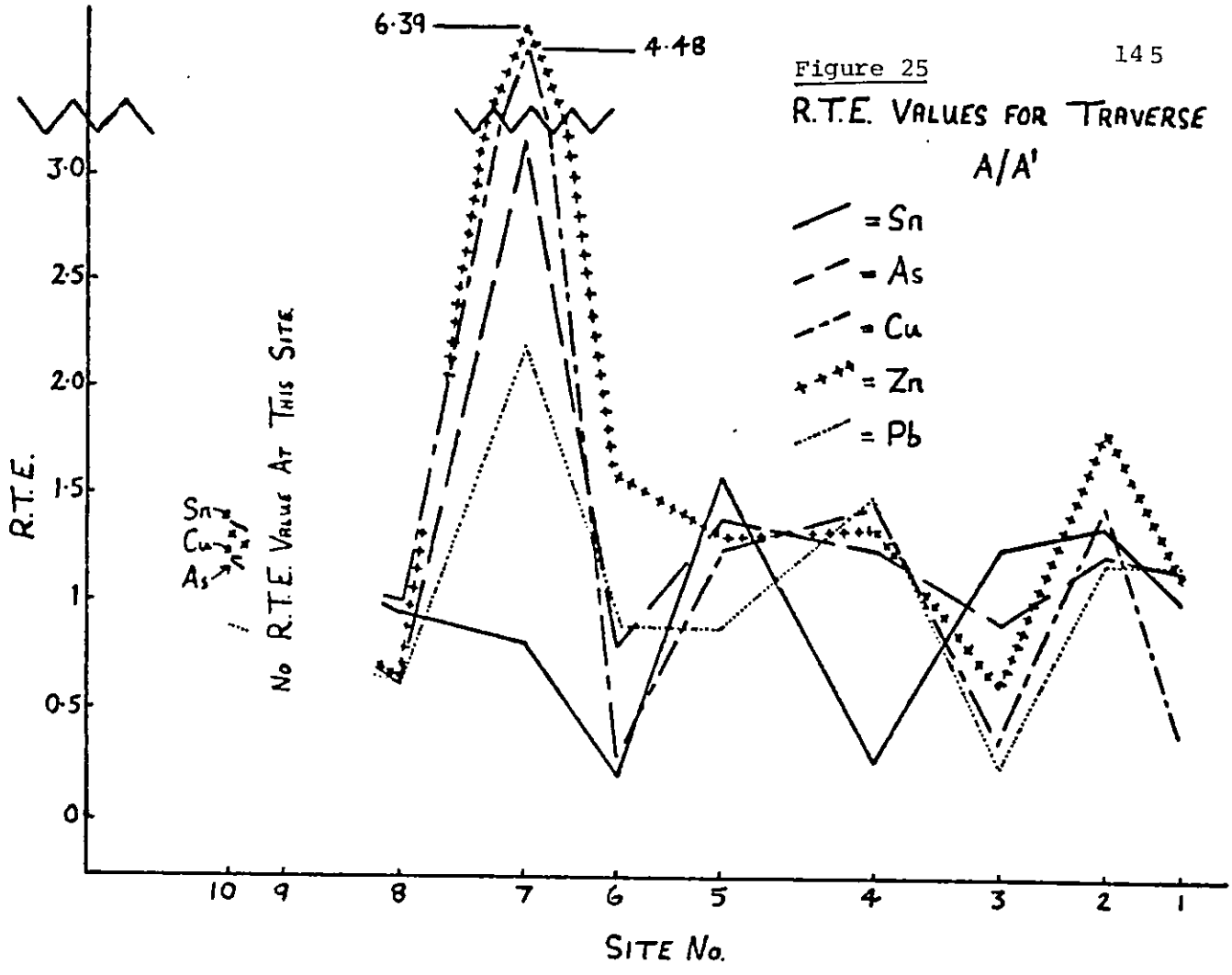
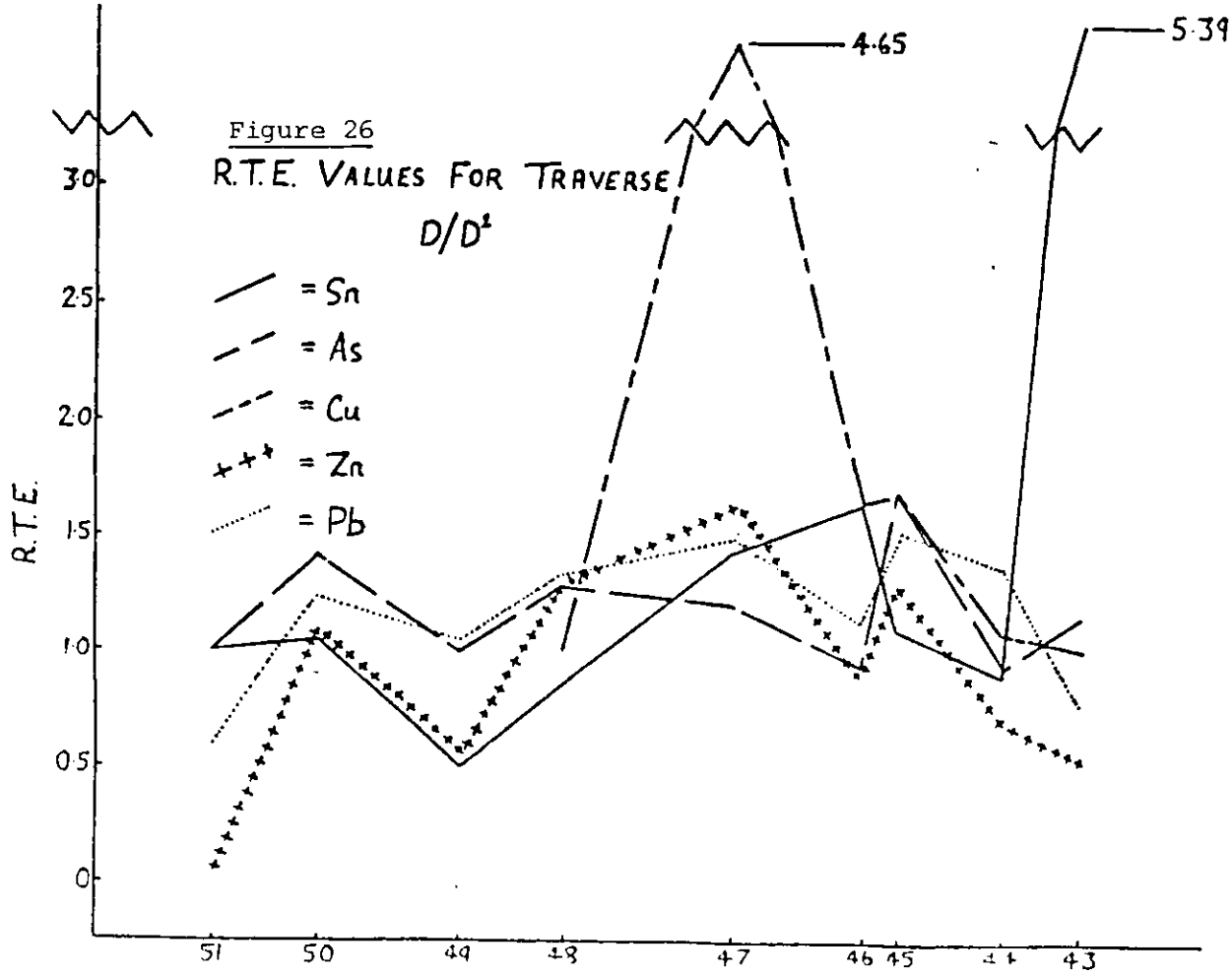


Figure 26

R.T.E. VALUES FOR TRAVERSE D/D²



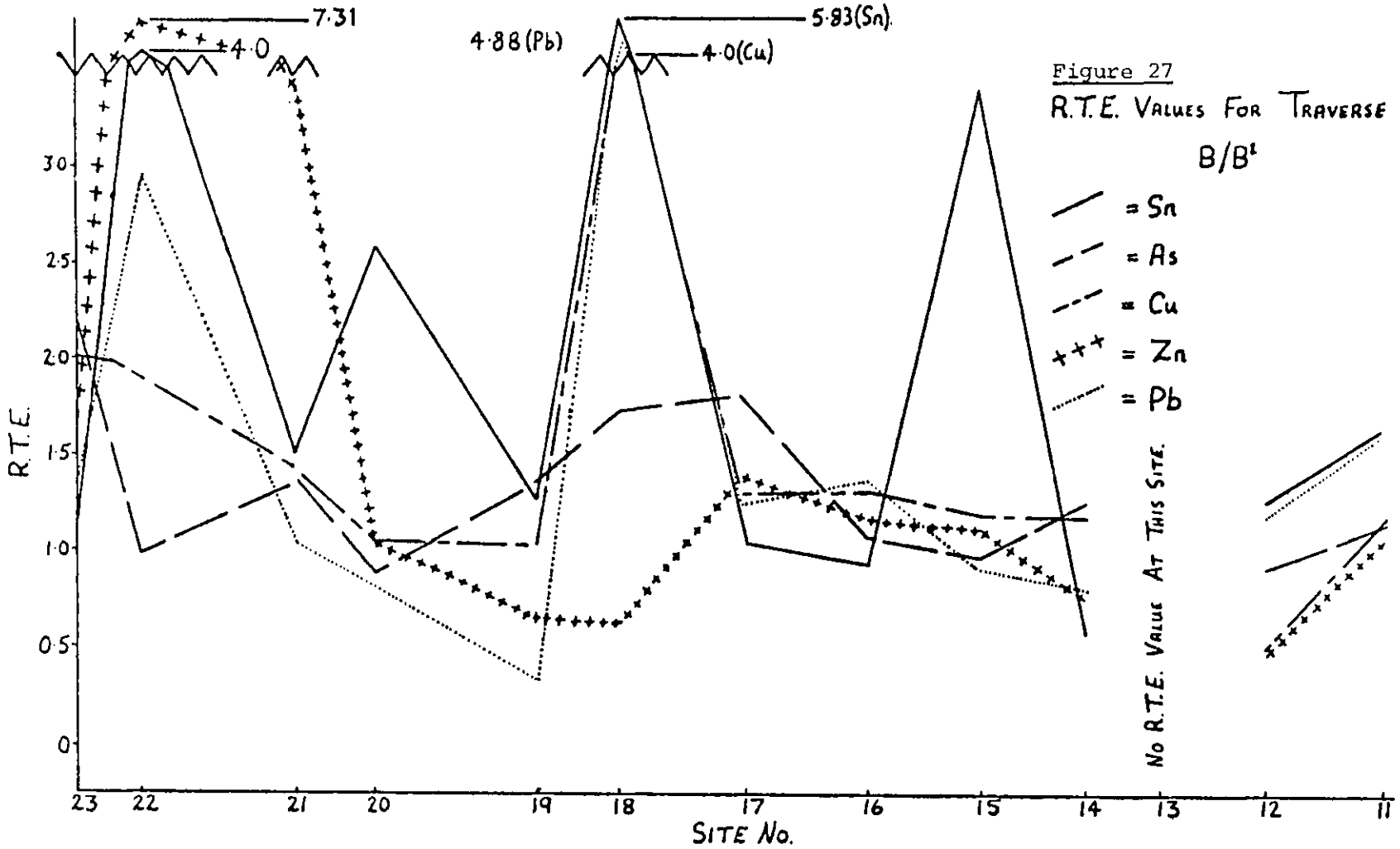
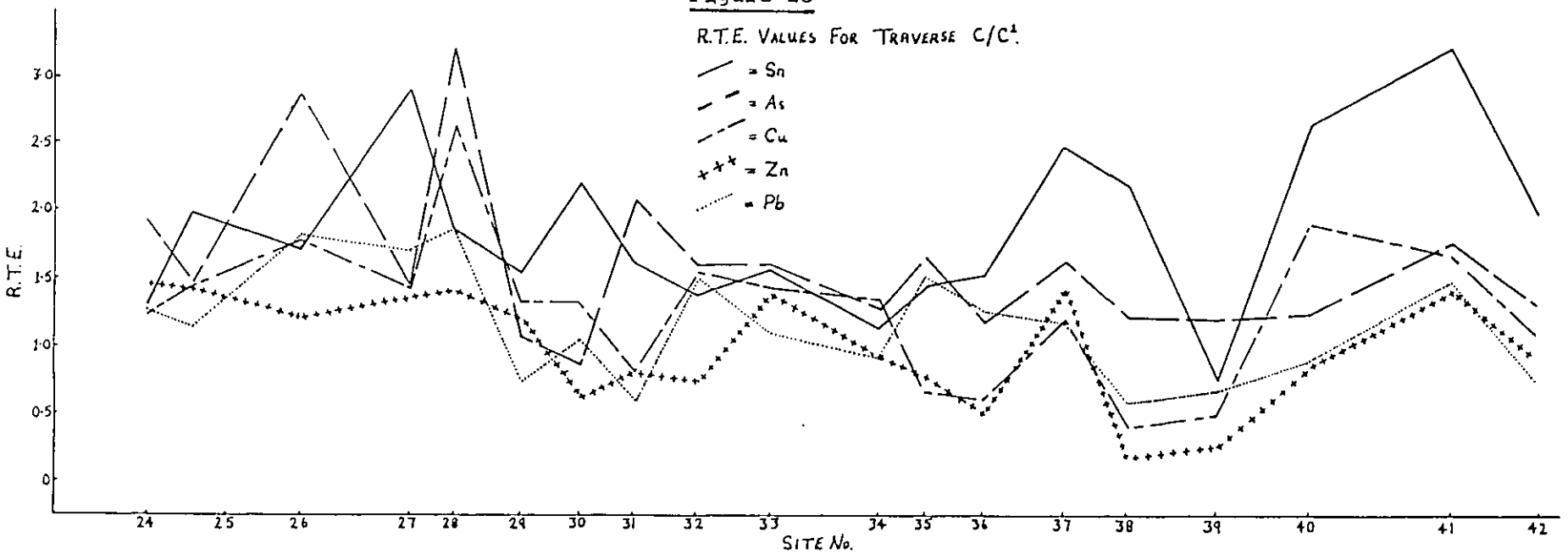


Figure 27

R.T.E. Values For Traverse B/B¹

Figure 28


R.T.E. Values For Traverse C/C¹.
= Sn
= As
= Cu
= Zn
= Pb
R.T.E.
3·0
2·5
2·0
1·5
1·0
0·5
0
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
Site No.

may also be contributing to the high concentrations observed at depth. However, some topsoils may be significantly elevated in their trace-element content compared to the underlying subsoils. Maximum R.T.E. ratios for Sn (5.83 at site 18), As (3.2 at site 27), Cu (4.5 at site 47), Zn (7.3. at site 22) and Pb (4.88 at site 18) were calculated from the results of the reconnaissance survey. In contrast, some particularly elevated subsoil concentrations result in R.T.E. ratios well below unity. Of the five elements examined in detail, Zn shows the greatest range in R.T.E. values; the elevated ratio at site 22 (R.T.E. 7.31) contrasts to the low ratio value of 0.05 at site 51 caused by the extreme subsoil enrichment (Figure 24d).

Most of the trace-element anomalies observed in the soils for the elements Sn, As, Cu, Zn and Pb are associated with the mineralised and mined districts. The mineral zoning which strongly controlled the deposition of the ores is reflected, in part, by the trace-element content of the soils. For example, the soils within the Sn producing district at Trencrom Hill (i.e. site 6) are elevated only in their Sn and (to a lesser extent) Cu content. However, the soils within the Sn producing area at Wendron are additionally enriched in a number of other elements, especially Zn in the subsoils. This enrichment may be associated with the mineralisation, although further detailed sampling of both soils, the granite parent material, and ores from the district is required to confirm this observation. The local contamination of the topsoil at site 7 observed for a multitude of trace-elements including Cu, As, Zn and Pb, indicates a further possible association of these elements with mining activity at sites within a former emanative centre on the granite. However, the lack of a topsoil Sn anomaly at this site may well suggest an alternative source of these elements.

Soil contamination is also apparent outside the major mineralised and mined areas of the study region. This is particularly evident for Zn where the concentrations recorded at certain locations were higher than those in soils of the minealised areas. Zinc concentrations up to 692 μg/g are found in topsoils north of site 19 which result, consequently, in elevated R.T.E. ratios (Figure 27). The source of this enrichment, however, cannot be determined. Similarly, the high subsoil Zn concentrations recorded at some sites along traverse D/D' cannot be related to any known source, and no corresponding enrichment is observed at these sites for any other element (Figure 24). Analysis of ores from the district disclose the multi-element associations which exist in the mineral veins of the study area. Table 19 shows the particularly high concentrations of Cu and Cd which can be associated with sphalerite (ZnS) ores. Thus the subsoil enrichment of Zn alone from a mineralisation source at these sites on traverse D/D' may be considered unlikely.

Tin and As are particularly good indicators of contamination and mineralisation since the concentrations of these elements associated with normal uncontaminated soils are low (i.e. $<$ 10 μg/g, see Table 3). Concentrations of both elements throughout the survey area, however, are elevated above this threshold value and demonstrate that the effects of mineralisation and contamination extend beyond the major mineralised areas. This was particularly evident in the soils of traverse D/D'. Suitable control areas wherein background values of these two trace-elements could be determined were thus difficult to establish. Only the six locations at sites 31 to 36 within the central region of the Carnmenellis granite appear to be possibly uncontaminated, although even in these soils the Sn and As

concentrations exceed the established normal concentrations presented in Table 3.

Localised soil anomalies are found for Co and Mn in soils of the study area. Maximum concentrations of 66 μg Co/g in the subsoil at site 29, and 2960 μg Mn/g in the topsoil at site 7 were observed from the reconnaissance traverses. However, both elements do not occur widely in the mineral veins of the study area (Dines, 1956) and it is considered likely that the median concentrations of both elements calculated from the soils of Traverse D/D' are representative of true background values. Similarly median Pb, Fe, Ca and Al concentrations of these slate derived soils may be regarded as background values. Cadmium concentrations in soils of this traverse are also generally lower than those recorded from the soils of the mineralised and contaminated districts such as Camborne. The data for Cd must be viewed subjectively, however, due to the poor precision obtained (160%) from replicated samples (Appendix 2).

A comparison between the Pb, Co, Mn, Al and Fe concentrations of the slate soils of Traverse D/D' (Table 21) and the six granite soils of sites 31 to 36 (Table 20) reveals the geochemical differences of the two areas caused by the different parent materials. In all cases, concentrations of the five elements are higher on the slate soils than the granite counterparts. The natural geochemical differences for the elements Sn, As, Zn and Cu between these soils cannot be so easily determined because of the mineralisation/contamination effects discussed above. The natural concentrations of Ca in both the granite and slate soils, however, appear to be similar and reflect the non-calcareous nature of both parent materials. Elevated Ca concentrations at the sites investigated by the four soil traverses

are only observed at a few isolated localites apart from the soils bordering St. Ives Bay which have been goechemically influenced by wind blown calcareous dune sand. The sampling and analysis of sand from Hayle has confirmed this source of Ca to the soils, with sand Ca concentrations exceeding 28% (Table 22). Elevated As concentrations in the sand (maximum recorded = 133 µg/g) are also likely to be reflected in the trace-element content of these calcareous soils. However, the topsoil enrichment of Zn observed in these soils does not appear to be related to the influx of dune sand. Table 22 reveals a maximum of only 63 µg Zn/g occurring in the sands which border St. Ives Bay.

Elevated Ca concentrations are additionally observed in the plaggen soils of site 1, and are confirmed by the analysis of two additional soil samples selected south of this site (Figure 21k). A maximum concentration of 1.5% Ca recorded from the upper 15 cm of these soils, contrast to the mean value of 0.25% Ca recorded from the slate derived soils of Traverse D/D' (Table 21). The enrichment of this element in the man-made soils is due to the long tradition of applying beach sand which acts both as a mineral manure and as a means of improving the workability of the soil. Staines (1979) notes the use of both highly calcareous dune sand from Hayle, and Ca-poor 'lugg sand' from Mounts Bay, which were added along with seaweed, animal and vegetable manures and town refuse from Penzance by farmers of the district. The different Ca status of both sand types is reflected by the data presented in Table 22.

Sample locality	Depth of sample	Al(%)	As	Ca(%)	Cd	Co	Cu	Fe(%)	Mn	Pb	Zn
HAYLE	(0 -15 cm	0.96	133	13.6	0.8	7	51	1.64	240	16	63
SAMPLE A	(										
(Grid Ref: SW 574 407)	(30-45 cm	0.76	100	18.0	0.8	4	60	1.40	240	8	56
HAYLE	(0 -15 cm	0.56	35	28.8	1.6	10	26	0.76	160	6	55
SAMPLE B	(30-45 cm	0.52	45	27.6	1.4	5	23	0.66	120	16	50
(Grid Ref: SW 554 388)	(60-75 cm	0.45	41	28.0	1.6	9	24	0.60	120	15	47
MOUNTS BAY	(0 -15 cm	0.64	6	2.36	2.4	4	6	0.68	160	8	22
SAMPLE A	(										
(Grid Ref: SW 498 312)	(30-45 cm	0.64	11	2.08	2.0	8	8	0.68	160	10	24
MOUNTS BAY	(0 -15 cm	0.68	13	2.80	2.0	8	8	1.00	240	12	32
SAMPLE B	(										
(Grid Ref: SW 492 311	(30-45 cm	0.64	10	1.72	1.6	8	11	0.88	200	12	35

All values in µg/g unless specified.
Samplesnot analysed for Sn.

Table 22. Geochemical analysis of sand samples taken from Hayle and Mounts Bay

The data presented in this table also shows the elevated status of elements such as As, Cu and Zn in the sand samples of Hayle compared to samples from Mounts Bay. Such enrichment is caused either by the products of mining activity which are brought to the St. Ives Bay coastline by the contaminated Red River (Yim, 1979) or, in the case of Zn, by enrichment from the weathering of cliff lodes along the northern coastline (Hosking and Ong, 1963-64). The application of these sands to the man-made soils may thus influence their trace-element content. This may, for example, be a source of As to the soils which contain up to 97 µg/g of this element (Figure 21c). However, the concentrations recorded from the beach sands (Table 22) cannot fully account for the elevated amounts of trace-elements such as Cu (maximum concentration recorded 212 µg/g), Pb (maximum 708 µg/g) or Zn (maximum 255 µg/g) found in the man-made soils. It therefore seems likely that these concentrations are due to the other additives which have been applied to the land. Previous research has shown that contamination of both urban and rural soils for a number of elements including Cu, Pb and Zn can occur by the application of domestic waste including soot, coal ash and municipal compost (Davies, 1975; Purves 1967, 1972 and 1977). In this research, analysis of pottery shards which occur commonly in these man-made soils are enriched in Pb and Co, presumably due to the association of these elements with the ceramic glaze. Lead concentrations are particularly elevated and range in value from 100 µg/g to 25000 µg/g (Table 23). Chisholm (1971) records the U.S. maximum permissible amount of Pb in glazes as 7 µg/g, and further notes that the element can be leached from glazed earthenware. The high amounts of Pb associated with the man-made soils may thus be derived, at least in part, from this source.

Sample identity	Co	Pb
P1	50	100
P2	20	9100
P3	260	720
P4	170	3200
P5	50	25000
P6	190	1280
P7	380	5000
P8	300	4000
P9	50	2800
P10	260	4200

All trace-element concentrations in µg/g.

Table 23. Lead and cobalt concentrations in shards of pottery found in the man-made soils south of the Lands End granite.

(III) THE DISTRIBUTION OF TRACE-ELEMENTS IN SOIL PROFILES OF THE STUDY AREA

As a follow-up to the reconnaissance work undertaken on the four soil traverses, 15 soil profiles were sampled in both mineralised and non-mineralised areas within the study region. In addition, three profiles representing the man-made soils south of the Lands End granite were also selected for further detailed examination. The soils were sampled with a Jarrett auger of 10 cm diameter. Samples were taken every 15 cm to a depth of 1 m or, if a shallower soil was sampled, until bedrock was encountered. Because this work was only intended to give a preliminary indication of the distribution of the elements down the soil profile, many parameters such as pH, texture and organic matter content were not determined. Information regarding these important soil characteristics can, however, be found in the Soil Survey Record of the area (Staines, 1979).

All the samples were analysed for Al, As, Ca, Cd, Co, Cu, Fe, Mn, Pb and Zn; analysis for Sn could not be undertaken because of time considerations. The data for Cd is not discussed in this study due to the poor analytical precision obtained as noted previously in this chapter. However, the soils were additionally analysed for potassium pyrophosphate extractable Fe (P.Fe) since this important soil parameter is useful in the classification of soils as the data relates to the fractions of Fe produced by recent weathering and eluviation (Bascombe, 1968). In helping to describe the analytical results obtained from the profile samples, R.T.E. ratios between the 0-15 cm/30-45 cm samples and the uppermost 15 cm/deepest 15 cm soil samples have been calculated. All ratio values, analytical data and information relating to the location of the soil profiles are outlined, in full, in Appendix 4.

a) Soils of the slate lowland

i) Soils developed over mineralised slates

Profile 1: The decline and low amounts of P.Fe found at depth confirms the classification of this soil as being a brown earth of the Highweek series. Total Fe and Al concentrations, however, increase with depth and do not correlate with the pyrophosphate distribution.

Arsenic and Cu are both enriched throughout the profile, with the highest concentrations occurring within the top 30 cm. Concentrations in the topsoil reach a maximum of 351 μg As/g and 268 μg Cu/g. Zinc enrichment in the topsoil is not as high (217 μg/g) although the distribution throughout the profile is similar to that of As and Cu. Lead concentrations are lower than Zn and approximate to the average concentration recorded from the soils of Traverse D/D' (Table 21), thus suggesting that no enrichment of this element has occurred in this soil through mineralisation or contamination. The R.T.E. (Pb) data presented in Appendix 4 reveals the accumulation of this element in the topsoil. In comparison, Ca, Co and Mn concentrations are variable throughout the profile, although there is clear evidence of both topsoil accumulation and enrichment at depth for the latter two elements.

Profiles 2, 3 and 4: Pyrophosphate extractable Fe concentrations in the subsoils of these three profiles confirm these soils as belonging to the Dartington series (i.e. brown podzolics). In particular, an advanced development of podzolisation in Profile 3 is suggested by the large amounts of P.Fe in the subsoil, which reaches a maximum concentration of 0.62% at 30-45 cm depth. The

highest amounts of both 'total' Fe (4.08%) and Al (6.52%) recorded from this profile are associated with the same sample, and the illuviated horizon is thus clearly defined. In contrast, total Fe and Al concentrations within Profile 2 do not show any clear pattern of accumulation, depletion or redistribution, whilst concentrations of both elements increase with depth within Profile 4. Maximum concentrations of 4.48% Fe and 9.20% Al are recorded from the 60-75 cm sample from this latter profile. The low amounts of P.Fe (0.04%) associated with this sample indicates that these elevated concentrations are not attibutable to podzolisation processes. High concentrations of As (133 μg/g), Cu (352 μg/g), Co (120 μg/g), Mn (4000 μg/g) and Pb (368 μg/g) in this sample suggest that the underlying enrichment is derived from a mineralisation source. Relative topsoil enhancement ratios between this sample and the topsoil for all these elements except As are below unity. However, the mineralisation may not be accounting for the Al enrichment observed at depth since this element does not appear to be associated with the metallic ores of the study area (Table 19).

The highest concentrations of both As and Cu are recorded from the topsoil of Profile 2 (762 μg As/g, 480 μg Cu/g) which was sampled within the heavily contaminated area at Camborne. Subsoil concentrations of both elements are also elevated, and within Profile 3 similar concentrations of both elements persist to a depth of 60 cm before noticeably declining. Topsoil accumulations of Pb, Zn, Mn and Ca are also apparent in profiles 2 and 3; Co differs little with depth. The Ca concentrations within all three profiles reflect the non-calcareous nature of the slate as noted previously from the soil traverse reconnaissance work, although an anomalous Ca value of 2.04%

occurs within the 30-45 cm sample of Profile 2. The source leading to this isolated anomaly remains unclear.

ii) Soils developed over non-mineralised slates

Profiles 5 and 6: Both these soil types are brown earths of the Highweek series which are developed on slates outside the main mineralised areas. The concentrations of specific elements from samples of these profiles, however, clearly indicate that both soils have been geochemically influenced by either mineralisation or contamination. Profile 6 was sampled at the same location as site 41 on soil traverse C/C' (Figure 20). This preliminary investigation revealed elevated concentrations of Pb and Zn which are confirmed by the analysis of the profile samples. Concentrations of 384 µg Pb/g and 305 µg Zn/g occur in the upper 15 cm of this soil, and increase with depth to a maximum of 496 µg Pb/g and 405 µg Zn/g in the 45-60 cm sample; the deepest soil sample analysed. This pattern of distribution suggests that underlying mineralisation is contributing both elements to the soil, although no mineral veins are indicated on geological maps of the area where the samples were obtained. The concentrations of As are also elevated in this soil but remain constant throughout the profile. Copper concentrations, in comparison, do not appear to be elevated through contamination or mineralisation. A maximum of 62 µg Cu/g occurs in the top 15 cm of the soil.

Concentrations of As in the topsoil of Profile 5 attain a maximum of 228 µg/g and contrast to the lower concentrations of the element recorded in the subsoil. This results in a large R.T.E. (As) ratio of 7.86 between the 0-15 cm/60-75 cm samples. This site appears to have been affected by the deposition of atmospheric

particulates from an unidentifiable source. An elevated concentration of 112 μg Cu/g in the top 15 cm of this soil further suggests that this profile has been affected by surface contamination.

The results obtained by the analysis of these two profiles show that elevated concentrations of certain trace-elements can occur in soils outside the major mineralised areas. The As and Cu data recorded from Profile 5 suggests that aerial contamination has influenced the trace-element status of the topsoil. Since this profile is located outside the mineralised area, large R.T.E. ratio values, particularly for As, occur due to the relatively limited input of both trace-elements from the underlying parent material. It is worth noting, however, that the As concentrations in the subsoil of this profile are still elevated over the normal soil concentrations quoted in Table 3. The data recorded from the samples of Profile 6 however, indicates that mineralisation and its effect on the trace-element status of soils may also occur outside the mineralised areas mapped by the Geological Survey. Raised concentrations of As, Pb and Zn are observed throughout the profile, and R.T.E. ratios are consequently low.

Profiles 7, 8 and 9: All three profiles were originally classified in the field as brown earths of the Highweek series. However, despite the absence of a brightly coloured ochreous Bs horizon, the persistence of elevated P.Fe concentrations (i.e. > 0.3%) at depth suggests that these soils are brown podzolics belonging to the Dartington series (Staines, 1979). Total Fe and Al concentrations do not correlate well with the P.Fe data since the distribution of the former elements do not necessarily coincide

with the distribution of the P.Fe. This is particularly evident in Profile 8 where the Fe and Al concentrations increase with depth and attain a maximum in the deepest samples which are low in P.Fe.

The concentrations of both As and Cu are considerably lower in these three soil profiles than those recorded from Profiles 1-6. With the exception of the As concentrations recorded from Profile 8, the concentrations of both As and Cu are also lower than the average amounts of both elements calculated from the slate soils of Traverse D/D' (Table 21). It seems possible, therefore, that the As and Cu concentrations recorded from profiles 7 and 9 may be representative of the normal or uncontaminated concentrations of the slate-derived soils. The elevated values of Pb (maximum 224 μg/g in the 15-30 cm sample) and Zn (maximum 201 μg/g in the 60-75 cm sample) found in Profile 8 suggest that this soil is affected by either contamination or mineralisation which may also be influencing the As status of the soil at this particular site. Arsenic concentrations within this soil attain a maxima of approximately 60 μg/g in both the topsoil and also the deepest soil samples analysed. In comparison, within Profile 7 and 9 a pronounced topsoil accumulation of this element is apparent (45 μg/g in both soils), and concentrations decrease with increasing depth. Topsoil accumulation in all three profiles also occurs for the elements Cu, Pb and Ca, although the R.T.E. ratios for these elements are not particularly elevated.

Manganese and Zn concentrations observed from these three profiles appear to be variable in their distribution, whilst Co concentrations increase with depth although the total variation of this element within all three profiles differs to only a small degree. Concentrations of this element within Profile 9, for example, vary by only 4 μg/g.

iii) Man-made (plaggen) soils developed on the slates

Profiles 10, 11 and 12: These three profiles were sampled on the slate south of the Lands End granite. The preliminary soil reconnaissance survey had revealed that elevated concentrations of a number of elements including Ca, Cu, As, Pb and Zn occur in these soils. Further research, discussed in detail in section IIc of this chapter, has indicated that the raised concentrations of these elements observed in the man-made soils are due, at least in part, to the application of beach sand and town refuse (including, possibly, shards of pottery).

The high concentrations of Ca can be directly attributed to the beach sand which has long been added to these soils. A maximum concentration of 1.52% Ca is recorded from the topsoil of these profiles, but the elevated concentrations of this element at depths up to 75 cm (the maximum sampling point of these soils) indicates the thickness of the Ap horizons. Thus, a minimum concentration of 0.4% Ca is recorded at depth within Profile 12; this can be compared to the mean subsoil (i.e. 30-45 cm) concentration of 0.19% Ca calculated from the slate soils of traverse D/D' (Table 21).

Associated with the thick Ap horizons, elevated concentrations of As, Cu, Pb and Zn occur throughout the three profiles, although for the latter three elements there is a distinct accumulation within the upper 15 cm. Maximum concentrations of 78 µg As/g, 172 µg Cu/g, 308 µg Pb/g and 255 µg Zn/g are recorded from the top 15 cm of these soils. In comparison, the concentrations of Al, Co, Fe and Mn do not appear to be elevated in these soils, since the concentrations are similar to those of the slate soils of Traverse D/D' (Table 21).

b) Soils of the granite hills

i) Soils developed over mineralised granites

Profiles 13, 14, 15 and 16: Staines (1979) records that all the freely drained soils of the granite hills are podzolised to a varying extent. In the present research documented in this thesis, three different soil series on the granites have been investigated. Profiles 13 and 15 are brown podzolic soils of the Moretonhampstead series, Profile 14 is a humic brown podzolic soil of the Moor Gate series, whilst Profile 16 is a podzol of the Cucurrian series. The morphologies of these three different soil series are illustrated in Figure 29.

In all four profiles, elevated P.Fe concentrations occur in the subsoils, and indicate the location of the Bs horizons. High concentrations are particularly observed at a depth of 30-45 cm within Profile 14 (1.95% P.Fe) and 15 (0.57% P.Fe), and at a depth of 30-60 cm within Profile 16 (average concentration 0.8% P.Fe). These concentrations are higher than those recorded in almost all the podzolic soils developed on the slate (the exception being Profile 3) and probably are the result of a more advanced degree of podzolisation

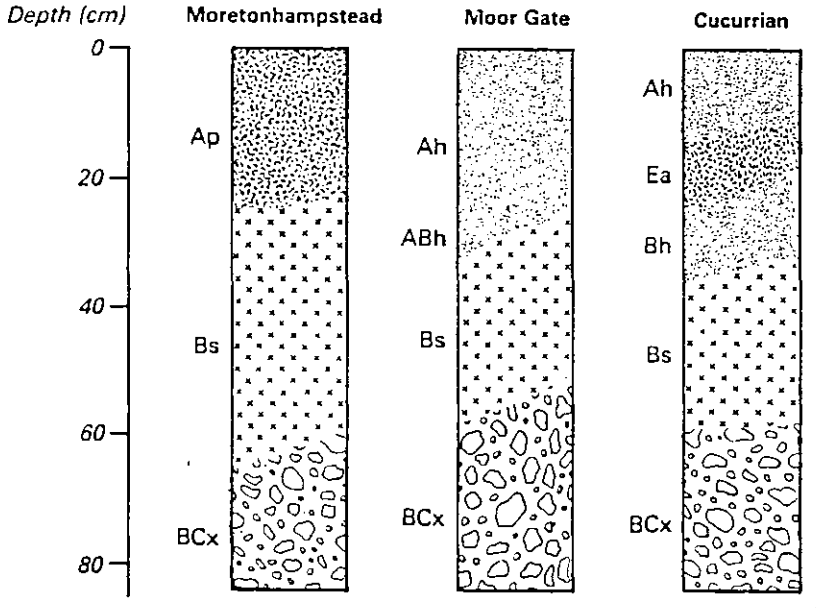


Figure 29. Profile morphology of 3 granite soils investigated in this research (from Staines, 1979).

development. Staines has pointed out in a personal communication that the brown podzolic soils developed on the slates do not show much evidence of downward movement of elements such as Fe and Al by podzolisation: the sesquioxides instead are produced more or less in situ by clay destruction. Within Profiles 14, 15 and 16, the total Fe distribution peaks with the soil samples of high P.Fe content. The highest Al concentrations within these soils, however, occur in the samples immediately below the horizons containing the high amounts of P.Fe. This evidence suggests that the Al may be translocated by the podzolisation processes to depths greater than recorded for Fe. This has been observed in some podzolic soils in Wales where the net redistribution of Fe and Al have been related to differences in response of both elements to the pH and oxidation/reduction conditions which influence their re-precipitation behaviour within the soils (Adams et al., 1980).

Concentrations of 440 µg As/g and 384 µg Cu/g occur in the upper 15 cm of Profile 13 and are clearly the result of atmospheric contamination since the subsoil concentrations are lower in comparison. Relative topsoil enhancement ratios between the 0-15/30-45 cm soil samples are 6.57 for As and 5.82 for Cu. Elevated concentrations of both elements occur in both the upper and deepest soil samples collected from Profile 14, and suggest an input of both elements from a mineralisation as well as an atmospheric source. The concentrations of these elements recorded from both Profiles 13 and 14 are comparable to those recorded from the contaminated and mineralised slate soils, and show that the effects of mineralisation and mining can equally affect the As and metal content of soils developed on the granite.

Both profiles were sampled immediately south of the heavily mineralised Camborne district. In comparison, Profiles 15 (located at Wendron) and 16 (Trencrom Hill) were sampled in areas important for Sn mining only. This is reflected in the lower As and Cu concentrations of both soils, since the topsoils attain a maxima of only 58 µg As/g (Profile 16) and 54 µg Cu/g (Profile 15). However, a comparison of these values to those of the unmineralised granite soils located within the centre of the Carnmenellis granite (Table 20), indicates that small scale enrichment of both elements has taken place within the soils developed in the Sn mining districts. The subsoil concentrations of the profile sampled at Wendron does not, however, confirm the very high concentrations of Cu, Pb and Zn which were disclosed by the earlier soil reconnaissance survey.

ii) Soils developed over unmineralised granites

Profiles 17 and 18: The amounts and distribution of P.Fe in these two soils clearly show their podzolised nature. A particularly high concentration (2.03%) occurs at 30-45 cm depth within Profile 17, and the total Fe and Al distribution similarly peaks in this horizon. In Profile 18, high concentrations of P.Fe occur between 30 to 75 cm. Total Fe concentrations attain a maxima of 2.96% at a depth of 45-60 cm within this profile, whilst the highest Al concentration (3.88%) occurs at a depth of 60-75 cm.

Both the As and Cu concentrations in these two soils are lower than those recorded from Profiles 13-16, and suggest that these profiles have been little affected by contamination. Concentrations

of both elements only slightly differ throughout the profile. This is particularly evident for Cu where the total variation of this element differs by 5 µg/g within Profile 17, and 6 µg/g within Profile 18. Despite this small variation, an accumulation of both elements in the topsoil is observed. A slight peak in As concentration is also associated with the illuviated sesquioxide-enriched horizons. For example, a concentration of 34 µg As/g is recorded at a depth of 30-45 cm within Profile 17, thus coinciding with the zone of elevated P.Fe. Concentrations of As above and below this sample are lower than this value.

The distribution of the remaining trace-elements in the two profiles are variable. Both Pb and Ca decline in concentration with depth, whilst Zn concentrations increase. Manganese and Co have a variable distribution throughout the two profiles, although for the former trace-element an enrichment in the topsoils is apparent.

c) Discussion

Analysis of the 15 granite and slate derived soil profiles confirms many of the earlier observations made from the results of the soil reconnaissance survey. Elevated concentrations of both As and Cu- and to a lesser extent Zn and Pb- can occur in soils previously thought to be unaffected by mineralisation and contamination. This presents a difficulty in determining the natural distribution and concentrations of these trace-elements in the soils of the study area. However, evidence from some of the soil samples collected within the unmineralised areas indicates that an accumulation of certain trace-elements including As, Ca, Cu, Pb and Zn occurs in the topsoils. For

some of these elements, this observation may be the result of low level contamination caused by distant mining activities. For example, Hughes (1979) has demonstrated that the topsoils of sand pararendzinas and peats can be slightly contaminated by As in districts of west Cornwall remote from the mined areas. Alternatively, the topsoil accumulation noted in this present research may be due to natural pedological processes caused by the biogeochemical cycling of the five elements between the soil-plant interface, and the accumulation of the trace-elements by organic complexing (Chapter 1). Agricultural practices may further influence the trace-element content of the topsoils, since the Ca content of soils will be affected by applications of lime. In addition, the historical practice of burning turf on the granite hills may affect the chemistry of the soils. This system of agriculture, known as 'Beat Burn' or 'Devonshiring', was commonly undertaken some 100-200 years ago, and has resulted in the 'fixing' of loose organically bound Cu in the topsoils (Hosking, personal communication).

It is clear from the discussion above that the distinction between uncontaminated soils and those soils which have been influenced by low levels of mining contamination has not been fully determined in this research. This is due firstly to the complicated mining history and extensive areas of mineralisation within the Hayle/ Camborne-Redruth area. Secondly, the limited outcrop of the Devonian Mylor slates meant that sampling could not be undertaken on this parent material at distances well away from the mineralised regions. The sampling of uncontaminated soils developed from similar argillaceous parent materials elsewhere in South-west England was not considered to be satisfactory in this study, since published scientific literature

had indicated the trace-element enriched nature of the Mylor slates compared to the other geological formations encountered in South-west England (Chapter 5). Thus, control values derived from these latter formations would be unlikely to be representative of the soils developed on the Mylor slates.

Higher levels of contamination are more clearly reflected in the trace-element content of soils within the study region. For example, maximum concentrations of 720 μg As/g and 480 μg Cu/g in the topsoil of Profile 2 located at Camborne clearly defines the most intensively mined area in South-West England. The data obtained from Profiles 5 and 13 indicates that topsoil enrichment of both elements through contamination especially affects the upper 30 cm of the soil. Thus, relative topsoil enhancement ratios for both elements between the 0-15/30-45 cm samples are elevated. More usually, however, high subsoil concentrations of these elements are associated with the contaminated topsoils which results in comparatively low R.T.E. ratios. The high subsoil concentrations can be attributed mainly to mineralisation; for example the raised concentrations of As (133 μg/g), Cu (352 μg/g), Co (120 μg/g), Mn (4000 μg/g) and Pb (368 μg/g) at depth within Profile 4 indicates the multi-element enrichment of the soils which can occur because of the complex mineral ores of the district.

Whilst mineralisation may be the main source of high trace-element concentrations found in the subsoils, other pedological processes operating within these soils may also influence the trace-element content of the lower soil horizons. The highest concentrations of potassium pyrophosphate extractable Fe occur in the ochreous (podzolised) Bs horizons of the granite soils sampled in Profiles

14-18. A peak in the total Fe content coincides with the P.Fe enrichment, whilst Al may be translocated to a greater depth by the podzolisation process. A similar enrichment of P.Fe and total Fe and Al is observed in the 30-45 cm sample of Profile 3 developed on the slate. In comparison, the remaining podzolised slate soils (and also Profile 13 developed on the granite) contain lower concentrations of P.Fe within the illuviated horizons, and also show little association between the distributions of P.Fe and total Fe and Al. These observations suggest that the degree of podzolisation development is generally more advanced in the granite soils rather than the slate counterparts. The limited movement of Fe and Al down the profile of the slate derived brown podzolic soils has been previously suggested by Staines, whose theory on their formation has been outlined earlier in this chapter.

From the limited amount of data available in this study, an association between the distribution of As and the podzolisation process may be postulated. Within the granite soils sampled in Profiles 15 to 18, a slight enrichment of As is evident in the Bs horizons. For example, within Profile 17 an As concentration of 34 µg/g is associated with the Bs horizon which contains over 2% P.Fe at 30-45 cm depth. The soil samples above and below this horizon contain lower amounts of As. A number of workers have found the sorption of As to be closely related to the sesquioxide content of soils (Thomas, 1955; Jacobs et al., 1970b; Korte et al., 1976; Wauchorpe, 1975; Woolson et al., 1971a, 1971b) with consequent enrichment of the element in B horizons (Boyle and Jonasson, 1973; Presant, 1966, 1971; Presant and Tupper, 1966). The observations put forward in this research, however, must remain tentative because of the limited amount of

data available due to the contamination and mineralisation effects which elevate and mask the natural As distribution and concentrations recorded from most of the soils studied. Nevertheless, it is interesting to note that no similar enrichment of As occurs in the Bs horizons of the slate derived brown podzolic soils sampled in Profiles 7, 8 and 9. This may promote the idea that a more advanced degree of podzolisation and profile development - as occurs in the granite soils - is necessary before a marked variation in the As distribution is observed. A similar theory of trace-element redistribution in soil profiles was indicated by Swaine and Mitchell (1960) following an extensive study of Scottish soils.

No other trace-element studied in this research appears to be influenced by the podzolisation processes operating within the soils of the study area. An enrichment of Pb (40 μg/g) associated with the illuviated horizon within Profile 17 is not observed in any of the remaining podzol profiles. However, enrichment of this element together with As, Ca, Cu and Zn in the man-made soils south of the Lands End granite can occur throughout the upper 75 cm of these soils. The distribution of these elements in the man-made soils correlate with the thick Ap horizon developed by man through the addition of beach sand and town refuse to the soils. These additives appear to be responsible for the raised concentrations of these five elements observed in the soil profiles.

(IV) THE CONTAMINATION OF SOILS THROUGHOUT THE SOUTH-WESTERN PENINSULA

a) Statistical correlations between the trace-element concentrations of the soils and stream sediments within the Hayle/Camborne-Redruth study area

Previous scientific research undertaken in South-West England has used statistical techniques in delinating areas of soil contamination. Soils sampled along control traverses have been analysed, and the means ($\bar{x}$) and standard deviations (σ) of the trace-element concentrations calculated. Using these statistical parameters, threshold values indicating soil contamination have been computed by Davies (1971) (Threshold = $\bar{x} + 3\sigma$) and by Colbourn (1976) (Threshold = $\bar{x} + 2\sigma$). The previous sections of this chapter, however, indicates the difficulty in selecting suitable control traverses within the Hayle/Camborne-Redruth study area due to the widespread metalliferous soil contamination. Furthermore, the analytical data obtained from the few apparently uncontaminated sites sampled in this study suggest that there is a natural difference between the trace-element content of soils derived from the granites and those from the slate/greenstone. Thus, the contamination threshold values calculated from the granite soils would not be applicable to the slate/greenstone sites, and vice-versa. In order to overcome these problems, therefore, the topsoil and subsoil data for each of the elements, Sn, As, Cu, Pb and Zn, determined from the four reconnaissance soil traverses sampled in the Hayle/Camborne-Redruth study area, were combined and contamination threshold boundaries selected on a percentile basis. The 70th and 90th percentiles

were chosen arbitrarily to delinate those soils which are moderately contaminated with each of the five elements. Soils with Sn, As, Cu, Pb or Zn concentrations exceeding the 90th percentile are considered to be highly contaminated with respect to the particular element concerned, whilst soils with concentrations less than the 70th percentile are either slightly contaminated or uncontaminated.

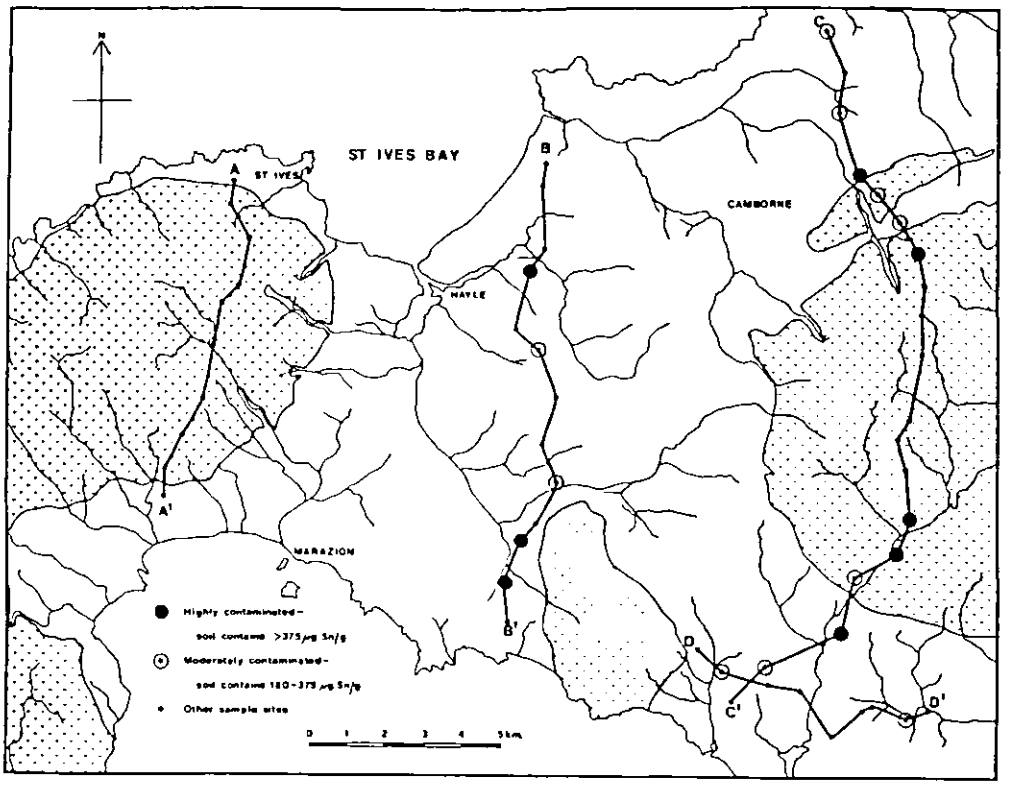
The contamination threshold values calculated in this way are presented in Table 24, and the distribution of the moderately or highly contaminated soils within the Hayle/Camborne-Redruth district are shown in Figures 30-34. Table 25 summarises the number of topsoils and subsoils which are either moderately or highly contaminated. This table shows that the highest concentrations of all five trace-elements are generally associated with the upper 15 cm of the soil profile. The distribution of the five trace-elements studied along the soil reconnaissance traverses has been discussed in Section II of this chapter, and accordingly the patterns of trace-element concentration disclosed in Figures 30-34 will not be outlined in full here. However, the diagrams clearly show that raised concentrations of Sn, As, Cu, Zn and Pb in the soils of the Hayle/Camborne-Redruth study area are closely related to the distribution of the mining fields shown in Figure 9. Elevated concentrations of Sn, As, Cu and, particularly, Pb and Zn are additionally found south of the Carnmenellis granite; the discussion in Section II of this chapter attributes such raised concentrations to the effects of mineralisation and contamination, or to the underlying Devonian Mylor slates. In contrast, the granites are not associated with many highly or moderately contaminated soils. Mineralisation, particularly for the

Element	Moderately contaminated	Highly contaminated
Sn	180 - 375	>375
As	110 - 190	>190
Cu	125 - 235	>235
Zn	190 - 300	>300
Pb	105 - 145	>145

(all values in µg/g)

TABLE 24. Contamination threshold values calculated from the soilssampled along four traverses within the Hayle/Camborne-Redruth study area.

a) Topsoil



b) Subsoil

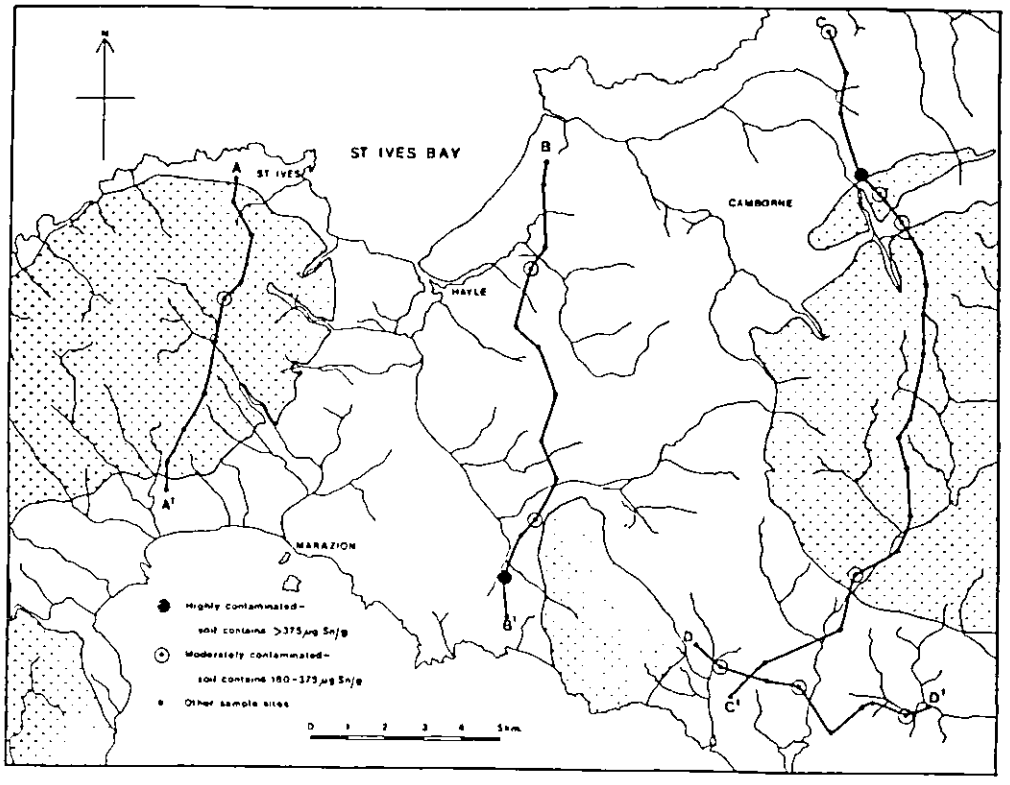
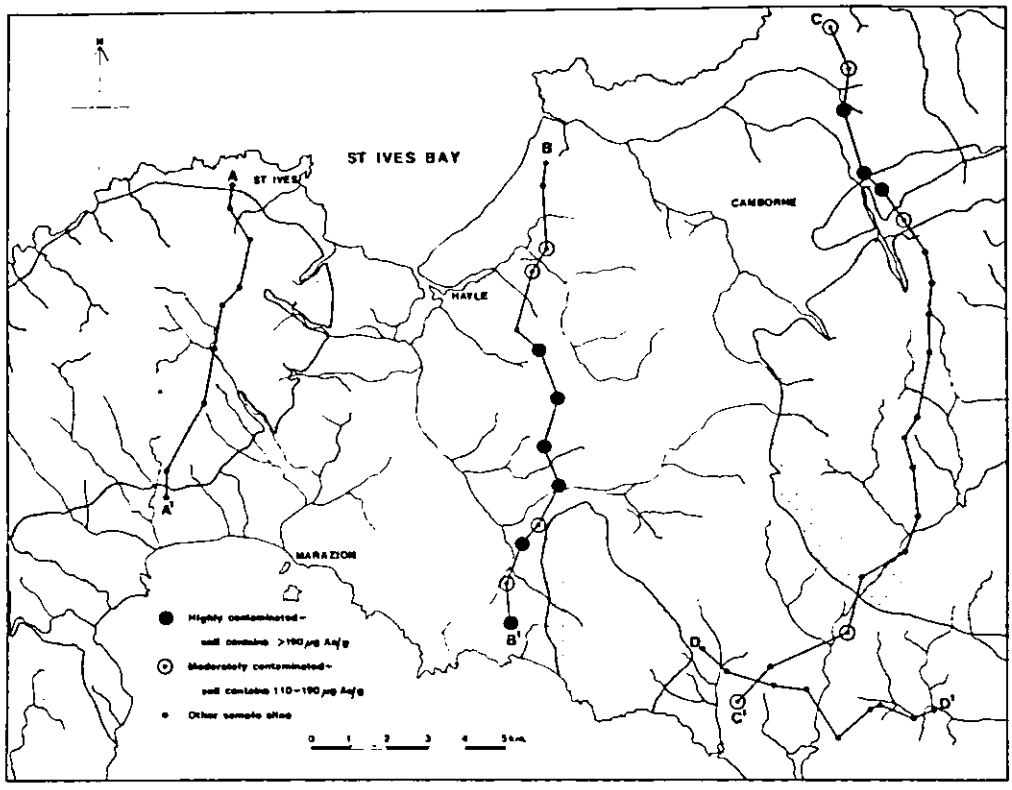


FIGURE 30. The distribution of soils contaminated with tin within the Hayle/Camborne-Redruth study area.

a) Topsoil



b) Subsoil

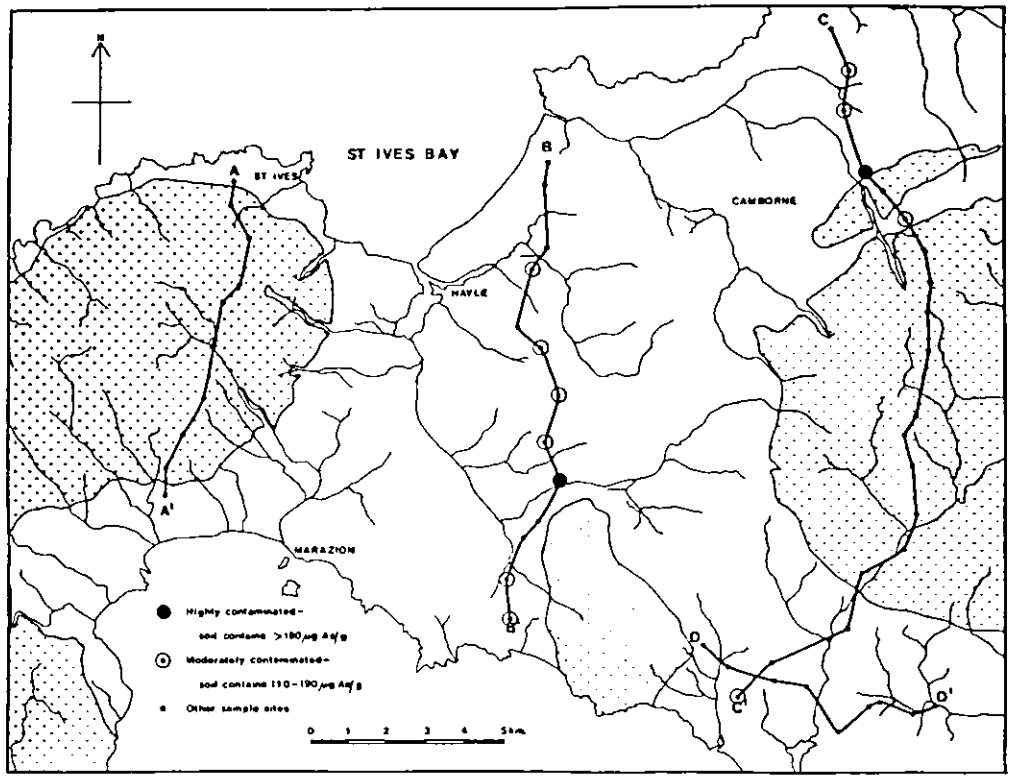
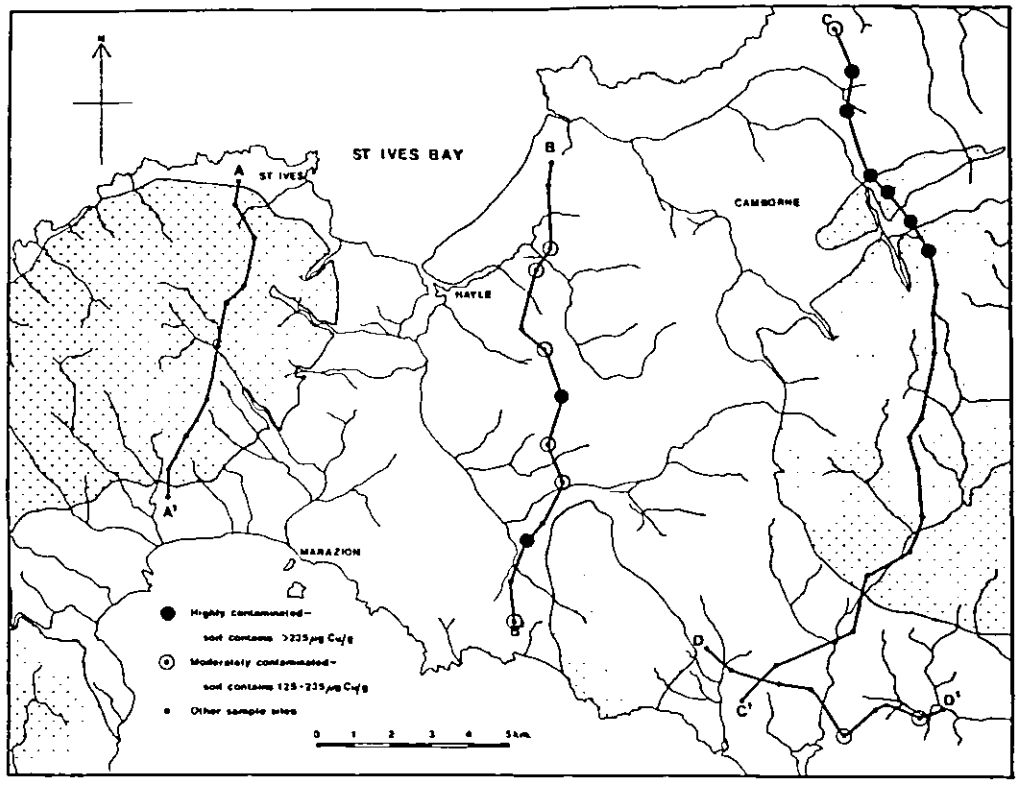


FIGURE 31. The distribution of soils contaminated with arsenic within the Hayle/Camborne-Redruth study area.

a) Topsoil



b) Subsoil

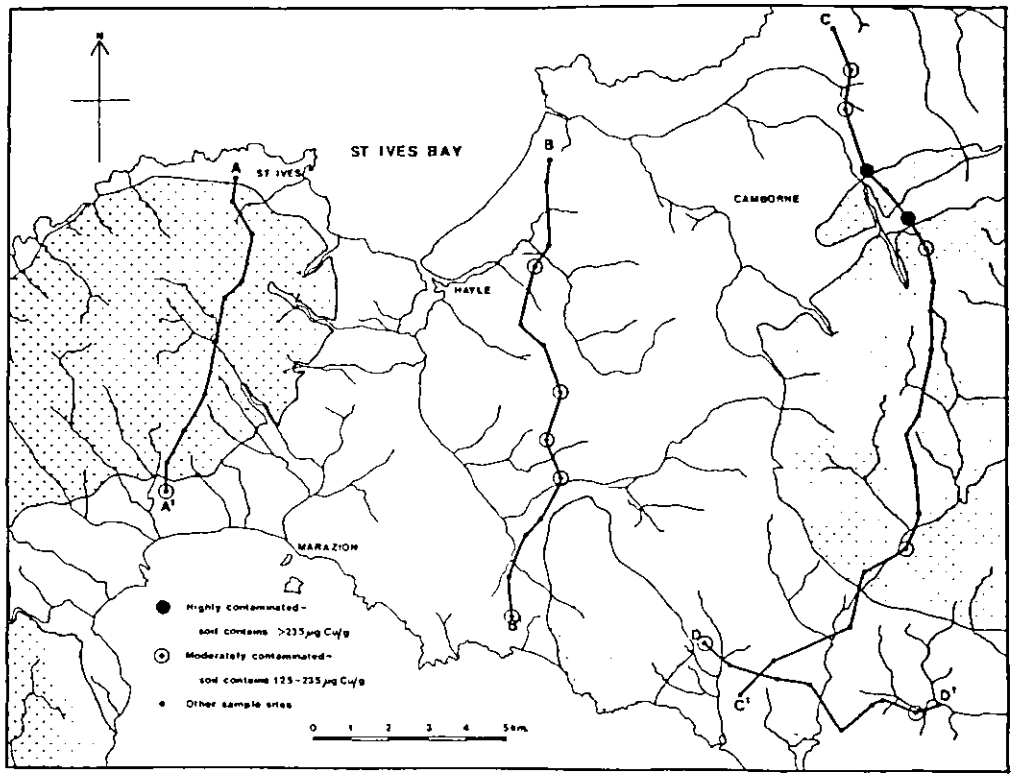
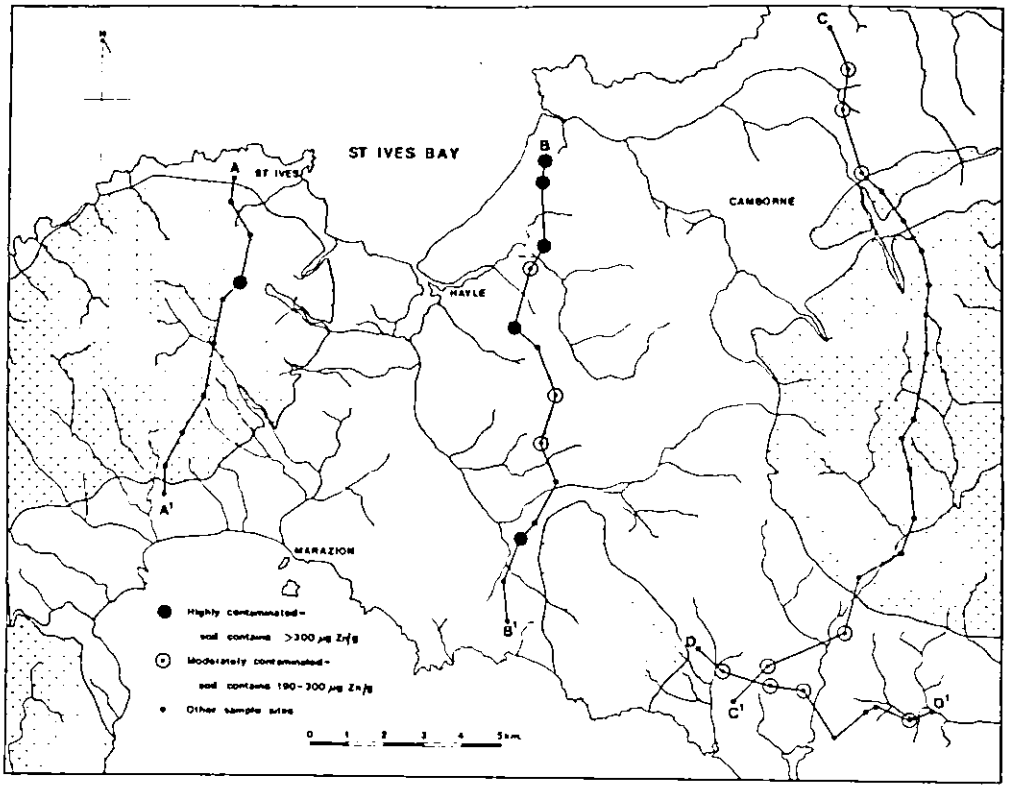


FIGURE 32. The distribution of soils contaminated with copper within the Hayle/Camborne-Redruth study area.

a) Topsoil



b) Subsoil

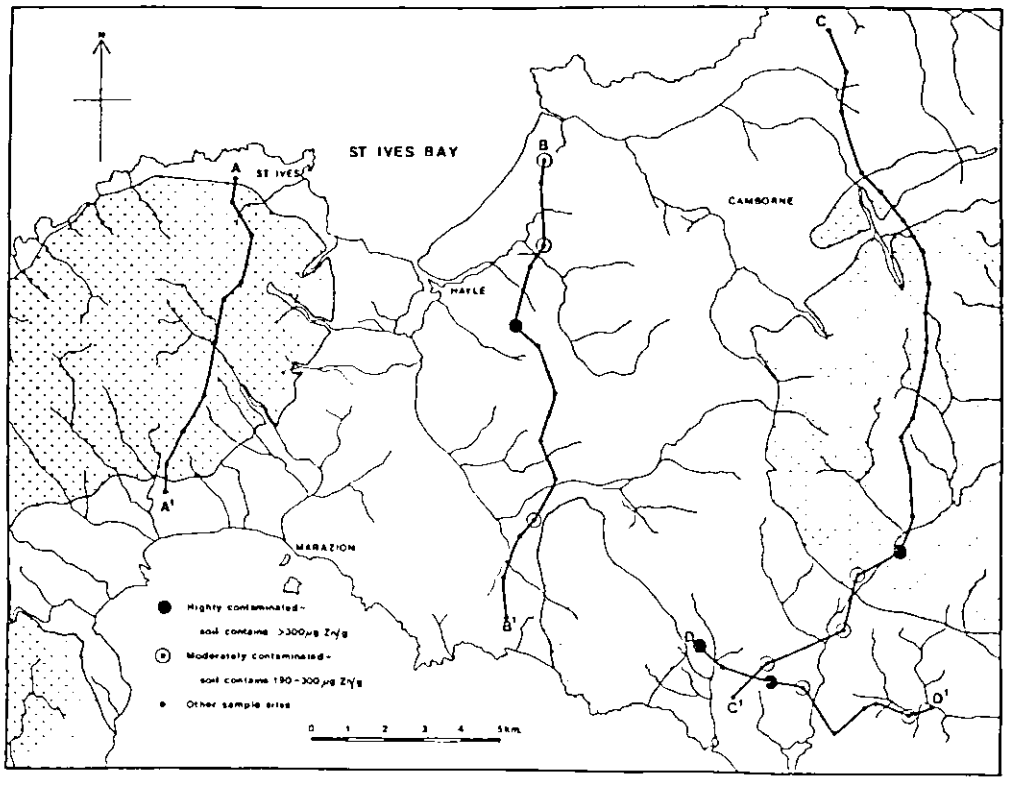
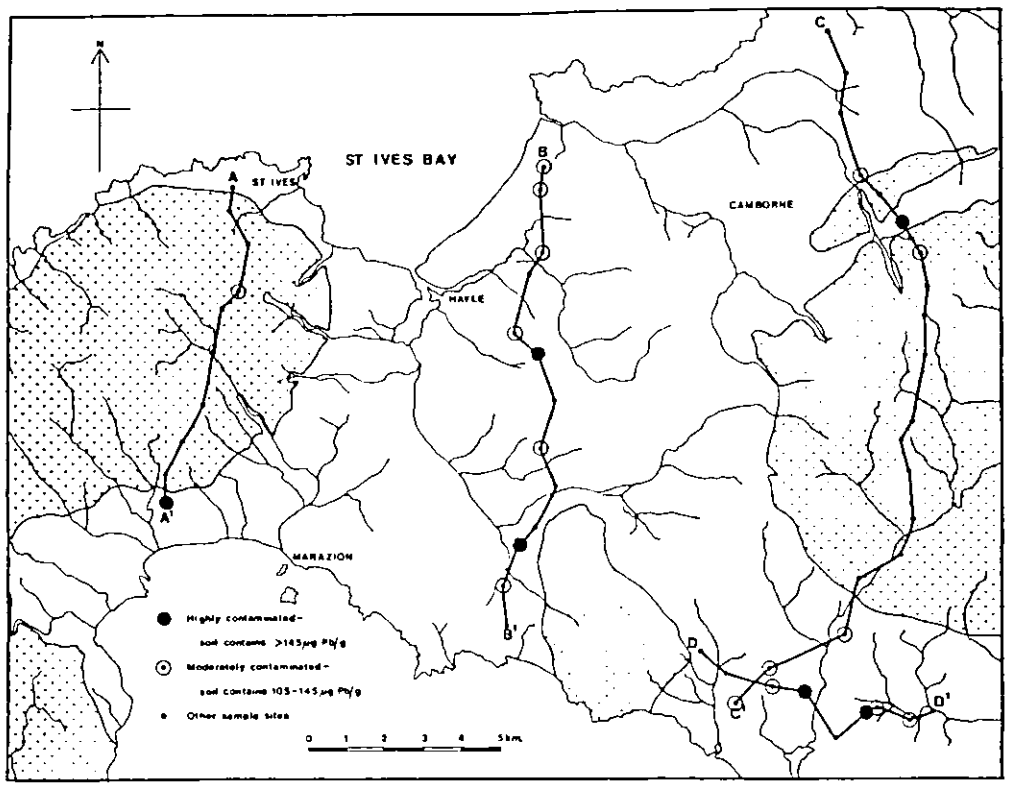


FIGURE 33. The distribution of soils contaminated with zinc within the Hayle/Camborne-Redruth study area.

a) Topsoil



b) Subsoil

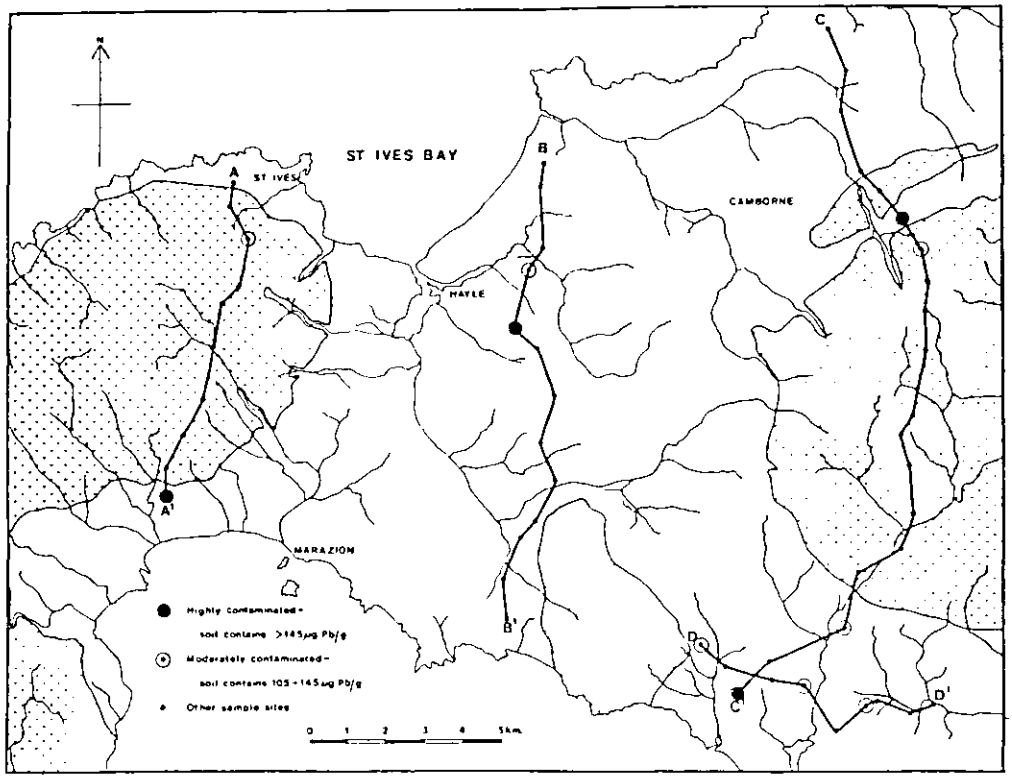


FIGURE 34. The distribution of soils contaminated with lead within the Hayle/Camborne-Redruth study area.

	Sn	As	Cu	Zn	Pb
Topsoil (0-15cm)					
Highly contaminated	8	8	8	6	6
Moderately contaminated	10	10	9	12	15
TOTAL	18	18	17	18	21
Subsoil (30-45cm)					
Highly contaminated	2	2	2	4	4
Moderately contaminated	10	10	12	8	7
TOTAL	12	12	14	12	11
Topsoil + subsoil TOTAL	30	30	31*	30	32*

*Grand total exceeds 30 due to more than one sample site corresponding to the 70th percentile soil concentration.

TABLE 25. The number of highly and moderately contaminated topsoils and subsoils within the Hayle/Camborne-Redruth study area.

elements As, Cu, Pb and Zn, is not widespread within the granites (Figure 9), and the trace-element concentrations of these four elements associated with the igneous bodies are considerably lower than the concentrations recorded from the Mylor slates (Chapter 5).

Statistically, the distribution of the contaminated soils recorded in Figures 31-34 can be compared with the stream sediment reconnaissance data outlined in Section IVc of Chapter 3 (Figures 15-18) by constructing a 3 x 3 contingency table*. Both the stream sediment and soil data presented in Figures 15-18 and 31-34 are subdivided into highly, moderately and uncontaminated classes. If the soils and stream sediments of the study area are perfectly correlated, therefore, all the highly contaminated soils should occur within the boundaries delineating the highly contaminated stream sediments. The same should also apply to the moderately contaminated and uncontaminated soil and stream sediment data. As an example, Figure 35 shows the relationship which exists between the topsoil As contamination classes and the stream sediment As classes. Note that data from soil sampling sites too close to a mapped stream sediment contamination boundary have been discarded in the statistical appraisal: the stream sediment contamination boundaries are based on human interpretation and may thus not be totally accurate. A null hypothesis can be considered, which in this case would be that there is no relationship between the soil and stream sediment distributions. The chi-square test can then be used to permit a comparison of the real (observed) data in the

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* NB Sn could not be statistically compared in this way since this element was not analysed during the stream sediment reconnaissance follow-up survey.

soil:	stream sediment: highly contaminated	moderately contaminated	slight/uncontaminated
highly contaminated	xxxx	xxxx	
moderately contaminated	xx	xxxxxx	
slight/ uncontaminated	x	xxxxxxxxx	xxxxxxxxxx xxxxxxxxxx x

n = 47

FIGURE 35: An example of a 3 x 3 contingency table - topsoil As versus stream sediment As. The x's indicate the number of times soils belonging to a certain contamination class are located within the specified stream sediment contamination zones.

3 x 3 contingency table with those which would be expected if there was no relationship between the two variables. The test statistic is:

$$\chi^2 = \frac{\sum_{1}^{n}(E_i - O_i)^2}{E_i}$$

where O_i is an observed value and E_i is the corresponding expected value.

The calculated χ^2 value can be compared against a tabulated value and, providing the former is higher than that in the table, the null hypothesis can be rejected. Table 26 outlines the calculated χ^2 values obtained from the relationship observed between the soil and stream sediment distributions. The topsoils of all four elements studied in this way are significantly correlated with the stream sediment reconnaissance maps. However, only the subsoil As and Pb concentrations are related to the stream sediment trace-element distributions. Thus, the stream sediments in the Hayle/Camborne-Redruth study area more accurately reflect the trace-element content of the topsoils than the subsoils. This may be expected, since the widespread surface enrichment caused by mining contamination - as noted earlier in this chapter - is more likely to affect both the topsoils and stream sediments than the underlying soil samples.

b) The extent of trace-element contamination throughout South-west England

On the basis of the statistical correlations outlined above, the stream sediment data comprising the Wolfson Geochemical Atlas of England and Wales can be used to delineate the areas of topsoil

Correlation between the trace-element distribution of the stream sediments and topsoils:

	Calculated X^2 value
As	24.41**
Cu	22.42**
Zn	21.50**
Pb	12.53*

Correlation between the trace-element distribution of the stream sediments and subsoils:

	Calculated X^2 value
As	27.30**
Cu	6.94
Zn	2.03
Pb	14.22**

** = significant at p = 0.01; * = significant at p = 0.05; 4 degrees of freedom

TABLE 26. Calculated X^2 values obtained by comparing the distribution patterns of the soils and stream sediments within the Hayle/Camborne-Redruth study area.

As, Cu, Zn and Pb contamination - and subsoil As and Pb contamination - throughout South-west England. Using the same stream sediment contamination thresholds outlined in Figures 15-18, areas of high or moderate stream sediment contamination within the province can be delineated by plotting the Wolfson Geochemical Atlas data using the computer programme FMAP developed by Kinniburgh (personal communication). Because of the statistical correlations calculated in Section IVa of this chapter, the areas of high or moderate stream sediment enrichment should also be areas where the soils are similarly enhanced in their As, Cu, Pb and Zn content.

The 'grey-scale' maps produced in this way from the Wolfson Geochemical Atlas data are presented in Figures 36-39. Such maps are comprised of map cells, each of which represents a surface area of 6.5 km^2. These map cells are obtained by spatial smoothing techniques in order to reduce sampling and analytical 'noise' and to bring out reliable regional patterns (Webb et al., 1978). The distribution of As, Cu, Zn and Pb in Figures 36-39 can be compared with Figure 6 which outlines the mining fields and mineralised areas of the province. The stream sediment maps indicate two major areas of trace-element enrichment:

i) Hayle/Camborne-Redruth/St. Day/St. Agnes-Cligga granite: The elevated trace-element concentrations found previously within the Hayle/Camborne-Redruth study area is shown by all four maps to extend outside this region to encompass the St. Day mining field, east of Redruth. Further contamination is associated with the St. Agnes district, and high Zn and Pb concentrations occur in the stream sediments of the St. Agnes and Cligga granite areas. The importance of Pb mineralisation and its output from the St. Agnes district in

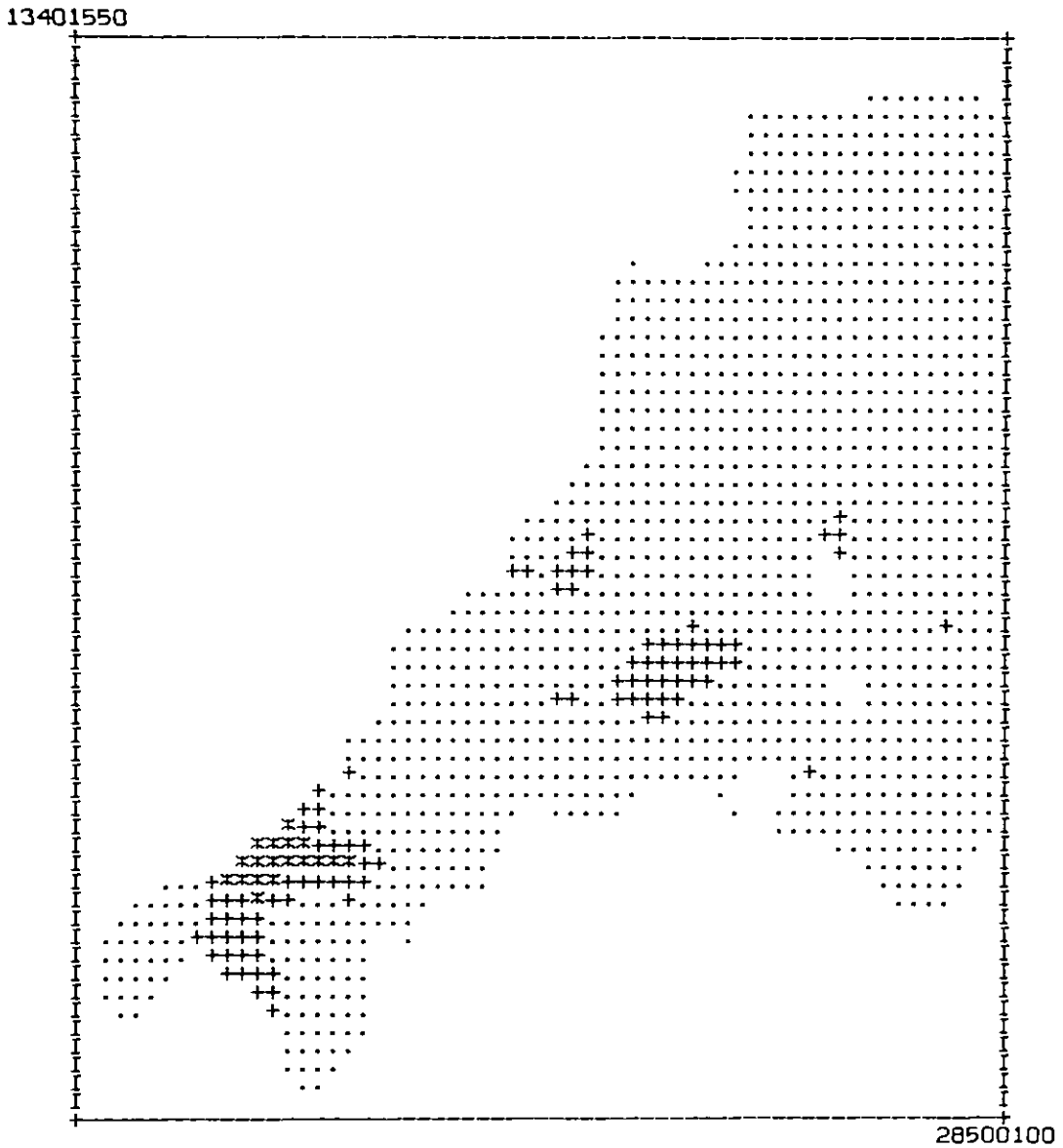


FIGURE 36. The distribution of land contaminated with arsenic in South-west England.

Key

Stream sediment values	Map Symbol	Number of map cells	Percentage of total land area surveyed
Uncontaminated (<100ug As/g)	·	1297	92.1
Moderately contaminated (100 - 500ug As/g)	+	93	6.6
Highly contaminated (>500ug As/g)	×	18	1.3

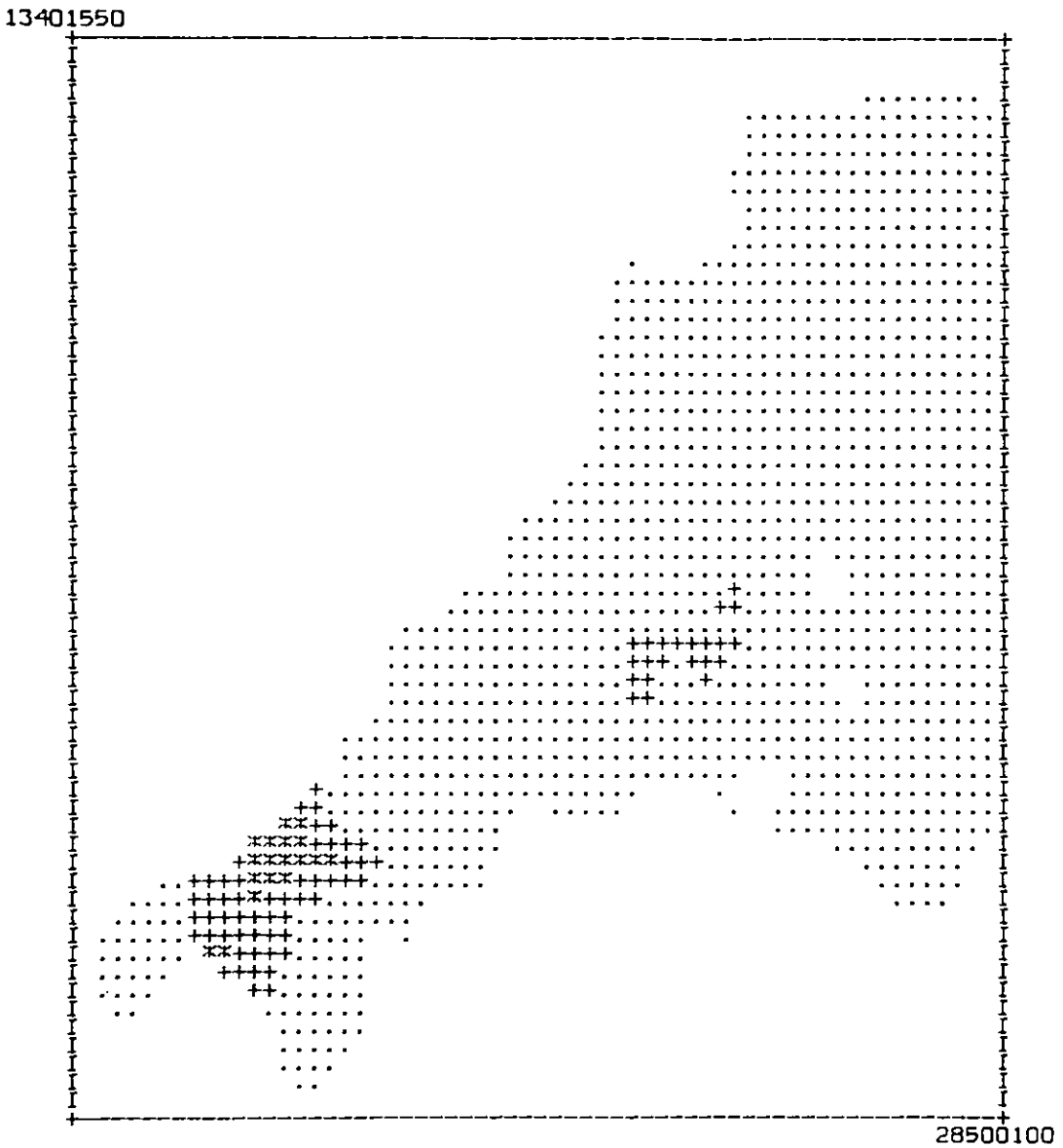


FIGURE 37. The distribution of land contaminated with copper in South-west England.

Key

Stream sediment values	Map symbol	Number of map cells	Percentage of total land area surveyed
Uncontaminated (<100 µg Cu/g)	·	1314	93.3
Moderately Contaminated (100-500 µg Cu/g)	+	76	5.4
Highly Contaminated (>500 µg Cu/g)	x	18	1.3

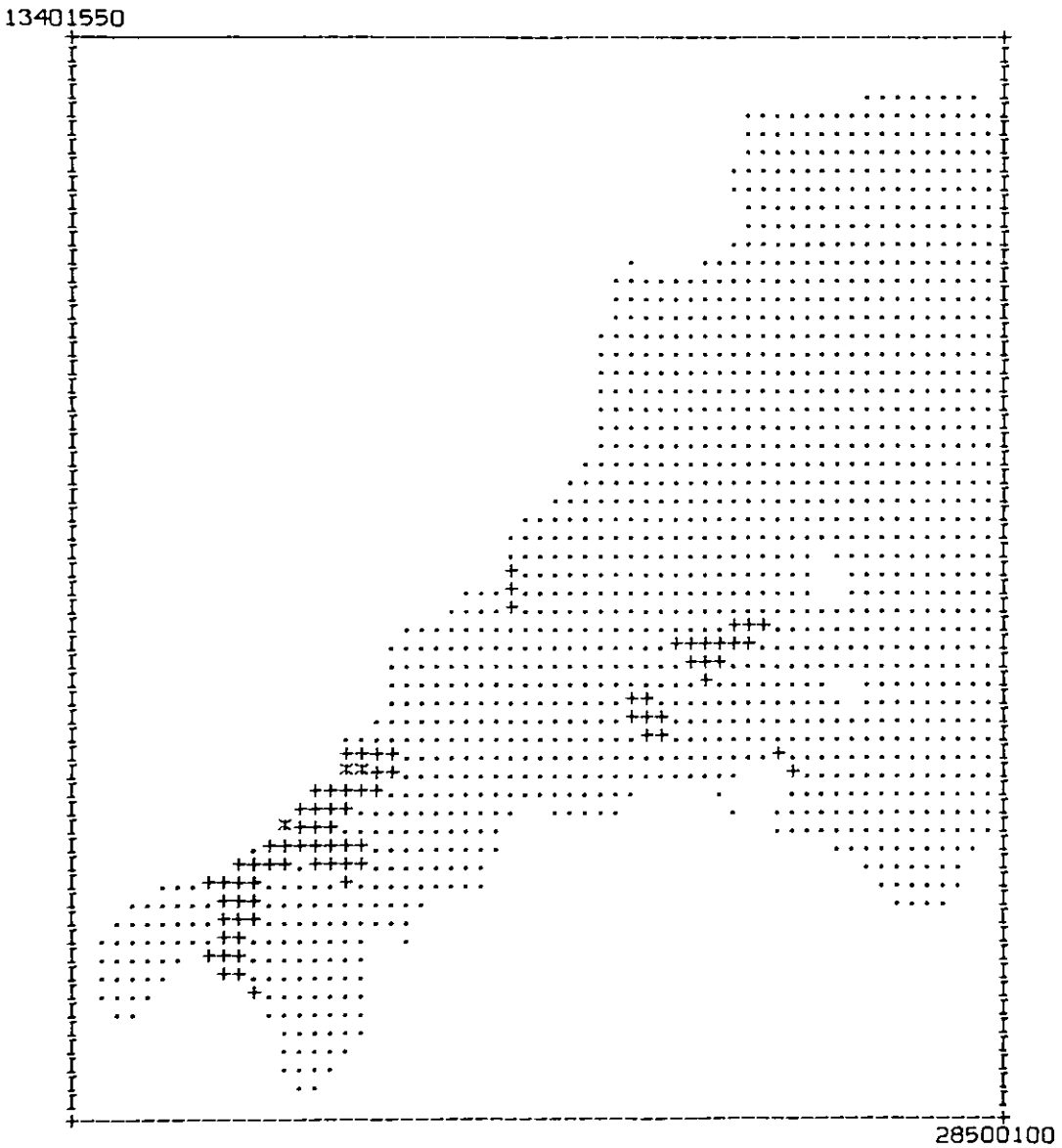


FIGURE 38. The distribution of land contaminated with zinc in South-west England.

Key

Stream sediment values	Map symbol	Number of map cells	Percentage of total land area surveyed
Uncontaminated (<300 µg Zn /g)	·	1328	94.3
Moderately Contaminated (300 µg - 700µg Zn /g)	+	77	5.5
Highly Contaminated (>700 µg Zn/g)	x	3	0.2

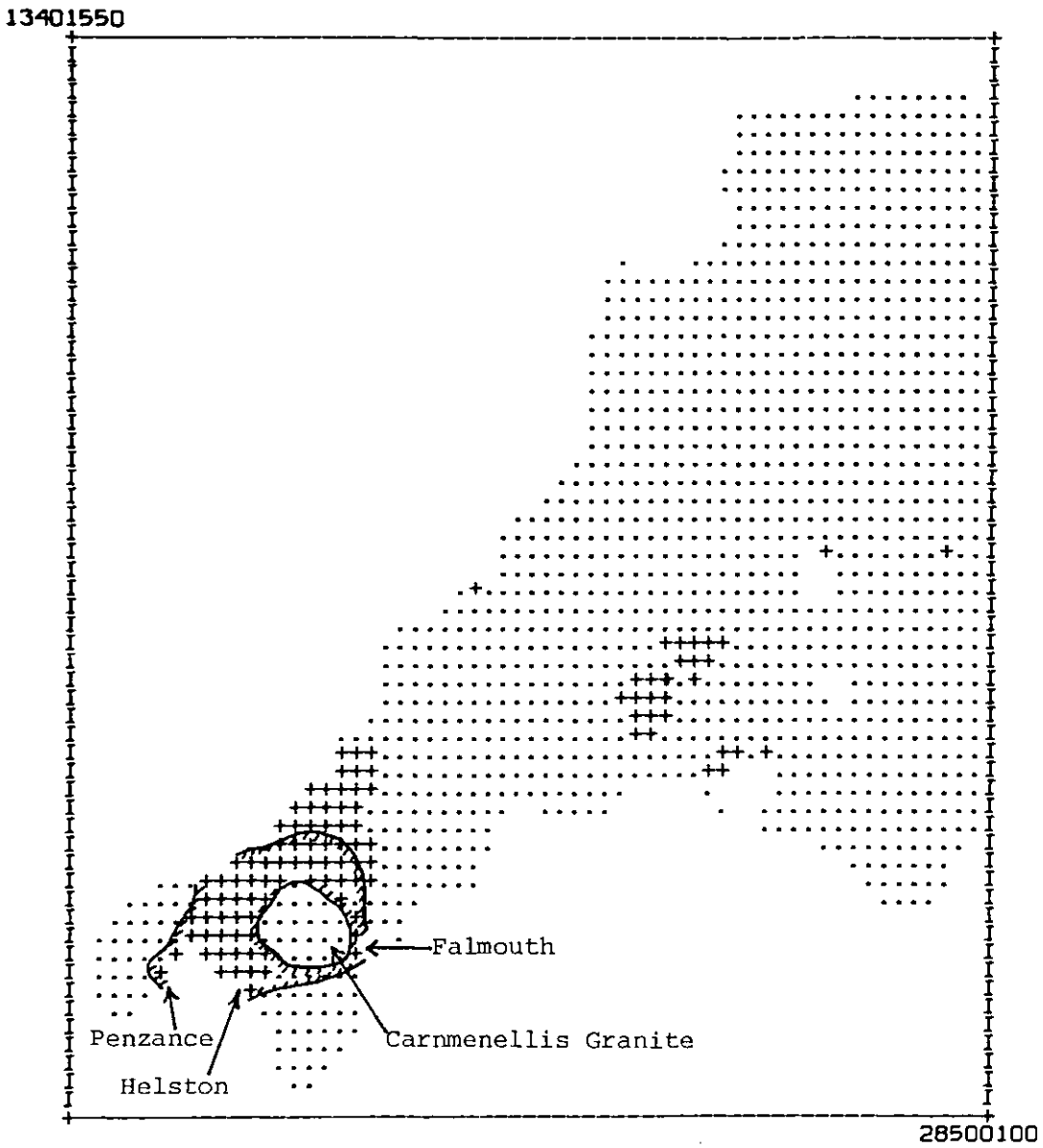


FIGURE 39. The distribution of land contaminated with lead in South-west England.

Key

Stream sediment values	Map Symbol	Number of map cells	Percentage of total land area surveyed
Uncontaminated (<100 µg Pb /g)	.	1298	92.2
Moderately contaminated (100 - 500 µg Pb/g)	+	110	7.8
Boundary of Mylor Slate Outcrop	=		

relation to the remaining areas of South-west England is noted in Table 11. Dines (1956) further indicates that St. Agnes was the most important producer of Zn within South-west England, producing some 75% of the total 85,000 tons extracted from the province.

ii) Liskeard/Callington/Tavistock: elevated concentrations of As, Cu, Pb and Zn are associated with these three important mining regions. It can be assumed that such raised concentrations are attributable to the joint effects of both mineralisation and mining contamination.

In addition to the two major areas of trace-element enrichment outlined above, several minor areas of raised trace-element concentrations are observed within South-west England. In particular, As concentrations are enriched within the north-western district of Dartmoor, and additionally around the Camelford area where small scale Pb and Zn enrichment is also evident (Figures 36, 38 and 39). In both areas, however, mineralisation and mining activity was considerably limited compared to the major contaminated regions outlined above. Both Dines (1956) and Reid et al. (1910) indicate the small output of As associated with the Camelford and north-west Dartmoor areas.

A further zone of trace-element enrichment, notably for the elements Pb and Zn, occur in the stream sediments surrounding the Plymouth region. Although no detailed follow-up work has been undertaken in this area, such contamination is possibly associated with sources related to the urban conurbation, and is not attributable to metalliferous mining activities.

Since each map cell represents 6.5 km², a compilation of the data comprising these stream sediment maps allows the total area of trace-element contamination within South-west England to be calculated. For example, Table 27 indicates that some 722 km² of land within the province is contaminated with As. Of this total figure, 618 km² of land is associated with the two major contaminated areas outlined earlier. A further breakdown of the data shows that 117 km² of South-west England is highly contaminated with both As and Cu (Table 28). Figures 36 and 37 reveal that the highly contaminated stream sediments occur mainly within the Hayle/Camborne-Redruth/St. Day mining areas. In comparison, land highly contaminated with Zn is severely restricted (20 km²), and the stream sediment maps further indicate that no part of the South-western peninsula is highly contaminated with Pb, despite the fact that such elevated concentrations have been recorded in the stream sediments within the Hayle/Camborne-Redruth study area (Figure 18). This is attributable to the smoothing techniques undertaken in plotting the stream sediment data shown in Figure 39.

A comparison of the trace-element distributions shown in Figures 36-39 indicates the multi-element contamination of the stream sediments which occurs because of the close association between the four trace-elements and the mineralisation/mining sources. Some stream sediments are not contaminated with all of the four elements, however, and by visually superimposing the data from Figures 36-39 together, the total area of land either highly or moderately contaminated with one or more of the trace-elements investigated can be calculated as 1,092 km². This is equivalent to 11.9% of the total land surface surveyed in this study.

	As	Cu	Pb	Zn
1. Hayle/Camborne-Redruth/St. Day/St. Agnes-Cligga granites	410	468	526.5	358
2. Liskeard/Callington/Tavistock	208	143	136.5	130
3. Camelford district	65	0	6.5	20
4. North-west Dartmoor	26	0	6.5	0
5. Plymouth district	6.5	0	32.5	13
6. Others	6.5	0	6.5	0
TOTAL (km^2)	722	611	715	521

TABLE 27. The distribution and extent of the areas in South-west England contaminated by As, Cu, Pb and Zn.

	As	Cu	Pb	Zn
Highly contaminated:				
(i) In km^2	117	117	0	20
(ii) percentage of the land area of S.W. England	1.3	1.3	0	0.2
Moderately contaminated:				
(i) In km^2	605	494	715	501
(ii) percentage of the land area of S.W. England	6.6	5.4	7.8	5.5
Total:				
(i) In km^2	722	611	715	521
(ii) percentage of the land area of S.W. England	7.9	6.7	7.8	5.7

note:- area of S.W. England surveyed = 9152 km^2.

TABLE 28. The total extent of As, Cu, Pb and Zn contamination in South-west England.

c) Discussion and conclusions

On the basis of statistical correlations between the distribution of trace-elements in soils and stream sediments within the Hayle/Camborne-Redruth study area, the Wolfson Geochemical Atlas stream sediment data have been used to delineate further areas of soil As, Cu, Pb and Zn contamination throughout South-west England. Two major areas of soil contamination are indicated by this research. Firstly, the contamination initially recorded in this study within the Hayle/Camborne-Redruth region is shown to extend east and north-eastwards to encompass the mining areas centred around St. Day, St. Agnes and Cligga granite. The second area of contamination is shown to occur in the Liskeard, Callington and Tavistock regions. Although no follow-up soil reconnaissance work has been undertaken in these latter areas, soils have been previously shown to be contaminated in certain districts of these regions by numerous workers (Millman, 1957; Davies, 1971; Aguilar Ravello, 1974; Colbourn et al., 1975; Colbourn, 1976; Hogan, 1977; Thoresby and Thornton, 1979).

Minor areas of elevated trace-element concentrations are centred on the north-west Dartmoor district, Camelford and the area surrounding Plymouth. It is presumed that the Pb and Zn enrichment at this latter locality is attributable to sources associated with the urban conurbation since there is no mineralisation or associated metalliferous industries located within the region. Both Hosking et al. (1965) and Hosking and Obial (1966) have indicated, for example, that elevated Zn concentrations can occur in stream sediments near settlements because of domestic sources such as raw sewage. No follow-up soil reconnaissance work has been undertaken in the Plymouth area,

however, to check on these possible sources of metal contamination, or to determine if the trace-element concentrations of the stream sediments are reflected in the soils. Similarly, no detailed follow-up soil research has been centred on the Camelford and north-west Dartmoor areas. Within both districts, As has been shown by stream sediment sampling to occur in localised elevated concentrations despite the limited recorded output of this element from the mines of both regions. The northern Dartmoor area, however, has been studied extensively by Aguilar Ravello (1974) who recorded stream sediment concentrations in the district as ranging from 10 to 2,500 μg As/g. Such concentrations were related to alluvial material and enrichment through known mineralisation and possible hidden (unknown) ore deposits. However, with the exception of soils developed at the granite margin, the soils of the north Dartmoor region did not reflect the raised stream sediment concentrations. Aguilar Ravello (op.cit.) attributed this to the leaching of As from the soils, although no detailed soil profile work was undertaken to confirm this observation. Clearly, more research is needed in the Camelford, north-west Dartmoor and Plymouth areas to confirm the proposed relationships between stream sediments and soils put forward in this present research. If, however, the work of Aguilar Ravello is confirmed, then the total area of contaminated land in South-west England proposed in this research (i.e. 1,092 km^2) may be an overestimation.

Land highly contaminated with both As and Cu is indicated by the stream sediment maps as occurring principally in the Hayle/Camborne-Redruth/St. Day mineralised areas. In comparison, land highly contaminated with Zn is restricted to the St. Agnes-Cligga

granite region; this reflects, in part, the lesser importance of Zn ores in the mines of South-west England compared to the ores of Cu and As. This applies also to Pb, since no areas of land highly contaminated with this element is shown by the stream sediment map to occur within the province. In part, however, the limited occurrence of highly contaminated Pb and Zn areas is due to the smoothing technique employed in plotting the stream sediment maps. Thus, the highly contaminated Pb and Zn regions found previously by detailed stream sediment sampling within the Hayle/Camborne-Redruth study area, are not delineated on the stream sediment maps representing the whole of South-west England.

Whilst part of the contamination proposed as occurring within the province of South-west England may be attributable to natural enrichment (e.g. north-west Dartmoor) or urban sources (e.g. the Plymouth district), there is little doubt that most of the As, Cu and Zn enrichment is caused by mineralisation and mining activities within the Hayle/Camborne-Redruth/St. Day/St. Agnes-Cligga granite areas and the Liskeard/Callington/Tavistock districts. Lead enrichment within these areas may also be attributable to mineralisation and mining contamination, although some of the elevated concentrations of this element found within South-west England may also be caused through the underlying parent material. Analysis of the soils sampled along the four reconnaissance traverses within the Hayle-Camborne-Redruth study area has indicated that enrichment of Pb through mineralisation and mining contamination appears to be limited to only a few sites (Section IIb, Chapter 4). Consequently, the selection of soils 'contaminated' with Pb by

using the 70th percentile as outlined earlier in Section IVa of this chapter, will pick out those soils affected by mineralisation and mining together with those soils which are naturally elevated in their Pb content. Within the Hayle/Camborne-Redruth district, the soils with an elevated natural content of Pb are developed on the Devonian Mylor slates. Studies outlined in Chapter 5 of this thesis have shown that the slates contain, on average, twice the amount of Pb normally associated with argillaceous rocks. In comparison, the Pb concentrations of the granites are considerably lower. Consequently, the stream sediment map showing the distribution of Pb throughout South-west England clearly defines the boundary of the Mylor slates in the relatively unmineralised districts of Penzance, Helston and Falmouth (Figure 39).

CHAPTER 5

THE SOURCES OF ANOMALOUS TRACE-ELEMENT CONCENTRATIONS IN THE HAYLE/CAMBORNE-REDRUTH DISTRICT

(I) INTRODUCTION

The high concentrations of a number of trace-elements found in the Hayle/Camborne-Redruth study area are clearly related to mineralisation and past metalliferous mining activities, although from the evidence presented in Chapter 4 it appears that in addition soils of the district have been naturally enriched in certain trace-elements by the weathering of the underlying parent materials. This chapter, therefore, is sub-divided into two separate sections, the first part of which examines the trace-element content of the rock formations underlying the study area, whilst the second section investigates the dispersion of contaminants into soils from mine spoil and tin and arsenic smelting sources within the district.

(II) GEOCHEMISTRY OF THE MAJOR GEOLOGICAL FORMATIONS

a) Analytical results obtained from the rock samples

Unweathered rock samples were collected in the Hayle/Camborne-Redruth district from each of the three major geological formations (slate, granite and greenstone) found within the study area. Due to the limited number of exposures and the present day overgrown state of the numerous quarries which have operated in the past within the district, many of the samples were collected from coastal sections. These rocks were crushed and analysed

using the techniques outlined in Appendix 1. The analytical data and sample locations are listed in full in Appendix 5, and are summarised in Table 29.

A comparison of the data for the three rock types shows the close geochemical similarity between the slates and greenstones. The only major geochemical difference between these two rock types is in their Ca content; a median concentration of 0.116% Ca obtained from the slate samples compares to a median of 2.04% Ca from the greenstones. The presence of Ca-bearing minerals including plagioclase feldspars, amphiboles and pyroxenes in the greenstone rocks of west Cornwall has been summarised by Floyd and Al-Sammon (1980), and is presumably responsible for the higher concentrations of this element associated with these rocks. In contrast, the Mylor slates are essentially non-calcareous, although local enrichment as found at Praa Sands can occur (Appendix 5). Both slates and greenstones differ appreciably in their trace-element content when compared to the granites. With the exception of Ca and Sn, concentrations of all the elements in the latter rocks are less than those of the former.

Average concentrations of trace elements in shales (the unmetamorphosed equivalent of slate), basalts (i.e. typical basic igneous rocks such as the greenstones of the study area) and granites have been summarised by Taylor (1964) and Turekian and Wedepohl (1961), and are presented in Table 30. A comparison between these average values and the data summarised in Table 29 indicates an enrichment of elements in the slates (As, Cd, Pb and Zn), greenstones (As, Cd, Pb, Sn and Zn) and granites (As, Cd, Co and Sn) of the study area. Comparatively low concentrations of Al and Ca in the

	Al(%)	As	Ca	Cd	Co	Cu	Fe(%)	Mn	Pb	Sn	Zn
Mylor Slates											
n=35 (13 for Sn)											
Mean ($\bar{x}$)	6.23	44	4247	2.01	24	81	5.44	832	64	10	174
Median ($\bar{x}m$)	6.04	32	1160	2.00	24	52	5.20	840	40	4.25	172
Standard deviation (σ)	1.36	38.75	8384	0.58	9.4	88	1.03	305	53	10.8	62
Range	1.88-8.40	5.9-224	N.D-32880	1.2-3.2	8-68	13-436	3.20-7.92	240-1560	Trace-212	N.D-33	53-317
Granites											
n=24 (9 for Sn)											
Mean ($\bar{x}$)	1.79	17	2275	0.7	9.3	17.5	1.29	237	+	11.7	33
Median ($\bar{x}m$)	1.78	12	2220	0.8	8.0	8.5	1.32	208	+	8.0	32
Standard deviation (σ)	0.55	11.7	750	0.46	3.1	26.5	0.46	99	+	9.8	11.3
Range	0.88-3.20	1.5-45	920-4080	N.D-2.0	N.D-16	4-132	0.40-2.40	120-520	Trace-28	3.5-34	15-59
Greenstones											
n=9 (3 for Sn)											
Mean ($\bar{x}$)	5.19	73	20556	2.04	31	91	6.15	1156	47	4.9	175
Median ($\bar{x}m$)	5.84	33	20400	2.00	31	82	5.68	880	24	5.0	160
Standard deviation (σ)	1.37	111	13913	0.51	5.1	89	3.42	660	46	2.04	68
Range	2.68-6.40	10-379	680-44880	1.2-2.8	25-44	10-312	0.76-14.4	640-2880	20-172	2.3-7.3	109-344

All values in µg/g unless specified.

+ = cannot be computed. N.D. = Not detected. Detection limits : Cd = 0·24µg/g ; Co = 1·2µg/g ; Sn = 0·2µg/g ; Ca = 2µg/g.

TABLE 29. Summary of the analytical data obtained from the slate, granite and greenstone rock samples.

		Al(%)	As	Ca(%)	Cd	Co	Cu	Fe(%)	Mn	Pb	Sn	Zn
Taylor (1964)	Basalt	8.76	2	6.72	0.20	48	100	8.56	1500	5	1	100
	Granite	7.70	1.5	1.58	0.20	1	10	2.70	400	20	3	40
Turekian and Wedepohl (1961)	Basalt	7.80	2	7.60	0.22	48	87	8.65	1500	6	1.5	105
	Granite	7.20	1.5	0.51	0.13	1	10	1.42	390	19	3	39
	Shale	8.00	13	2.21	0.30	19	45	4.72	850	20	6	95

All values in µg/g unless specified.

TABLE 30. Average concentrations of selected trace-elements in basalts, granites and shales.

slates, Al, Ca, Fe and Mn in the greenstones, and Al, Ca and Mn in the granites are also apparent.

b) Discussion

A close relationship between the trace-element content of the soils and rocks of the study area can be expected because of the limited importance of solifluction in the district (Staines, 1979). The natural or inherent trace-element content of soils within the study area, therefore, is likely to closely reflect the underlying parent materials, with the degree to which elements are incorporated in these soils being dependent upon the types of minerals present in the rocks, their rates of weathering, and their redistribution within the soil profile (Chapter 1). Although the rates of weathering between the slates and greenstones are likely to differ, it is probable that because of their close petrological geochemistry, the soils of both parent materials are likely to be similar in their natural trace-element concentrations. However, because of the widespread contamination and the limited outcrop of the greenstones, this assumption cannot be proved by soil analysis. The greenstone derived soil sampled at site 10 on the initial soil reconnaissance survey, for example, is contaminated as shown by the raised Sn concentrations recorded from both the topsoil (173 μg/g) and subsoil (126 μg/g) (Chapter 4). However, the elevated Ca concentrations associated with this soil (1.28% in the topsoil, 0.88% in the subsoil) may reflect the high Ca content of the greenstone rocks at this site.

The trace-element differences between the unmineralised slate and granite soils observed in the soil traverse reconnaissance survey (Chapter 4) are attributable to the lower amounts of the trace-elements which are associated with the granite rocks. Elevated concentrations of certain elements in the unmineralised granite soils, however, were recorded by the earlier soil reconnaissance survey. In particular, both Sn and As soil concentrations at the unmineralised sites (e.g. average topsoil concentrations of 49 μg Sn/g and 26 μg As/g in the centre of the Carnmenellis granite; see Table 20) exceeded the concentrations of both elements which are considered normal in soils (Table 3). Pedological processes may, in part, be responsible for such elevated concentrations. For example, a slight enrichment of As in the organic topsoils and illuviated ochreous horizons of granite profiles may be atrributable to organic complexing and podzolisation processes (Chapter 4). However, a comparison of Tables 29 and 30 indicates that the granites of South-west England are enriched in As, Cd, Co and Sn compared to the world average concentrations calculated by Taylor and Turekian and Wedepohl (Table 30). It is likely, therefore, that such elevated concentrations will be reflected in the granite soils. The enrichment of these elements in the granites of South-west England has been confirmed by Hosking (1965) and Edwards (1976) who further provide evidence of Pb enrichment in these rocks. The work of Hosking, however, does not confirm the Co enrichment observed in the granite rocks studied in this present research.

In contrast, the granites of South-west England have low concentrations of Al, Ca and Mn compared to those quoted by Taylor (1964) and Turekian and Wedepohl (1961). These trace-element concentrations are reflected by the low soil concentrations of these elements observed during the earlier soil reconnaissance survey (Chapter 4).

A number of researchers have noted the trace-element enriched nature of the Devonian metasediments (Henley, 1974; Edwards, 1976) and theories about possible mechanisms of mineralisation caused by the granitisation of the metal enriched sediments (Hosking, 1964; Hosking et al., 1965), or by the leaching of elements from the sediments by circulating waters have been postulated (Dangerfield and Hawkes, 1969; Alderton, 1975, 1978). The Mylor slates have, in particular, been noted with regard to their elevated trace-element status, and have consequently been used in elucidating stratigraphical and structural problems (Valrey, 1965-66). In this present study, no Cu enrichment of the slates was observed when the average concentrations were compared to those of Taylor and Turekian and Wedepohl (Table 30). This observation agrees with those of Edwards (1976), although Bird (1981) has indicated that the slates in mineralised areas may contain elevated amounts of Cu presumably due to wall rock alteration during mineral emplacement. A definite enrichment of As, Cd, Pb and Zn has been found in the slates studied in this research. This may lead to naturally occurring elevated amounts of these elements in the overlying slate-derived soils. The As concentrations of any uncontaminated soils will, in particular, exceed those amounts considered normal for agricultural soils elsewhere in Great Britain. Soils formed from the greenstones will be similarly affected, although within both slate and greenstone derived soils the concentrations

found will also be dependent upon the various pedogenic processes which influence the distribution of the trace-elements within the soil profile.

(III) THE DISPERSION OF CONTAMINANTS FROM MINE SPOIL AND SMELTING SOURCES WITHIN THE HAYLE/CAMBORNE-REDRUTH DISTRICT

a) Introduction

Numerous potential sources of contamination are evident within the study area. Dines lists some 400 underground mines which have operated in the Hayle/Camborne-Redruth area in the past, although a study of old mining journals coupled with detailed field investigations is likely to locate other mineralised sites (Rottenbury, 1974). Hosking (1955-56, 1970) outlines in detail the contamination of soils and river waters from sources which include mine dumps, smelters, calciners, leats, settling pits, mine adits, walls constructed of mine waste, and pathways which were used regularly by the miners. In this particular survey, the contamination of soils from mine spoil, tin smelters and arsenic calciners has been investigated on a local scale.

b) The contamination of agricultural land from spoil heaps

Although mining activity has largely ceased within the study area, the importance and extent of the industry is still clearly recognisable by the extensive areas of land which are covered by mine dumps. Of the 93 km^2 of west Cornwall surveyed by Staines (1979), some 405 ha (i.e. 4% of the total area surveyed) of land has been lost to agriculture through the dumping of mine waste. Such waste consists not only of barren unmineralised country

rock, but also of residual ores which have not been extracted either because of inefficient metallurgical techniques or because of some other consideration (e.g. ores of As, Zn and U were originally dumped by the miners as they were once considered to be an undesirable constituent of the lode-stuff). Thus high concentrations of a number of elements may be associated with these wastes, and redistribution of such elements onto and into the surrounding agricultural soils is likely to occur through the joint effect of wind and water dispersion (Johnson et al., 1978).

Detailed studies on the redistribution of As and metals from mine spoil was undertaken at two sites, Wheal Tremayne located on the Devonian slates, and Wheal Sisters sited on the Lands End granite. Soils sampled as linear transects were taken at 0-15 cm and 30-45 cm depth up to 250 m away from the mine waste in order to observe the effects of the spoil on the surrounding agricultural land. Five samples of mine spoil were additionally taken from both localities. Details regarding the location and mining history of both sites, together with the geochemical data relating to the mine spoil are outlined in Tables 31 and 32.

i) Wheal Tremayne: ratios calculated by dividing the median concentration of each element obtained from the five mine spoil samples by the median concentrations of each element found in the Mylor slates (the latter obtained from Table 29 in this chapter) indicate the degree of enrichment of the mine spoil caused by the mineralisation (Table 33). Thus, the importance of both As and Cu ores in the mineralisation of this particular area is reflected

Location: SW 588348

Geology: Mylor Slate

Site characteristics: Flat topography, with pasture surrounding the heap

Mine output: Dines (1956) records that the mine was particularly important for the production of Sn and Cu. According to Henwood (1843) the lodes are of slate with quartz carrying pyrite and chalcopyrite. Argentiferous mispickel, uranite, native silver and 'road-eye' tin are also recorded.

Spoil Analysis:	Al(%)	As	Ca	Cd	Co	Cu	Fe(%)	Mn	Pb	Zn
1.	5.92	2517	3680	2.4	24	1168	7.24	840	312	320
2.	4.08	2649	5600	7.2	100	8200	9.20	2240	1000	2120
3.	6.00	N.A.	6960	4.0	80	2320	7.92	1680	208	1184
4.	6.40	1915	2280	3.6	68	3000	7.20	1320	212	960
5.	6.32	1582	1920	2.8	20	800	6.36	640	252	188

N.A. = Not analysed

All values in µg/g unless specified

TABLE 31. Details of Wheal Tremayne, Fraddam.

Location: SW 500366

Geology: Granite

Site characteristics: Flat pasture to the west of the spoil; gently sloping pasture to the east

Mine output: Lodes of this mine have yielded both Sn and Cu ores (Dines, 1956)

Spoil analysis:	Al(%)	As	Ca	Cd	Co	Cu	Fe(%)	Mn	Pb	Zn
1.	3.44	37	6000	2.0	12	224	2.72	448	48	70
2.	3.56	53	6480	1.6	16	248	3.08	464	64	79
3.	3.08	100	5200	1.2	8	208	2.04	368	40	64
4.	2.76	22	4880	1.2	12	200	1.88	304	36	51
5.	3.16	35	5600	1.2	12	180	2.12	440	68	53

All values in µg/g unless specified

TABLE 32. Details of Wheal Sisters, Brunnion.

	Al	As	Ca	Cd	Co	Cu	Fe	Mn	Pb	Zn
Wheal Tremayne										
Median mine spoil concentration	6.00%	2216	3680	3.6	68	2320	7.24%	1320	252	960
Median Mylor slate concentration (obtained from Table 29)	6.04%	32	1160	2.0	24	52	5.2%	840	40	172
mine spoil/slate rock ratio	0.99	69.25	3.17	1.8	2.83	44.62	1.39	1.57	6.30	5.58
Wheal Sisters										
Median mine spoil concentration	3.16%	37	5600	1.2	12	208	2.12%	440	48	64
Median granite concentration (obtained from Table 29)	1.78%	12	2200	0.8	8	8.5	1.32%	208	+	32
mine spoil/granite rock ratio	1.78	3.08	2.55	1.5	1.5	24.47	1.61	2.12	-	2.00

+ = cannot be calculated

All concentrations in µg/g unless stated

TABLE 33. Enrichment of the mine spoil at Wheal Tremayne and Wheal Sisters caused by the mineralisation.

by high ratio values of 69 and 45 respectively*. These high ratios are due to the elevated amounts of both elements in the mine spoil; maximum concentrations of 2649 µg As/g and 8200 µg Cu/g were recorded from the spoil at this site (Table 31). In comparison, the mine spoil/Mylor slate ratios calculated for Zn and Pb are considerably lower (both approximately 6), and demonstrate the lesser importance of these two elements in the mineralisation at this particular site. Maximum concentrations of 2120 µg Zn/g and 1000 µg Pb/g were recorded from the mine spoil samples.

The presence of Ca, Cd, Co, Fe and Mn associated in minor amounts with the lode-stuff is also shown by the mine spoil/Mylor slate raio values which exceed unity. Aluminium, however, does not show any enrichment in the minespoil when compared to the concentrations associated with the Mylor slates. Data on the analysis of ore materials from the west Cornwall district confirm the low concentrations of this element associated with the ores of the region (Bird, 1981) (Table 19).

Soil sampling at Wheal Tremayne extended to 150 m south of the spoil heap, and to 250 m north of the waste material. The northern extension of the traverse was disjointed due to the presence of a mineral lode with associated mine waste. Accordingly, the sampling points at 100 m, 150 m, 200 m and 250 m distance from the spoil were selected on a separate traverse line well away from the mineral vein and the sampling sites at 0- 50 m distance (Figure 40).

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* NB Sn was not determined in this survey.

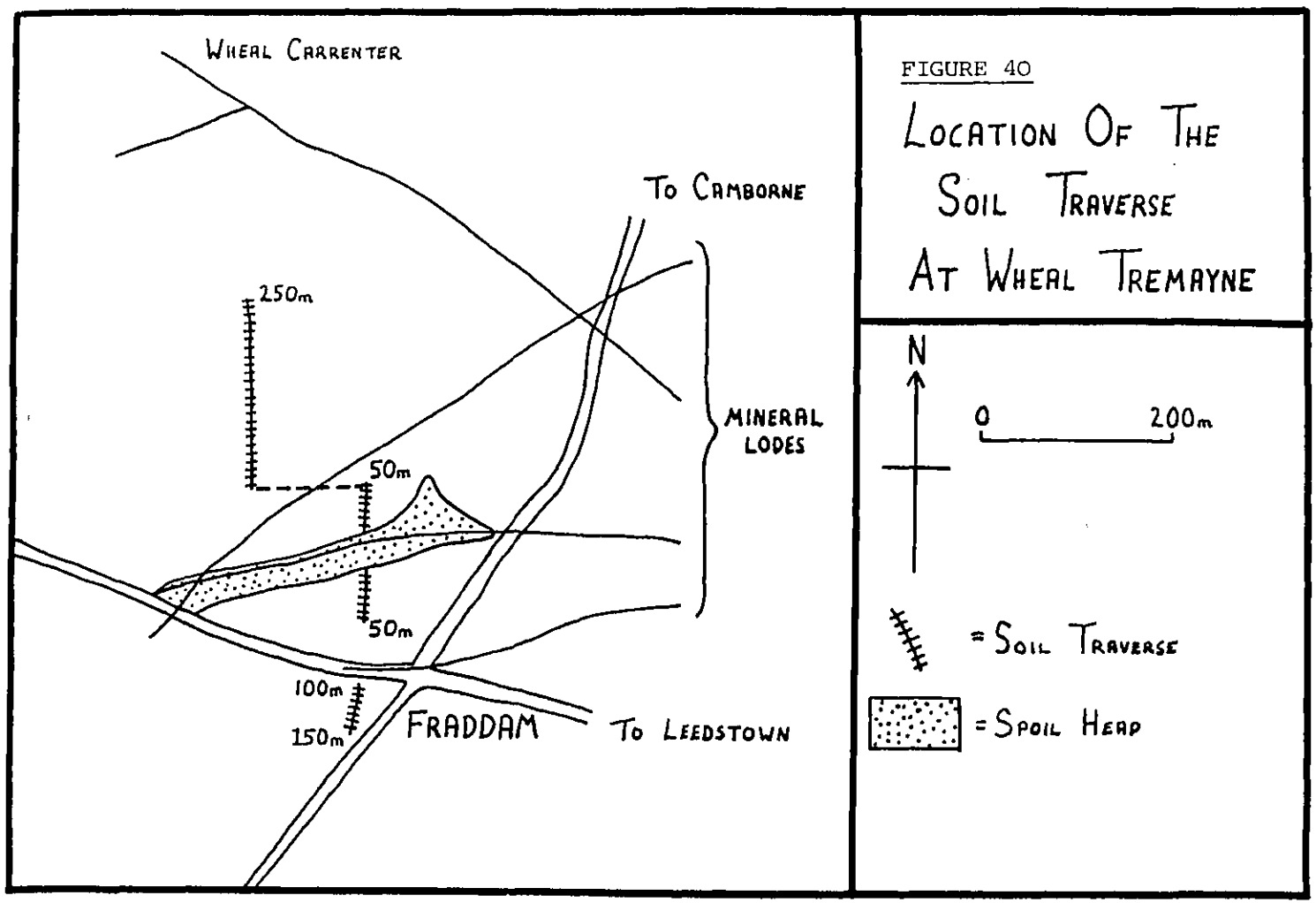
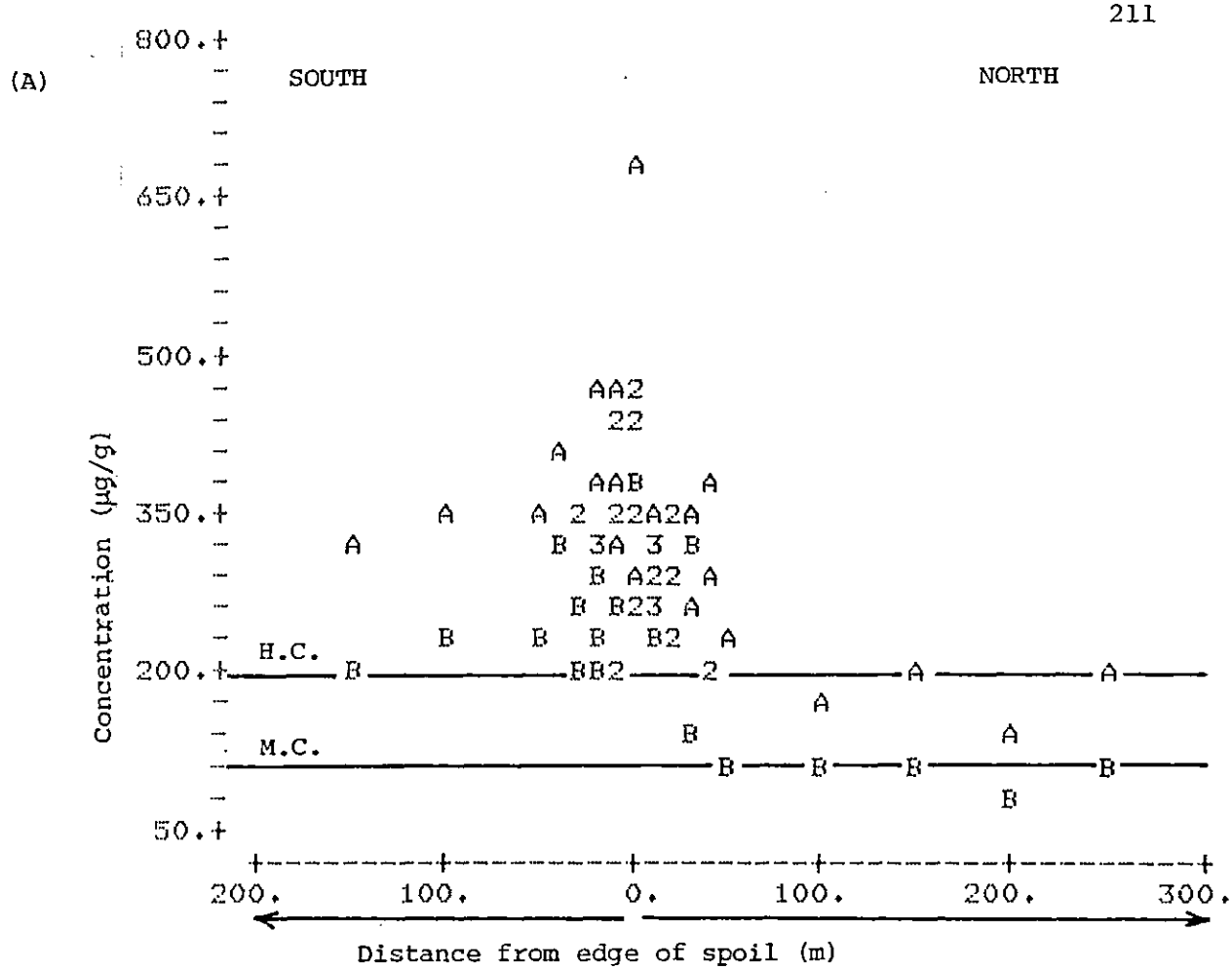


FIGURE 40

LOCATION OF THE SOIL TRAVERSE AT WHEAL TREMAYNE

The As, Cu, Zn and Pb data obtained by the analysis of these soil samples is presented graphically in Figures 41a-44a; the data for these and the other 6 elements analysed are further outlined in tabular form in Appendix 6. The As and metal concentrations observed in the soils either side of the spoil material reflect the elevated trace-element composition of the mine spoil. Maximum concentrations of 860 µg Cu/g, 686 µg As/g, 616 µg Zn/g and 228 µg Pb/g were found in the topsoils immediately surrounding the spoil heap, with the concentrations then decreasing significantly with increasing distance from the spoil (Table 34). The moderately contaminated and highly contaminated soil threshold values quoted in Table 24 are included on Figures 41a-44a. These diagrams show that the contamination of the soils adjacent to the mine spoil is more widespread for As and Cu than compared to the elements Pb and Zn. This reflects the increased concentrations of the former elements in the mine spoil. The data further indicates that topsoils highly contaminated with Cu persist up to at least 150 m from the spoil material, whilst soils highly contaminated with As may occur up to at least 250 m (i.e. the maximum distance sampled) from the mine waste.

In addition to the four elements outlined above, Ca, Cd, Co, Fe and Mn concentrations, in general, decrease with increasing distance away from the mine spoil. This reflects firstly the elevated trace-element content of these elements associated with the mine waste, and secondly the potential of such mine waste in releasing a multitude of trace-elements into the surrounding environment. Consequently, significant inverse correlation trends between the concentrations of these elements and the distance of the soil



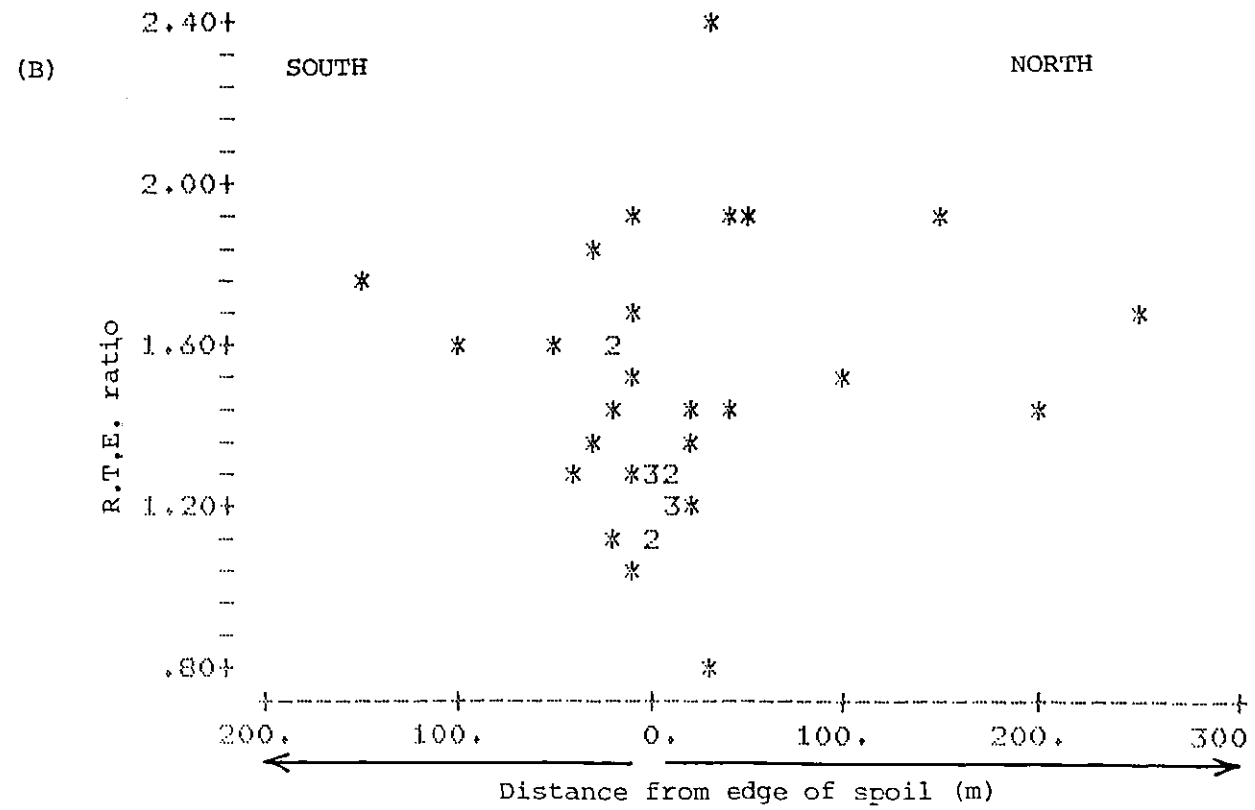
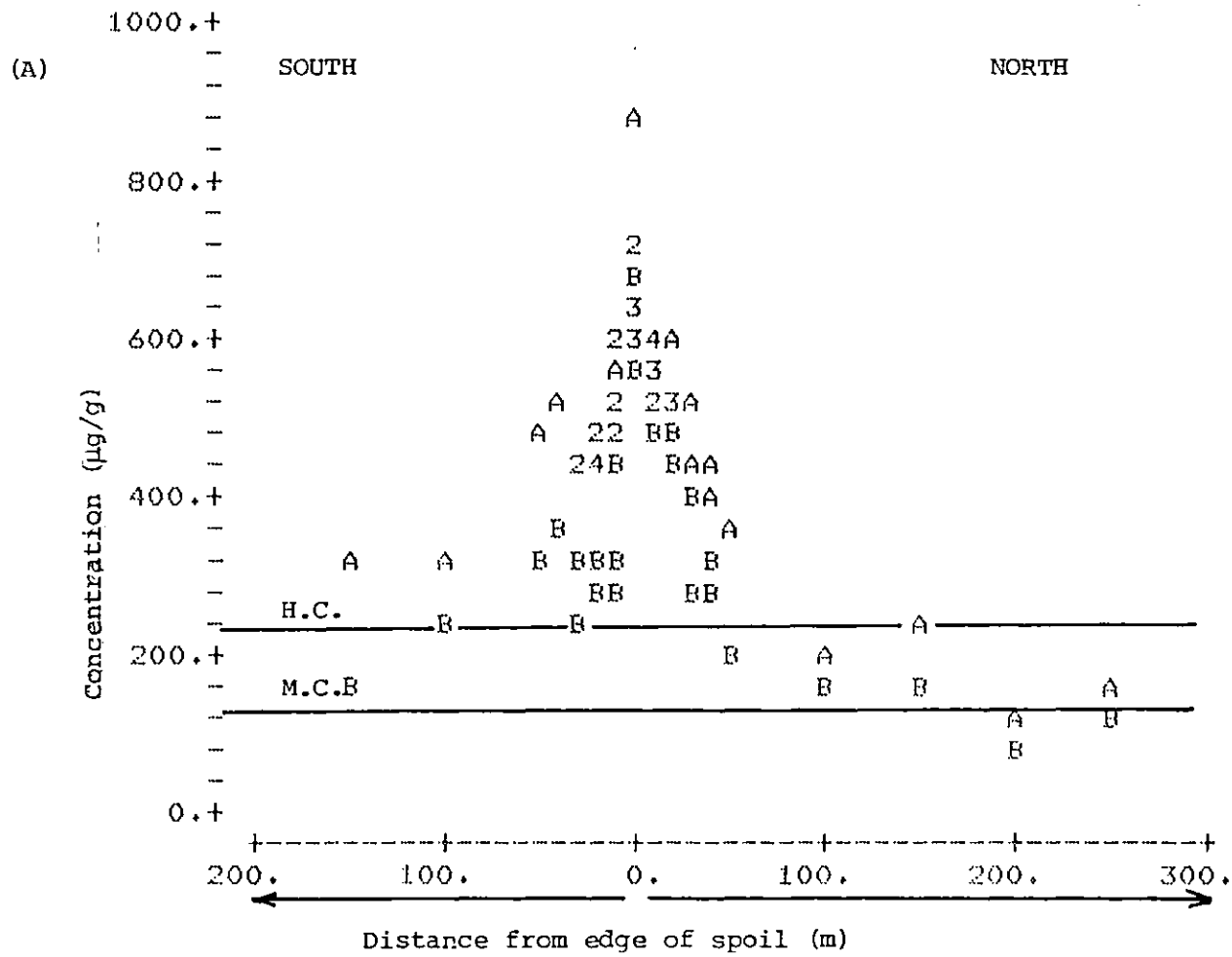


Figure 41. (A) Concentrations of arsenic found in the soils at Wheal Tremayne. (A=Topsoil, B=Subsoil, H.C.=Heavily contaminated soil threshold, M.C.=Moderately contaminated soil threshold).
(B) Arsenic R.T.E. ratios at Wheal Tremayne.



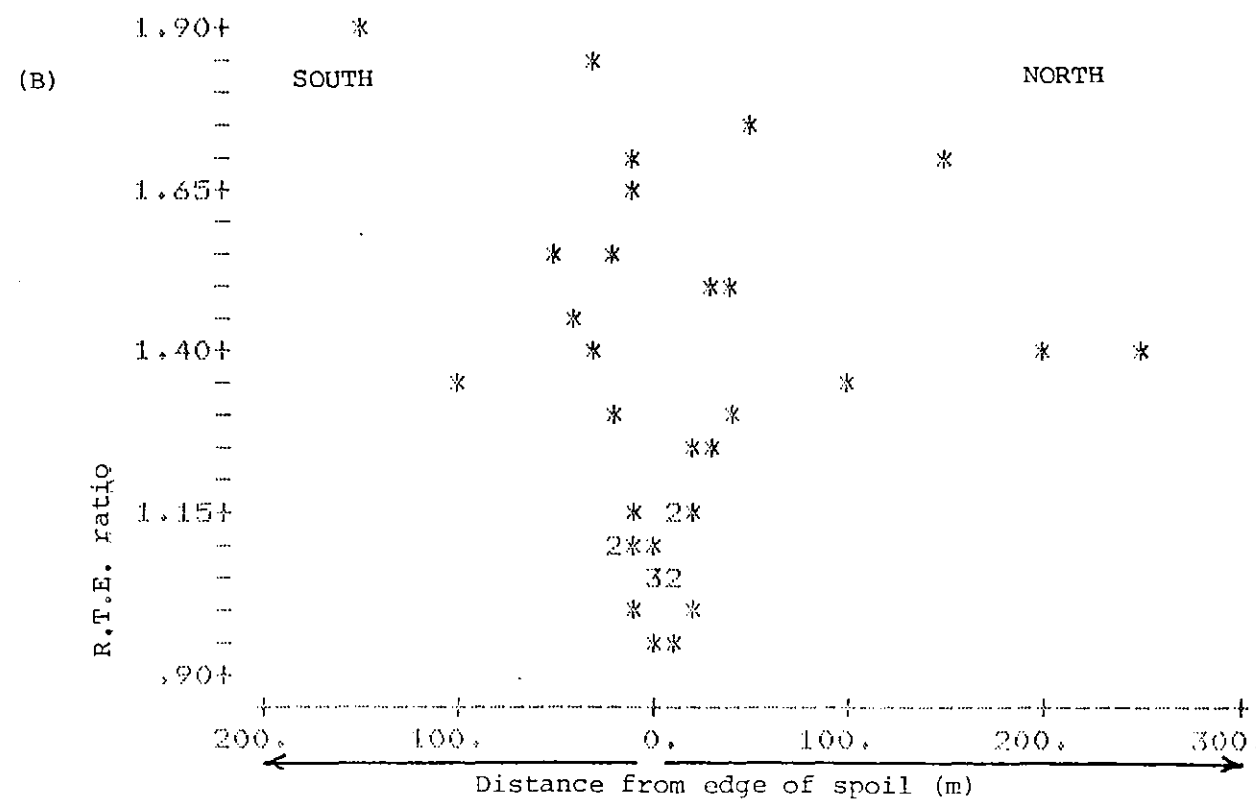


Figure 42. (A) Concentrations of copper found in the soils at Wheal Tremayne. (A=Topsoil, B=Subsoil, H.C.=Heavily contaminated soil threshold, M.C.=Moderately contaminated soil threshold).

(B) Copper R.T.E. ratios at Wheal Tremayne.

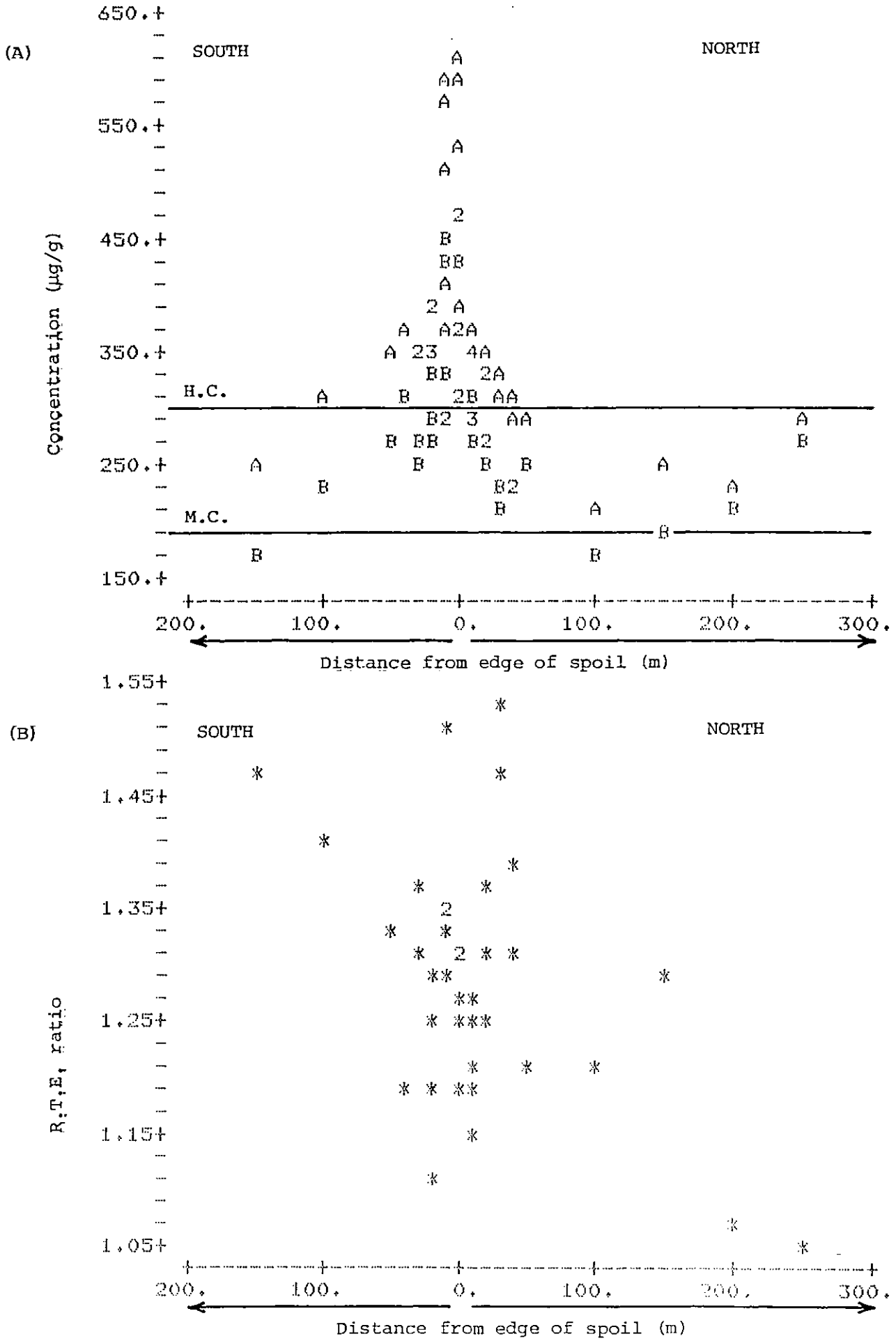
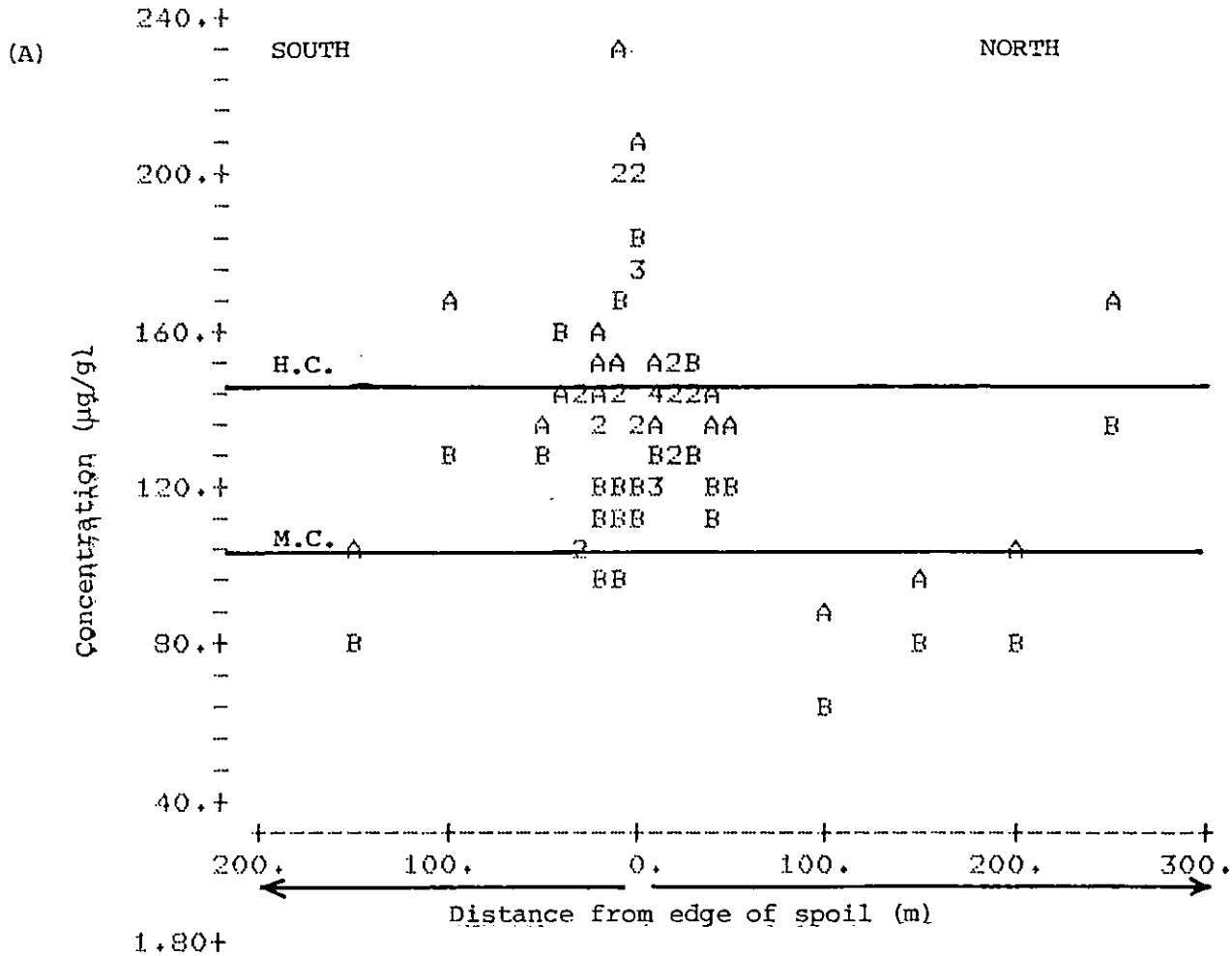


Figure 43. (A) Concentrations of zinc found in the soils at Wheal Tremayne. (A=Topsoil, B=Subsoil, H.C.=Heavily contaminated soil threshold, M.C.=Moderately contaminated soil threshold).
(B) Zinc R.T.E. ratios at Wheal Tremayne.



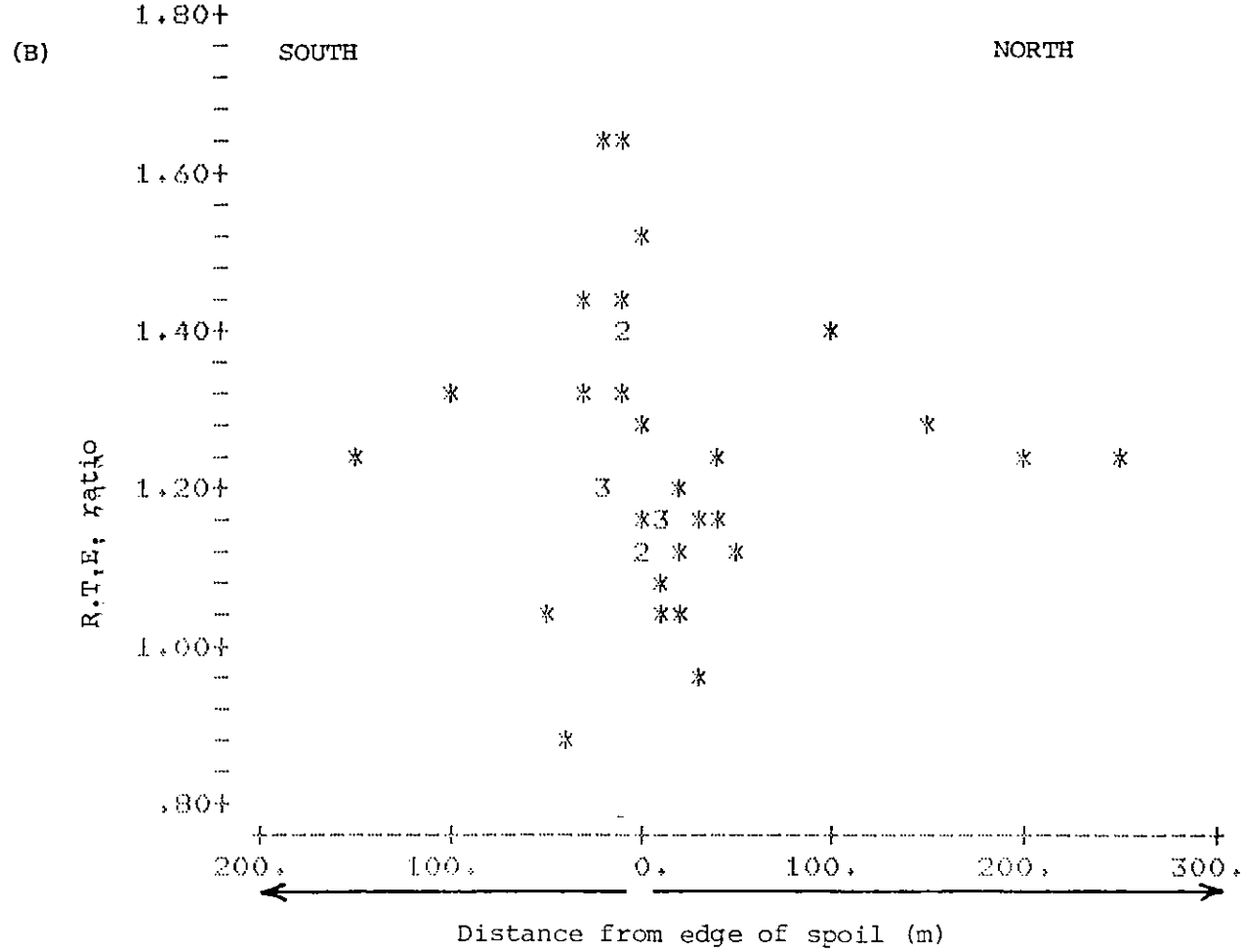


Figure 44. (A) Concentrations of lead found in the soils at Wheal Tremayne. (A=Topsoil, B=Subsoil, H.C.=Heavily contaminated soil threshold, M.C.=Moderately contaminated soil threshold).
(B) Lead R.T.E. ratios at Wheal Tremayne.

samples from the mine spoil are observed (Table 34). In comparison, Al correlation coefficients are particularly poor, and reflect the fact that elevated concentrations of this element do not occur in the mine spoil.

The observations made above, however, do not consider two variables which may influence the soil trace-element concentrations recorded at Wheal Tremayne. Firstly, a mineral lode is recorded by geological maps as outcropping near to the 100 m sampling point south of the mine spoil (Figure 40); the influence of this lode on the trace-element concentrations obtained by analysis cannot be determined in this present research. Secondly, the possible effect of the mineral workings at Wheal Carpenter, north of Wheal Tremayne, remain unclear (Figure 40). It is possible that at least some of the soils sampled in the survey at Wheal Tremayne are affected also by the mineralisation and mining activities of this northern site. In addition, the soil Co, Fe and Mn concentrations are all elevated at the 100 to 250 m sample sites north of Wheal Tremayne, and suggest that the workings associated with Wheal Tremayne are not the only source of trace-element enrichment within this particular area.

The concentration and distribution of the trace-elements in the subsoils of the traverse closely reflect those observed in the topsoils (Table 34), and indicate that enrichment has occurred at depth. Relative topsoil enhancement (R.T.E.) ratios are thus close to unity (e.g. Figures 41b-44b). For some elements, most notably As, Cu and Pb, the R.T.E. ratios are especially low near to the site of the spoil heap. These ratio values may reflect enrichment of the subsoils caused by the mineralisation at Wheal Tremayne, since

		South of spoil n - topsoils = 18 subsoils = 17	North of Spoil n - topsoils) = 20+ subsoils)
Al:	Topsoil	.052	.144
	Subsoil	-.454*	-.159
As:	Topsoil	-.422*	-.796***
	Subsoil	-.457*	-.767***
Ca:	Topsoil	-.387	-.683***
	Subsoil	.118	-.166
Cd:	Topsoil	-.512**	-.479**
	Subsoil	-.436*	-.267
Co:	Topsoil	-.521**	.132
	Subsoil	-.768***	-.617**
Cu:	Topsoil	-.677***	-.905***
	Subsoil	-.650***	-.825***
Fe:	Topsoil	-.635***	-.883***
	Subsoil	-.770***	-.881***
Mn:	Topsoil	-.785***	-.873***
	Subsoil	-.594***	-.925***
Pb:	Topsoil	-.603***	-.371
	Subsoil	-.435*	-.465**
Zn:	Topsoil	-.673***	-.691***
	Subsoil	-.715***	-.451**

*** = significant at p = 0.01 (1%)

** = significant at p = 0.05 (5%)

* = significant at p = 0.1 (10%)

+ the Co, Fe and Mn data at the 100, 150, 200 and 250m sample sites are excluded from the statistical appraisal due to suspected contamination of these 3 elements at these sites from a source independent of the mine spoil at Wheal Tremayne.

TABLE 34. Correlation coefficients between the soil concentrations and the distance of the soil samples from the spoil at Wheal Tremayne

the lode outcrop corresponds to the location of the mine waste (Figure 40). However, the elevated Al subsoil concentrations and the low R.T.E. ratios observed for this element in the vicinity of the spoil heap and mineralisation (Figure 45), indicates that this theory may not be totally valid since the association of Al with the mineral ores of the mine has been disproved earlier in this section. A number of alternative soil processes may account for the trace-element concentrations observed in the subsoils at this site. These include the leaching and dispersion of trace-elements from the mine spoil by water (a process which is likely to affect both topsoil and subsoils), the disturbance of the soil by man during the working of the mine itself, or the mixing of the soil caused as a result of soil fauna activity. The contamination of soils by wind blown particulates derived from the mine spoil is likely to especially affect the topsoils. However, it is possible that trace-elements may be leached from these particulates, with subsequent enrichment at depth. Detailed investigations into the possible mobilisation of trace-elements within the soils by such processes are clearly required before any of the above theories can be validated.

ii) Wheal Sisters: This mine is situated in the Trencrom Hill district which is recorded by Dines (1956) as being a former emanative centre of mineralisation. Because of the mineralisation controls, Sn and Cu were solely produced from the mine. The ratio between the median Cu concentrations of the mine spoil (Table 32) and the granite rocks of the study area (Table 29) indicate the occurrence of Cu in the mineral lodes at this site (Table 33)*. Similarly, the mine

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* N.B. Sn was not determined in this survey.

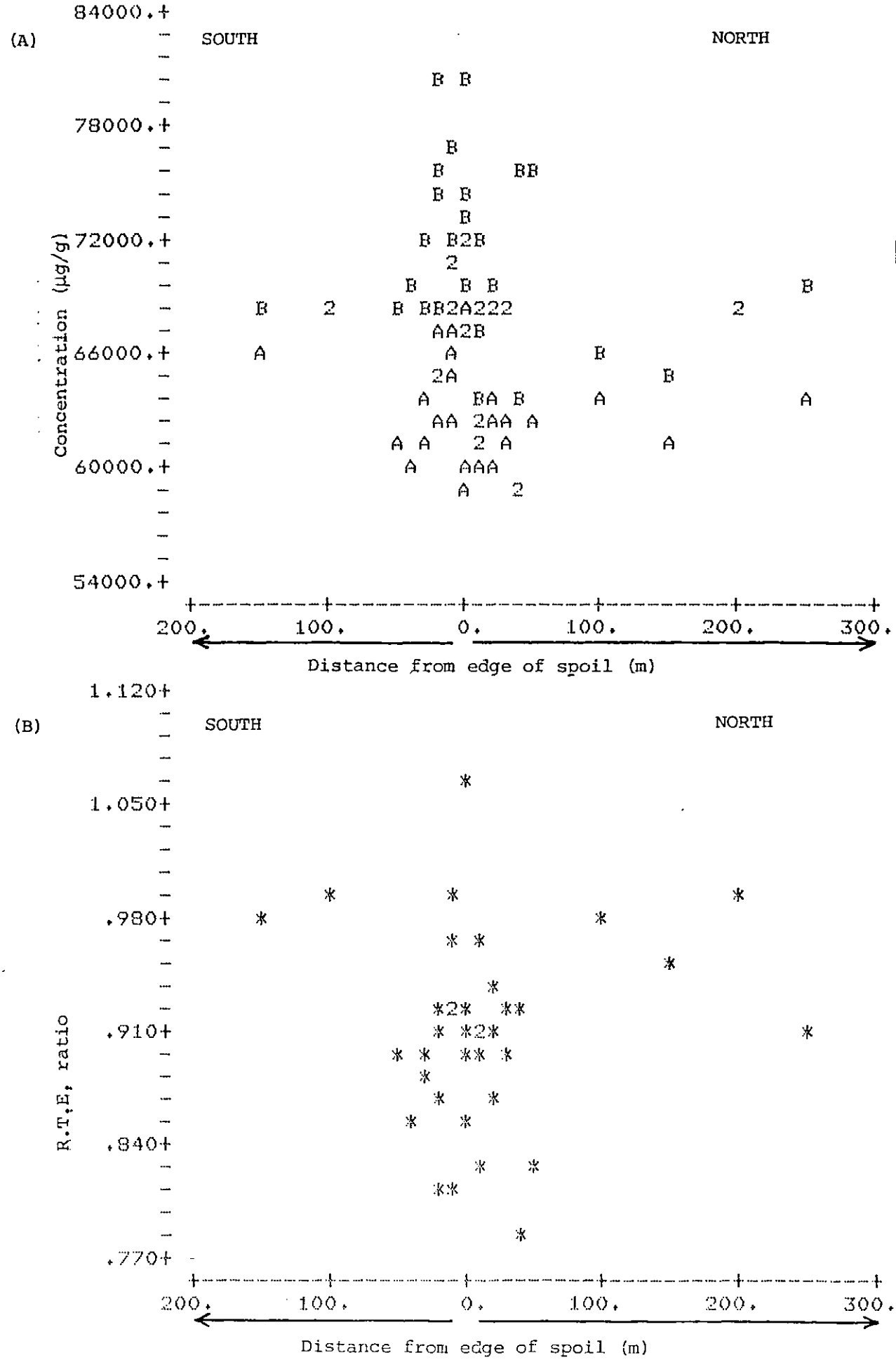


Figure 45. (A) Concentrations of aluminium found in the soils at Wheal Tremayne. (A=Topsoil, B=Subsoil).

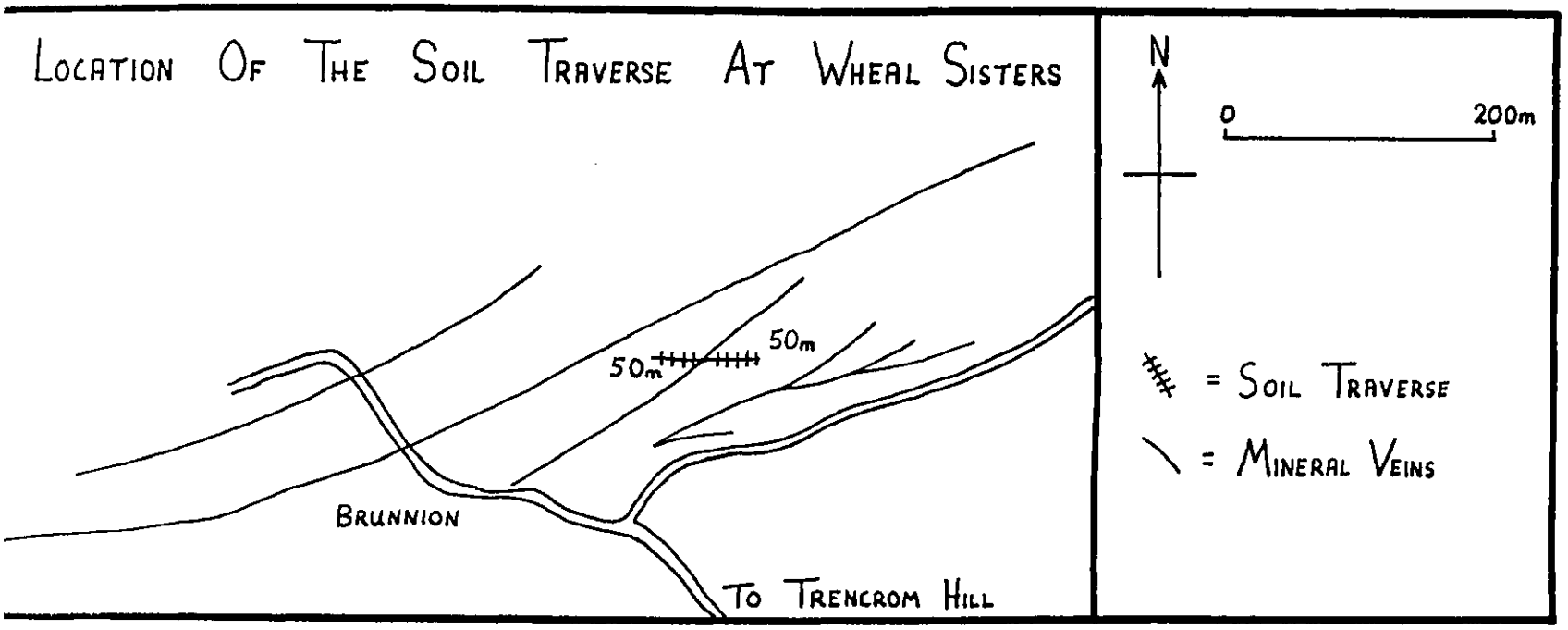
(B) Aluminium R.T.E. ratios at Wheal Tremayne.

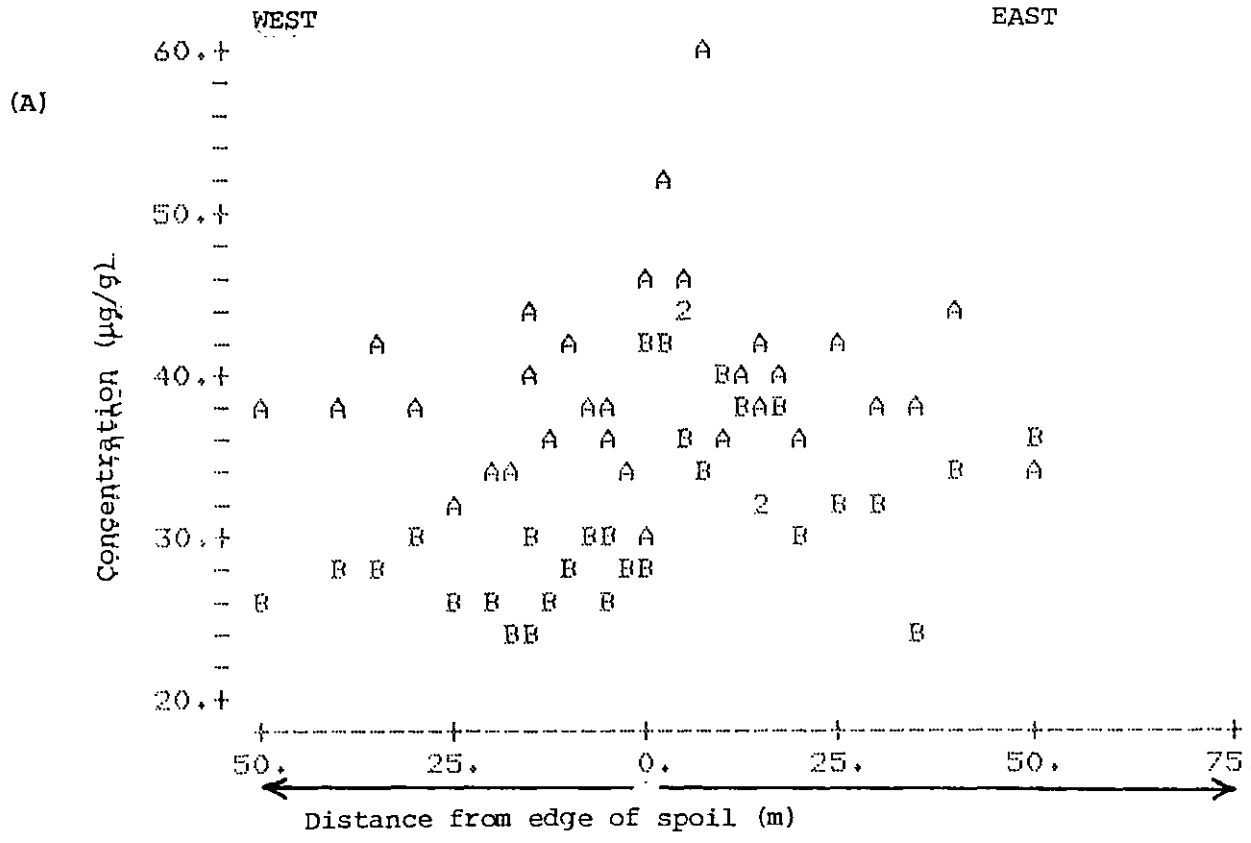
spoil/granite rock ratios calculated for the remaining trace-elements studied in this survey, exceed unity and indicate an association of these elements with the mineralisation. However, these latter ratio values are all considerably lower than the Cu ratio, and thus demonstrate the minor importance of these elements in the mineral ores of the district. The enrichment of Al in the mine spoil at this site is unlikely to be associated with the mineralisation due to the reasons outlined earlier in this chapter. It is probable that the enrichment of this element in the mine spoil at this site is due to increased weathering of the exposed granite, with the resulting formation of Al-rich kaolin clays. This theory may also explain the raised Al concentrations observed in the mineralised granite soils south of Camborne, disclosed by the earlier soil reconnaissance survey (page 133, Chapter 4).

The trace-element concentrations of the mine spoil at this site are considerably less than those recorded from the spoil at Wheal Tremayne. This applies even to Cu (median mine spoil concentration = 208 μg Cu/g) despite the elevated mine spoil/granite rock ratio noted for this element in the paragraph above. Such concentrations demonstrate not only the mineralisation controls which were operative during the emplacement of the mineral lodes, but also the low As and metal content of the granite parent material compared to the slate at Wheal Tremayne. Only the Ca content of the mine spoil at Wheal Sisters exceeds the concentrations recorded from the spoil at Wheal Tremayne (Table 33).

Soils were sampled at Wheal Sisters up to a distance of 50 m away from the mine spoil (Figure 46). The comparitively low concentrations of As and metals in the mine spoil at this site results in poorly defined dispersion haloes in the adjacent soils. The concentrations of As, Cu, Zn and Pb in the soils sampled at this site are presented graphically in Figures 47a-50a; the complete analytical data obtained at this site is presented in Appendix 6. The contamination at Wheal Sisters is clearly limited, with none of the As, Cu, Pb or Zn soil concentrations exceeding the contamination threshold values outlined previously in Table 24. Correlation coefficients between the soil trace-element concentrations and the soil sample distance from the spoil are variable (Table 35), and R.T.E. ratios for all the elements examined disclose no appreciable enrichment of the topsoils or subsoils (e.g. Figures 47b-50b). It is of interest to note, however, the highly significant negative correlation coefficients observed between the sample distance and the soil As, Zn, Cu and Ca concentrations east of the spoil (Table 35). This may indicate the dispersion of these four elements from the mine spoil. Such dispersion may be attributable to the erosion and subsequent deposition of mine spoil particulates into the adjacent agricultural soils caused as a result of the westerly winds which are dominant within the study area (Figure 51). Hydromorphic dispersion may also be important, however, due to the slope of the land east of the mine spoil which could influence ground water movements.

FIGURE 46


LOCATION OF THE SOIL TRAVERSE AT WHEAL SISTERS
N
0
200m
50m
50m
= SOIL TRAVERSE
= MINERAL VEINS
BRUNNION
TO TRENCROM HILL



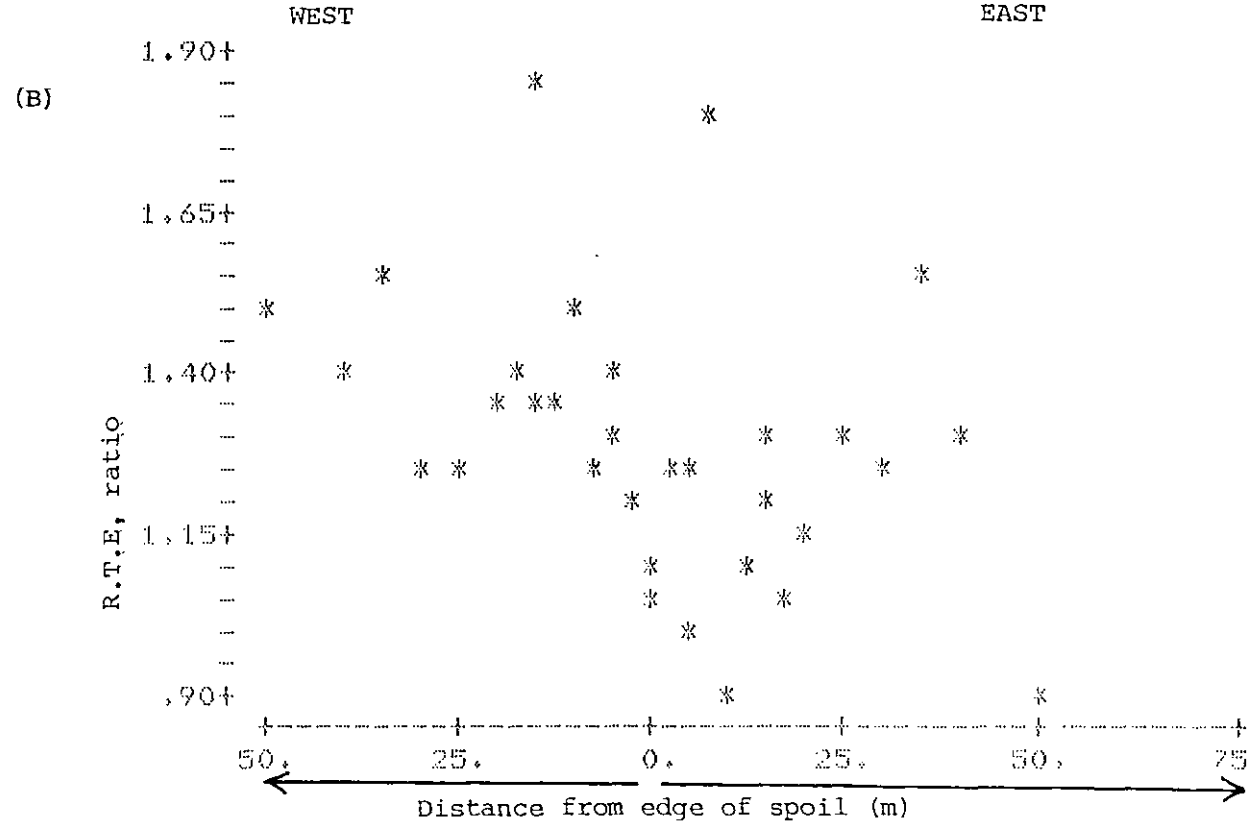
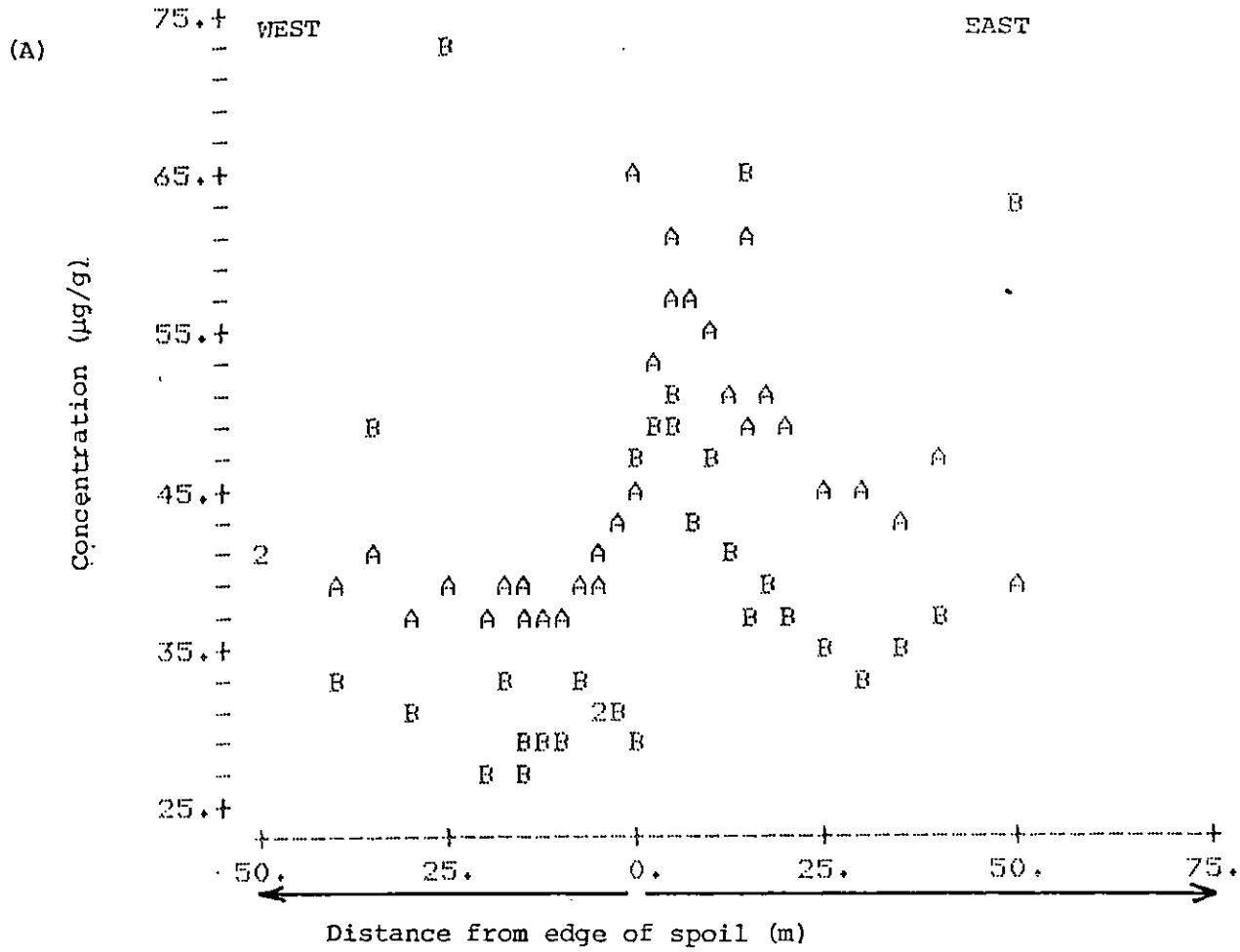


Figure 47. (A) Concentrations of arsenic found in the soils at Wheal Sisters. (A = Topsoil, B = Subsoil).
(B) Arsenic R.T.E. ratios at Wheal Sisters.



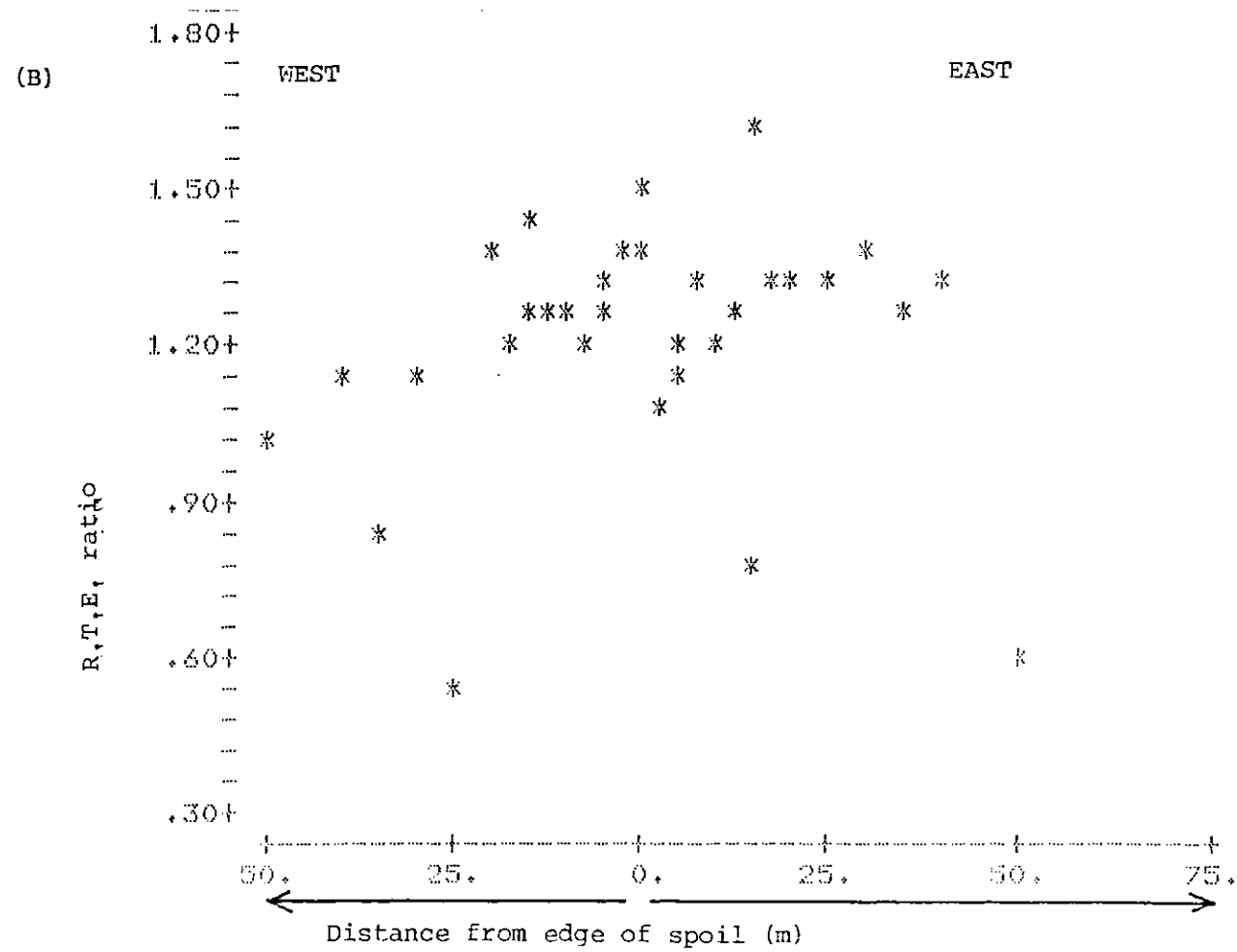
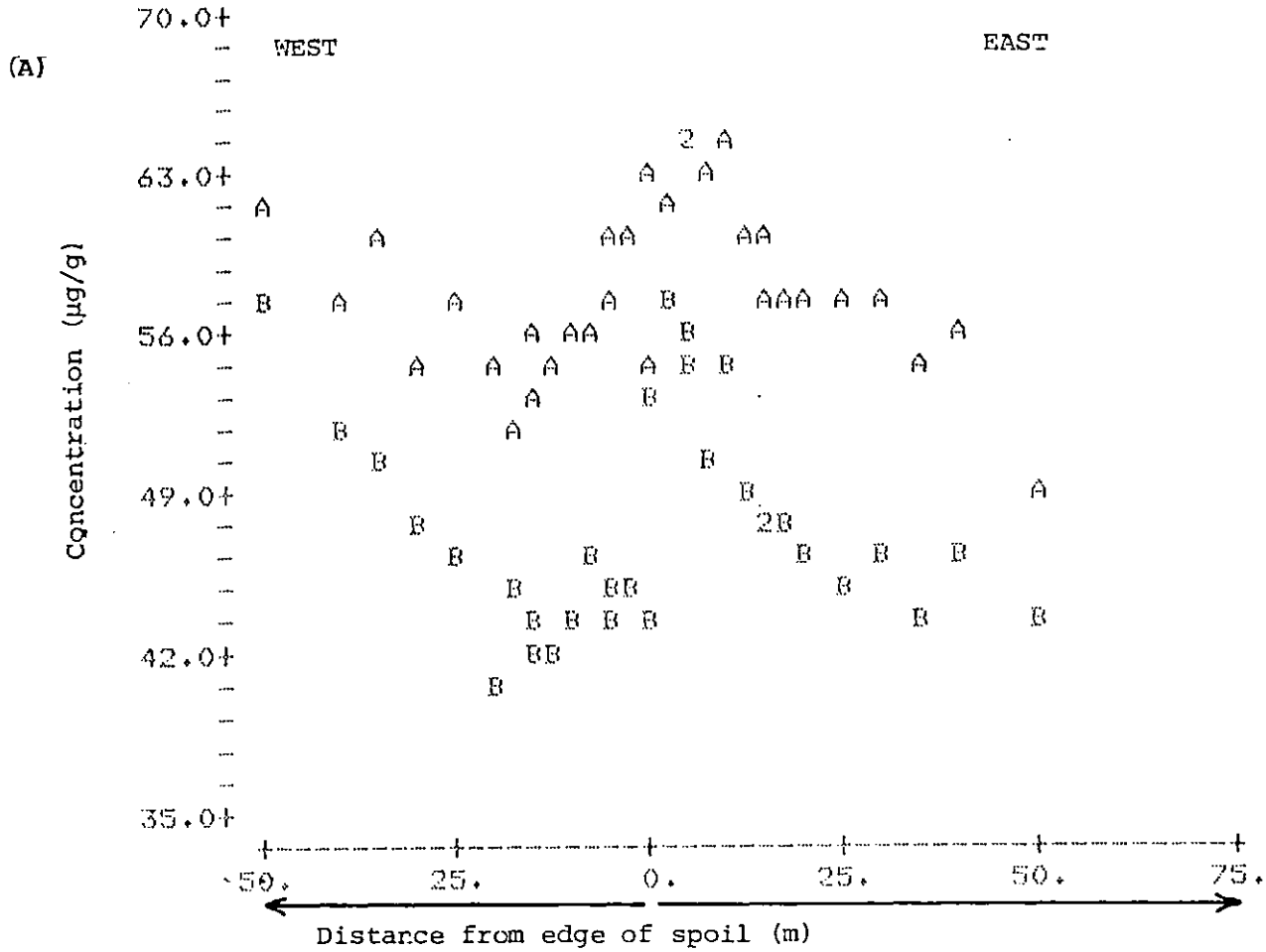


Figure 48. (A) Concentrations of copper found in the soils at Wheal Sisters. (A = Topsoil, B = Subsoil).
(B) Copper R.T.E. ratios at Wheal Sisters.



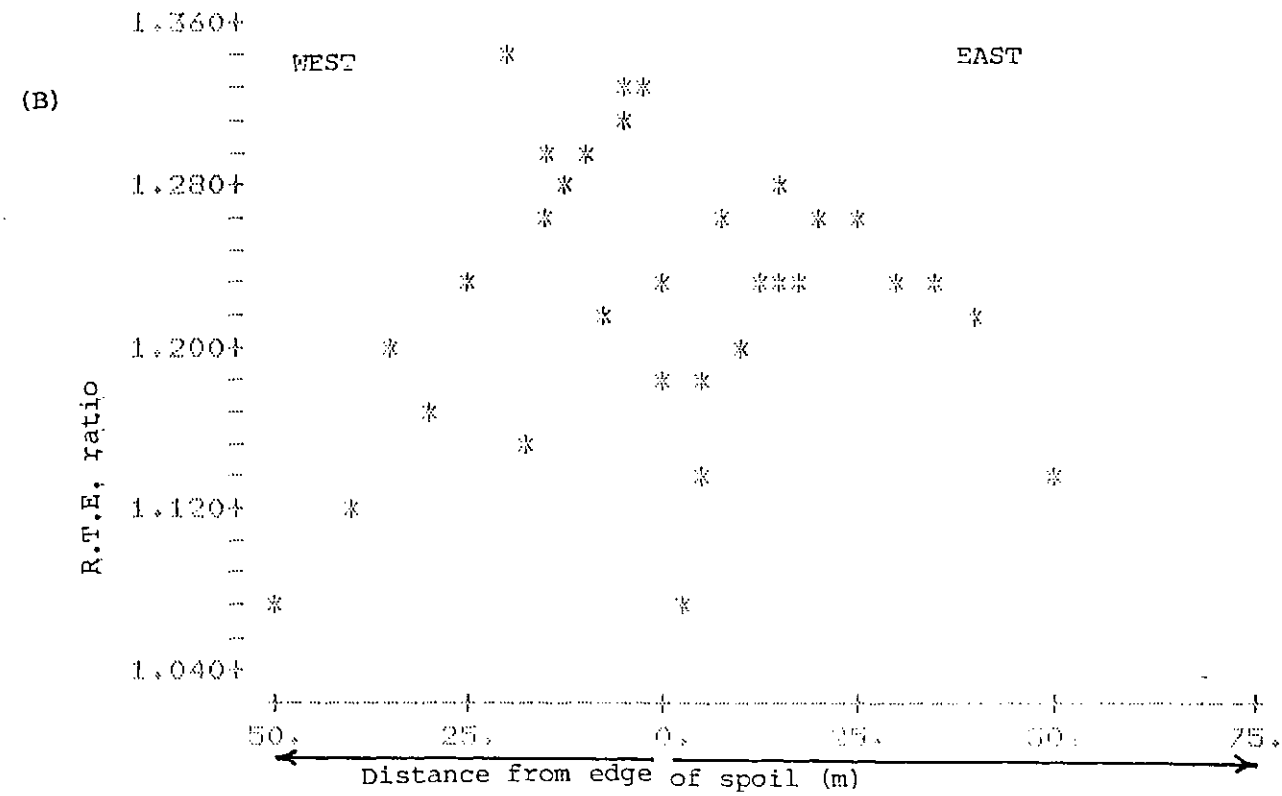


Figure 49. (A) Concentrations of zinc found in the soils at Wheal Sisters. (A = Topsoil, B = Subsoil).
(B) Zinc R.T.E. ratios at Wheal Sisters.

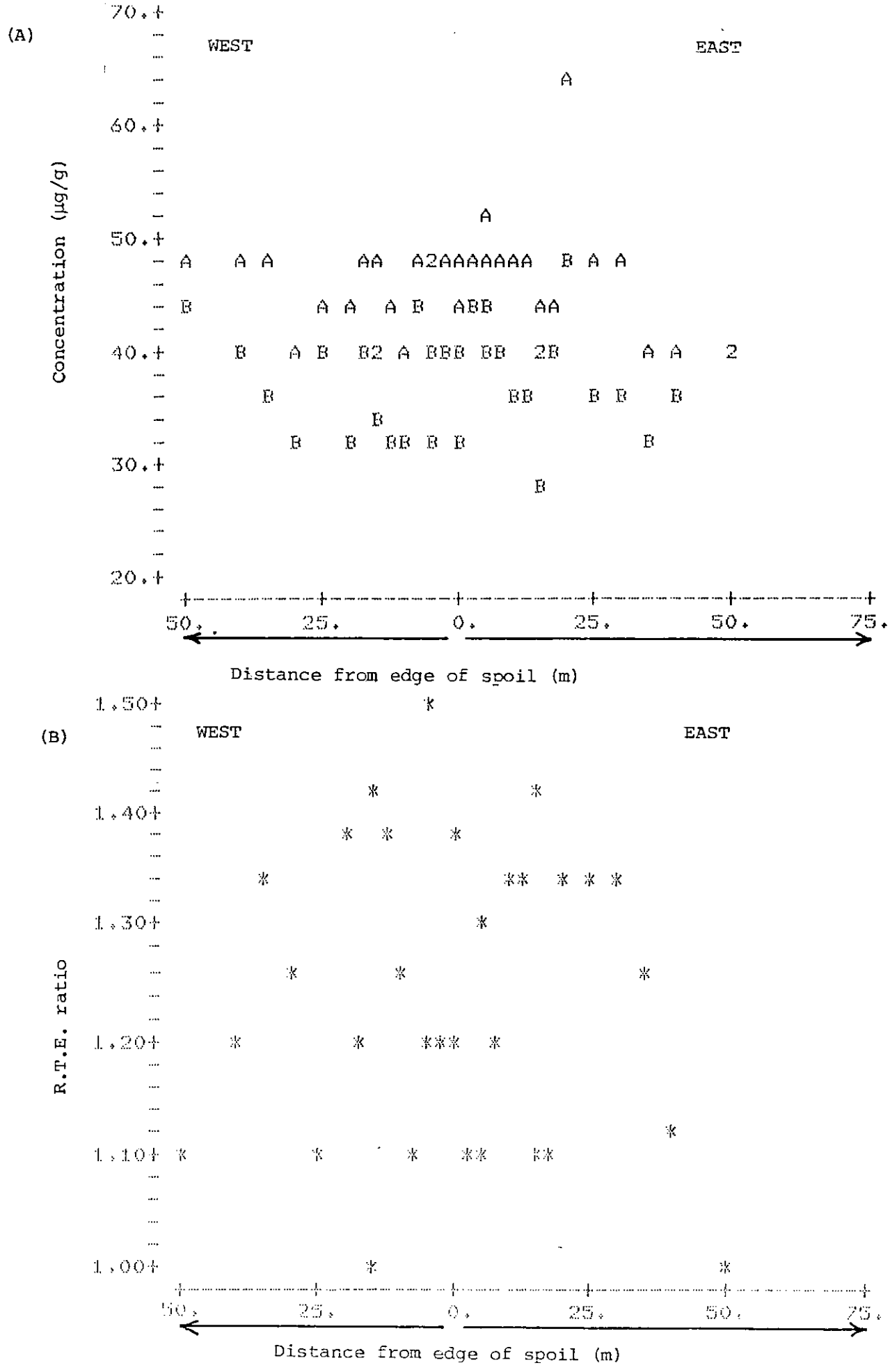


Figure 50. (A) Concentrations of lead found in the soils at Wheal Sisters. (A = Topsoil, B = Subsoil).
(B) Lead R.T.E. ratios at Wheal Sisters.

		West of spoil (n = 16)	East of Spoil (n = 16)
Al:	Topsoil	.161	.713***
	Subsoil	.502**	.322
As:	Topsoil	.279	-.539**
	Subsoil	-.220	-.536**
Ca:	Topsoil	-.060	-.616**
	Subsoil	.185	.432*
Cd:	Topsoil	-.325	.161
	Subsoil	-.099	.504**
Co:	Topsoil	-	-.464*
	Subsoil	-	-.133
Cu:	Topsoil	-.255	-.849***
	Subsoil	.411	-.110
Fe:	Topsoil	.103	-.366
	Subsoil	.320	.013
Mn:	Topsoil	.365	.276
	Subsoil	.738***	.558**
Pb:	Topsoil	-.030	-.371
	Subsoil	.172	-.138
Zn:	Topsoil	.329	-.928***
	Subsoil	.780***	-.830***

Level of significance:- *** = significant at p = 0.01 (1%)
** = significant at p = 0.05 (5%)
* = significant at p = 0.1 (10%)

TABLE 35. Correlation coefficients between the soil concentrations and the distance of the soil samples from the spoil at Wheal Sisters

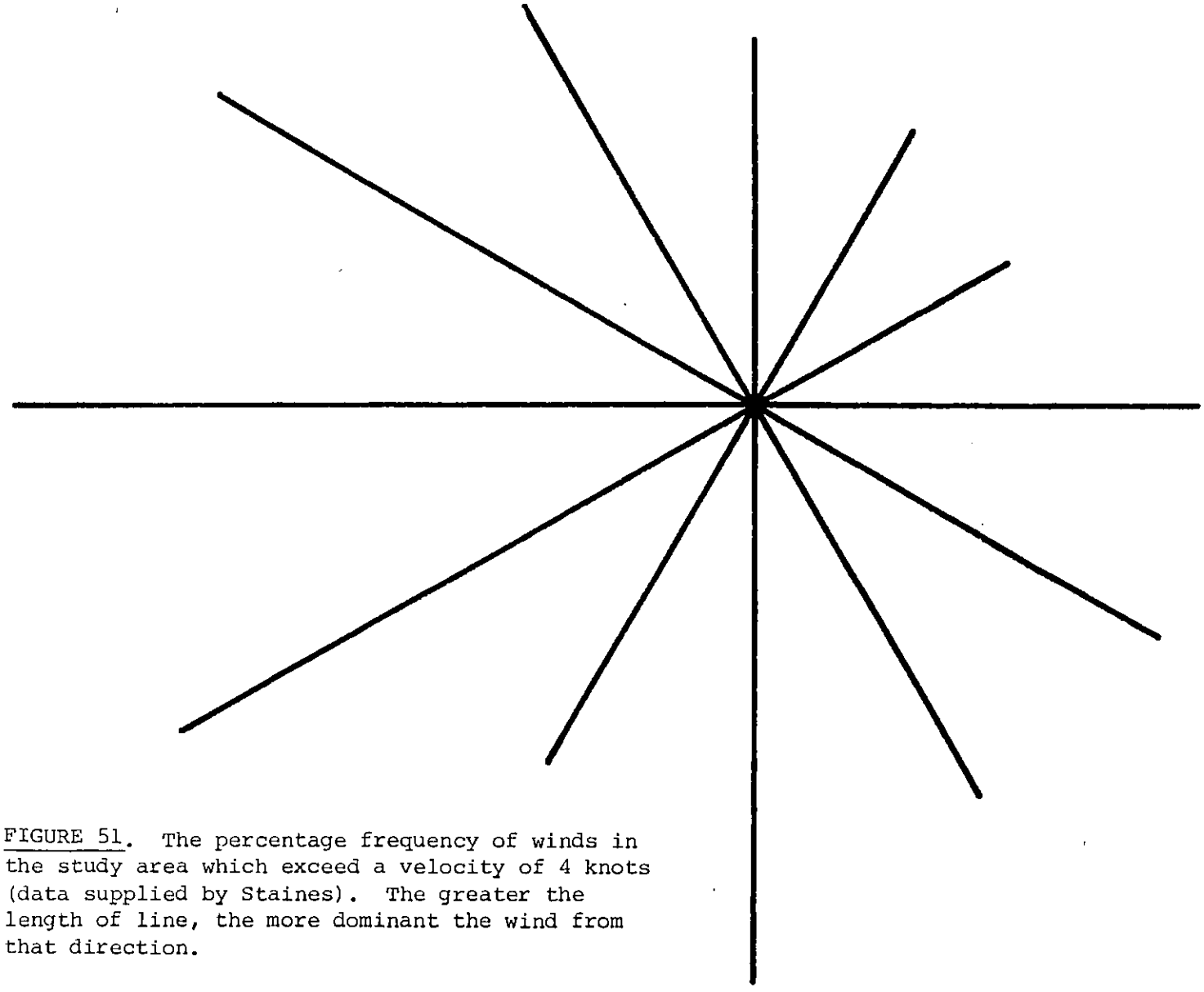


FIGURE 51. The percentage frequency of winds in the study area which exceed a velocity of 4 knots (data supplied by Staines). The greater the length of line, the more dominant the wind from that direction.

c) Contamination due to smelting operations in the province

The production of Cu and Sn ores in Cornwall remained, until recently, as separate distinct entities rather than two sides of the same industry. The differences between them were considerable, but all stemmed from the fact that tin mining was a more ancient industry, governed and ruled by customs and regulations that had evolved with it, and to none of which the more recently developed copper industry was subject. The greatest difference lay in the smelting, the former being required to be produced solely within the county, whilst the latter, for economic reasons, had become almost entirely the province of smelters situated on the South Wales coalfield. Although copper was smelted at a few localities (e.g. Hayle and the St. Austell district), none of the ventures in Cornwall lasted any great time (Barton, 1968a). In contrast, Barton (1967) lists 28 Cornish tin smelting houses, but notes that there were others scattered throughout the county (Figure 52). In addition, the location of some smelters are unknown; this is particularly true of the site of the 'blowing houses', the forerunners of the tin smelters.

Soil sampling was centred around the site of the former smelting works at Trereife, west of Penzance (Figure 52). Geological maps reveal that this area is not mineralised, although local knowledge has disclosed the presence of ancient Sn works at Trewidden (G.R. SW 443296), approximately 1 km west of the smelter. Mylor slates and greenstones comprise the two parent materials found within the vicinity of the former smelting works. In addition, river alluvium may also be present along the banks of the stream. Trereife smelting works itself was established prior to 1732, and finally

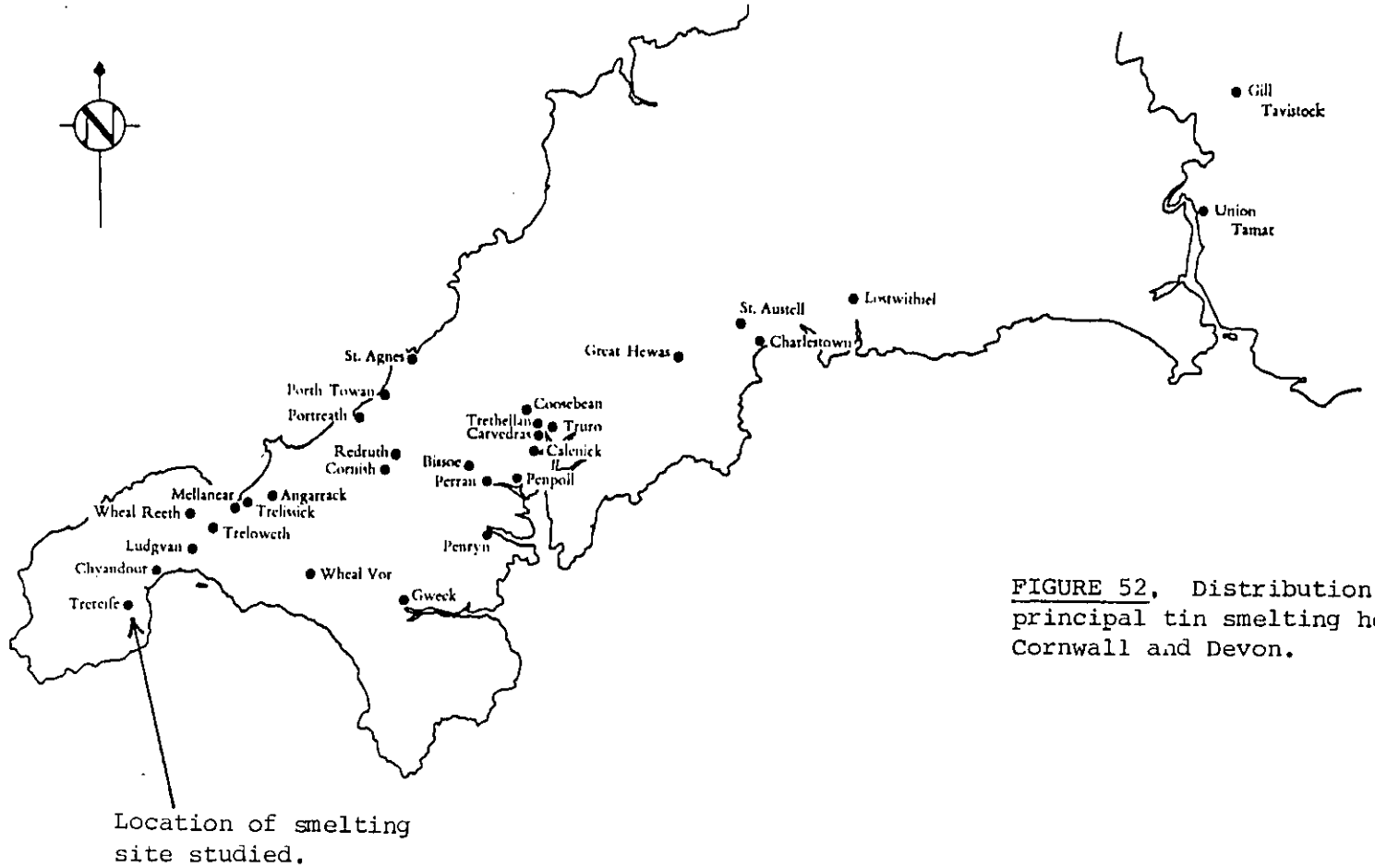


FIGURE 52. Distribution of the principal tin smelting houses in Cornwall and Devon.

closed in 1896 (Barton, 1967). The presence of the smelter at this particular site was probably influenced by the proximity of the stream which was sufficiently powerful enough to drive the water wheel stamps used for breaking up the 'hard head' furnace slags for re-smelting. Penzance, immediately to the east of the smelter site, developed into an important coinage town where the smelted Sn ingots were assayed and weighed prior to taxation. Furthermore, culm and firebricks needed for the smelter could easily be brought into the port. These factors explain why the near proximity of the mines were not necessarily a major factor in the locational siting of the smelting works.

Thirty eight topsoil (0-15 cm) and 35 subsoil (30-45 cm) samples were selected around the former smelting site on an approximate grid pattern (Figure 53). Such a system of sampling could not be accomplished precisely due to a number of difficulties. To the east of sample sites S31 and S33, recent building had just been completed, whilst to the west of site S30, S32 and S34, the land was partly derelict and inaccessible. Further derelict land lay immediately to the east of the former smelter; at the time when the tin smelter was operational, first edition Ordnance Survey maps indicate that this land was afforested.

The soils were analysed for As, Cu and Sn, and the results are presented in table form in Appendix 7. Using the contamination thresholds in Table 24, 35 of the topsoils and 24 of the subsoil samples can be described as being either moderately or highly contaminated with Sn. Five of these sample sites (S5, S11, S20-S22) are heavily contaminated in this element due, at least in part,

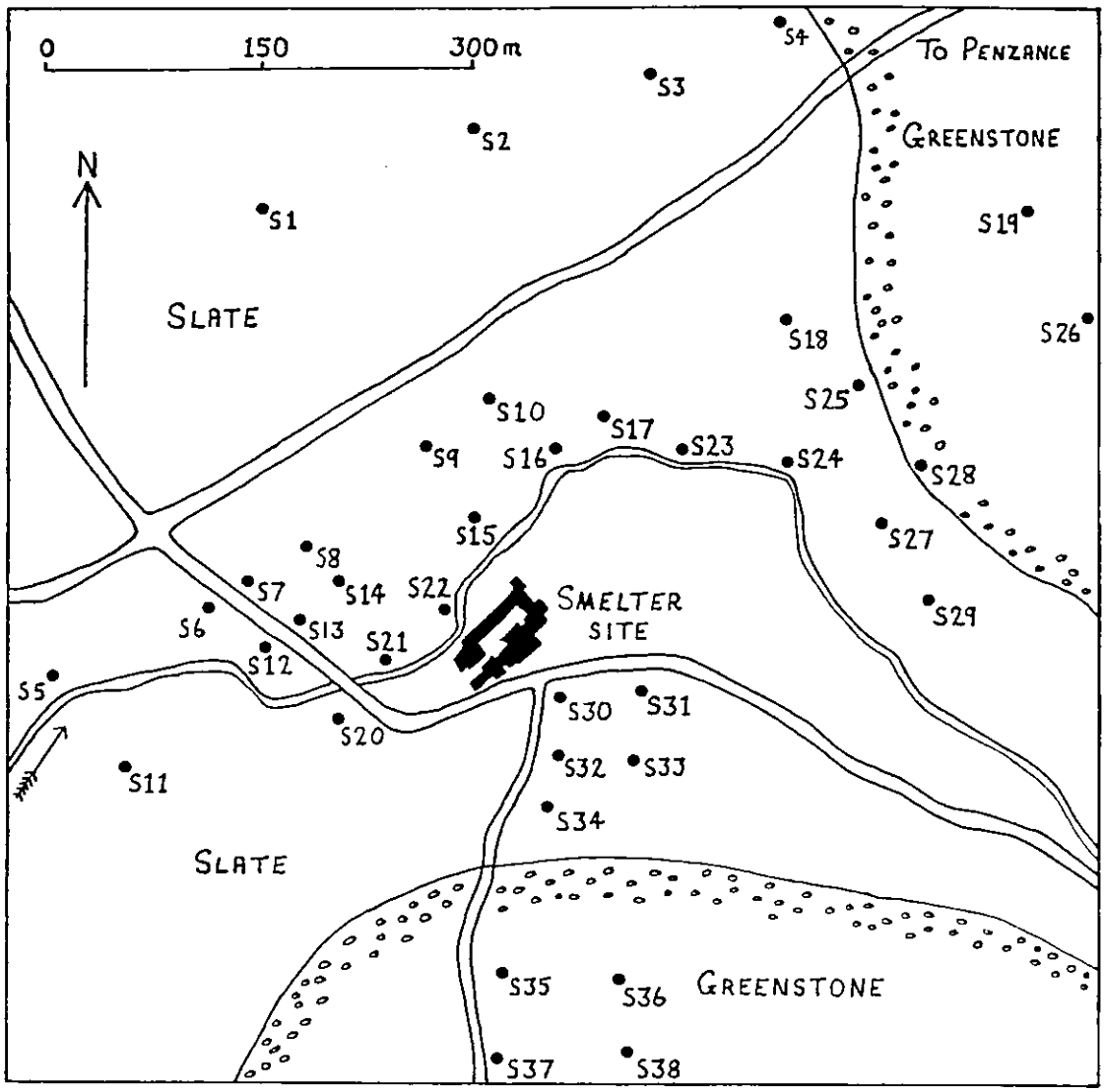


FIGURE 53. Sample site locations around the former smelting works at Trereife.

to the near proximity of the stream and the incorporation of stream sediment material into these soils during times of flooding. A maximum concentration of 2,398 μg Sn/g was recorded from the subsoil sample at site S20. These soils are distinguishable from the soils of the remaining sample sites by their coarse texture. Stream sediment reconnaissance work has confirmed the elevated Sn concentrations of the stream sediments at this location (Webb et al., 1978), and local residents claim that interest in the Sn content of the stream bed load has been evident in the past by mineral exploration companies.

On the basis of texture, the remaining soil sample sites do not appear to have been affected by the local stream. Clearly, some other contamination source is indicated by the high concentrations of Sn recorded at these sites. Analysis of variance has been used as a statistical test to assess the effect of the smelter on the surrounding soils. Ignoring the five sample sites influenced geochemically by the local stream, and those locations where no subsoil could be sampled, the remaining soils were grouped into three zones designated A, B and C according to the distance of the sample site from the smelter. Soils at distances of up to 150 m from the smelter were grouped into Zone A, those between 150 m and 300 m were grouped into Zone B, whilst those sampled at a distance greater than 300 m were classified into Zone C. The mean topsoil and subsoil Sn concentrations of each zone were then determined, and the null hypothesis constructed:

$$H_o = \bar{x}_A = \bar{x}_B = \bar{x}_C$$

The mean concentration of Sn in both the topsoils and subsoils decreases with increasing distance from the smelter source (Table 36). The calculated F value of 10.28 for the topsoil Sn concentrations, and 12.47 for the subsoil Sn concentrations, exceed the tabulated value of 5.49 for F at a significance level of $p = 0.01$ (1%). It can thus be concluded that the sample means are different, and the null hypothesis is rejected. The observed significant inverse trend between the mean Sn concentrations of the three zones and the distance of the zones away from the former smelting works, pinpoints the smelter as a contamination source of Sn with the severest contamination occurring in the immediate vicinity of the work site. Soil contamination thresholds calculated earlier in this research (Table 24) show that soils designated as being highly contaminated in Sn (i.e. > 375 µg/g) occur mainly within 150 m from the smelter site (i.e. within Zone A where the topsoil average is 377 µg Sn/g and the subsoil average is 379 µg Sn/g). The elevated mean concentration of Sn in the topsoils of Zone C ($\bar{x}$ = 232 µg/g) exceeds the moderately contaminated threshold value of 180 µg Sn/g, and clearly shows that the contamination derived from the smelter persists over a greater area than sampled.

Research undertaken during the early part of this century showed that several elements including As were released to the environment through the smelting of sulphide Cu ores (Harkins and Swain, 1907). Hutchinson (1979) draws attention to the fact that this early work set the scene for the now well established principle that aerial discharges from smelters offer the possibility of multi-element toxicities since more than one metal may be emitted. Consequently, the soils sampled in this present research at Trereife have been

analysed for As and Cu due to the close association of both elements with the Sn ores of South-west England. The concentrations of As in soils surrounding the smelter are particularly elevated (Appendix 7). Using the soil contamination threshold values outlined in Table 24, 25 topsoils and 25 subsoils can be described as being either moderately or highly contaminated with this element. The mean concentrations of soil As calculated in Zones A, B and C surrounding the former smelting works, however, do not follow the inverse trend observed for Sn, and the analysis of variance discloses no significant difference between the three soil mean As concentrations (Table 36). This statistical evidence suggests that the Sn smelting process was not responsible for the elevated As concentrations recorded around the site. A review of the literature has indicated that As had to be removed from the Sn ores prior to the smelting of Sn (Barton, 1968b). The black Sn, as delivered to the smelter, was thus already in a relatively pure state. It is of no surprise, therefore, that the As concentrations in the soils surrounding Trereife smelting works do not appear to be associated with the location and operation of the former smelter. The actual source of the high soil As concentrations recorded at Trereife has thus not been determined in this present study.

Copper concentrations in the soils surrounding the former smelting site are not as elevated as those observed for Sn and As. Only four topsoil and five subsoil samples exceed the moderately contaminated threshold value of 125 µg Cu/g quoted in Table 24. The analysis of variance discloses no significant difference between the mean soil Cu concentrations of Zones A, B or C. The operation of the Sn smelter at Trereife, therefore, does not appear to have appreciably affected the Cu content of the surrounding soils.

		Mean Concentration (µg/g)			
		Zone A (n=10)	Zone B (n=10)	Zone C (n=10)	F Ratio
Sn:	Topsoil	376.9	298.6	231.7	10.28***
	Subsoil	379.2	237.6	173.1	12.47***
As:	Topsoil	131.1	140.0	179.5	2.39
	Subsoil	148.3	155.8	200.2	1.35
Cu:	Topsoil	82.0	86.7	104.0	2.15
	Subsoil	89.4	102.9	146.8	2.09

*** = significant at p = 0.01 (1%)

$F_{crit.}$ (p = 0.01) = 5.4881; $F_{crit.}$ (p = 0.05) = 3.3541

TABLE 36. The mean concentrations of tin, arsenic and copper found in soils around the former tin smelter at Treriefe.

The concentrations of Sn, As and Cu in the subsoils at Trereife are generally similar to the topsoil concentrations (Table 36). Consequently, R.T.E. ratios approximate to unity in this contaminated but relatively unmineralised locality (Appendix 7). The significance of this observation may be important if the Sn concentrations are considered. The contamination of the soils by Sn particulates from the smelter is likely to principally affect the surface soil, especially since the metal is chemically inert and is thus unlikely to be leached down the soil profile. The high subsoil Sn concentrations, however, closely reflect the topsoils (Table 36) which suggests that Sn is being translocated down the soil profile. Since chemical movement is unlikely, the mechanical movement of Sn particulates into the lower horizons seems probable. The mechanism of such movement remains unclear, but the activities of soil fauna, or the ploughing of the land and the constant remixing of the upper layers of the soil profile over the many years since the smelter was first established, may offer a possible explanation. More detailed research involving the sampling of soil profiles at depth at this location is required in order to investigate these theories.

d) Contamination due to the calcination of arsenic ores

Even before As became a commercially viable product in the 1870's, its common association with Sn ores was of prime concern to the miners of South-west England. As any trace amounts of the element would produce a relatively hard, less lustrous and less ductile Sn product after smelting, it had to be removed by roasting

or calcination (Barton, 1968b). Once a demand for As arose through the chemical industry, the production of the element became an important by-product of many Sn mines. Dines (1956) records the process of calcination in detail. Following crushing and concentration, the ores were calcined and the vapours passed through the chambers or flues where arsenic oxide accumulated as a grey powder known as 'arsenic soot' or 'crude arsenic'. This crude arsenic contained from 80 to over 90% of As_2O_3 along with certain impurities including C and/or S compounds. Although it was often sold in this form, further calcination could improve the purity by producing 'refined' or 'white arsenic' containing 99.5% As_2O_3.

Such processes are known to have affected the local environment when they were operative. Barton (1967) records that in 1851 an action was brought against Perran Smelting House because of deaths of both cattle and other animals poisoned by As through grazing downwind of the stacks. Accordingly, samples were selected in this research around the site of a former calcining works at Newmill which operated up to 70 years ago. Geological maps reveal that the site lies outside the main belt of mineralised ground. Dines (1956) records, however, the existence of a small mine (Wheal Hartley) worked for Sn, Cu and Zn, located immediately to the south of the works.

Mylor slates of Devonian age constitute the parent material of this smelting site on which have developed loamy brown rankers belonging to the Powys series. Accordingly, sampling was restricted to topsoils (0-15 cm) due to the shallow nature of the soil. The

roasting of the ores took place in ovens at the valley bottom, although the stack through which any emissions of particulate material would occur is built at the top of the slope (Plates 8 and 9). Sampling was thus centred around the chimney, with one traverse line extending to the opposite valley slope (Figure 54). Meteorological data indicates that this extended traverse line coincides with the dominant wind direction (Figure 51).

A total of 58 samples were collected in this survey. Using the soil contamination threshold values quoted in Table 24, some 51 samples contained As in concentrations exceeding the moderately contaminated threshold of 110 µg As/g (Figure 55). Soils high in As were found immediately adjacent to the chimney; at sites C23 and C24 the As concentrations were 652 µg/g and 980 µg/g respectively. However, soils elevated in the element are not confined to the immediate vicinity of the stack. For example, concentrations of 59, 132 µg As/g and 1, 219 µg As/g were recorded from sample sites C47 and C49 on the southernmost traverse line. Unfortunately, it cannot be determined in this present research whether such high concentrations are related solely to emissions from the arsenic calciner or from some other source. More detailed and extensive sampling is clearly required to fully investigate the extent and effects of the calciner on the As content of the surrounding soils. The data recorded from this present study suggests that contamination of As persists over a greater area than has been surveyed.

PLATE 8



PLATE 9



PLATE 8. Remains of the calcining ovens at Newmill.

PLATE 9. The chimney stack at Newmill.

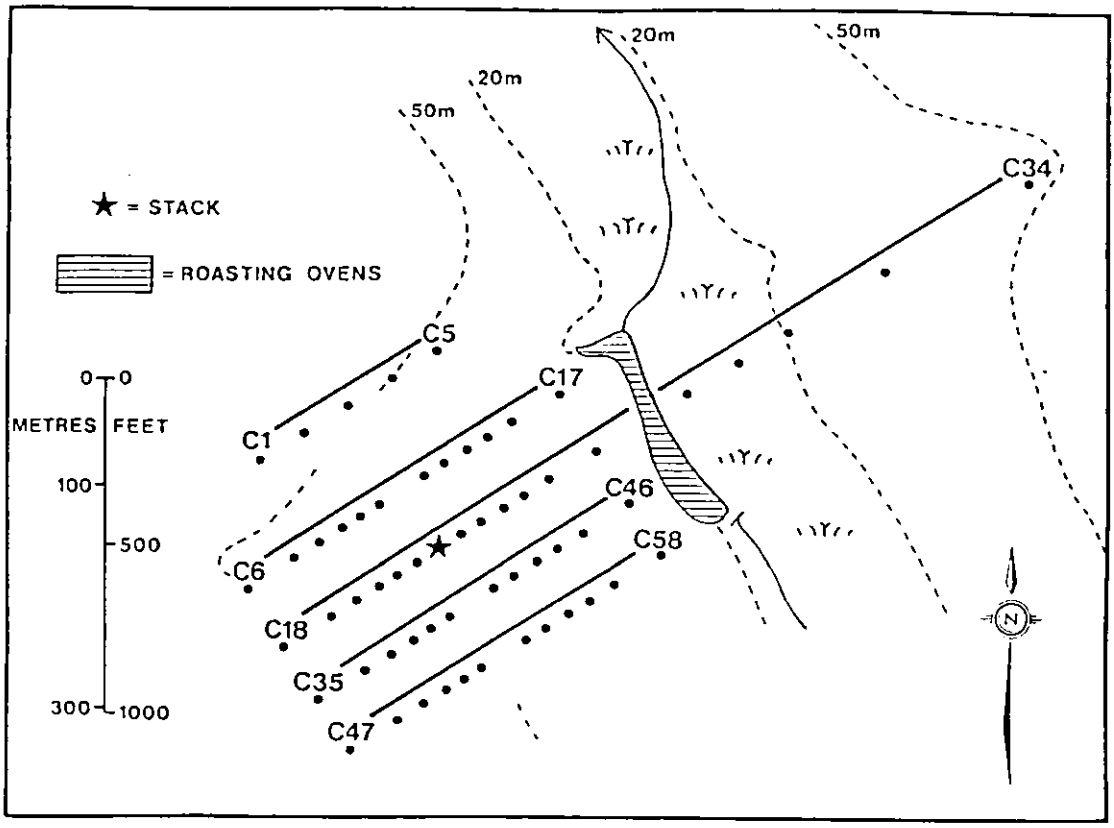


FIGURE 54. Location of sites around the stack of the arsenic works at Newmill.

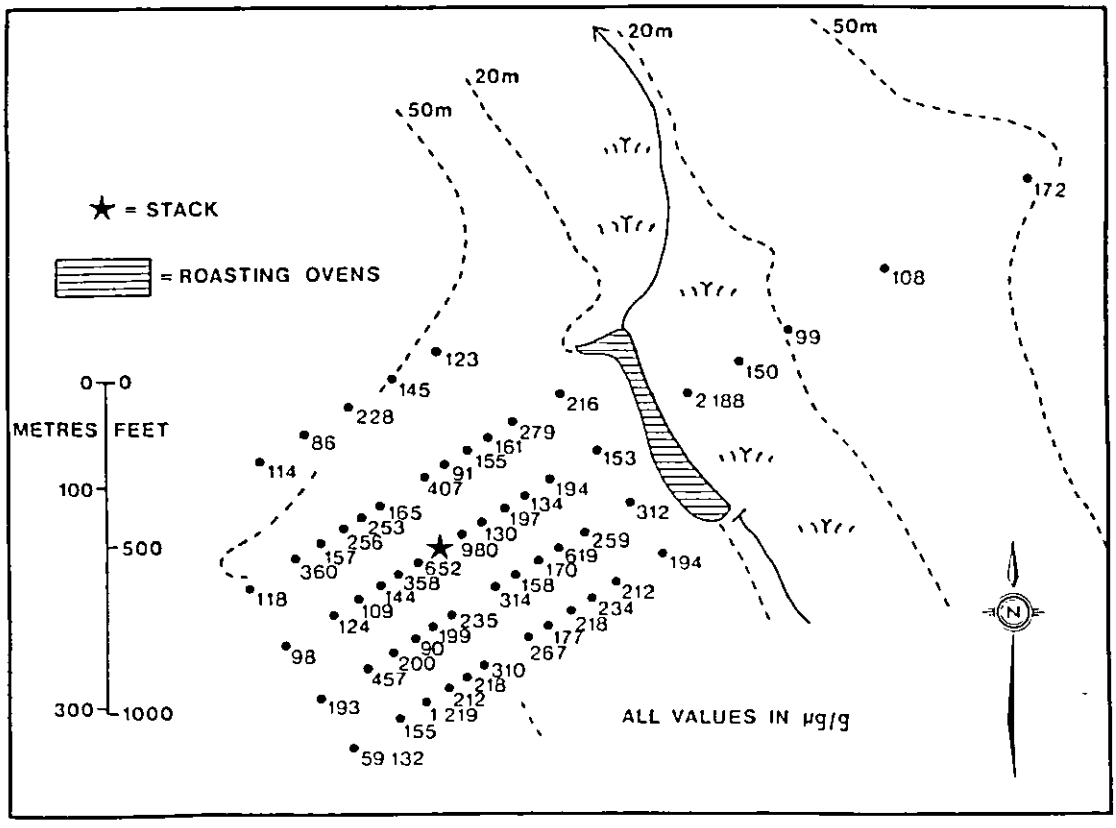


FIGURE 55. Arsenic concentrations in the soils at Newmill.

Negligible Sn and Cu contamination is associated with the roasting of As ores. Only four sites have soil Sn concentrations which exceed the moderately contaminated threshold value of 180 μg/g, whilst five soils exceed the threshold limit of 125 μg Cu/g (Figures 56 and 57). The highest concentrations of Sn (620 μg/g) and Cu (1,248 μg/g) are located at sample site C30. This is an alluvial soil which possibly reflects the effect of flooding from the stream which drains the mineralised ground to the south of the calcining works. High As concentrations may also be associated with these alluvial soils; analysis of soil from the same sample site revealed a concentration of 2,188 μg As/g (Figure 55).

(IV) SUMMARY ON THE SOURCES OF TRACE-ELEMENTS TO THE SOILS OF SOUTH-WEST ENGLAND

Research on the trace-element content of rocks within the study region has revealed that concentrations of specific elements may exceed those amounts normally associated with slate, granitic and basic igneous rocks. Due to the limited amount of solifluction which has occurred within the study region, the trace-element content of soils considered to be relatively unaffected by mineralisation or contamination will closely relate to the underlying parent material. Thus the soils of the study region may contain trace-elements in concentrations greater than normal for soils developed on slate, granite, or basic igneous parent materials. This is especially likely for As, since the normal soil concentrations of this element are low.

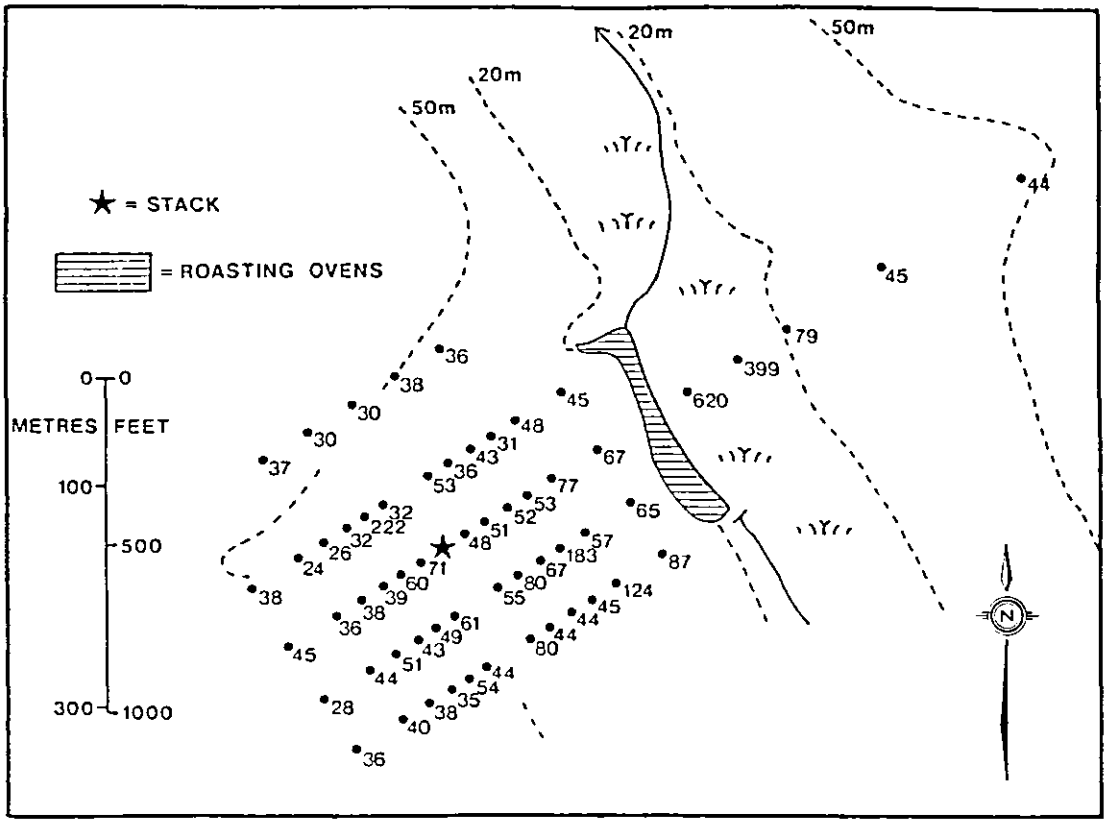


FIGURE 56. Tin concentrations in the soils at Newmill (values in µg/g).

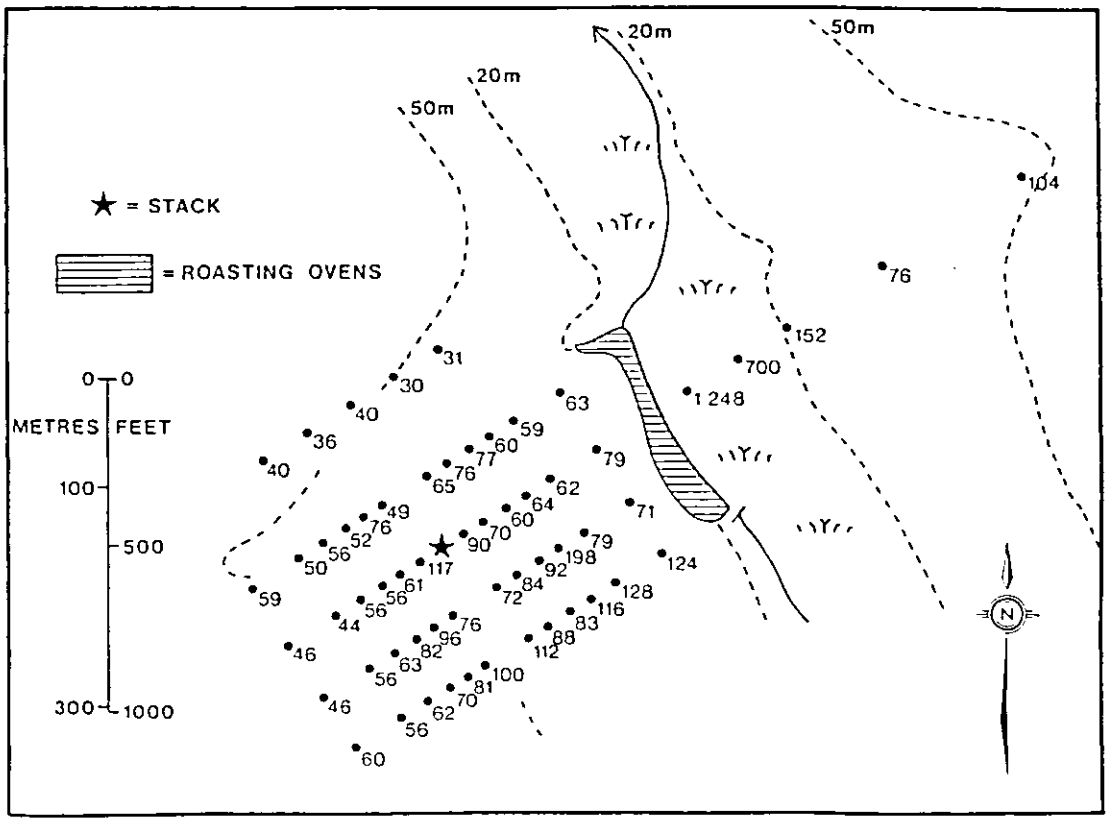


FIGURE 57. Copper concentrations in the soils at Newmill (values in µg/g).

Soils of the district may be further enriched naturally by the weathering of mineralised ore-bodies. Such an investigation has not been studied in this present research, but details by Hale (1980) and Wraith (1982) clearly show that soil concentrations of elements including As and Cu are elevated in soils adjacent to mineralisation. For example, Wraith (op.cit.), working in a relatively uncontaminated area of Cornwall, recorded concentrations of up to 250 μg Cu/g and 90 μg As/g in soils (at 30 cm depth) adjacent to outcropping mineral lodes. The dispersion halo of As in the soils was found to be 90 m.

Further research by Bird (1981) has shown the extremely large amounts of elements including As, Cu, Cd, Fe, Pb and Zn which are associated with the mineral ores of the district. This work also reveals the complex mineralogy and trace-element associations which occur in the mineral ores. Research undertaken in this present study and centred at the sites of two former mines, Wheal Tremayne and Wheal Sisters, has revealed that these trace-element associations are reflected in the mine spoil. The trace-element concentrations of the mine spoil, however, are closely related to the geological controls which influenced mineralisation. Thus, the mine spoil associated with Wheal Sisters contains comparatively low concentrations of all the trace-elements studied, since this mine is centred within an emanative centre of mineralisation where Sn was the dominant mine product. Contamination of agricultural soils adjacent to the mine spoil at this site is therefore limited. In comparison, soils at Wheal Tremayne are contaminated with a number of trace-elements including As, Cd, Co, Cu, Fe, Mn, Pb and Zn, due to the higher

concentrations of these elements associated with the mine spoil at this particular site. The importance of Cu and As at this mine is reflected in the large concentrations of both elements ($\bar{X}m$ = 2,320 µg Cu/g and 2,216 µg As/g) associated with the mine spoil. Consequently, concentrations of both elements are particularly elevated in the soils immediately adjacent to the waste. However, the dispersion patterns revealed at this site show that the contamination of both elements persist up to distances greater than 250 m away from the mine spoil; the maximum distance sampled in this survey.

Whilst a number of elements may be released into soils from mine spoil, it would appear that tin smelting only released significant amounts of Sn into the environment. The high concentrations of As found in soils surrounding the tin smelter studied in this present research are not statistically associated with the site of the former works; this suggests that the As is derived from an alternate and, as yet, undetermined source. Similarly, of the three trace-elements studied at the site of a former arsenic works, only As is found in widespread and elevated concentrations in soils around the site. Since the proximity of mineralisation does not appear to have been a necessity in the locational siting of both tin smelters and arsenic calciners, the contamination from both industries has resulted in elevated concentrations of both Sn and As outside the major mineralised areas. The soil sampling undertaken around the former tin smelter and arsenic works investigated in this research was localised, and the data generated in both surveys suggest that the contamination of Sn and As extends over a greater area than sampled. Barton (1968b) for example, records that the extremely poisonous emissions from lead smelters in Cornwall persisted up to distances of 4 or 5 miles

from the smelters on tranquil days. More detailed and extensive sampling is thus required at both sites investigated in this present research to determine the full effects of the tin smelter and the arsenic calciner on the surrounding soils.

The high concentrations of trace-elements found in soils surrounding the sites of old mines and former arsenic and tin smelting works, indicates that the contamination persists in the soils long after the mining operations have ceased. Hosking (1970) considered that the oxides of As derived from the calciners may ultimately convert to arsenate ions which become fixed in the soil as relatively insoluble ferric arsenate. Organic matter and clay minerals may also provide reactive surfaces which limit the removal of the trace-elements from the soil profile. Tin is especially likely to remain in the soils of the province due to the chemically inert nature of cassiterite (SnO_2), the major Sn mineral of South-west England. However, the concentrations of this element in the subsoils surrounding the former smelting works in the unmineralised area of Trereife, strongly suggests that Sn can be moved down the soil profile by mechanical processes which may involve ploughing and the constant remixing of the upper soil horizons, or the activities of soil fauna. Further sampling of subsoils is required, however, to confirm this observation.

> . . . the sterility may be great, where metals and minerals abound, of which no place perhaps affords more frequent instances than Cornwall; for here the coarsest grounds abound most in metals, and on the other hand, there is the greatest plenty of corn, grass, plants and trees, where no metals or minerals have ever appeared.
>
> W. Borlase (1758)

CHAPTER 6

TRACE-ELEMENT UPTAKE BY PASTURE HERBAGE ON THE CONTAMINATED SOILS OF SOUTH-WEST ENGLAND

(I) INTRODUCTION

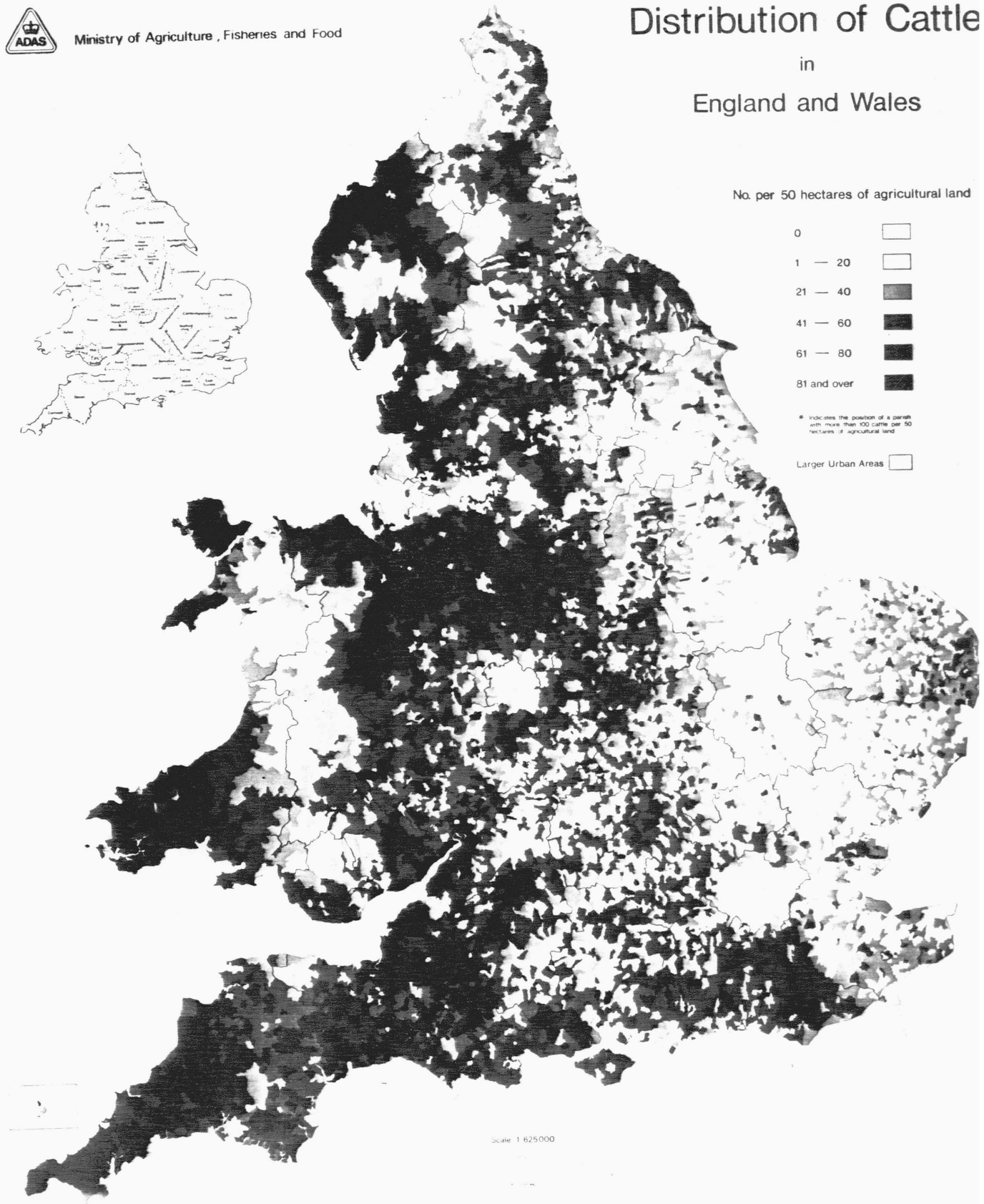
The guidelines which have been proposed by Government or other agencies relating soil contamination to agricultural productivity are difficult to apply to the contaminated soils of South-west England. Recent tentative guidelines by the Department of the Environment (Smith, 1980; D.O.E., 1980) do not apply to agricultural land, whilst other guidelines on geochemistry related to animal nutrition (e.g. E.E.C., 1972) do not include elements such as As and Sn, possibly because the biological significance of such elements has not been fully realised until recently (Davies, 1981). Previous geochemical work relating the soil contamination in South-west England to agriculture has been confined mainly to trace-element uptake studies by barley, broccoli, lettuce, strawberries and pasture herbage (Colbourn, 1976; Hughes, 1979; Thoresby and

Thornton, 1979). Following the advice of ADAS specialists (Dr. David Hughes and Mr. Rowland Thomas), the agricultural aspects of this thesis have been confined to the possible effects of the metal contamination on the health of cattle, and to the quality of the pasture sward. Detailed mapping of the distribution of cattle in England and Wales reveals the importance of livestock to the agriculture of South-west England (Figure 58).

(II) TRACE-ELEMENT UPTAKE BY PASTURE HERBAGE

Using the stream sediment and soil traverse reconnaissance data (Chapters 3 and 4), 12 farms (referred to as sites 1-12) which geochemically reflected the range of trace-elements found within the soils of the Hayle/Camborne-Redruth area, were selected to evaluate the agricultural significance of the As and heavy metal contamination (Figure 8). Following consultation with each farmer, a representative field was selected at each farm, within which three 3 x 3 m^2 plots (designated as plots A, B and C) were established along the centre of the field. Nine soil sub-samples of topsoil (0-15 cm) were collected with a hand screw auger and bulked from each plot, following which composite samples of pasture herbage were cut with stainless steel shears at 2.5 cm above ground level (to avoid unnecessary soil contamination) in late April, late June and late August. In the laboratory, the herbage was split into two separate sub-samples, one sub-sample being washed three times in de-ionised water before oven drying at 80°C. Differences between washed and unwashed herbage samples could then be examined. Methods of sample preparation and analysis of both soils and herbage are more fully outlined in Appendix 1.

FIGURE 58


ADAS
Ministry of Agriculture, Fisheries and Food
Distribution of Cattle
in
England and Wales
No. per 50 hectares of agricultural land
0
1 — 20
21 — 40
41 — 60
61 — 80
81 and over
* Indicates the position of a parish with more than 100 cattle per 50 hectares of agricultural land
Larger Urban Areas
Scale 1:625000

Full details regarding the 12 farms and the analytical data obtained by analysis are presented in Appendix 8. All the soil and herbage samples were analysed for As, Cu, Fe, Mn, Pb and Zn. Problems were encountered with the Pb analysis, however, since the concentrations of this element in the herbage by the method outlined in Appendix 1 were near to the detection limit (4 μg/g) and could not be recorded accurately. Accordingly, all the data for this element is disregarded in the following discussion and is not presented in Appendix 8. The lack of this analytical data in this present research, however, is not regarded as being important since this metal is not a major contaminant within the study area.

(III) SEASONAL VARIATIONS IN THE ARSENIC AND METAL CONTENT OF THE PASTURE HERBAGE

a) The contamination of pasture herbage by soil

True trace-element variations in pasture herbage can only be determined by the analysis of washed herbage since soil contamination arising from soil splash or ruminant poaching can mask and enhance the apparent trace-element content of the plant. A simple unwashed herbage/washed herbage ratio - referred to in this thesis as the contamination ratio - can be used to assess the degree of soil contamination. A high ratio indicates extreme soil contamination, whilst ratio values close to unity indicate negligible soil contamination of the unwashed herbage. Ratio values of less than 1 may occur through analytical error.

Titanium is a particularly good indicator of soil contamination, since this element has a high soil/plant ratio caused by negligible uptake by plants (Mitchell, 1960). In this respect, Fe may also be a useful indicator of soil contamination because of the high amounts of this element found in most soils, and the relatively limited amount of this element which is taken up and translocated by plants (David Kinniburgh, personal communication). Unwashed herbage samples contaminated with soil particules may thus yield high Fe concentrations when analysed. Consequently, contamination ratios (unwashed herbage concentration ÷ washed herbage concentration) were calculated for each of the elements studied in this work, including Fe, and their relation to each other and to the time of sampling can be noted from the data presented in Appendix 8.

As expected, Fe is a reasonably good indicator of soil contaminated herbage, with 32 contamination ratio values (out of the total of 108 calculated) exceeding the value of 2 or more. Unwashed herbage Fe concentrations may be up to 10 times greater than the amounts found associated with the washed herbage at the same site. In comparison, relatively little difference is observed between the Cu, Mn and Zn concentrations of the washed and unwashed herbage samples. Herbage contaminated with soil As appears to be more serious however, since 48 contamination ratio values for this element exceed the value of 2. This research has revealed that unwashed herbage concentrations may be up to 63 times greater than recorded from the washed herbage samples. This clearly indicates the importance of an efficient washing technique when undertaking trace-element uptake studies.

Relative accumulation ratios can be calculated by dividing the washed herbage content of an element by the soil concentration. The relative accumulation ratios calculated in this research are presented in Appendix 8, and indicate two major points of interest. Firstly, relative accumulation is dependent upon soil concentration, with low ratio values coinciding with the more heavily contaminated soils, and high ratio values corresponding with the soils which are lower in their trace-element content. This characteristic of relative accumulation is outlined in greater detail in Section IVc of this chapter. Secondly, the relative accumulation ratios clearly show that under the soil conditions examined in South-west England, the relative accumulation of As is considerably lower than that observed for the elements Cu, Mn and Zn. Most relative accumulation ratio values for As are below 0.01, whilst in comparison all the ratio values for Cu, Mn and Zn are above this value with minimum values of 0.033 for Cu, 0.037 for Mn and 0.07 for Zn being recorded. The relative accumulation of Fe falls between those recorded for As and the three elements Cu, Mn and Zn.

These relative accumulation ratios explain why herbage is susceptible to both Fe and As soil contamination. Since Cu, Mn and Zn are more easily taken up and translocated within the pasture herbage, the difference between the soil and herbage concentrations for these three trace-elements is less than will occur for As and Fe. Herbage is thus particularly susceptible to soil As and Fe contamination, which results consequently in elevated contamination ratios for these two elements. However, some contamination ratios for both As and Fe are below unity and show that at some sites the washed herbage concentrations for these two elements are higher than those recorded from the unwashed samples. A closer examination

of the Fe data reveals that this feature is particularly apparent at four soil plots, viz:

i) site 9, plot C, late August

ii) site 7, plot C, late June

iii) site 7, plot A, late August

iv) site 7, plot B, late August.

Since theoretically the washed herbage Fe concentrations should never exceed the values associated with the unwashed samples, the Fe herbage concentrations recorded from the four plots above must be regarded as questionable. Accordingly, all the analytical data relating to these plots are not considered in the following sections dealing with trace-element uptake by the pasture herbage.

b) The concentrations of trace-elements in the pasture herbage of South-west England

An examination of the trace-element concentrations derived by the analysis of the washed herbage samples shows that the late June herbage concentrations generally appear to be lower than those recorded from the late April and late August samples (Appendix 8). This trend is particularly observed for Fe but is also apparent, in part, for the other elements. However, at some plots this general trend does not occur (e.g. all the elements recorded from the washed herbage samples of the three plots within site 5). Seasonal variation in the trace-element content of plant materials has been attributed to processes within the plant, or to differences in the seasonal availability of trace-elements within the soil (Chapter 1). The limited nature of the work outlined in this thesis cannot disclose the reasons for the seasonal trace-element variations observed in

pasture herbage of the study area. However, the general seasonal trend disclosed in this research has been noted by other workers. In the Tamar Valley district, minimum concentrations of As, Cu, Pb and Zn were recorded from pasture herbage in July, compared to March and November (Thoresby and Thornton, 1979). Further research by Colbourn (1976) found As to be the only element which exhibited any marked seasonal variations. Concentrations of this element tended to be higher in October herbage than those recorded in May.

Within the sampling period April to August, the trace-element content of pasture herbage may vary to a large degree. Table 37 reveals the maximum extent to which such variation within a single plot may occur. Concentrations of Fe are particularly variable (maximum variation 1,183 μg/g), although on a percentage basis the variation observed for As may also be significant compared to the elements Cu, Mn and Zn. Greater variations may be expected for the trace-element content of unwashed herbage due to the extreme values recorded as a result of soil contamination. A study of the data in Appendix 8 reveals that herbage in late April is particularly sensitive to such contamination. It was noted during sampling that the grass at this time of the year was very short and thus susceptible to the effects of soil splash and ruminant poaching. Site 9 during this sampling period is particularly affected by soil contamination with maximum values of 58 μg As/g, 74 μg Cu/g, 11,750 μg Fe/g, 300 μg Mn/g and 103 μg Zn/g being recorded in the unwashed herbage of plot C. In comparison, the washed herbage concentrations at this plot during late April were 1.05 μg As/g, 17 μg Cu/g, 1,360 μg Fe/g, 138 μg Mn/g and 49 μg Zn/g.

	Range (µg/g)	Difference between maximum and minimum concentration (µg/g)	% difference (i.e. $\frac{\text{maximum}}{\text{minimum}} \times 100$)	Site at which observed
As	0.28-1.42	1.14	507	Site 11 (plot A)
Cu	9 - 24	15	267	Site 4 (plot B)
	11 - 26	15	236	Site 8 (plot B)
Fe	177 -1360	1183	768	Site 9 (plot C)
Mn	113 - 325	212	288	Site 2 (plot A)
Zn	38 - 77	39	203	Site 8 (plot A)

TABLE 37. The maximum variation of arsenic, copper, iron, manganese and zinc observed in washed pasture herbage between the late April, late June and late August sampling periods.

(IV) FACTORS INFLUENCING THE TRACE-ELEMENT CONTENT OF PASTURE HERBAGE

a) The relationship between the trace-element content of the pasture herbage and the 'total' soil trace-element concentrations

The As and metal content of the soils is only reflected to a limited extent in the trace-element content of the pasture herbage. Diagrams showing the relationship between the trace-element concentrations of the soils and pasture herbage in late April are presented in Figures 59a-e. These diagrams show that of the 5 elements studied, only the As and Cu content of the pasture herbage increases significantly with increasing soil content. However, in terms of concentration, for both elements the observed increase in pasture herbage content on the heavily contaminated sites is relatively small compared to the large range (17-388 µg As/g and 9-334 µg Cu/g) of both elements recorded in the soil samples representing the 36 plots studied.

Iron and Zn herbage concentrations are not significantly correlated with soil content. The correlation (R^2) values are low and Figures 59(c) and 59(e) reveal little relationship between the simple linear regression equations and the data plots. In comparison, manganese concentrations in herbage decrease significantly with soil Mn content. Figure 59(d) shows that pasture growing on soils containing 2,000 µg Mn/g can contain up to approximately 200 µg Mn/g less than pastures established on soils containing 100-200 µg Mn/g. This pattern of Mn uptake is probably strongly influenced by soil parameters independent of the soil concentration. In this research, the low Mn sites (i.e. < 300 µg/g) are developed on granites, where

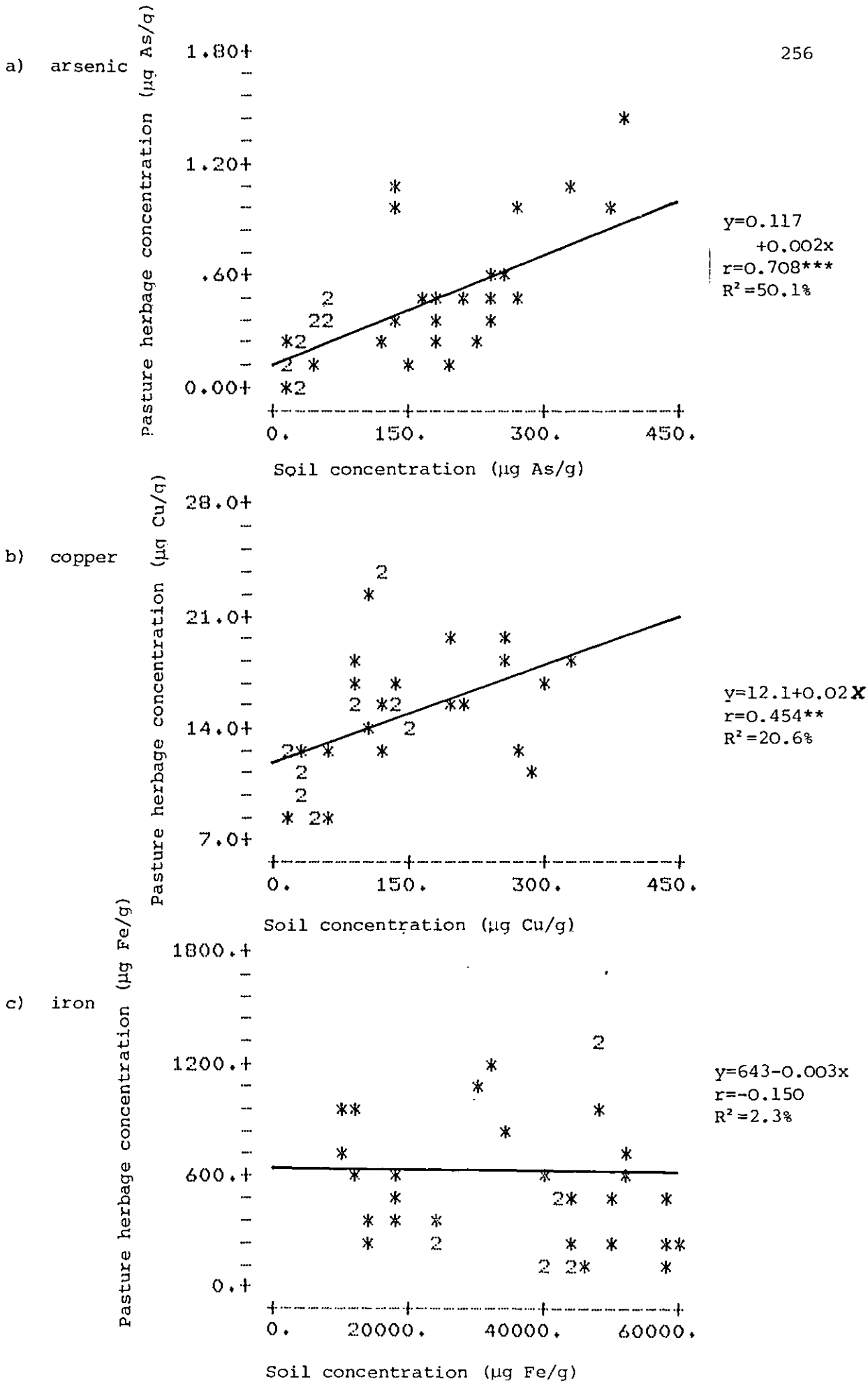
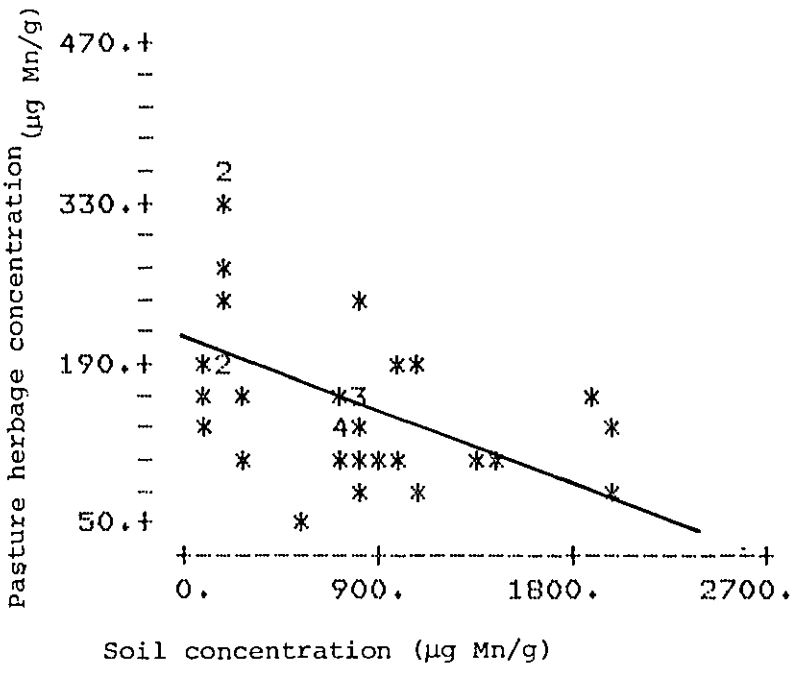


FIGURE 59a-c. Arsenic, copper and iron concentrations in pasture herbage sampled during late April.

d) manganese



e) zinc

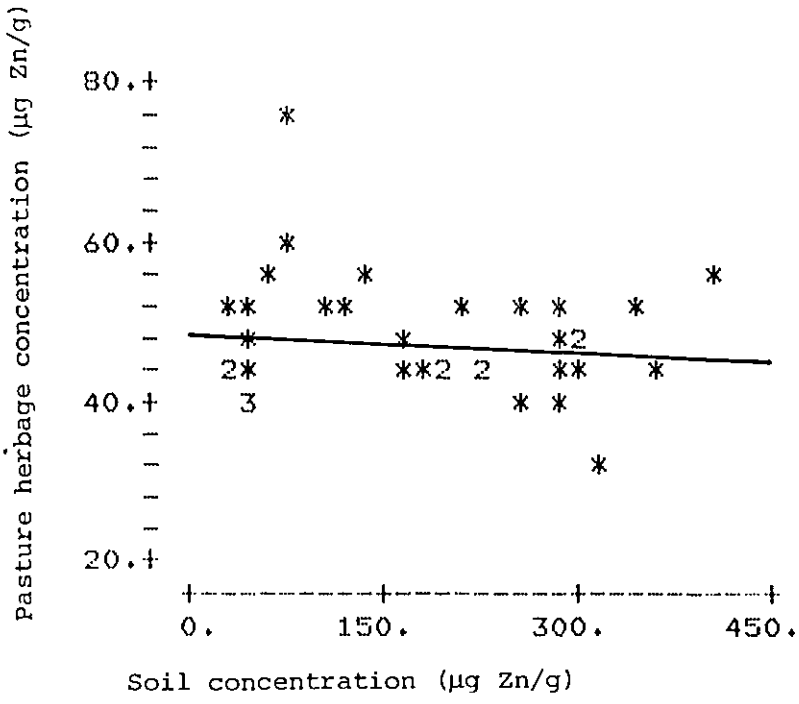


FIGURE 58d-e. Manganese and zinc concentrations in pasture herbage sampled during late April.

**=significant at p=0.01(1%)

soil variables such as pH and organic matter content differ from the slate soils which all have greater concentrations of the element. The possible influence of such variables on Mn uptake is discussed more fully in section IV(b) of this chapter.

Diagrams relating the trace-element concentrations of the pasture herbage to the soils during late June and August are not presented in the text of this thesis. However, Pearson correlation coefficients between the herbage and soil concentrations for these two sampling periods are included in Table 38. These correlation coefficients indicate a similar relationship between soil and herbage trace-element concentrations as observed in late April.

b) The use of multiple-regression techniques in investigating the uptake of trace-elements by pasture herbage

The Pearson correlation coefficients determined from the relationship between soil and pasture herbage trace-element concentrations (Table 38) indicate that the assimilation by pasture of any of the five elements studied in this research is not totally related to the soil concentrations. The work of a number of researchers on plant uptake is briefly summarised in Chapter 1, and indicates the complex nature of trace-element uptake. Variables such as pH, organic matter content and the presence of associated ions in the soil may all be important in determining the uptake of an element by pasture herbage. Thus, regression of the 'total' content of a specific element in the pasture herbage against more than one variable may allow for the development of models which account for a greater proportion of the variation of the total plant content than does the simple linear regression analysis presented in the section above.

	Sampling period		
	late April (n = 36)	late June (n = 35)	late August (n = 33)
Arsenic	0.708***	0.753***	0.621***
Copper	0.454**	0.468**	0.324
Iron	-0.150	0.252	0.283
Manganese	-0.486**	-0.506**	-0.456**
Zinc	-0.145	0.183	0.194

*** = significant at p = 0.001 (0.1%)

** = significant at p = 0.01 (1%)

TABLE 38. Pearson correlation coefficients determined from the relationships between the five trace-elements in soils and herbage.

The method most commonly employed to describe the relation of one variable to a number of other independent (predictor) variables is multiple linear regression. However, one problem with this technique is that correlations between predictor variables tend to produce multiple correlation coefficients which are too high and often of the wrong sign (Turner, 1980). Correlation between the concentrations of the five trace-elements, pH and organic matter content of the 36 soil plots investigated in this research show that many of the variables are significantly correlated (Table 39). Ridge regression analysis can overcome these problems, however, since this technique removes the effects of the correlations from the regression analysis. Such a technique has been used in this research, using a computer programme developed by Dr. Richard Howarth of the Applied Geochemistry Research Group.

The procedure for ridge regression involves the addition of a small constant 'k' to the diagonal elements of the covariance matrix. The estimates of regression coefficients obtained in this way are biased, but have small sums of squares deviations between the coefficients and their estimates (Turner, 1980). The optimum value for k is determined by the data itself; a plot of standard estimators against k, called the ridge trace, is used as a means of determining subjectively the value of k. Turner (op.cit.) gives the following criteria to be used in the selection of k:

i. At the chosen value, all changes of sign and all the major changes in relative importance of the estimators should have occurred.

ii. Coefficients with an apparently incorrect sign at k=0 will have changed to the proper sign.

	Soil As	Soil Cu	Soil Zn	Soil Fe	Soil Mn	Soil pH
Soil Cu	.886***					
Soil Zn	.809***	.858***				
Soil Fe	.735***	.747***	.913***			
Soil Mn	.435*	.622***	.835***	.854***		
Soil pH	.254	.112	.402*	.430*	.398*	
O.M.	-.242	-.328	-.357*	-.359*	-.397*	-.332*

*** = significant at p = 0.001 (0.1%)

* = significant at p = 0.05 (5%)

O.M. = organic matter content

TABLE 39. Correlations between variables measured from the 36 soil plots investigated in this research.

iii. Variance inflation factors should be approximately equal to unity.

iv. The sum of inverse eigenvalues will be approximately equal to the number of variables in the model.

v. The residual sum of squares will not have been inflated to an unreasonable value.

vi. The coefficients (estimators) will not have unreasonable values with respect to the factors for which they are representing rates of change.

The use of the ridge regression technique on the As content of pasture during late April (i.e. the dependent variable) can be presented in the text of this thesis in order to explain how the method is used. Initially, in this particular case, the ridge regression model was tried using eleven predictor or independent variables which were:

i. The As, Cu, Zn, Fe and Mn soil concentrations (five predictors referred to as AS, CU, ZN, FE and MN in the following computer output).

ii. The Cu, Zn, Fe and Mn concentrations of the herbage sampled in late April (four predictors referred to as CUAP, ZNAP, FEAP and MNAP in the following computer output).

iii. The pH and organic matter content of the 36 soil plots (two predictors referred to as PH and OM in the following computer output).

Reference to the table of ridge constants calculated by the computer progamme shows the ordinary least squares solution to occur where k=0 (Table 40). Had this method of multiple linear

36 SAMPLES INPUT
DATA MATRIX : 36 OBSERVATIONS 12 VARIABLES

STANDARDIZED ESTIMATORS

	RIDGE CONSTANT					
	0.00	.02	.04	.06	.08	.10	.15
AS	.3416	.4547	.4804	.4852	.4824	.4762	.4559
CU	.9844	.6718	.5485	.4815	.4387	.4086	.3604
CUAP	-.0332	.0059	.0230	.0327	.0391	.0437	.0512
ZN	-.7560	-.4193	-.2757	-.1966	-.1465	-.1120	-.0598
ZNAP	.1686	.1431	.1282	.1172	.1084	.1010	.0864
FE	.4425	.2384	.1595	.1179	.0925	.0758	.0522
FEAP	.1909	.2329	.2469	.2522	.2539	.2538	.2497
MN	-.4304	-.3882	-.3698	-.3547	-.3411	-.3283	-.2998
MNAP	.2310	.1917	.1716	.1579	.1472	.1385	.1216
PH	.5628	.4523	.3982	.3623	.3352	.3133	.2713
OM	.0062	-.0259	-.0405	-.0494	-.0556	-.0602	-.0677
AVERAGE VIF	10.24	6.28	4.77	3.93	3.39	3.01	2.38

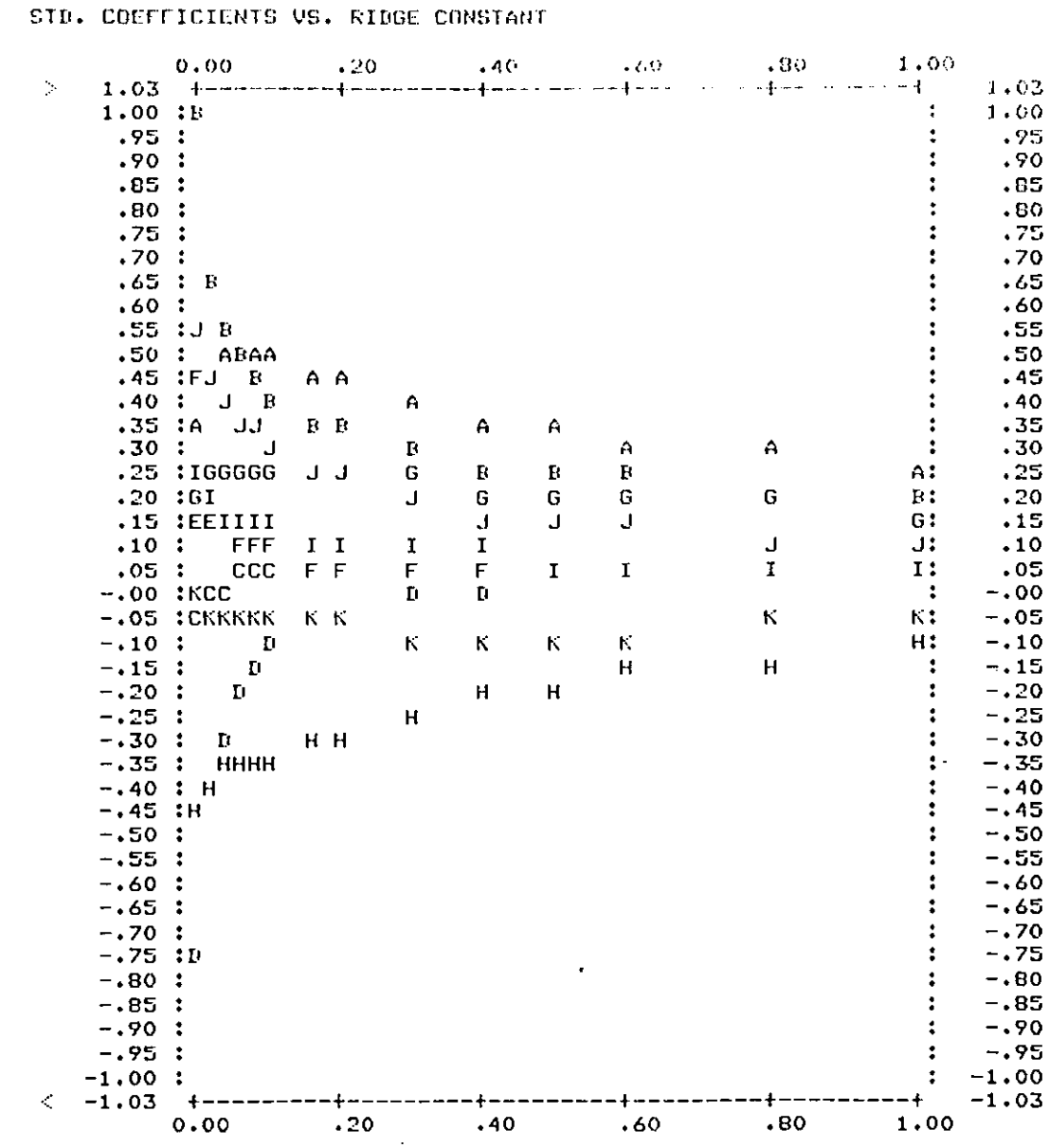
STANDARDIZED ESTIMATORS

	RIDGE CONSTANT					
	.20	.30	.40	.50	.60	.80	1.00
AS	.4346	.3960	.3639	.3370	.3144	.2783	.2507
CU	.3305	.2926	.2675	.2487	.2337	.2102	.1924
CUAP	.0558	.0613	.0644	.0663	.0674	.0681	.0677
ZN	-.0306	.0007	.0170	.0268	.0332	.0408	.0448
ZNAP	.0756	.0605	.0506	.0436	.0384	.0314	.0268
FE	.0409	.0319	.0295	.0294	.0302	.0322	.0341
FEAP	.2435	.2299	.2168	.2048	.1939	.1751	.1596
MN	-.2753	-.2353	-.2041	-.1792	-.1588	-.1274	-.1046
MNAP	.1088	.0900	.0765	.0663	.0581	.0458	.0370
PH	.2404	.1964	.1661	.1439	.1269	.1029	.0867
OM	-.0720	-.0760	-.0770	-.0766	-.0755	-.0725	-.0692
AVERAGE VIF	2.00	1.55	1.28	1.10	.96	.78	.66

TABLE 40. Standardised estimator values derived by regression of the arsenic content of pasture herbage sampled during late April against 11 predictor variables (36 observations).

regression been employed, soil Cu, soil pH, soil As and soil Fe would have been the strongest positive estimators, and soil Zn and soil Mn the strongest negative predictors. With a small increase in K, however, several of these estimators, most notably soil Zn, decrease in predictive importance. This is reflected by the ridge trace (Figure 60) which thus clearly demonstrates the value of ridge regression analysis in clarifying relationships which would otherwise be affected by correlations between the predictor variables. The optimum value of k was chosen as 0.2, since the stability of the ridge trace had been achieved at this value, and all the criteria given above for the choice of k are satisfied. Table 41 shows the regression estimators and statistics comparing the least squares model with the ridge equation model when k=0.2. The multiple R^2 value has been reduced from 83.7% to 77.1%, but the latter ridge model should be more reliable than the least squares estimate, which is partly evidenced by the reduction in the total variance of the estimators from 0.0062 to 0.0039.

However, the residual probability plot presented in Figure 61 shows that four data points do not 'fit' well to the model when k=0.2. The three points with the largest residuals represent instances where the actual concentration of As recorded in the pasture herbage is larger than that predicted by the model. Conversely, the point with the largest negative residual represents a site where the concentration of As in the herbage is much smaller than that predicted by the model. These outliers are difficult to explain, although the large negative residual is due to the extremely low concentration of As (0.09 μg/g) recorded at site 6 (plot C) (Appendix 8); such an abnormally low concentration may



KEY

A=AS B=CU C=CUAP D=ZN E=ZNAP F=FE G=FEAP H=MN I=MNAP
J=PH K=OM

FIGURE 60. Ridge trace of the data presented in Table 40.

Regression estimators:

	Ridge (k=0.2)		Least squares (k=0)	
	Estimator	Standard error	Estimator	Standard error
Intercept	-0.7698		-2.1426	
AS	.001347	.000470	.001058	.001142
CU	.001226	.000598	.003650	.001305
CUAP	.004613	.009949	-.002742	.011624
ZN	-.000090	.000520	-.002209	.001242
ZNAP	.003484	.005252	.007770	.005824
FE	.000087	.000351	.000941	.000665
FEAP	.023110	.010293	.018118	.011854
MN	-.017671	.009618	-.027631	.022086
MNAP	.000485	.000587	.001030	.000700
PH	.115870	.055374	.27126	.069915
OM	-.015994	.022603	.001373	.023063

Total variance of estimators:	Ridge	Least squares
	.0039	.0062

Analysis of variance:

Source of variation	Degrees of freedom	Ridge (k=0.2)			Least squares (k=0)		
		Sum of squares	Mean squares	F-ratio	Sum of squares	Mean squares	F-ratio
Regression	11	3.04	0.28	7.339	3.30	0.30	11.215
Residual	24	0.90	0.04		0.64	0.03	
Total variation	35	3.94			3.94		

	Ridge	Least squares
Multiple R^2(%)	77.08	83.71
Standard error of estimator	0.1939	0.1635
Variance of error term	0.0376	0.0267
Sum of inverse eigenvalues	22.05	112.64

TABLE 41. Comparison of ridge regression and least squares multiple regression - the arsenic pasture herbage (late April) data is regressed against 11 predictor variables.

(36 observations)

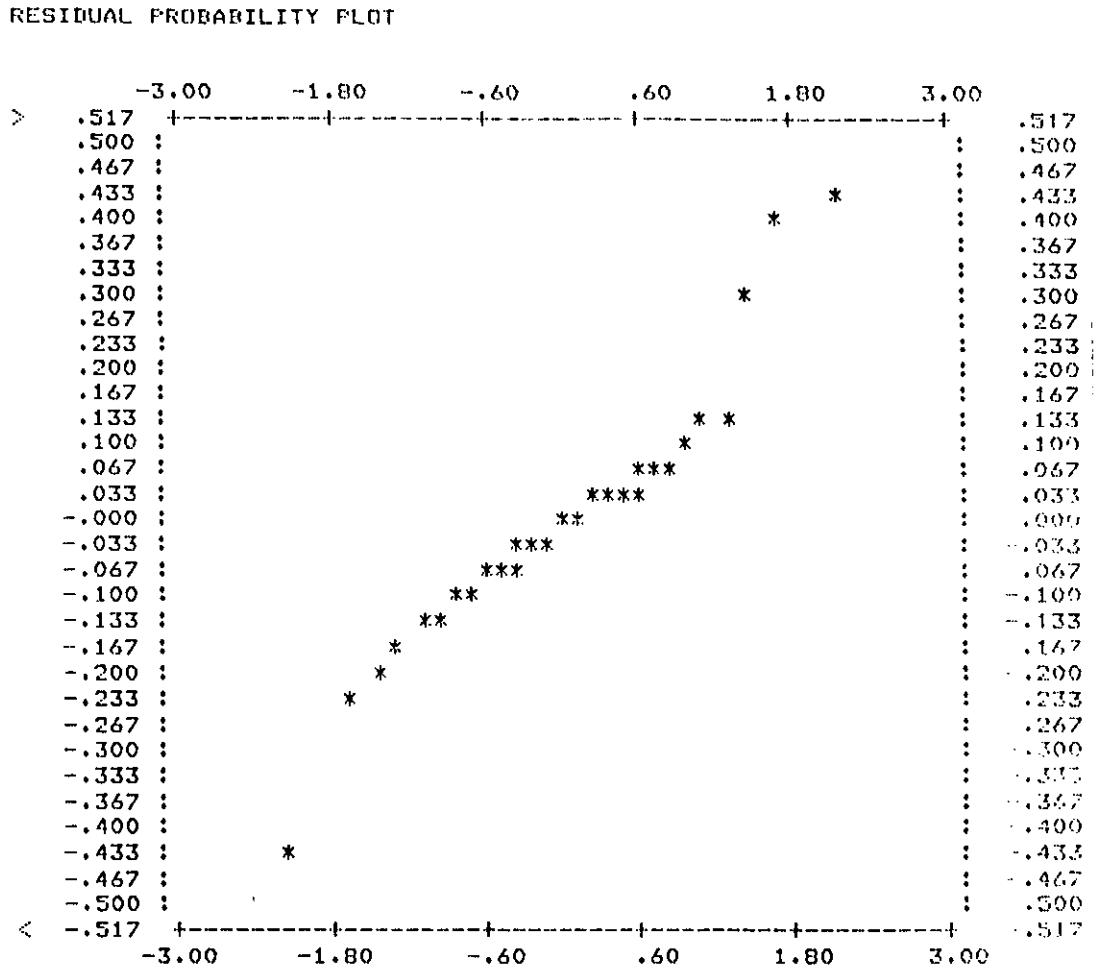


FIGURE 61. Residual probability plot for the regression of the arsenic content of pasture in late April against 11 predictor variables (36 observations).

well be due to analytical error. Accordingly, the ridge regression model may be re-run with the data relating to these four outliers excluded from the statistical analysis. Reference to the 'new' table of ridge constants (Table 42(a)) show that the optimum value of k can now be chosen as 0.15. At this value, four predictor variables - AS, CU, MN and FEAP - have standardised estimator values greater than 0.15. This latter figure is considered by Howarth to be a threshold value indicating which predictors are particularly important in accounting for the variation observed in the dependent variable. This is further indicated by the standard error of the estimated coefficients representing these four predictor variables which are less than the coefficient values themselves (Table 42b). Accordingly, the ridge regression technique can be repeated yet again using only the four predictors quoted above as the independent variables. Ridge regression is thus a statistical technique wherein a number of models can be tested by varying the predictor variables and eliminating any outliers. For the problem posed above, the most statistically sound solution was found by running the ridge regression technique with the four predictor variables indicated previously. The elimination of six outliers further improved the multiple correlation R^2 value from 67.3% to 86.8% and the F Ratio from 15.98 to 41.12. Accepting the run which eliminated the six outliers as producing a more statistically sound result, the regression equation which accounts for 86.8% of the variation in the As content of pasture herbage during April is expressed as:

herbage As content (April) = 0.054 + 0.0011 soil As content + 0.0011 soil Cu content + 0.022 herbage Fe (April) content - 0.0084 soil Mn content.

36 SAMPLES INPUT
DATA MATRIX : 32 OBSERVATIONS 12 VARIABLES

a)

STANDARDIZED ESTIMATORS

	RIDGE CONSTANT						
	0.00	.02	.04	.06	.08	.10	.15
AS	.6758	.6581	.6373	.6176	.5993	.5822	.5445
CU	.6931	.5388	.4787	.4448	.4219	.4047	.3743
CUAP	.0466	.0710	.0785	.0816	.0830	.0837	.0842
ZN	-.4258	-.1694	-.0757	-.0276	.0013	.0204	.0476
ZNAP	.1032	.0780	.0655	.0570	.0505	.0453	.0355
FE	.1239	.0333	.0057	-.0053	-.0098	-.0113	-.0096
FEAP	.2712	.2884	.2912	.2901	.2873	.2838	.2737
MN	-.3523	-.3601	-.3526	-.3415	-.3294	-.3174	-.2894
MNAP	.2302	.2048	.1896	.1779	.1681	.1595	.1416
PH	.3098	.2339	.1965	.1711	.1515	.1355	.1050
OM	.0071	.0079	.0080	.0079	.0077	.0073	.0062
AVERAGE VIF	12.44	7.28	5.44	4.45	3.82	3.38	2.67

STANDARDIZED ESTIMATORS

	RIDGE CONSTANT						
	.20	.30	.40	.50	.60	.80	1.00
AS	.5124	.4604	.4198	.3869	.3596	.3166	.2841
CU	.3527	.3213	.2978	.2789	.2630	.2374	.2174
CUAP	.0842	.0837	.0831	.0823	.0814	.0794	.0771
ZN	.0615	.0743	.0794	.0815	.0821	.0815	.0795
ZNAP	.0285	.0196	.0142	.0107	.0084	.0056	.0042
FE	-.0053	.0039	.0118	.0181	.0231	.0302	.0347
FEAP	.2634	.2439	.2267	.2117	.1985	.1766	.1591
MN	-.2650	-.2251	-.1942	-.1696	-.1496	-.1191	-.0969
MNAP	.1273	.1053	.0891	.0766	.0666	.0518	.0413
PH	.0829	.0531	.0344	.0220	.0135	.0033	-.0019
OM	.0049	.0021	-.0005	-.0030	-.0051	-.0087	-.0114
AVERAGE VIF	2.24	1.72	1.42	1.22	1.07	.86	.73

Regression estimators:

b)

	Least squares (k=0)		Ridge (k=0.15)	
	Estimator	Standard error	Estimator	Standard error
Intercept	-1.0296		-.4046	
AS	.00161	.00073	.00130	.00033
CU	.00200	.00086	.00108	.00043
CUAP	.00281	.00727	.00508	.00635
ZN	-.00089	.00084	.00010	.00036
ZNAP	.00339	.00370	.00116	.00332
FE	.00018	.00047	-.00001	.00023
FEAP	.01887	.00726	.01904	.00656
MN	-.01608	.01521	-.01321	.00665
MNAP	.00073	.00043	.00045	.00037
PH	.12221	.05332	.04140	.04005
OM	.00146	.01974	.00127	.01890

TOTAL VARIANCE OF ESTIMATORS	Least squares	Ridge
	.0036	.0021

TABLE 42(a). Standardised estimator values derived by the regression of the arsenic content of pasture herbage during late April against 11 predictor variables (32 observations).

TABLE 42(b). Standard errors of the regression estimators.

The ridge regression equations derived for the remaining dependent variables are presented in Tables 43-47. Statistical data relating to the simple linear regression models discussed in Section IVa of this chapter are presented alongside the ridge regression data for the sake of comparison. The predictors outlined in the ridge regression equations indicate which variables are significantly associated with the uptake and assimilation of the five elements in the pasture herbage. However, for each element certain predictors are not included in all the three equations representing the period of the growing season studied. For example, soil Cu appears only as a predictor of herbage As content in April, and not in the June and August equations. Consequently, the relationship between soil Cu and its influence on the As concentrations in the pasture herbage of South-west England remains unclear. It is probable that if the ridge regression analysis is to give an accurate indication as to which variables determine the trace-element content of herbage, then as many independent variables as possible should be included in the predictive model. For example, it is likely that the inclusion of soil and herbage P as independent variables into the data set will alter the equations outlined in Table 43, since the influence of this element on As uptake is now widely acknowledged (Woolson et al., 1973).

Despite this problem, some associations disclosed by the ridge regression equations merit a closer investigation. The equations outlined in Table 43, for example, show a relationship between the herbage concentrations of Fe and As throughout the growing season studied. An association between these two elements was suggested earlier in this research from soil samples collected from podzolised profiles (Chapter 4), and the positive relationship

	Simple linear regression model	Ridge Regression Model
(a) in April		
Regression eqn.	herbage As content = 0.117+0.002 soil As content	herbage As content = 0.054+0.0011 soil As content + 0.0011 soil Cu content + 0.022 herbage Fe (April) content - 0.0084 soil Mn content
R^2	50.1%	86.8%
F Ratio	-	41.12*
Value of K	-	0.2
n	36	30
(b) in June		
Regression eqn.	herbage As content = 0.07+0.002 soil As content	herbage As content = -0.072+0.0011 soil As content + 0.1 herbage As (April) content + 0.0019 herbage Fe (June) content - 0.0059 soil Mn content
R^2	56.7%	84.3%
F Ratio	-	38.86**
Value of K	-	0.15
n	35	34
(c) in August		
Regression eqn.	herbage As content = 0.19+0.002 soil As content	herbage As content = - 0.1691+0.0005 soil As content +0.3 herbage As (June) content + 0.0007 soil Fe content + 0.0009 herbage Fe (August) content
R^2	38.5	97.03%
F Ratio	-	195.69***
Value of K	-	0.2
n	33	29

* Critical $F_{.05} = 2.76$
** Critical $F_{.05} = 2.70$
*** Critical $F_{.05} = 2.78$

TABLE 43. Predictive equations for the content of arsenic in pasture herbage.

	Simple Linear Regression Model	Ridge Regression Model
(a) in April		
Regression eqn.	herbage Cu content = 12.1 + 0.02 soil Cu content	herbage Cu content = 8.6439 + 0.0066 soil As content + 0.0086 soil Fe content + 0.21 herbage Fe (April) content
R^2	20.6%	67%
F Ratio	-	19.6309*
Value of K	-	0.4
n	36	33
(b) in June		
Regression eqn.	herbage Cu content = 8.08 + 0.01 soil Cu content	herbage Cu content = 7.5267 + 0.0030 soil As content + 0.0073 soil Cu content + 0.096 herbage Zn (June) content - 0.0069 herbage Fe (June) content + 0.0054 herbage Mn (June) content - 0.22 organic matter content
R^2	21.9%	88.75%
F Ratio	-	28.9322**
Value of K	-	0.15
n	35	29
(c) in August		
Regression eqn.	herbage Cu content = 10.8 + 0.14 soil Cu content	herbage Cu content = 5.0236 + 0.14 herbage Cu (April) content + 0.46 herbage Cu (June) content + 0.19 Zn herbage (August) content + 0.25 herbage Fe (April) content
R^2	10.5%	83.35%
F Ratio	-	33.7982***
Value of K	-	0.0
n	33	32

* Critical $F_{.05}$ = 2.93
** Critical $F_{.05}$ = 2.55
*** Critical $F_{.05}^{.05}$ = 2.73

TABLE 44. Predictive equations for the content of copper in pasture herbage.

	Simple Linear Regression Model	Ridge Regression Model
(a) in April		
Regression eqn.	herbage Fe content = 643 + 0.0034 soil Fe content	herbage Fe content = - 19.45 - 0.0109 soil As content + 4.2153 herbage As (April) content + 0.4030 herbage Cu (April) content - 0.0075 soil Zn content
R^2	2.3%	75.1%
F Ratio	-	19.6319*
Value of K	-	0.15
n	36	31
(b) in June		
Regression eqn.	herbage Fe content = 79.3 + 0.001 soil Fe content	herbage Fe content = 2.4752 + 51.529 herbage As (June) content + 2.1115 herbage Zn (June) content + 4.4507 herbage Fe (April) content - 0.1009 herbage Mn (April) content
R^2	6.3%	68.2%
F Ratio	-	13.9623**
Value of K	-	0.0
n	35	31
(c) in August		
Regression eqn.	herbage Fe content = 129 + 0.003 soil Fe content	herbage Fe content = 181.4548 - 0.6708 soil As content + 279.53 herbage As (August) content + 9.1679 herbage Fe (April) content + 0.5842 herbage Fe (June) content + 3.492 soil Mn content - 13.015 organic matter content
R^2	8%	87.14%
F Ratio	-	32.7426***
Value of K	-	0.15
n	33	36

* Critical $F_{.05}$ = 2.74
** Critical $F_{.05}$ = 2.74
*** Critical $F_{.05}$ = 2.43

TABLE 45. Predictive equations for the content of iron in pasture herbage.

	Simple Linear Regression Model	Ridge Regression Model
(a) in April		
Regression eqn.	herbage Mn content=212- 0.07 soil Mn content	herbage Mn content = 87.7116 + 4.9233 herbage Zn (April) content - 0.2181 soil Fe content - 14.159 soil pH
R^2	23.6%	78.84%
F Ratio	-	34.7732*
Value of K	-	0.0
n	36	32
(b) in June		
Regression eqn.	herbage Mn content = 191 - 0.07 soil Mn content	herbage Mn content = 142.4018 + 5.9719 herbage Cu (June) content - 0.1387 soil Fe content + 0.4097 herbage Mn (April) content - 13.67 soil pH
R^2	25.6%	81.58%
F Ratio	-	33.2137**
Value of K	-	0.15
n	35	35
(c) in August		
Regression eqn.	herbage Mn content = 185 - 0.49 soil Mn content	herbage Mn content = 121.4438 + 1.1940 herbage Zn (August) content + 0.3968 herbage Mn (June) content - 13.399 soil pH
R^2	20.8%	67.37%
F Ratio	-	19.9592***
Value of K	-	0.02
n	33	33

* Critical $F_{.05}$ = 2.95
** Critical $F_{.05}$ = 2.69
*** Critical $F_{.05}$ = 2.93

TABLE 46. Predictive equations for the content of manganese in pasture herbage.

	Simple Linear Regression Model	Ridge Regression Model
(a) in April		
Regression eqn.	herbage Zn content = 48.8 - 0.009 soil Zn content	herbage Zn content = 42.1046 - 0.0098 soil As content + 0.61 herbage Cu (April) content + 0.24 soil Mn content + 0.035 herbage Mn (April) content - 1.7 soil pH
R^2	2.1%	61.21%
F Ratio	-	8.8356*
Value of K	-	0.1
n	36	34
(b) in June		
Regression eqn.	herbage Zn content = 33.8 + 0.016 soil Zn content	herbage Zn content = 0.4046 + 0.026 soil Cu content - 0.9448 herbage Cu (April) content + 1.3185 herbage Cu (June) content + 0.5803 herbage Zn (April) content + 0.3588 soil Mn content + 0.0189 herbage Mn (June) content
R^2	3.3%	85.79%
F Ratio	-	25.1561**
Value of K	-	0.15
n	35	32
(c) in August		
Regression eqn.	herbage Zn content = 38.9 + 0.016 soil Zn content	herbage Zn content = 34.1461 + 1.3782 herbage Cu (August) content + 0.2118 herbage Zn (June) content - 0.2149 herbage Fe (April) content + 0.0101 herbage Fe (August) content - 3.3228 soil pH
R^2	3.8%	81.93%
F Ratio	-	23.5817***
Value of K	-	0.15
n	33	32

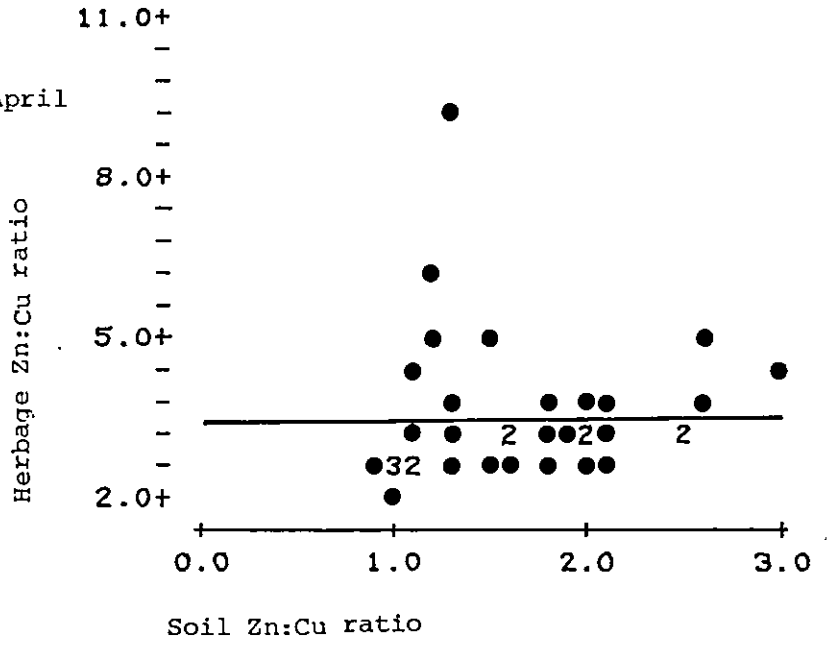
* Critical $F_{.05}$ = 2.56
** Critical $F_{.05}$ = 2.49
*** Critical $F_{.05}$ = 2.59

TABLE 47. Predictive equations for the content of zinc in pasture herbage.

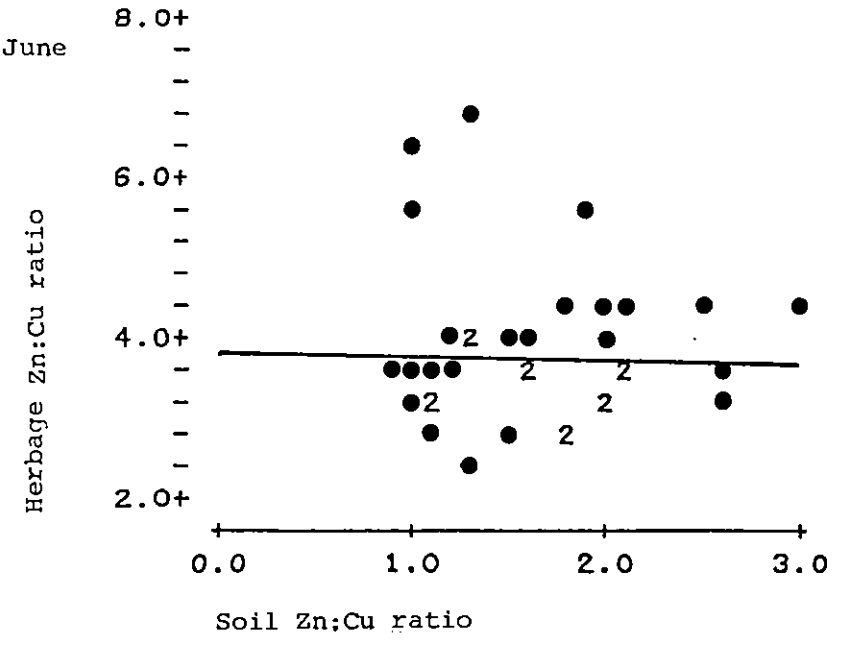
observed from the three equations of Table 43 may suggest a continued close relationship between the two elements in plant material. Similarly, herbage As concentrations appear as strong predictors of herbage Fe, although soil As during April and August is inversely related to this dependent variable (Table 45). The precise nature of the relationship appertaining to these two elements at the soil-plant interface remains, therefore, uncertain.

Soil Mn has a negative influence on As uptake which may indicate an antagonistic relationship between the two variables. In contrast, soil Mn is positively related to the Zn content of herbage (Table 47). A positive relationship between the Zn and Cu content of pasture herbage is also indicated by the ridge equations outlined in Tables 44 and 47. This latter relationship is particularly interesting since the Zn:Cu ratios of herbage in soil contaminated areas has been considered as a possible cause of Cu deficiency in cattle (Iain Thornton, personal communication). This theory is based on the assumption that excess Zn concentrations within the soil will lead to an increased uptake of Zn in pasture herbage at the expense of Cu. However, the ridge regression equations do not readily support this theory, and Zn:Cu ratios in the herbage samples analysed in this survey are not significantly correlated with the differing Zn:Cu ratios of the 36 soil plots studied (Figures 62a-c). This evidence suggests that Zn does not seriously suppress the Cu content of pasture herbage in the study area. It is of interest to note that the Hayle/Camborne-Redruth area is a region associated with a low incidence of bovine copper deficiency (Leech et al., 1982).

a) late April



b) late June



c) late August

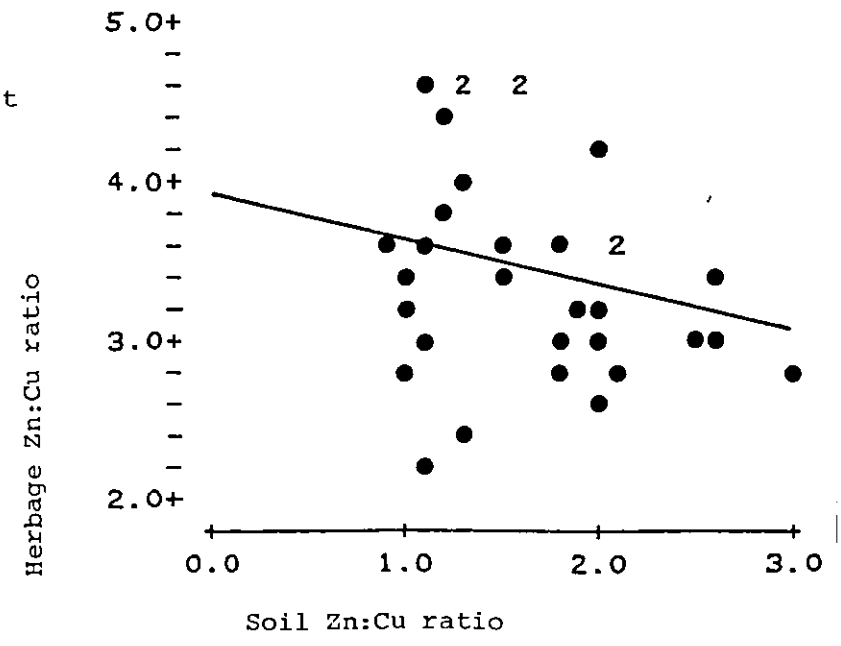


FIGURE 62a-c. The relationship between Zn:Cu ratios in the soil and late April, late June and late August pasture herbage samples.

From the ridge regression equations presented in Tables 46 and 47, soil pH is observed as an important predictor influencing the Mn and Zn concentrations of the pasture herbage. Inverse relationships with pH are shown for both elements, suggesting that under the soil pH conditions prevailing in South-west England, both Mn and Zn uptake is restricted on the sites with an elevated pH. Such sites tend to be developed on the slates due to agricultural liming (Table 12). Thus uptake of both Zn and Mn is likely to be enhanced on the more acidic granite soils. This may explain the relatively high concentrations of Mn associated with pasture herbage at the granite sites which are themselves low in soil Mn (Figure 59(d)). For the remaining three elements studied in this research, soil pH appears to be a less important variable in influencing the trace-element content of pasture herbage. Similarly, soil organic matter content has an insignificant role in determining the trace-element content of pasture, since this variable is included in only two of the fifteen ridge equations presented in Tables 43-47. Organic matter has previously been shown to be an important soil constituent in adsorbing Cu (Beckwith, 1955; McLaren and Crawford, 1973a, 1973b), which may thus restrict its uptake by plants. However, such an inverse relationship is not disclosed by the April and August ridge regression equations for this element.

The ridge equations further show that the trace-element status of pasture early in the growing season can be useful in predicting the content later in the year. For example, the As content of herbage in April appears as a predictor in determining the content of the element in June, whilst the June concentration is an important predictor of the As pasture herbage content in August. This

characteristic applies for all the five trace-elements studied. Furthermore, the April content may also be important as a predictor of the August concentrations (as observed for the elements Cu and Fe), although more commonly the content of herbage during August appears to be more directly related to the previous sampling period in June. This may be due to the seasonal fluctuations in the trace-element content of the pasture as noted earlier in this chapter.

c) The relative accumulation of As, Cu, Fe, Mn and Zn by pasture herbage

It is of some interest that the ridge regression equations presented in the previous section indicate that the content of Cu, Fe, Mn and Zn in pasture herbage do not appear to be directly related to the corresponding soil concentrations. Only soil As is a consistently important predictor in accounting for the concentrations of this element found in the herbage. Further interpretation of the data recorded from the 12 sites does show, however, that the content of all five trace-elements in the pasture herbage is related to the soil concentrations. For the elements Cu, Mn and Zn, diagrams showing the relative accumulation (i.e. amount in plant ÷ amount in soil) of each element plotted against the soil concentrations give an approximation to a hyperbolic curve; for As and Fe this hyperbolic tendency is also apparent despite a greater variation of the plotted points. This feature of relative accumulation is illustrated in Figures 63(a-e) which present the data relating to the concentrations of the five trace-elements recorded from the late April herbage samples. Similar plots were computed however, from the data obtained from the two remaining sampling periods.

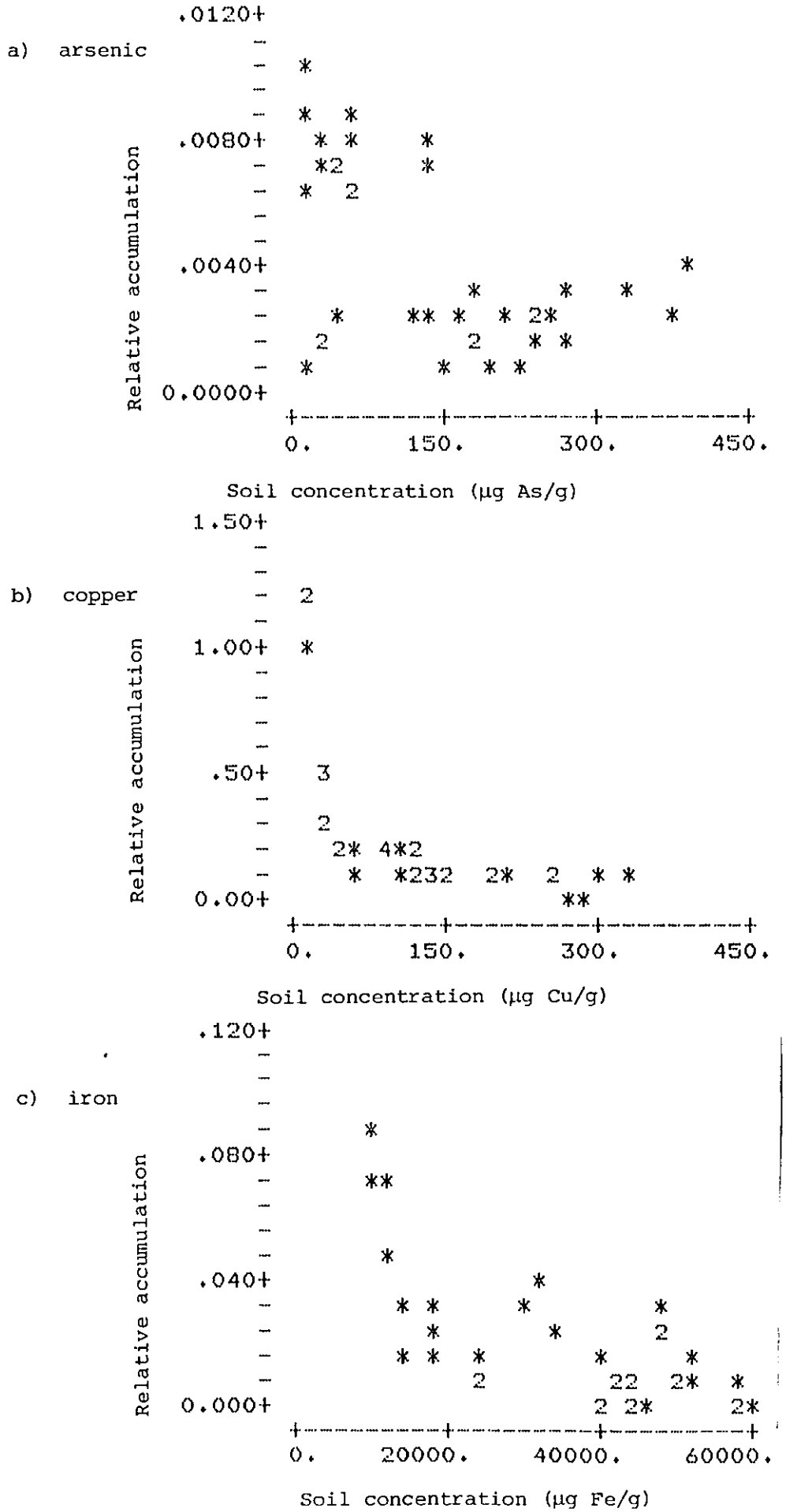


FIGURE 63a-c. The relative accumulation of arsenic, copper and iron by pasture during late April.

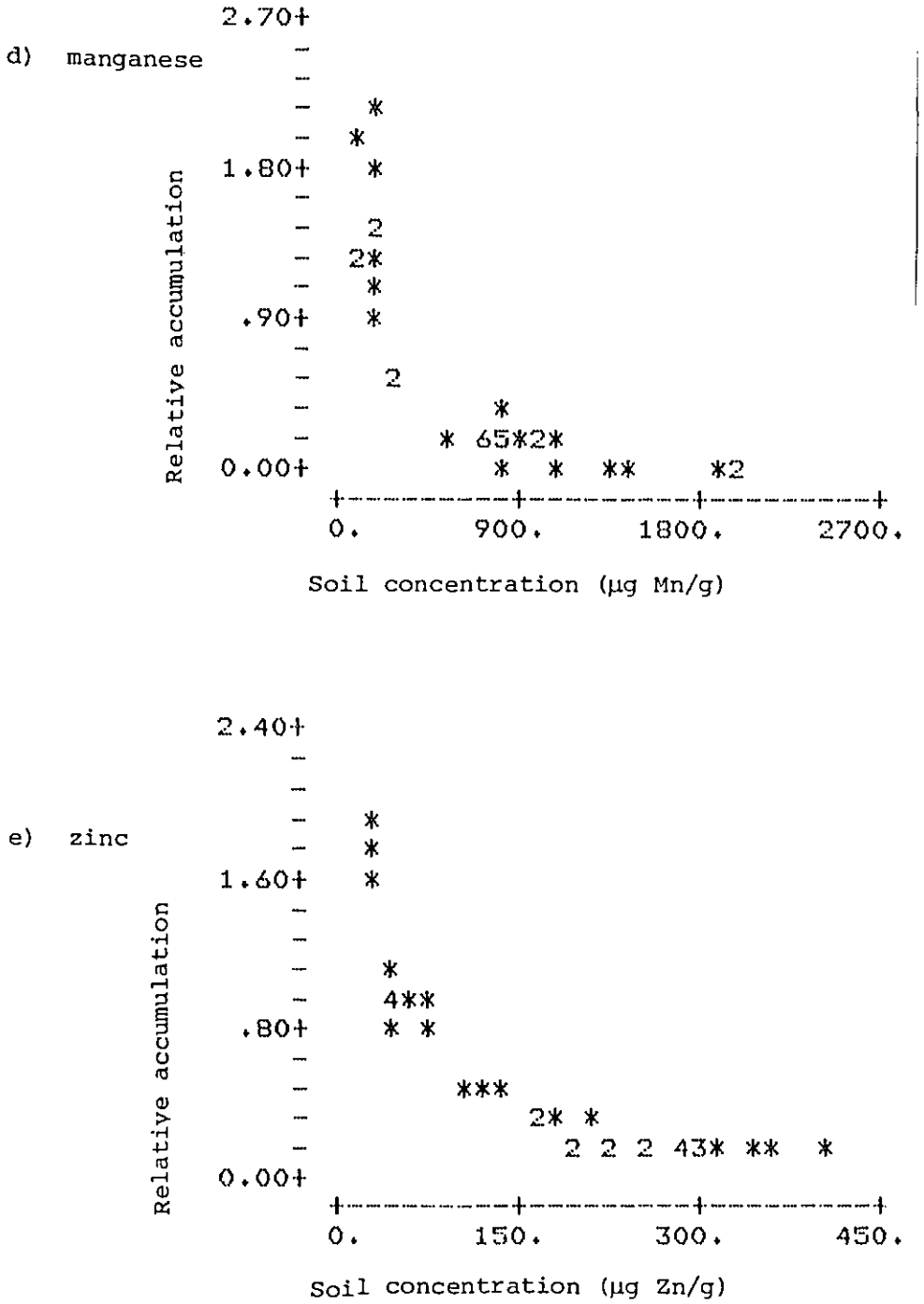


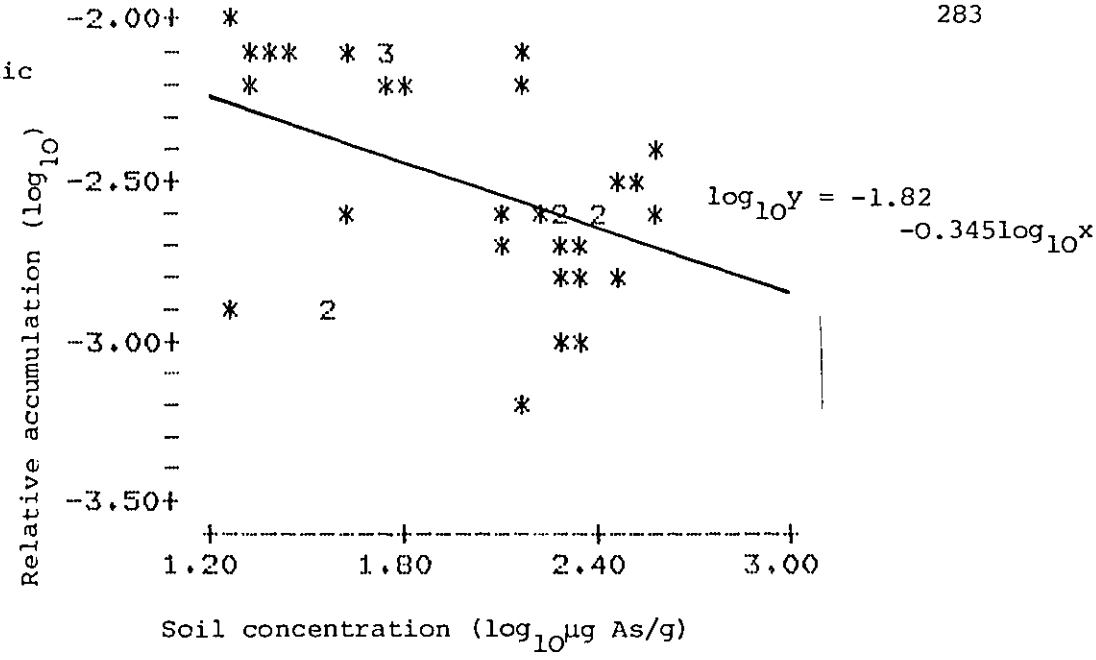
FIGURE 63d-e. The relative accumulation of manganese and zinc during late April.

Logarithmic transformation of the data co-ordinates transforms the hyperbolic curves into linear lines with a significant inverse trend (e.g. Figures 64(a-e)). The correlation coefficients for the log-transformed Cu, Mn and Zn data are highly significant, and correlation R^2 values range from 88% to 97% (Table 48). The correlation coefficients for Fe and As are also significant although the correlation R^2 values are lower than those presented above (maximum = 50%). In particular, the inverse trend observed for As is not as highly significant as calculated from the relationships appertaining to the elements Cu, Mn, Zn and Fe (Table 48). Arsenic uptake cannot, therefore, be predicted accurately from these log-transformed relative accumulation plots compared to the remaining four trace-elements.

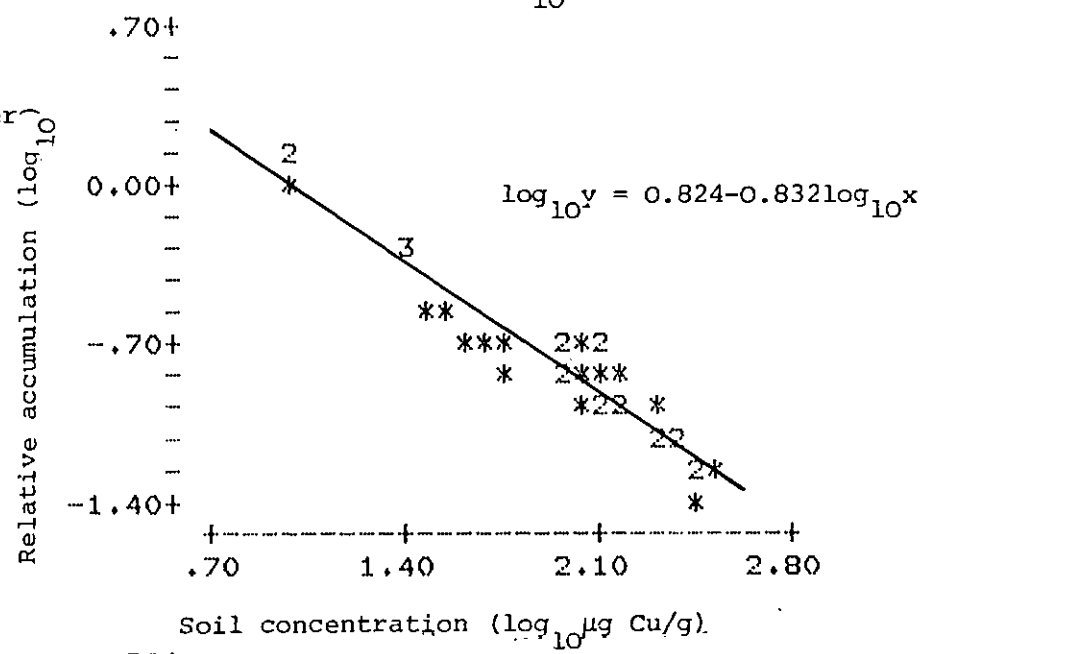
(V) DISCUSSION AND CONCLUSIONS RELATING TO THE TRACE-ELEMENT UPTAKE OF As, Cu, Fe, Mn AND Zn BY PASTURE HERBAGE

Diagrams showing the relationship between the As, Cu, Fe, Mn and Zn content of pasture herbage and the soil concentrations, indicate that the plants have a differing response in uptake and translocation characteristics depending upon the element concerned. Data from the 36 soil plots studied in South-west England shows that the Cu and As content of pasture herbage increases slightly with increasing soil content, Mn pasture concentrations decrease, whilst Fe and Zn pasture herbage concentrations show no apparent relationship with soil Fe and Zn content. These relationships between soil and herbage concentrations were observed during all the three sampling periods studied, although the actual trace-element content of the pasture was found to vary according to the season of sampling. Generally, the minimum concentrations of all five trace-

a) arsenic



b) copper



c) iron

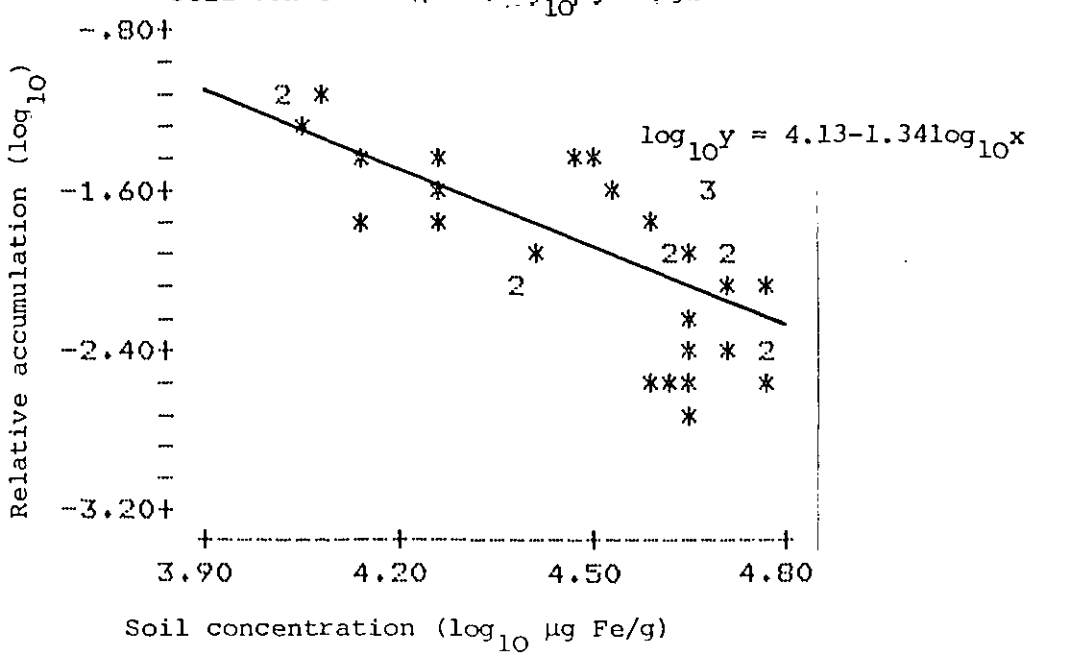


FIGURE 64a-c. Logarithmic transformation of the soil and relative accumulation arsenic, copper and iron data observed during

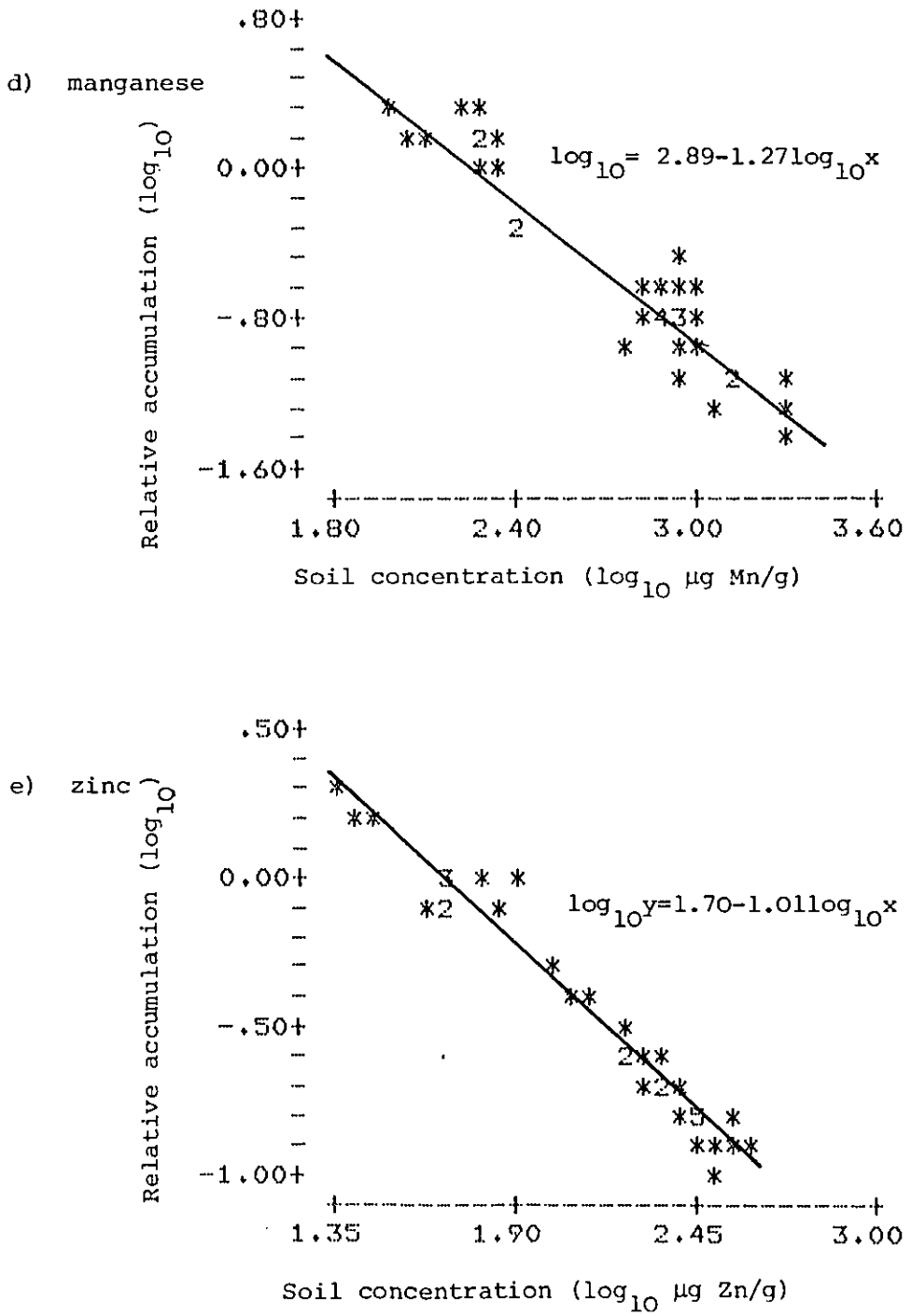


FIGURE 64d-e. Logarithmic transformation of the soil and relative accumulation manganese and zinc data observed during late April.

mpling period		Arsenic	Copper	Iron	Manganese	Zinc
te April:	regression equation	$\log_{10}y=-1.82-0.345\log_{10}x$	$\log_{10}y=0.824-0.832\log_{10}x$	$\log_{10}y=4.13-1.34\log_{10}x$	$\log_{10}y=2.89-1.27\log_{10}x$	$\log_{10}y=1.70-1.01\log_{10}x$
	correlation coefficient (r)	-0.443**	-0.965***	-0.708***	-0.949***	-0.986***
	correlation coefficient (R^2)	19.6%	93.1%	50.1%	90.0%	97.2%
	n = 36					
te June:	regression equation	$\log_{10}y=-2.08-0.275\log_{10}x$	$\log_{10}y=0.83-0.925\log_{10}x$	$\log_{10}y=1.24-0.833\log_{10}x$	$\log_{10}y=3.04-1.35\log_{10}x$	$\log_{10}y=1.44-0.948\log_{10}x$
	correlation coefficient (r)	-0.376*	-0.962***	-0.638***	-0.938***	-0.953***
	correlation coefficient (R^2)	14.1%	92.5%	40.7%	88%	90.8%
	n = 35					
te August:	regression equation	$\log_{10}y=-1.96-0.239\log_{10}x$	$\log_{10}y=0.939-0.926\log_{10}x$	$\log_{10}y=0.448-0.59\log_{10}x$	$\log_{10}y=2.63-1.17\log_{10}x$	$\log_{10}y=1.49-0.944\log_{10}x$
	correlation coefficient (r)	-0.351*	-0.965***	-0.501**	-0.957***	-0.970***
	correlation coefficient (R^2)	12.4%	93.1%	26%	91.6%	94%
	n = 33					

*** = significant at p = 0.001 (0.1%); ** = significant at p = 0.01 (1.0%); * = significant at p = 0.05 (5%)

TABLE 48. Statistical data relating to the logarithmic relationship observed between the pasture herbage relative accumulation ratios and the soil As, Cu, Fe, Mn and Zn concentrations.

elements were found to occur in the herbage sampled during late June. This observation agrees with those presented by Thoresby and Thornton (1979).

The relationship between soil and pasture herbage trace-element concentrations has been further studied by the use of ridge regression. This statistical technique outlines those variables which are particularly important in accounting for the variation observed in the trace-element content of the pasture herbage. A number of associations acounting for the trace-element content of the pasture herbage has been revealed in this study, although it is considered likely that further research using more independent or predictor variables in the statistical technique will further the observations made in this thesis.

The ridge regression equations reveal that soil organic matter content plays an insignificant role in determining the As, Cu, Fe, Mn or Zn status of pasture herbage in South-west England. In comparison, the Mn and Zn content of pasture herbage is shown by the ridge regression equations to be inversely related to soil pH. This may thus account for the increased uptake of Mn by herbage on the acidic granite soils which are themselves comparitively low in this element. The ridge equations further indicate that the presence of associated ions within the soil may also influence the trace-element status of pasture. For example, soil Mn may have an antagonistic influence on As accumulation in the pasture herbage. This research has further indicated, however, that excess Zn concentrations in the soil do not significantly lower the Cu concentrations of the pasture herbage.

Whilst the trace-element content of pasture herbage is dependent upon variables including those mentioned above, it is clear from the research described in this thesis that the plants themselves further control the uptake and translocation of As, Cu, Fe, Mn and Zn. The hyperbolic curves produced by plotting the relative accumulation of the five trace-elements against their respective soil concentrations show that pasture herbage excludes, to a certain extent, the uptake of all five elements on soils with an elevated As, Cu, Fe, Mn and Zn content. Research undertaken in New Zealand on the uptake of Cu and Zn by a number of plant species has yielded similar results. (Timperley et al., 1970). Since Cu and Zn are known to be essential for plant nutrition, these authors considered that when the concentration of these elements in soils are below the physiological requirement level, the plants will readily accumulate both elements until the required concentration is achieved. At soil concentrations higher than the required level, the plants will partially exclude the element concerned. This theory must now be considered with care, however, since the relative accumulation of Pb (a non-essential element) by pasture herbage has since been found to follow a hyperbolic curve similar to that observed for Cu and Zn (AGRG, unpublished data). The decrease in relative accumulation of the five elements studied in this research is therefore not necessarily indicative of essentiallity. Indeed, the nutritional importance of As for plant metabolism still remains unclear, although a number of researchers have found that plant growth can be stimulated by its presence (Woolson et al., 1971a; Porter, 1976).. This may be due, however, to arsenate which displaces phsophate from the soil with a resultant increase in phosphate availability (Jacobs et al., 1970a).

Logarithmic transformation of the relative accumulation and soil co-ordinates produces linear inverse plots for all the five elements studied. The Pearson correlation r and R^2 coefficients show that pasture herbage Cu, Mn, Fe and Zn concentrations can be predicted very accurately from these logarithmic plots. The correlation R^2 values for As, however, are low (range 12.4% - 19.6%) and the Pearson correlation (r) coefficients not as highly significant compared to the other four elements. Consequently, pasture As concentrations can be predicted more accurately from the simple linear regression equations calculated from the relationships observed between soil and herbage As (e.g. Figure 59a). The ridge equations can be used to predict the pasture concentrations of all five elements with a fairly good degree of accuracy as shown by the multiple correlation R^2 and F ratios presented in Tables 43-47. These equations only relate to the general pattern of trace-element accumulation, however, since any outliers were eliminated from the statistical analysis.

CHAPTER 7

TRACE-ELEMENT INTAKE BY CATTLE IN SOUTH-WEST ENGLAND

(I) INTRODUCTION

The intake of the trace-elements As, Cu, Fe, Mn and Zn by cattle was investigated at the same 12 sites which were used to determine the uptake of these elements by pasture herbage (Chapter 6). Surface soils (0-15 cm), comprising 20 sub-samples bulked from a 'W' traverse within each field grazed, were collected and analysed in order to determine the As and metal status of the complete field. In order to determine fully the trace-element intake of these five trace-elements by cattle, analytical data relating to the trace-element content of washed herbage is also required. In this study, such data was obtained by calculating the mean of the washed herbage concentrations derived from the three plots of each site used in the pasture herbage uptake survey (Chapter 6).

Twenty bulked cow faecal samples were also taken from each site during the three sampling periods in late April, late June and late August. Factors governing the nutritional status of cattle are outlined in Chapter 1 of this thesis; one such factor, the involuntary ingestion of soil, may be important to the nutrition of cattle. In this study, the Ti content of faeces has been used as a stable marker of soil ingestion, since the element is usually present in relatively high concentrations in soils (several thousand μg/g) and in very small amounts in clean herbage (usually < 10 μg/g). Any Ti recorded in the faecal samples can thus be assumed to originate from a soil source. Soil ingestion has been calculated,

assuming a digestibility of 70% and a dietary intake of 13.6 kg/day, using the equation:

$$\% \text{ soil ingestion} = \frac{(1-Dh)Ti_f \times 100}{Ti_s - DhTi_f}$$

where Dh = digestibility of herbage

Ti_s = Ti content of soil

Ti_f = Ti content of faeces.

In order to differentiate between the 12 study locations, the soil As data was used to classify the fields into low, medium and high As sites. The threshold parameters used for this purpose are outlined in Table 24. Sites 1 to 5 are all comparitively low in soil As, 6 and 7 are moderate, and 9 to 12 high in As (Tables 49-60). High concentrations of As were also recorded initially at site 8; however, in June and August the cattle were moved to an adjacent field which differed appreciably in its soil trace-element content from the original site (Table 56). Since no washed herbage data is available from this site for the late June and August periods, many of the observations discussed in this section do not include the data from this latter field.

Correlation coefficients reveal that sites high in As are also usually elevated in Cu, Zn, Fe and Mn (Table 39). The reason for this is twofold; firstly, soils contaminated by As are also prone to be contaminated to a varying degree by the other elements. Secondly, with the exception of site 4, all the low As sites studied in this work are located on granite parent material. This parent material contributes less of all five trace-elements to the soil than the remaining sites developed on greenstone and slate (Chapter 5).

SITE: 1

Farm type: Low As Parent Material: Granite

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc. (µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	2.74			0.17	12	1.51	28	8.9	10.4	2.2	159	11.1	169	80	6.2
June	0.63	24	28	0.03	8.5	0.94	38	2.1	2.4	0.4	115	2.5	117	84	2.1
August	2.58			0.1	9.25	1.61	24	8.4	9.8	1.3	123	9.7	133	87	7.4
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	2.74			43	469	117	1744	21	6782	569	6204	590	12986	3.6	52
June	0.63	56	18200	27	61	113	1050	4.8	1559	365	824	370	2383	1.3	65
August	2.58			32	104	129	1825	20	6386	424	1378	444	7764	4.5	82
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	2.74				235		450		68		3108		3176		2.1
June	0.63		182		158		488		16		2135		2151		0.7
August	2.58				249		625		64		3299		3363		1.9

TABLE 49. The daily intake of arsenic, copper, iron, manganese and zinc at Site 1.

SITE: 2

Farm type: Low As Parent Material: Granite

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	3.35			0.13	11	2.08	36	8.7	5.5	1.7	145	10.4	150	84	3.7
June	3.91	19	12	0.15	9.0	1.77	46	10	6.4	2.0	118	12.0	124	83	5.2
August	3.51			0.16	13	2.56	34	9.1	5.7	2.1	171	11.2	177	81	3.2
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	3.35			46	871	140	2069	13	4920	605	11449	618	16369	2.1	30
June	3.91	29	10800	34	111	162	1456	15	5743	444	1451	459	7194	3.3	80
August	3.51			40	220	119	2775	14	5155	525	2887	539	8042	2.6	64
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	3.35				155		275		55		2037		2092		2.6
June	3.91		120		221		469		64		2888		2952		2.2
August	3.51				126		375		57		1653		1710		3.3

TABLE 50. The daily intake of arsenic, copper, iron, manganese and zinc at Site 2.

SITE: 3

Farm type: Low As Parent Material: Granite

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	5.37			0.06	9.7	2.08	25	28	26	0.8	125	29	151	97	17
June	1.22	39	36	0.06	8.0	1.06	40	6.5	6.0	0.8	107	7.3	113	89	5.3
August	3.58			0.10	9.5	1.6	46	19	18	1.3	125	20	143	95	13
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	5.37			43	259	90	2694	41	17528	553	3333	594	20861	6.9	84
June	1.22	56	24000	31	68	133	1237	9.3	3982	416	914	425	4896	2.2	81
August	3.58			39	134	109	2225	27	11685	511	1757	538	13442	5.0	87
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	5.37				154		325		190		1982		2172		8.7
June	1.22		260		125		450		43		1679		1722		2.5
August	3.58				158		425		127		2072		2199		5.8

TABLE 51. The daily intake of arsenic, copper, iron, manganese and zinc at Site 3.

SITE: 4

Farm type: Low As Parent Material: Greenstone

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	6.04			0.44	23	15	57	48	102	5.6	294	54	396	89	26
June	3.44	58	124	0.22	8.6	4.4	64	27	58	2.9	113	30	171	90	34
August	4.66			0.75	15	5.1	54	37	79	9.7	194	47	273	79	29
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	6.04			54	1027	135	6994	116	26286	690	13124	806	39410	14	67
June	3.44	141	32000	36	164	196	4000	66	14971	473	2154	539	17125	12	87
August	4.66			51	560	142	5750	89	20280	661	7261	750	27541	12	74
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	6.04				182		450		690		2326		3016		23
June	3.44		840		162		650		393		2127		2520		16
August	4.66				183		525		532		2373		2905		18

TABLE 52. The daily intake of arsenic, copper, iron, manganese and zinc at Site 4.

SITE: 5

Farm type: Low As Parent Material: Granite

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	17.93			0.34	9.7	3.15	39	122	154	3.8	108	126	262	97	59
June	0.56	50	63	0.34	11	1.84	31	3.8	4.8	4.6	149	8.4	154	45	3.1
August	3.18			0.08	10	2.29	32	22	27	1.1	132	23	159	96	17
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	17.93			62	412	102	2569	222	39503	692	4599	914	44102	24	90
June	0.56	91	16200	51	113	111	1125	6.9	1234	690	1528	697	2762	1.0	45
August	3.18			44	94	104	1750	39	7001	579	1238	618	8239	6.3	85
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	17.93				346		425		585		3862		4447		13
June	0.56		240		300		463		18		4057		4075		0.4
August	3.18				215		325		104		2831		2935		3.5

TABLE 53. The daily intake of arsenic, copper, iron, manganese and zinc at Site 5.

SITE: 6

Farm type: Moderate As

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	7.53			0.69	17	20	54	143	96	8.7	214	152	310	94	31
June	0.29	140	94	0.22	11	3.0	44	5.5	3.7	3.0	149	8.5	153	65	2.4
August	2.78			0.48	12	5.2	33	53	36	6.3	159	59	195	90	18
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	7.53			46	511	138	11500	179	44035	578	6426	757	50461	24	87
June	0.29	175	43000	37	90	105	1737	6.9	1696	502	1220	509	2916	1.4	58
August	2.78			34	290	89	3850	66	16257	450	3834	516	20091	13	81
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	7.53				130		500		696		1635		2331		30
June	0.29		680		92		338		27		1248		1275		2.1
August	2.78				97		350		257		1283		1540		17

TABLE 54. The daily intake of arsenic, copper, iron, manganese and zinc at Site 6.

SITE: 7

Farm type: Moderate As

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	5.68			0.34	15	16	62	122	96	4.4	192	126	288	97	33
June	1.33	158	124	0.71	7.75	8	38	29	22	9.5	104	38.5	126	75	17
August	3.34			1.01	13	12	45	72	56	13	171	85	227	85	25
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	5.68			44	528	153	9000	222	37697	564	6773	786	44470	28	85
June	1.33	287	48800	33	275	123	4737	52	8827	443	3690	495	12517	11	71
August	3.34			38	512	127	7250	130	22167	500	6731	630	28898	21	77
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	5.68				106		575		1020		1360		2380		43
June	1.33		1320		88		863		239		1181		1420		17
August	3.34				113		625		600		1485		2085		29

TABLE 55. The daily intake of arsenic, copper, iron, manganese and zinc at Site 7.

SITE: 8

Farm type: High/low As* *Daily intake cannot be calculated at this site due to the lack of washed herbage data

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	4.35	320	236	0.5	13	8.9	62	189	140	6.5	169	196	309	96	45
June	2.25	49	21	-	-	46	33	15	6.4	-	-	-	-	-	-
August	2.46					4.3	28	16	7.0						
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	4.35	285	46800	38	101	182	5494	169	27687	494	1314	663	29001	25	95
June	2.25	93	19600	-	-	95	2412	28	5998	-	-	-	-	-	-
August	2.46					87	3025	31	6557						
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	4.35		1000		90		500		592		1171		1763		34
June	2.25		224		-		400		69		-		-		-
August	2.46						325		75						

TABLE 56. The daily intake of arsenic, copper, iron, manganese and zinc at Site 8.

SITE: 9

Farm type: High As

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	2.44			1.1	18	14	61	84	90	15	239	99	329	85	27
June	1.36	254	272	0.77	12	7.8	63	47	50	10	161	57	211	82	24
August	1.36			0.81	13	9.8	57	47	50	11	174	58	224	81	22
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	2.44			50	1224	107	6994	84	16194	663	16240	747	32434	11	50
June	1.36	253	48800	47	174	133	3112	47	9026	631	2334	678	11360	6.9	79
August	1.36			39	261	110	4500	47	9026	523	3501	570	12527	8.2	72
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	2.44				551		375		252		7311		7563		3.3
June	1.36		760		138		400		141		1851		1992		7.1
August	1.36				127		350		141		1704		1845		7.6

TABLE 57. The daily intake of arsenic, copper, iron, manganese and zinc at Site 9.

SITE: 10

Farm type: High As

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	7.24			0.54	16	20	64	188	122	6.8	202	195	324	96	38
June	0.18	191	124	0.51	9.6	6.9	55	4.7	3.0	6.9	130	11.6	133	41	2.3
August	3.88			0.9	11	10	40	101	65	12	144	113	209	89	31
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	7.24			46	459	137	9744	218	49232	580	5790	798	55022	27	89
June	0.18	221	50000	31	102	116	1800	5.4	1224	421	1385	426	2609	1.3	47
August	3.88			35	237	92	6000	117	26384	458	3098	575	29482	20	89
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	7.24				139		400		1448		1754		3202		45
June	0.18		680		101		375		17		1371		1388		1.2
August	3.88				147		350		359		1922		2281		16

TABLE 58. The daily intake of arsenic, copper, iron, manganese and zinc at Site 10.

SITE: 11

Farm type: High As

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc. (µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	1.47			0.26	16	6.8	66	44	64	3.5	214	48	278	92	23
June	1.42	222	319	0.22	13	9.5	59	43	62	2.9	174	46	236	93	26
August	1.64			0.94	9.5	8.2	55	50	71	13	127	63	198	79	36
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	1.47			50	197	205	4475	73	11735	670	2640	743	14375	10	82
June	1.42	365	58700	47	120	138	4112	70	11336	630	1609	700	12945	10	88
August	1.64			44	353	129	2875	81	13092	589	4722	670	17814	12	73
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	1.47				101		400		330		1353		1683		20
June	1.42		1650		95		313		319		1274		1593		20
August	1.64				114		300		368		1525		1893		19

TABLE 59. The daily intake of arsenic, copper, iron, manganese and zinc at Site 11.

SITE: 12

Farm type: High As

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M)		Faeces conc. (µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage (mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	3.58			0.49	15	12	59	102	63	6.4	197	108	260	94	24
June	1.26	210	130	0.26	15	8	38	36	22	3.5	201	40	223	90	10
August	3.20			0.50	13	11	73	91	57	6.6	171	98	228	93	25
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	3.58			45	200	172	5182	145	21715	590	2623	735	24338	20	89
June	1.26	297	44600	25	42	129	3175	51	7643	336	564	387	8207	13	93
August	3.20			40	132	209	4125	129	19410	527	1738	656	21148	20	92
			Mn		Mn		Mn		Mn		Mn		Mn		Mn
April	3.58				108		325		225		1416		1641		14
June	1.26		463		47		600		79		631		710		11
August	3.20				87		400		201		1145		1346		15

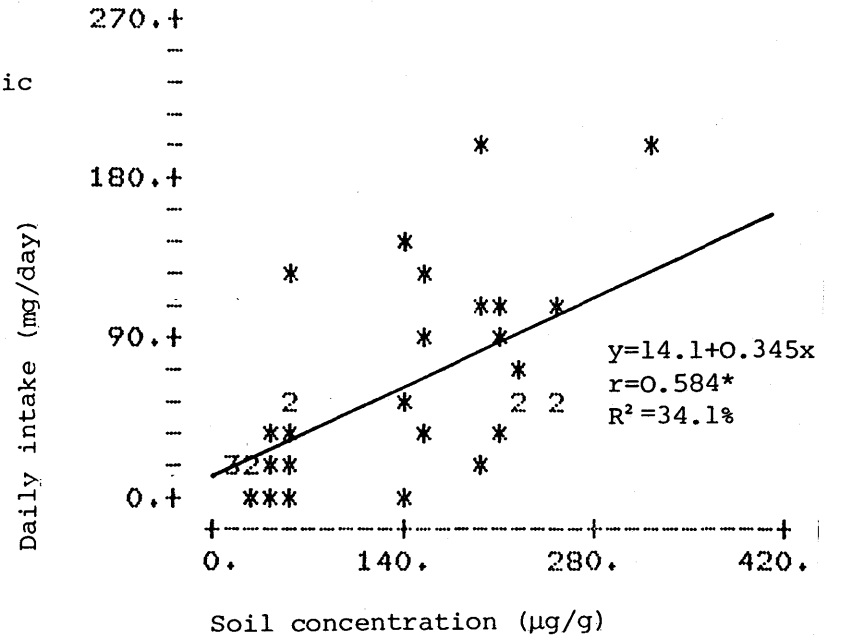
TABLE 60. The daily intake of arsenic, copper, iron, manganese and zinc at Site 12.

(II) THE TOTAL DAILY INTAKE OF TRACE-ELEMENTS BY CATTLE GRAZING WITHIN THE HAYLE/CAMBORNE-REDRUTH STUDY AREA

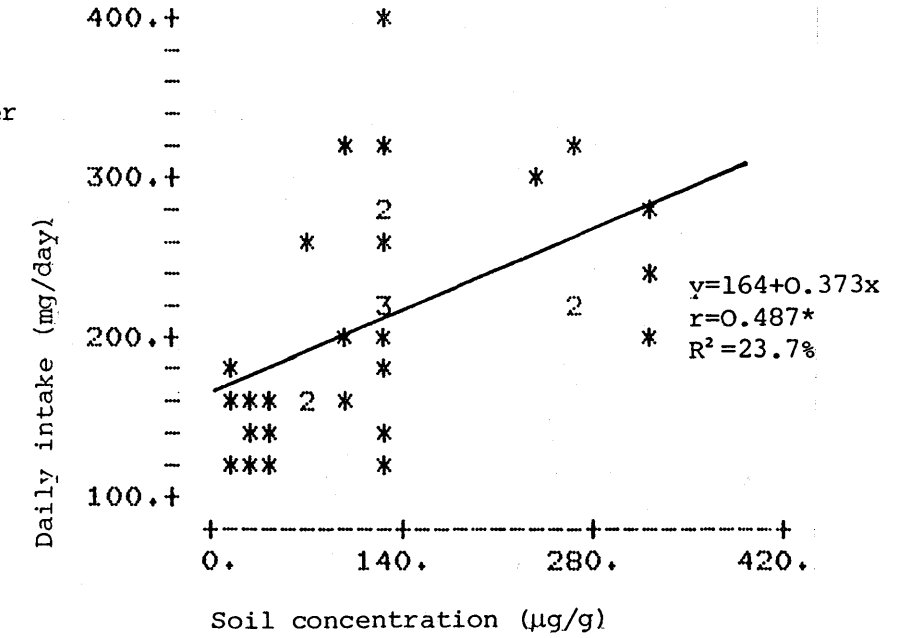
The total daily intake of the five elements can be calculated by assuming a dietary intake of 13.6 kg/day, and by calculating the rate of soil ingestion together with the soil and washed herbage trace-element concentrations (Tables 49-60). Figures 65a-e incorporate all the total daily intake values recorded for each element during the three periods of sampling. For the trace-elements As and Cu, the total daily intake is positively correlated with the soil concentrations of the fields studied; no significant trend is observed, however, for the elements Fe, Mn and Zn. The correlation R^2 values calculated from Figures 65a-e range from 3.7% for Mn to 34% for As, and indicate that much of the variation observed for the daily intake rates are not fully related to the soil concentrations of the 12 fields studied. This can be attributed to two factors:

i) The trace-element concentrations of the pasture herbage: research outlined in Chapter 6 indicates the trace-element variability of the pasture herbage in response to the soil concentration. For example, the correlation R^2 values calculated from Figures 59a-e range from 2.1% for Mn to 50.1% for As. The As and Cu content of the pasture herbage increases slightly but significantly with soil As and Cu concentrations. In comparison, Fe and Zn concentrations of the herbage do not reflect the soil content of these elements, whilst Mn concentrations in the pasture herbage decline with increasing soil Mn content, possibly due to the effects of soil pH. In addition to these observations, the trace-element concentrations of the herbage varies according to the season. Research outlined in Chapter 6 indicates that the trace-element content of the pasture herbage is generally lower in late June than in late April or late August.

a) arsenic



b) copper



c) iron

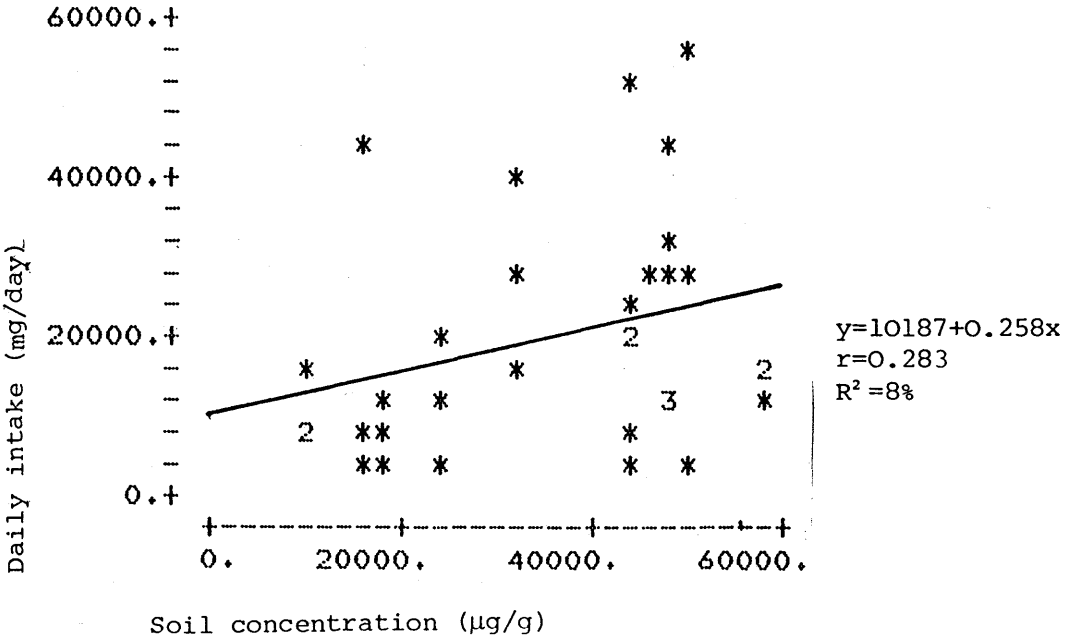
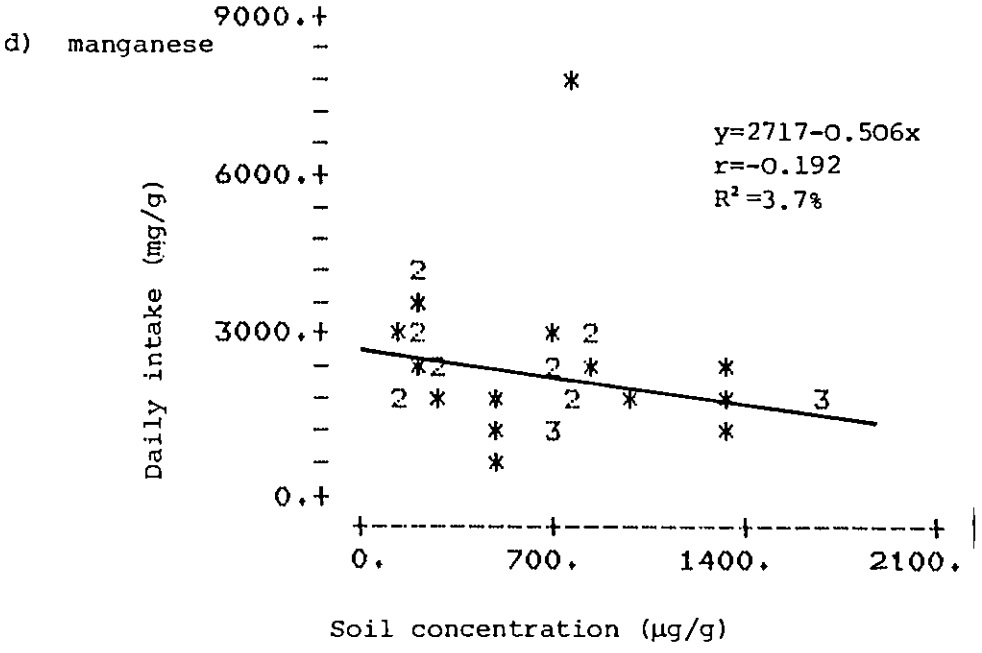


FIGURE 65a-c. Daily intake of arsenic, copper and iron related to soil content.

*=significant at p=0.05 (5%)



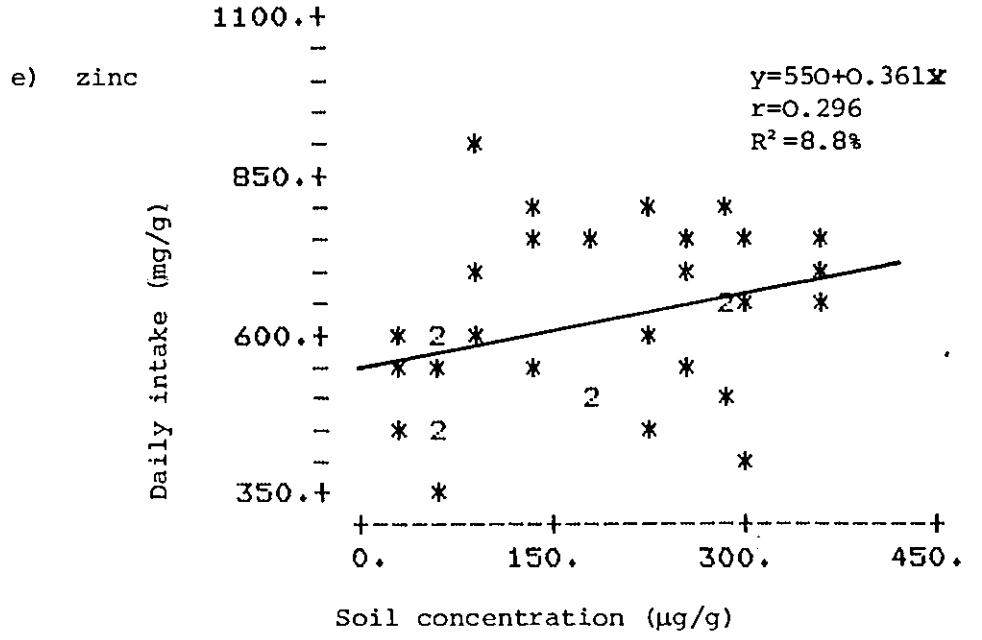


FIGURE 65d-e. Daily intake of manganese and zinc related to soil content.

ii) Soil ingestion: the analysis of faecal Ti indicates that soil may be an important constituent of the ruminant diet. Soil may account for up to 18% of the total dry matter intake (Table 53). Because soil contamination of the pasture herbage can significantly increase the As and Fe concentrations relative to 'clean' pasture herbage contents (Section III, Chapter 6) soil ingestion is a particularly important source of these two elements to grazing cattle. The percentage of As ingested as soil varies from 41% to 97% ($\bar{X}$=85%), whilst for Fe the percentage ingested as soil varies from 30% to 95% ($\bar{X}$=76%). In comparison, the percentage range for Cu is 2.1% to 59%, for Mn the range is 0.4% to 45%, and for Zn the range is 1% to 28% (Tables 49-60).

The total daily intake of the five trace-elements studied can be significantly increased as a result of soil ingestion by the ruminant. Site 5, located within an area associated with relatively low soil trace-elements, provides a particularly good example where the high soil ingestion rate during late April (17.9%) appreciably raises the total daily intake of As (126 mg/day), Fe (44,102 mg/day) and, to a lesser extent, Cu (262 mg/day), Zn (914 mg/day) and Mn (4,447 mg/day). These figures can be compared with the median values obtained for the same month at the other low As sites (19.7 mg As/day, 18,165 mg Fe/day, 160 mg Cu/day, 606 mg Zn/day and 2,594 mg Mn/day). Conversely, periods of low soil ingestion may significantly decrease the total daily intake of trace-elements. For example, the low rate of soil ingestion at site 10 during late June (0.18%) results in a daily intake of 11.6 mg As/day compared to the median of 46 mg As/day observed from the remaining high As sites.

On nearly all the 12 farms studied, the rate of soil ingestion was found to vary with the season of sampling. Soil ingestion is particularly elevated during the period of late April (maximum recorded value = 17.9% of the total dry matter intake) and thus reflects the time of raised unwashed pasture herbage trace-element concentrations caused as a result of soil contamination(Section III, Chapter 6). Soil ingestion falls rapidly in early summer with the flush of new pasture growth, and increases again in the late summer when grass is less abundant (Table 61). This seasonal trend in the rate of soil ingestion corresponds to the general seasonal concentrations of the five trace-elements in the pasture herbage. As a result, the total daily intake of the five elements follows a similar trend, with the lowest intake rates being associated with the late June period.

(III) COMPARISON OF THE FAECAL TRACE-ELEMENT CONCENTRATIONS WITH THE DAILY INTAKE OF As, Cu, Fe, Mn AND Zn

The trace-element content of faecal samples need not be directly related to the total daily intake of an element, since the faecal trace-element concentrations represent both the unabsorbed portion of the element in the total diet, and also a variable proportion of the trace-element which is re-excreted from the animal. The Mn and Zn content of faecal material analysed in this work is not significantly related to the total daily rate of Mn and Zn intake (Figures 66d and e). Correlation R^2 values are low for both of these observations (0.1% for Mn, 3.9% for Zn), and indicate that much of the variation in the faecal Mn and Zn concentrations do

Sample period	Percentage Soil Ingested	
	Mean ($\bar{x}$)	Range
late April	5.64%	1.47 - 17.93%
late June	1.49%	0.18 - 3.91%
late August	3.01%	1.36 - 4.66%

n = 12 for each sampling period

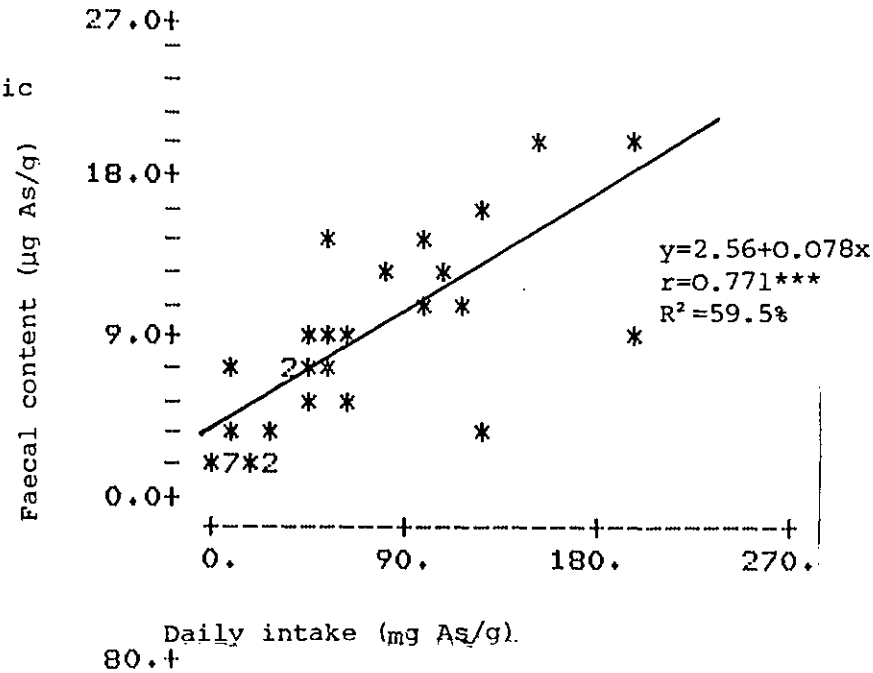
TABLE 61. Seasonal variation of soil ingested by cattle at the 12 farms investigated in South-West England.

not appear to be directly related to the rates of intake by the cattle. In comparison, Pearson correlation coefficients between the faecal content of the remaining three trace-elements studied and the daily intake of these elements are significant (Figures 66a-d). The particularly good relationships observed for As (R^2 = 60%) and Fe (R^2 = 73%) are probably due to the fact that soil (which is less readily absorbed than herbage) is the major input of both elements to the diet (Gwyneth Lewis, personal communication). However, this cannot explain the significant trend observed for Cu, since the percentage of this element ingested as soil approximates more to the amounts associated with the elements Mn and Zn. This suggests that different biochemical reactions influencing the absorption of Cu, Mn and Zn is occurring within the gastro-intestinal tract of the cattle. Such differing reactions may be related to ingested soil; for example, initial research has shown that ingested soil may reduce the availability of Cu, but may release and thus increase the availability of Zn (Suttle, et al., 1975).

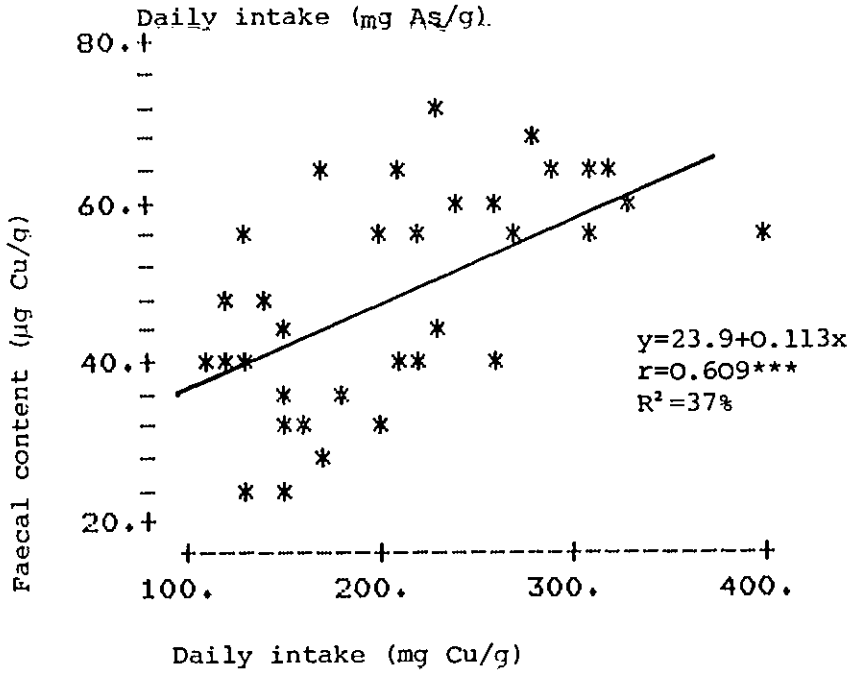
(IV) THE THEORETICAL INTAKE OF TRACE-ELEMENTS BY CATTLE GRAZING UNCONTAMINATED SOILS OUTSIDE THE SOUTH-WEST ENGLAND PENINSULA

The relevance of the trace-element dietary intake values outlined in Section II of this chapter remain largely unclear due to the lack of biochemical information in the literature. Whilst toxicological reviews, information relating to the trace-element content of animal foodstuffs, and trace-element requirement threshold values are available (Underwood, 1971; EEC, 1972; Clarke et al.,

a) arsenic



b) copper



c) iron

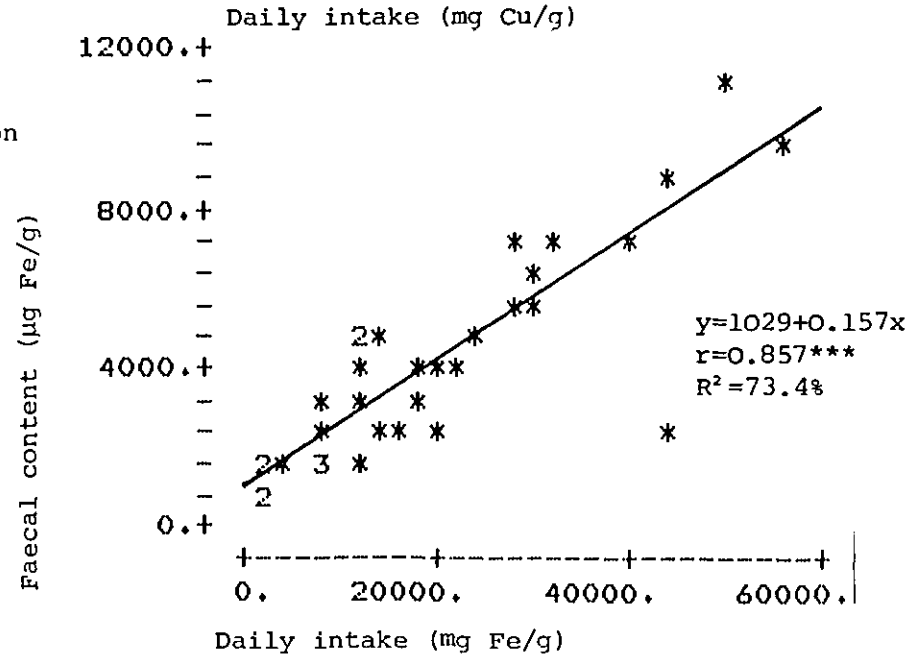
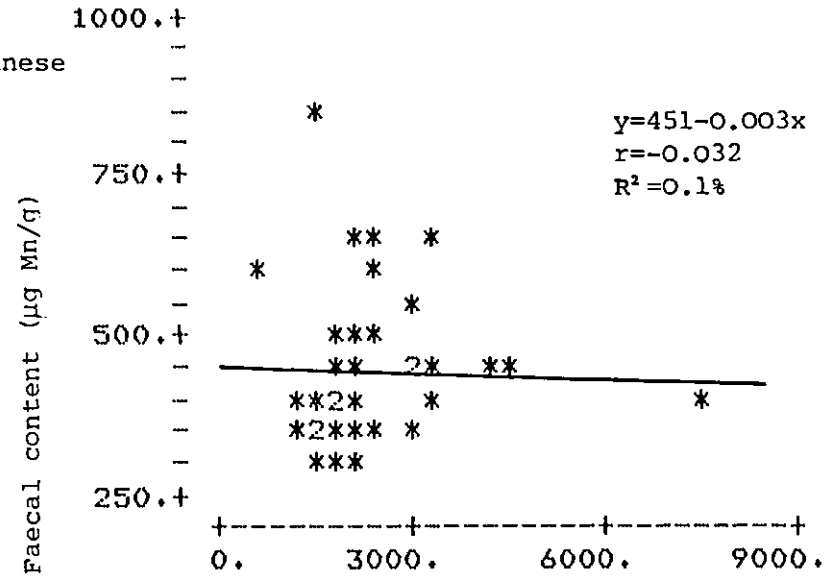


FIGURE 66a-c. The faecal content of arsenic, copper and iron related to total daily intake.

*** = significant at p=0.001 (0.1%)

d) Manganese



e) zinc

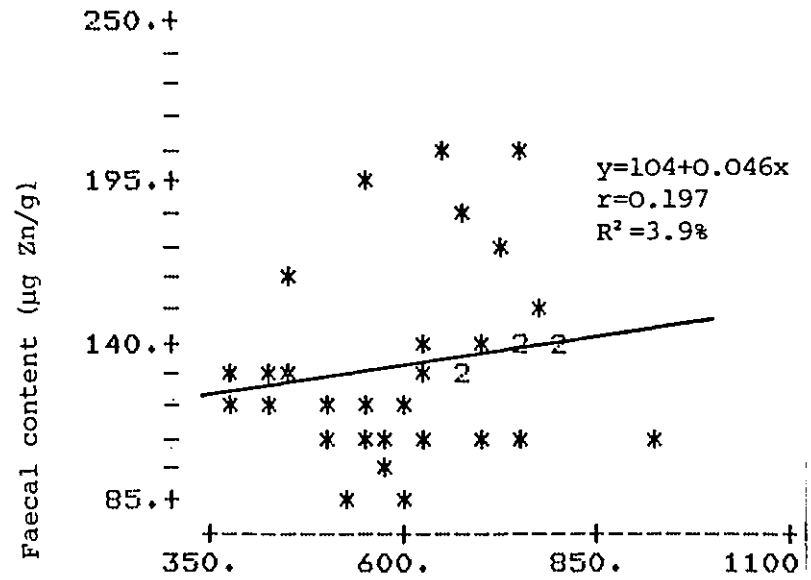


FIGURE 66d-e. The faecal content of manganese and zinc related to total daily intake.

1981; ARC, 1980; Bartic and Piskač, 1981), much of the information is difficult to apply to the practical situation which exists in South-west England. In order to assess the importance of the widespread soil As and metal contamination which persists in this region of Britain, however, a theoretical model indicating the trace-element intake of As, Cu, Fe, Mn and Zn by cattle grazing soils of normal trace-element content can be calculated. The details relating to this theoretical model are outlined in Table 62, and is based on a number of assumptions:

i) that the rate of soil ingestion is similar to that observed at the sites investigated in South-west England. The rates of soil ingestion shown in the theoretical control model were calculated by computing the means of the data outlined in Tables 49-60. These mean values had previously been calculated in this chapter (Table 61).

ii) the theoretical model requires typical uncontaminated soil concentrations for the calculation of daily intake rates. This data was obtained from information supplied by Berrow and Burridge (1979b) (Table 3).

iii) the theoretical model requires the washed herbage concentrations which can be expected to be associated with the uncontaminated soils outlined in section (ii) above. Such concentrations were calculated by using various regression equations presented in Chapter 6. For the elements Cu, Fe, Mn and Zn the herbage concentrations were derived from the equations relating to the relative accumulation logarithmic plots (Table 48). For As, the linear regression equations derived by plotting herbage As versus soil As concentrations (Table 43) were used for the prediction.

The theoretical daily intake values shown in Table 62 can be taken to represent a control situation against which the daily

	Soil ingested (%)	Soil conc. (µg/g)		Washed herbage conc.(µg/g D.M.)		Daily intake as soil (mg/day)		Daily intake as herbage(mg/day)		Total daily intake (mg/day)		% element ingested as soil	
		As	Cu	As	Cu	As	Cu	As	Cu	As	Cu	As	Cu
April	5.64			0.13	11	4.6	15	1.7	141	6.3	156	73	9.6
June	1.49	6	20	0.08	8	1.2	4.1	1.1	107	2.3	111	52	3.7
August	3.01			0.20	11	2.5	8.2	2.6	145	5.1	153	49	5.4
		Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
April	5.64			48	368	38	30682	616	4723	654	35405	5.8	87
June	1.49	50	40000	34	102	10	8106	456	1367	466	9473	2.1	86
August	3.01			38	216	20	16374	501	2849	521	19223	3.8	85
			Mn		Mn		Mn		Mn		Mn		Mn
April	5.64				128		614		1643		2257		27
June	1.49		800		106		162		1420		1582		10
August	3.01				137		327		1807		2134		15

TABLE 62. The theoretical daily intake of As, Cu, Fe, Mn and Zn by cattle grazing pastures established on soils with typical soil trace-element concentrations.

intake values found in South-west England can be compared. For As, the daily intake of the element via ingested pasture herbage indicated by the 'control' model is equivalent to, or even greater than, those amounts recorded from the low As sites studied in the Hayle/Camborne-Redruth study area. A comparison of the total daily intake rates, however, indicates clearly that the dietary intake of As on the low As sites (median values of 29 mg As/day in April, 8.4 mg As/day in June and 20 mg As/day in August) is greater than those of the control model (maximum proposed daily intake equals 6.3 mg As/day during late April). The disparity is due to the effects of ingested soil, where the median daily soil intake values of 28 mg As/day (April), 6.5 mg As/day (June) and 19 mg As/day (August) on the low As sites compare with the theoretical control values of 4.6 mg As/day (April), 1.2 mg As/day (June) and 2.5 mg As/day (August). This shows the importance of ingested soil in supplying As to the diet of cattle on the low As sites of South-west England. The theoretical model devised in this study, however, shows that even on soils with a normal As content, soil may still be an important source in supplying the trace-element to the animal (range 49-73% of the element ingested).

On the high As sites, the intake of As is particularly elevated. Median total daily intake rates of 108 mg As/day during late April, 43 mg As/day during late June and 81 mg/day during late August were calculated from the five high As sites investigated. A maximum of 196 mg As/day was recorded from site 8 during late April; of this total figure, 189 mg As/day (i.e. 96%) was ingested in the form of soil (Table 56). A comparison of the total daily intake of this element at site 8 with the value calculated from the control model, indicates that the intake of As may be up to 31 times

greater on the highly contaminated sites of South-west England compared to sites with typical uncontaminated soil concentrations.

The total daily intake of Cu and Zn outlined by the control model approximate to those sites in South-west England which are not elevated in their Cu and Zn soil concentrations (i.e. sites 1, 2, 3 and 5). These sites have soil Cu and Zn contents which are similar to those used in the control model. Thus the total daily intake of these two elements at these sites - median values 160 mg Cu/day and 606 mg Zn/day (April); 121 mg Cu/day and 442 mg Zn/day (June); 151 mg Cu/day and 539 mg Zn/day (August) - probably approximates to those amounts consumed by cattle throughout large areas of Britain. In comparison to As, ingested soil at these sites usually is of little importance in supplying both elements to the ruminant. The source of soil in supplying Cu and Zn only becomes more important at the contaminated sites. This may result in an elevated total daily intake of both elements. The raised Cu and Zn daily intake values, however, are not as elevated as those observed for As. The maximum total daily intake of Cu (396 mg/day at site 4) and Zn (914 mg/day at site 5) compare with values of 156 mg Cu/day and 654 mg Zn/day from the control model.

The total daily intake rates of both Fe and Mn in South-west England are closely related to the underlying parent materials which strongly influence the soil Fe and Mn concentrations of the study area. Mineralisation and mining activities are unlikely to seriously affect the soil concentrations of both trace-elements compared to As, Cu and Zn (Chapter 4). Since the soil Fe and Mn concentrations of the sites investigated on the slate/greenstone parent materials

are similar to those used in the theoretical control model, the daily intake rates on the farms located on the Mylor slates and greenstones can be considered normal (Table 63). The data generated from the control model shows that soil ingestion is likely to be an important source of dietary Fe to cattle over large areas of Britain (Table 62). In comparison, the total daily intake of Fe on the four granite sites investigated in this research shows that the intake of this element can be up to 2½ times less the amounts considered average as proposed by the control model. This can be attributed to the low Fe concentrations associated with the granite soils. The intake of Mn is not severely depressed on the granite parent material, however, despite the low concentrations of this element found within the granite derived soils. The high concentrations of Mn associated with the pasture herbage of the granite sites (Chapter 6), ensures that a normal intake of this element is maintained (Table 63).

(V) DISCUSSION AND CONCLUSIONS

The total daily intake of the elements As, Cu, Fe, Mn and Zn by cattle studied in this research is highly variable. This has been shown to be due to the trace-element variability of the two constituents, pasture herbage and soil, which determine the rate of trace-element intake. The proportion of each constituent to the diet of the cattle is also important. In particular, the rate of soil ingestion may significantly influence the trace-element intake by cattle. The total daily intake of the five elements can be substantially elevated on the low As sites during times of high soil ingestion, whilst conversely the total intake can be depressed on the contaminated sites provided the rate of soil ingestion is

		Season of grazing		
		late April	late June	late August
Total daily intake of Fe and Mn calculated in the control model (mg/day)	Fe	35405	9473	19223
	Mn	2257	1582	2134
Median total daily intake of Fe and Mn observed at the 8 slate/greenstone sitesinvestigated (mg/day)	Fe	35922	11360	21148
	Mn	2856	1420	1893
Median total daily intake of Fe and Mn observed at the 4 granite sites investigated (mg/day)	Fe	14678	3829	8141
	Mn	2674	2552	2567

TABLE 63. The total daily intake of iron and manganese at the slate/greenstone and granite sites compared to the proposed intake of both elements under 'control' conditions.

low. Such periods of low soil ingestion are associated with the late June period, presumably due to the plentiful supply of grass. Higher rates of ingested soil are associated with the late April and late August sampling periods. Personal experience in South west England has indicated that during late April the supply of grass to the ruminant is low. Theoretically, however, this should not be evident since temperate grasses have a characteristic pattern of production which is at a very low level during winter, but which accelerates to a spring peak before falling thereafter more or less rapidly to return to the low winter level in October or November (Corrall, 1978). This information suggests that the shortage of grass observed during late April is due to the fact that cattle are being turned out to the fields on too early a date following the winter period indoors. Consequently, although the grass may be actively growing, constant grazing during the spring period is limiting the grass supply and leads to an increased intake of soil as part of the diet. In addition, MAFF (1976) indicate that in Cornwall the growing season commences around February 20th and the grazing season some two weeks later, around March 4th. MAFF (op. cit.) further indicate that the end of capacity date in Cornwall is around April 27th. This latter date may be vital in terms of determining the supply of soil to cattle, since it marks the end of the period where rainfall exceeds the transpiration rate. Under the wet conditions prior to this date, pasture will be particularly susceptible to soil contamination through poaching and soil splash.

More detailed research is required to confirm these observations above, but the evidence does suggest that the farmer can largely control soil ingestion (if so required) by the correct form of farm

management (i.e. by ensuring that there is an adequate supply of grass). There is no evidence at this moment in time, however, to suggest that the widespread soil trace-element contamination in South-west England is seriously affecting agricultural productivity. Toxicity symptoms in grass species are restricted mainly to derelict mine sites of no importance to agriculture (Plate 5), whilst the contamination of soils by As in the province does not manifest itself in the large scale poisoning of farm animals (Thomas, 1979). It is known, however, that a certain amount of As is absorbed in cattle, since it has been noted that animals moved from a farm with little As contamination to one which is heavily contaminated (or vice versa) lose condition to a greater extent than normally expected as a result of a change of field or environment (Thomas, op.cit.). This change in condition can manifest itself clinically in the appearance of the animals coat (Thornton, 1978).

However, the exact biochemical role of As and associated elements affecting the cattle in South-west England remains to a large extent unknown. The relevance of the trace-element dietary intake values calculated from 12 farms within the Hayle/Camborne-Redruth area thus remain unclear. The construction of a model representing a control or uncontaminated locality has indicated the increased intake of As in South-west England caused as a result of the high soil contamination; cattle may ingest up to 31 times the amount of As in South-west England compared to the control situation. The ingestion of soil may account for up to 97% of the element in the diet. In comparison, the daily intake of Cu and Zn may also be elevated (although to a lesser extent than As), whilst Fe and Mn daily intake rates reflect the underlying geological parent materials, and

are not elevated due to the limited amount of soil Fe and Mn contamination within the province.

The significant correlation between the daily intake rates of As and the concentrations of this element in the faeces of cattle supports the view that a certain proportion of the trace-element is excreted in the faeces and is not biologically absorbed. This may be due to the fact that soil is the major source of the element to cattle. According to Hegan and Eagle (1944) (cited by Clarke et al., 1981), the rate of As excretion varies with the type of compound and is generally inversely related to the toxicology. It is probable that under the freely drained soil conditions found in South-west England, arsenate is the predominant inorganic species of the element (Peterson et al., 1981). This species is less toxic than the trivalent (arsenite) form, and apparently does not accumulate in vertebrates (Schroeder and Balassa, 1966). Further biochemical research is needed, however, to clarify the significance of the high As intake which is evident within South-west England. Some As will be absorbed and may be excreted in the milk of suckler cows (Clarke et al., 1981). Milk may thus be contaminated with unacceptable concentrations of this element which can be potentially dangerous to calves since they are particularly susceptible to trace-element excess (Thomas, 1979). No known research has yet been undertaken on this problem, however. Similarly, the possible antagonistic effects of trace-elements on the absorption of As within cattle still requires investigation. For example, the close association between Fe and As observed in the soils and pasture herbage of South-west England may persist within the ruminant. In this context, it is interesting to note that moist freshly prepared ferric hydroxide remains the classical antidote for As poisoning in animals (Clarke et al., 1981).

CHAPTER 8

SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

(I) THE CONCENTRATIONS, DISTRIBUTION AND SOURCES OF TRACE-ELEMENTS IN THE SOILS OF SOUTH-WEST ENGLAND

Widespread anomalies of trace-elements in the stream sediments of South-west England were delineated by the Wolfson Geochemical Atlas of England and Wales during the early 1970's. Further detailed studies undertaken by the Applied Geochemistry Research Group included the collection and analysis of stream sediment samples within the Hayle/Camborne-Redruth area. This survey accurately defined areas of high and moderate As, Cu, Pb and Zn contamination within the study region; the anomaly for Cd was of limited extent. In terms of both the concentrations found and the extent in area of the contamination, As and Cu were the major contaminants and thus reflected the importance of these two elements in the mineral ores of the study area. The contamination coincided with the major mineralised and mined areas located mainly within an area of Devonian Mylor slates. In contrast, the trace-element concentrations of the stream sediments draining the granite areas were generally not as elevated, although the concentrations recorded from these granite sites indicated a minor enrichment of As, Cu, Pb and Zn due either to mineralisation and/or a naturally enriched parent material.

Initial soil sampling undertaken in this research involved the collection of both topsoils (0-15 cm) and subsoils (30-45 cm) from four reconnaissance traverses selected on the basis of the

trace-element contamination patterns as defined by the detailed stream sediment maps of the Hayle/Camborne-Redruth area. This work was intended to both check and confirm the conclusions made from the stream sediment survey, and to observe to what extent the soil trace-element concentrations reflected those of the stream sediments. In addition to As, Cd, Co, Cu, Pb and Zn which were analysed in the stream sediment survey, each soil sample was also analysed for Al, Ca, Fe, Mn and Sn. The conclusions determined from this initial soil survey are outlined as follows:

1. For the main elements of interest to this research, the order of soil trace-element enrichment observed from the four soil traverses is Sn > As > Cu > Zn > Pb. Maximum concentrations of 1,088 μg Sn/g, 727 μg As/g, 564 μg Cu/g, 685 μg Zn/g and 268 μg Pb/g were determined from the topsoils of the traverse samples.

2. The soil contamination is mainly found within the areas of mineralisation and mining activity, and thus closely reflects the trace-element contamination patterns defined by the detailed stream sediment maps. The contamination is also closely linked with the geological controls which influenced the mineralisation and led to the deposition of the ores in zones around 'emanative centres of mineralisation'. Thus, the Sn mining regions located on the granites at the sites of former emanative centres of mineralisation, are generally areas which are comparitively low in soil trace-elements such as As and Cu, since these elements are not associated with the mineralisation at such sites.

3. The soil As, Cu, Pb and Zn concentrations determined from the soils of the four reconnaissance traverses have been statistically compared with the detailed stream sediment maps of the Hayle/Camborne-

Redruth area by using the χ^2 test. The topsoils of all four trace-elements studied in this way are significantly correlated with the stream sediment reconnaissance maps; only the As and Pb concentrations of the subsoils are related to the distribution of the trace-elements in the stream sediments. On the basis of these statistical correlations, the stream sediment data comprising the Wolfson Geochemical Atlas of England and Wales was used to delineate the areas of topsoil and subsoil contamination throughout South-west England. All four trace-elements are elevated in concentration within the Hayle/Camborne-Redruth/St. Day/St. Agnes-Cligga granite mining districts and the mining areas centred at Liskeard, Callington and Tavistock. The highest concentrations of both As and Cu occur in the Hayle/Camborne-Redruth/St. Day districts. Minor areas of trace-element enrichment also occur in the Camelford, north-west Dartmoor and Plymouth regions. The Pb and Zn contamination associated with the latter locality is believed to be related to sources associated with the urban environment. In all, a total of 1,092 km^2 of land - equivalent to 11.9% of the total area surveyed by this research - is believed to be contaminated by one or more of the elements As, Cu, Pb and Zn.

Further studies undertaken in this research involved the collection of samples from representative soil profiles within the Hayle/Camborne-Redruth area. In addition, soil samples were taken from fields adjacent to areas of mine spoil and around the sites of a former tin smelter and a former arsenic calciner. A number of slate, granite and greenstone rock samples were also collected; these three rock types comprise the main parent materials of the

Hayle/Camborne-Redruth area. The analysis of these samples complemented the research undertaken during the initial soil reconnaissance work, and has led to the following conclusions:

1. Raised trace-element concentrations can occur outside the major mineralised and mined districts of the Hayle/Camborne-Redruth area. These anomalies may be attributed to a number of sources. For example, soil concentrations of 496 µg Pb/g and 405 µg Zn/g found at a depth of 45-60 cm in a soil profile sampled supposedly in an unmineralised area, suggests that the mineralisation may be more widespread than indicated by geological maps of the region. Similarly, concentrations of 228 µg As/g and 112 µg Cu/g in a topsoil sample collected within an apparently unmineralised area, indicates the widespread effect of atmospheric contamination which can occur within the study region.

2. Additional soil trace-element anomalies found in the Hayle/Camborne-Redruth study area are not directly related to the mineralisation or mining contamination. The elevated Ca concentrations in soils bordering the coast north-east of Hayle are attributable to the calcareous dune sand which has blown inland. The addition of the calcareous dune sands from Hayle are also responsible for the elevated concentrations of Ca recorded from the man-made soils which are located on the southern slopes of the Lands End granite. These soils are additionally enriched in Cu, As, Pb and Zn; whilst this enrichment may be due to the application of the sand (e.g. As soil concentrations may be raised due to the contaminated nature of the sand), it is considered that the raised concentrations of these elements observed in these soils may additionally be due to the application of domestic waste from Penzance. The pottery shards found commonly within these soils, for example, may be a possible source of Pb contamination.

3. The analysis of the rock samples has revealed that the concentrations of As, Cd, Pb and Zn in the Devonian Mylor slates, As, Cd, Pb, Sn and Zn in the greenstones and As, Cd, Co and Sn in the granites of the Hayle/Camborne-Redruth study area are elevated compared to the published average concentrations of these elements associated with these three different rock types. Since the soils of the study area are little affected by solifluction and are more or less formed in-situ, the elevated trace-element concentrations of these three parent materials will probably result in soils which are naturally enriched in the trace-elements noted above. However, the widespread contamination found within the study area largely masks this natural enrichment.

4. Within the contaminated and mineralised areas, the anomalous trace-element concentrations are consistently high and suggest that soils may be severely affected by contamination well beyond the immediate vicinity of the mine workings. Detailed sampling undertaken around spoil heaps, a former tin smelter and a former arsenic calciner, has shown that the contamination persists in soils long after the mining operations have ceased. Mine spoil may release a large number of trace-elements including As, Ca, Cd, Co, Cu, Fe, Mn, Pb and Zn into the surrounding soils due to the multi-element nature of the mineral ores remaining in the waste. The extent of soil contamination derived from mine spoil is, in part, dependent upon the nature and trace-element composition of the waste itself. In comparison, whilst a number of elements may be released into soils from mine spoil, it would appear that tin smelting only released significant amounts of Sn into the surrounding environment. Similarly, of the three trace-elements studied at the site of a former arsenic works (Sn, Cu and As), only As is found in widespread and elevated concentrations around the site. Since the proximity of mineralisation

does not appear to have been a necessity in the locational siting of both the tin smelters and the arsenic calciners, the contamination from both industries has resulted in elevated concentrations of both Sn and As outside the major mineralised areas.

5. The highest concentrations of Sn, As, Cu, Pb and Zn in the Hayle/Camborne-Redruth study area are associated generally with the topsoils, and reflect the effects of surface contamination caused by the mining activity. The possible complexing of these trace-elements by organic matter, together with the effects of the 'Beat Burn' system of agriculture, may promote this topsoil enrichment by 'fixing' the trace-elements in the upper horizons of the soil. However, elevated concentrations of trace-elements are also found in the subsoils of the study region; for example, maximum concentrations of 400 μg Sn/g, 500 μg As/g, 394 μg Cu/g, 1,833 μg Zn/g and 379 μg Pb/g were recorded from the subsoil samples collected during the soil traverse reconnaissance survey work. These high subsoil concentrations result in Relative Topsoil Enhancement ratios which are generally close to unity. The elevated trace-element concentrations in the subsoils probably reflect the effects of the underlying mineralisation which has been shown by other research workers to be responsible for releasing high amounts of elements such as As and Cu into the overlying soils. The results obtained from this present research further indicates that the subsoil concentrations may be influenced by additional factors:

i) the analysis of soils sampled in the unmineralised area located around the former tin smelter at Trereife has revealed high concentrations of Sn in the subsoils which closely reflect the overlying topsoil concentrations. This evidence strongly suggests that Sn has been translocated down the soil profile by mechanical

processes which may involve soil fauna or the activities of man. Such processes will probably influence the distribution of other trace-elements within the soil.

ii) podzolisation has been found to be generally more advanced in the soils of the granites compared to the soils derived from the slates. Concentrations of both Fe and Al - and potassium pyrophosphate extractable Fe - particularly reflect this advanced stage of podzolisation, whilst a slight enrichment of As in the podzolised B horizons of the granite soils is also evident from the limited amount of data in this study.

(II) THE AGRICULTURAL SIGNIFICANCE OF THE RAISED SOIL TRACE-ELEMENT CONCENTRATIONS IN SOUTH-WEST ENGLAND

The uptake of As, Cu, Fe, Mn and Zn by pasture herbage was studied at twelve farms (36 soil plots) located within the Hayle/Camborne-Redruth district during late April, late June and late August. A study into the intake of these five elements by cattle was also undertaken during the same sampling periods. The conclusions determined from this work are outlined below:

1. The uptake and translocation of As, Cu, Fe, Mn and Zn by pasture herbage varies according to the trace-element concerned. The Cu and As content of the herbage increases slightly with increasing soil concentrations, whilst the Mn content of pasture herbage decreases on the slate soils which contain greater concentrations of the element compared to the granite derived soils. Concentrations of Fe and Zn in the pasture herbage show no apparent relationship with soil Fe and Zn content.

2. The trace-element content of the pasture herbage varies according to the time of sampling. Generally, the minimum concentrations of all five trace-elements investigated were found to occur in herbage sampled during late June. These observations agree with previously published research undertaken in South-west England.

3. The relationship between soil and the trace-element concentrations of the pasture herbage has been studied by ridge regression; a multi-variate technique which removes the effects of multicollinearity from the regression analysis. This statistical technique outlines the variables which are important in accounting for the variation observed in the trace-element content of the herbage. Some of the more interesting relationships revealed by the ridge regression analysis are:

i) both the Zn and Mn content of the herbage is shown by the ridge regression analysis to be inversely related to the soil pH. This may account for the increased concentrations of Mn in herbage associated with the acidic granite soils which are themselves low in this element.

ii) soil organic matter has an insignificant role in determining the As, Cu, Fe, Mn or Zn content of the herbage in South-west England.

iii) a positive relationship is observed between Zn and Cu concentrations in the herbage. This has led to a further investigation of Zn:Cu ratios in both the soils and herbage of the study area. Excess Zn concentrations in soils have been considered a possible cause of Cu deficiency in cattle. This theory is based on the assumption that excess Zn concentrations within the soil will lead to an increased uptake of Zn in pasture herbage at the expense

of Cu. However, this relationship was not evident in the soil and herbage samples studied within the Hayle/Camborne-Redruth district. The possibility of other trace-element interactions influencing the trace-element content of herbage is, however, indicated by the ridge regression equations outlined in this thesis. Soil Mn, for example, may have an antagonistic influence on As accumulation in the pasture herbage.

4. The relative accumulation (amount in plant ÷ amount in soil) of As, Cu, Fe, Mn and Zn by pasture herbage decreases on soils which are elevated in their soil trace-element content. This suggests that the plants may control (to an unknown extent) the uptake and translocation of these five trace-elements. The relative accumulation of both As and Fe is lower than for the elements Cu, Mn and Zn. Thus, herbage is particularly susceptible to soil As and Fe contamination. For example, the unwashed herbage concentrations of As may be up to 63 times greater than recorded from the washed herbage samples.

5. The total daily intake of As, Cu, Fe, Mn and Zn by cattle in the Hayle/Camborne-Redruth study area is variable, and dependent upon the trace-element concentrations of the two constituents of the diet, pasture herbage and soil, which determine the rate of trace-element intake. The proportion of each constituent to the diet of the cattle is also important. In particular, the rate of soil ingestion may significantly influence the trace-element intake, since the daily consumption of the five elements can be substantially elevated during times of high soil ingestion. Conversely, the total daily intake can be depressed when the supply of soil to the ruminant is limited.

6. The total daily intake of As, Cu, Fe, Mn and Zn by cattle is related to the time of year. The lowest intake rates are generally associated with the late June period; this coincides with the relatively low trace-element concentrations found in the herbage, and also the low rates of soil ingestion recorded at this time of the year (mean percentage soil ingested = 1.49%). Higher rates of soil ingestion were recorded during late April ($\bar{X}$ = 5.64%) and late August ($\bar{X}$ = 3.01%). The seasonal variability of soil ingestion may be related to the weather and to the supply of grass to the ruminant; farm management may strongly influence the latter variable.

7. The ingestion of soil is a particularly important source of both As and Fe to the ruminant due to the high soil concentrations of both elements relative to the pasture herbage concentrations. Thus, soil may account for up to 97% and 95% of the total daily intake of As and Fe respectively. In comparison, soil ingestion is not so important for Cu, Mn and Zn due to the higher relative accumulation ratios observed in pasture herbage for these three elements. Ingested soil may thus account for up to 59%, 45% and 28% of the Cu, Mn and Zn supply to the ruminant.

8. The construction of a model representing a control or uncontaminated locality has indicated the increased intake of As by cattle in the Hayle/Camborne-Redruth study area caused as a result of the high soil contamination. Cattle may ingest up to 31 times the amount of As compared to the control model. The intake of Cu and Zn may also be elevated on the contaminated sites, although the degree to which the intake rates of both elements is enriched is substantially less than observed for As. Due to the limited extent of soil Fe and Mn contamination in the study area, the daily intake rates of both of these elements are not elevated, but they do reflect

the Fe and Mn content of the slate and granite parent materials.

9. A significant correlation between the daily intake rates of As, Fe and Cu and the concentrations of these elements in the faeces of cattle, supports the view that a certain proportion of these three elements are readily excreted and are not biologically absorbed. For As and Fe, this may be attributed to the fact that the major input of both elements to the ruminant diet is in the form of soil.

(III) PROPOSALS FOR FUTURE WORK

Due to the widespread soil contamination found within the Hayle/Camborne-Redruth study area, the natural trace-element concentrations and distribution within the soil profile have proved difficult to fully determine. Further detailed research is required in order to investigate these parameters. The sampling and analysis of uncontaminated soils outside the Hayle/Camborne-Redruth district may not be satisfactory for this purpose, however, since the present research has indicated the trace-element enriched nature of the Mylor slates, granites and greenstones of the study area. The sampling and analysis of soils developed on other parent materials within South-west England, therefore, may be unsatisfactory since their 'natural' trace-element geochemistry may differ from those of the Hayle/Camborne-Redruth area.

Research investigating into the dispersion of trace-elements from contamination sources such as mine spoil and tin smelters has been limited in South-west England. A great deal more work can be undertaken on these problems. Lysimeters may prove useful in

determining the rates of leaching from mine spoil. Such mine waste may also be subject to wind erosion with subsequent deposition of the spoil particulates onto the surrounding soils. The sampling of atmospheric particulates by filtration techniques or deposit gauges (e.g. moss bags) may give some indication as to the extent of the present day dispersal of particulates from the waste. These techniques cannot be used for determining the extent of atmospheric contamination from the tin smelters or arsenic calciners since these industries are no longer operative within the province of South-west England. However, further detailed and extensive soil sampling around the former sites of both industries may delineate the extent of trace-element contamination from both sources.

The variables which account for the trace-element concentrations observed in the pasture herbage of the Hayle/Camborne-Redruth area have been determined in this study by ridge regression. It is considered likely that the inclusion of further predictor variables such as cation exchange capacity and 'total' P will further the observations made in this thesis. An examination of the trace-element content of soil waters may additionally help in understanding the uptake of elements by the herbage, since the soil solution provides the chemical environment of the plant roots. Similarly, the use of soil extractants such as ammonium acetate, EDTA, DTPA, and, for the elements As and P, 'Morgan's Reagent' will give some indication as to the various forms and potential availability of the trace-elements in the soils of South-west England. The trace-element content of the herbage is additionally dependent upon the translocation of the elements from the roots to the shoot. Further sampling and analysis is required in order to investigate the

translocation and redistribution of the trace-elements within the various pasture species.

The significance of the trace-element intake of As, Cu, Fe, Mn and Zn by cattle recorded in the Hayle/Camborne-Redruth study area remains unclear. An investigation into the possible antagonistic effects of the trace-elements in the nutrition of cattle, together with further research examining the effects of ingested soil in adsorbing or supplying trace-elements to the animal is required.

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APPENDIX 1

ANALYTICAL METHODS

(I) SAMPLE PREPARATION

a) Soils

Soil samples collected in the field were stored in kraft paper bags. Once in the laboratory, the field samples were either air dried at room temperature for 2-3 days or oven dried at c.80°C or 105°C, depending on the subsequent analysis for which they were required. Once fully dry, the soil samples were disaggregated using a porcelain pestle and mortar, and passed through a 2mm (10 mesh) nylon sieve. The oven dried (i.e. 80°C) soil samples were further homogenised by grinding the samples in an agate tema mill. These samples were then subsequently stored in paper bags in a cool dry place.

b) Rock and mine spoil samples

Samples of slate, granite and greenstone collected for trace-element analysis were crushed by hand with a pestle and mortar, prior to grinding in an agate tema mill. Samples of mine spoil were treated in a similar fashion.

c) Herbage

The mixed pasture herbage samples were divided into two sub-samples immediately after returning to the laboratory (generally within a few days of collection). One sample of each pair was repacked into a

clean sample bag and the other washed prior to repackaging. The washing technique involved vigorous agitation of the herbage samples in three rinses of de-ionised water. Surplus water was removed by shaking, and drying with paper towels. These samples together with the unwashed herbage were then dried in an air-circulation oven at 80°C for 3 days. The samples were milled in a Christy and Norris mill designed to reduce the risk of trace-element contamination. Prepared samples were stored in paper bags in a cool dry place.

d) Faeces

Following collection in the field, the cow faecal samples were placed in a large porcelain evaporating dish and dried at 80°C for a period of three days. The samples were milled in a Christy and Norris mill and stored in paper bags.

(II) ANALYTICAL TECHNIQUES

a) Determination of Al, Ca, Cd, Co, Cu, Fe, Mn, Pb and Zn in soil, rock and mine spoil samples

The method employed for the determination of these elements is fully outlined by Thompson and Wood (1982). A nitric-perchloric mixture (4:1 v.v.) was added to 0.25g of oven dried temad soil, and was evaporated to dryness. The residue was leached with 2ml of 6M hydrochloric acid, and the samples 'made-up' to 10ml with de-ionised water. The supernatant liquid was then analysed on a Perkin Elmer 403 atomic absorption spectrophotometer.

Calcium interference was determined from a number of standard sample solutions, and a correction factor was employed for the elements

Cd, Co, Cu, Pb and Zn on any sample which was elevated in its Ca content (i.e. >16,000µg/g). Only a few samples had to be corrected in this way, however, due to the low Ca status of most of the soils and rocks sampled.

b) Determination of As in soil, rock and mine spoil samples

The technique employed for the determination of As follows the initial nitric-perchloric procedure outlined above. Following the evaporation of the acid mixture, 7ml of concentrated hydrochloric acid and 8ml of 0.2% kI solution was then added to the residue. The As concentrations were determined by inductively coupled plasma emission spectrometry (ICP) following reduction to arsine by sodium tetrahydroborate.

c) Determination of Sn in soil and rock samples

Tin was determined by atomic absorption spectrophotometry (AAS). Oven dried (80°C) temaū samples were attacked by volatilisation with ammonium iodide, and the sublimate containing the Sn was dissolved in dilute tartaric acid (Gladwell et al, 1981; Thompson and Wood, 1982). The Sn was introduced into the atomiser of a Perkin-Elmer model 403 AAS in the form of its volatile hydride, SnH_4, which is formed from aqueous solution by reduction with sodium tetrahydroborate.

d) Determination of Ti in soil and cow faecal samples

In order to concentrate the Ti content of the cow faecal samples, approximately 5grams of oven-dried material was ignited in silica crucibles at 900°-950°C for 3 hours. The percentage loss of ignition was then determined as:

$$100 \times \frac{\text{Mass of oven-dried material - Mass of ignited material}}{\text{Mass of oven-dried material}}$$

Oven dried soil samples did not have to be concentrated by this method, since Ti occurs in soils in relatively high concentrations. (i.e. several thousand µg/g).

0.25grams of the soil and ignited faecal samples were digested in PTFE beakers using 6ml of a 1:1 nitric-perchloric mixture and 10ml of 40% hydrofluoric acid. The beakers were placed on a hot plate and the samples left to fume down. The samples were then refumed with 2ml of perchloric acid and the residue dissolved in 10ml of hydrochloric acid. These samples were then diluted to 50ml with de-ionised water.

A 1ml aliquot of each sample solution was mixed with 9ml of 'titanium reagent', a mixture of sulphuric acid, orthophosphoric acid and hydrogen peroxide.* A colour complex is then developed, and absorbance was measured by using a Pye-Unicam SP600 spectrophotometer at a wavelength of 400. The Ti content of the soils could be determined directly from the calibration curve plotted on graph paper. However, because of the ashing technique employed for concentrating the Ti content of the faecal samples, the following calculation was necessary for determining the faecal Ti content.

$$\text{Ti in faeces} = (\mu g\ \text{Ti/ml} \times \text{dilution factor}) \times \frac{\%\ \text{Ash}}{100}$$

where dilution factor = 2000

and % Ash = 100-% loss on ignition.

e) Determination of soil pH, organic matter content and potassium pyrophosphate extractable iron

Soil pH was determined on freshly sampled, air dried soil which

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* i.e. 50ml of H_2SO_4, 100ml each of H_2O_2 and H_3PO_4 made up to 1 litre with de-ionised water.

had been passed through a 10 mesh (<2mm) nylon sieve. The method used is outlined fully by Avery and Bascombe (1974), where the pH of a 1:2.5 ratio air dry soil and water suspension is determined using a pH electrode and meter.

The determination of soil organic matter content followed the technique outlined by Ball (1964). This method involves calculating the weight loss of oven dried (105°C) soil samples following ignition at 375°C for 16 hours. It was recognised at the time of analysis that this technique destroys elemental carbon in addition to organic forms.

Potassium pyrophosphate was used as an extractant in this study for the estimation of 'active' Fe oxides. The method used follows that of Avery and Bascombe (1974), and involves shaking of soil and 0.1M potassium pyrophosphate solution at a 1:100 weight to volume ratio for 16 hours, followed by centrifugation to produce a clear solution in which Fe was determined by AAS using a Perkin Elmer 403. The results are reported in this thesis as the percentage of the air dry, less than 2mm fraction of the soil.

f) Determination of Cu, Fe, Mn, Pb and Zn in pasture herbage samples

Oven dried, milled herbage samples were subjected to a nitric-perchloric acid digestion prior to analysis by AAS using a Perkin Elmer 403. This method is fully outlined by Thompson and Wood (1982). Following leaching with 5ml of 6M hydrochloric acid, the samples were transferred to a graduated flask and 'made-up' to 25ml with de-ionised water. The flasks were thoroughly shaken and then left for a few hours, allowing the insoluble silica residue to settle prior to analysis.

g) Determination of As in pasture herbage samples

For the determination of As in pasture herbage, a 1ml aliquot was taken from each of the 25ml graduated flasks mentioned in section f above. 4ml of concentrated hydrochloric acid and 5ml of 0.2% kI solution was then added to each sample. Arsenic was determined by ICP and hydride generation following reduction to arsine by sodium tetrahydroborate.

h) Determination of Pb and Co in pottery samples

The pottery shards collected from the man-made humus soils south of the Lands End granite were first crushed in a porcelain pestle, before being ground to a fine powder in an agate tema mill. The samples were then subjected to a hydrofluoric-nitric-perchloric acid digestion as outlined fully by Thompson and Wood (1982). Following the acid attack, the digested samples were then dissolved in 5ml 6M hydrochloric acid and made up to 25ml in volumetric flasks with de-ionised water. Analysis for both Pb and Co was determined by using a Perkin Elmer 403 atomic absorption spectrophotometer.

APPENDIX 2

ANALYTICAL QUALITY CONTROL

(I) INTRODUCTION

With all the analytical work used throughout this thesis, a number of basic procedures were observed in order to optimise the precision and accuracy of the results obtained. All glassware was first thoroughly washed with 'Teepol' before being leached with 10% 'Technical' grade nitric acid and rinsed, finally, with de-ionised water. The use of concentrated aqua regia (a 3:1 mixture of hydrochloric and nitric acid) was deemed necessary for washing the glassware used for the analysis of Sn. Previous research had shown that the glassware used for this latter experiment retained a 'memory' effect, and thus had to be subjected to a strong acid leach prior to their re-use (David Gladwell, personal communication).

'Analar' grade chemicals were used for all the analytical work undertaken in this research. At the time of analysis, all the samples were not identifiable to the analyst in order to obviate the otherwise unavoidable human tendency to give special attention to the analysis of important samples (e.g. duplicates), or to repeat the analysis if the expected result was not obtained at the first attempt (Thompson, 1983).

(II) CONTROL PROCEDURES UNDERTAKEN IN THE ANALYTICAL WORK

The following quality control procedures were used to assess

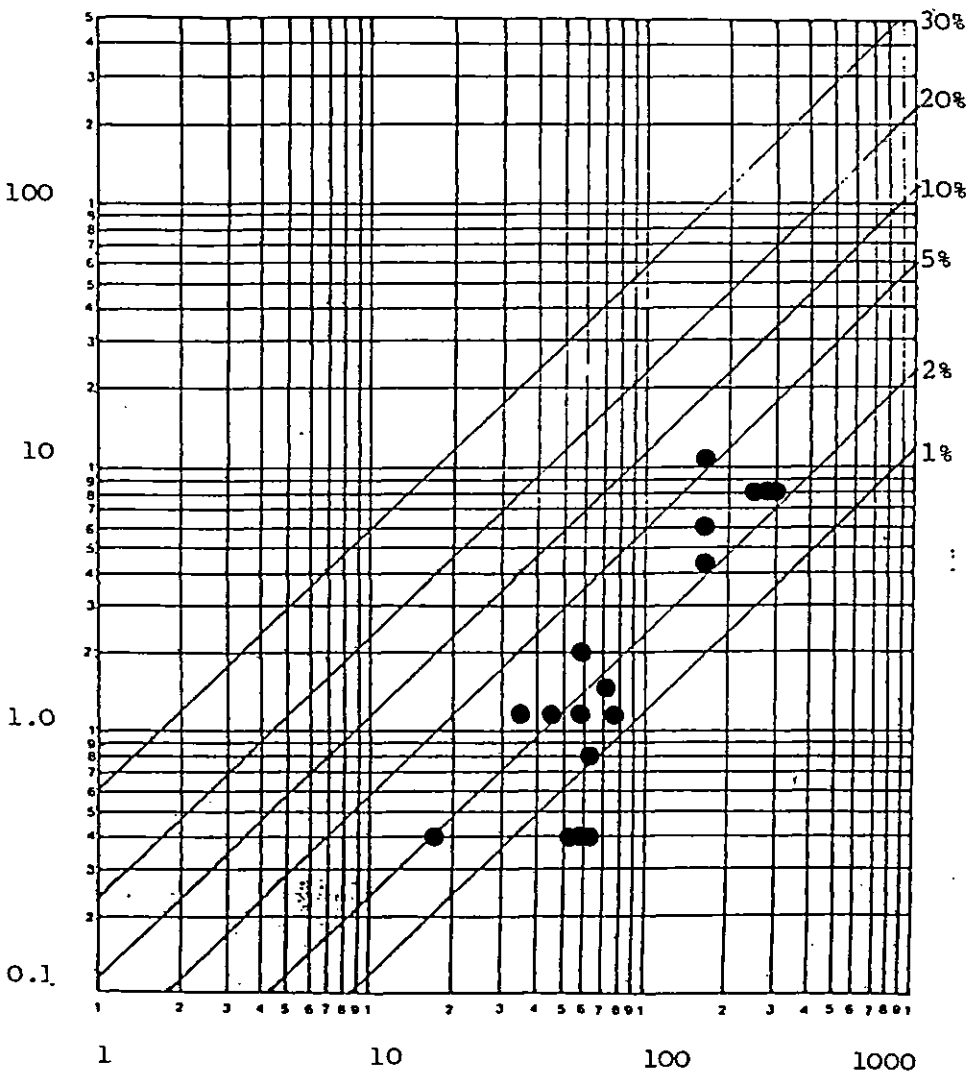
the accuracy and precision of the analytical results:

a) The use of machine calibrators to monitor AAS, ICP and colorimeter performance: These were prepared using BDH standard solutions and were made up in a matrix solution similar to that of the samples. The calibrators were distributed systematically within each analytical batch, and they comprised some 10% of the total samples analysed during each time of analysis.

b) The use of duplicate analysis of samples to monitor the reproducibility of the results: with each analytical 'run', some 10% of the samples were analysed in duplicate in order to determine the within batch precision. These duplicates were inserted randomly within the batch in order to minimise either analytical or human bias. The precision was obtained by using special charts provided by the Applied Geochemistry Research Group (Figure 67). Table 64 outlines the total analytical precision obtained for each trace-element by plotting all the replicated samples analysed throughout this research on the precision charts.

c) The use of reference materials (standards) to determine the accuracy of the analytical work: departmental reference materials were included randomly within each batch of samples analysed. These reference materials accounted for up to 5% of the total number of samples analysed at any one time. Tables 65 and 66 outline the accuracy of the analytical methods used.

d) The use of reagent blanks to assess background concentrations and possible contamination errors: reagent blanks were inserted in each analytical batch. These were again included randomly and made up to 5% of each batch. Table 67 outlines the analytical results obtained for all the blanks studied in this research. Concentrations of Zn were recorded from most of the blank samples, although the concentrations were usually low compared to those of the soil and herbage samples themselves.



In a set of duplicate measurements on many samples, 90% of the points will fall below the diagonal appropriate to the precision of the measurements at the 95% confidence limits.

FIGURE 67. Example of a precision control chart for duplicate results. This example shows duplicate results for soil Cu obtained from one analytical run - the precision is less than 5% in this particular case.

	Soils	Herbage
Al	±8%	-
As	±30%	±60%
Ca	±9%	-
Cd	±160%	-
Co	±35%	-
Cu	±15%	±7%
Fe	±6%	±18%
Mn	±9%	±6%
Pb	±18%	±15%
Sn	±40%	-
Zn	±15%	±6%

TABLE 64. Replicate sample precision obtained from soil and herbage samples analysed in this research.

Reference material	Result	Al(%)	As	Ca	Cd	Co	Cu	Fe(%)	Mn	Pb	Zn
	Established	5.63	*	195	1.1	7.25	25	1.96	154	39	46
	Found - $\bar{x}$	5.34	26	252	1.68	13.6	28.4	2.17	157	36.8	48
	σ	0.25	2.37	29.4	0.30	2.0	4.1	0.12	26	8.5	1.4
993013	Range	5.00-5.72	23-26	240-300	1.20-2.00	12-16	25-35	2.08-2.40	144-200	28-52	42-52
	n	5	3	5	5	5	5	5	5	5	5
	Accuracy (%)	5.2	-	29.2	52.7	87.6	13.6	10.7	1.9	5.6	4.3
	Established		7.13				32	2.00	570	*	125
	Found - $\bar{x}$		7.62				20.2	1.90	540	53	153
	σ		0.69				1.9	0.06	50	4.4	9.6
Z1	Range		6.8-8.99				18-24	1.84-2.00	440-600	48-60	140-169
	n		6				6	6	6	6	6
	Accuracy (%)		6.9				36.9	5	5.3	-	22.4
	Established		50				520	3.50	740	170	800
	Found - $\bar{x}$		49.9				556	3.72	834	170	872
	σ		6.0				11.7	0.15	28	3.6	17.2
Z3	Range		40-58				536-572	3.44-3.96	800-880	164-176	848-896
	n.		17				7	7	7	7	7
	Accuracy (%)		0.24				6.9	6.3	12.7	0	9

* = no established value

All values in µg/g unless specified

N.B. - Sn not included in table above. The use of two additional internal standards indicated an accuracy of 8.9% (n=10) and 11% (n=8) for this element by using the analytical technique outlined in Appendix 1.

TABLE 65. Accuracy of the nitric-perchloric digestion on three internal soil reference materials.

Reference material	Result	As	Cu	Fe	Mn	Zn
997003	Established	0.19	8.4	421	50	37
	Found - $\bar{x}$	0.18	8.7	460	54	35
	σ	0.06	0.59	70.7	2.56	2.04
	Range	0.1-0.28	6.5-10.3	375-625	50-60	32.5-43
	n	33	34	34	34	34
	Accuracy (%)	5.3	3.6	9.3	8.0	5.4

TABLE 66. Accuracy of the nitric-perchloric digestion on an internal herbage reference material.

	Al	As	Ca	Cd	Co	Cu	Fe	Mn	Pb	Sn	Zn
Total no. of 'blanks' included for analysis	28	37	28	28	28	36	36	36	36	13	36
No. of 'blank' samples where element was 'not detectable'	28	11	26	28	28	19	36	36	36	5	1
Maximum concentration found in remaining samples	-	2.6	320	-	-	2.4	-	-	-	10	30
Mean ($\bar{x}$)	-	0.5	320	-	-	1.2	-	-	-	4.2	5.1
Median ($\bar{x}m$)	-	0.08	320	-	-	1.2	-	-	-	4.2	4.0

TABLE 67. Concentrations of trace-elements in 'blanks' incorporated randomly within batches of soil and herbage samples.

This also applies for the elements As, Cu and Sn. However, whenever the blank concentration of these elements exceeded 10% of the soil/herbage sample values, the sample concentrations were 'blank deducted'.

APPENDIX 3

SOIL CLASSIFICATION IN SOUTH-WEST ENGLAND

The original soil series names as used by Staines (1979) are used throughout this thesis. Some of these names have now been superseded, however, and the table below clarifies the present situation:

Original soil series name	New soil series name
Highweek	<80cm deep - Denbigh >80cm deep - East Keswick
Trusham	<80cm deep - Trusham >80cm deep - Erisey
Dartington	<80cm deep - Manod >80cm deep - Meline
Moretonhampstead	Moretonhampstead
Moor Gate	Moor Gate
Trink	Trink

APPENDIX 4

SOIL PROFILE DATA



APPENDIX 5

SAMPLE LOCATIONS AND ANALYTICAL DATA DETERMINED FROM THE ROCK SAMPLES



APPENDIX 6

TRACE-ELEMENT DATA OBTAINED FROM THE TRAVERSE SAMPLES LOCATED AT WHEAL TREMAYNE AND WHEAL SISTERS



APPENDIX 7

CONCENTRATIONS OF Sn, Cu and As RECORDED AT TREREIFE SMELTING WORKS

Sample No.	Sn			As			Cu		
	Topsoil	Subsoil	RTE	Topsoil	Subsoil	RTE	Topsoil	Subsoil	RTE
S1	258	87	2.97	263	303	0.87	179	276	0.65
S2	243	185	1.31	177	169	1.05	95	104	0.91
S3	204	148	1.38	165	181	0.91	98	111	0.88
S4	253	162	1.56	130	118	1.10	79	88	0.90
S5*	722	628	1.15	93	84	1.11	60	53	1.13
S6**	388	-	-	92	-	-	66	-	-
S7	318	250	1.27	96	102	0.94	80	80	1.0
S8	310	263	1.18	106	153	0.69	81	100	0.81
S9	409	325	1.26	184	267	0.69	113	152	0.74
S10	349	290	1.20	165	178	0.93	90	98	0.92
S11*	874	604	1.45	95	99	0.96	65	60	1.08
S12	383	373	1.03	103	84	1.23	82	119	0.69
S13	335	409	0.82	140	101	1.39	75	100	0.75
S14	371	364	1.02	86	152	0.57	82	104	0.79
S15	338	391	0.86	210	242	0.87	112	114	0.98
S16	334	359	0.93	166	186	0.89	88	96	0.92
S17	395	338	1.17	189	238	0.79	98	104	0.94
S18	222	121	1.83	124	126	0.98	76	82	0.93
S19	264	318	0.83	190	240	0.79	158	400	0.40
S20*	1866	2398	0.78	162	134	1.21	88	70	1.26
S21*	854	1028	0.83	126	166	0.76	55	50	1.1
S22*	928	1707	0.54	121	155	0.78	37	44	0.84
S23**	218	-	-	271	-	-	162	-	-
S24	448	153	2.93	204	246	0.83	104	162	0.64
S25	203	166	1.22	167	188	0.89	94	108	0.87
S26**	324	-	-	239	-	-	132	-	-
S27	202	240	0.84	223	230	0.97	94	104	0.90
S28	225	153	1.47	195	176	1.11	80	82	0.98
S29	275	279	0.99	297	414	0.72	118	142	0.83

S30	534	488	1.09	99	102	0.97	72	55	1.31
S31	401	509	0.79	111	116	0.96	76	68	1.12
S32	357	141	2.53	98	110	0.89	69	72	0.96
S33	389	544	0.72	101	110	0.92	71	67	1.06
S34	301	262	1.15	116	97	1.20	62	64	0.97
S35	262	203	1.29	89	88	1.01	71	78	0.91
S36	166	141	1.18	93	104	0.89	66	70	0.94
S37	153	125	1.22	132	135	0.98	101	114	0.89
S38	170	112	1.52	87	87	1.00	63	75	0.84

All values in µg/g.

R.T.E. = Relative Topsoil Enhancement ratio

* signifies that the soil has been affected by the river flooding

** indicates a shallow soil where a topsoil could only be sampled.

APPENDIX 8

DETAILS RELATING TO THE 12 FARMS INVESTIGATED IN THIS RESEARCH

LOCATION AND SITE CHARACTERISTICS OF EACH FARM

	Grid Reference	Parent Material	Soil Series
'Low' As Sites (<110µg As/g)			
Site 1	SW 488341	Granite	Moretonhampstead
Site 2	SW 494352	Granite	Moor Gate
Site 3	SW 500368	Granite	Moretonhampstead
Site 4	SW 503400	Greenstone	Trusham
Site 5	SW 595298	Granite	Moretonhampstead
'Moderate' As Sites (soils contain 110-190µg As/g)			
Site 6	SW 533342	Slate	Highweek
Site 7	SW 586375	Slate/Greenstone	Highweek/Trusham
'High' As Sites (soils contain >190µg As/g)			
Site 8	SW 543338	Slate/Greenstone	Highweek/Trusham
Site 9	SW 587348	Slate	Highweek
Site 10	SW 594358	Slate	Highweek
Site 11	SW 589373	Slate/Greenstone	Highweek/Trusham
Site 12	SW 615373	Slate	Highweek

..../continued over

APPENDIX 1

Washed and unwashed herbage analytical data, contamination ratios and relative accumulation ratios derived from the 12 sites investigated.