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Release of Metals from Plant Surfaces

by

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Thesis submitted for the degree of Doctor of Philosophy in the University of London and for the Diploma of Membership of the Imperial College of Science and Technology.

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ABSTRACT.

Evidence is presented that plants lose metal-containing material from their foliage in particulate and volatile forms, as well as by leaching. It is argued that such processes may significantly influence atmospheric concentrations of trace elements. Particles collected from plant surfaces in London were enriched in many heavy metals compared to herbage and soil (dry weight basis), and this was attributed to atmospheric contamination. However, in mineralised rural areas of southwest England, local geochemistry was a significant factor influencing the concentrations of many elements in surface particles of Ulex europaeus. Data indicated that both soil dust and plant fragments were involved in these geochemical correlations. Leachates were obtained by collecting deposited materials under Pinus sylvestris forests and compared with the deposition on open ground. There was no appreciable foliar loss of Zn, Cu or Pb, with amounts collected depending on atmospheric fallout. Mn, K and Na, however, were significantly leached. 'Forest' deposition, less 'Open', ($kg.^{-1}$ $ha.^{-1}$ yr.) was 23.5 for Na, 22.4 for K and 1.1 for Mn. Greater apparent leachability and similar overall trends were observed with Sorbus aucuparia and Betula pendula, although results were complicated by extraneous dust on foliage. The processes of particulate loss and leaching were further investigated using radioactive isotopes absorbed by small conifers. In leaching experiments at pH 3.1, the loss of ^{65}Zn in 24h. from Cupressus leylandii averaged 0.1% of the isotope in foliage. From Tsuga heterophylla in similar conditions, 1% of ^{65}Zn and about 8% of ^{54}Mn were leached. Levels of radioactivity in particles on the plant surfaces and associated with evapotranspirates, however, were very low. The roles of vegetation as a source of trace elements in the atmosphere and as a 'sink' for particulate pollutants are discussed. The potential use in mineral exploration of particles collected from soil and plant surfaces is considered.

ACKNOWLEDGEMENTS.

I would like to thank my supervisor, Dr. J. Barber, for encouragement and valuable criticism, Dr. W. Beauford for help and advice, Dr. A.R. Barringer for continued interest in the work, and Ms. E. Roberts for her impeccable typing of this thesis.

I am grateful to Barringer Research Limited, Toronto, Canada and Mr. M.T. Luton for the analysis of numerous samples, Mr. P. Grant for assistance with electron microprobe analysis, Dr. P.W. Mueller and Mr. R.G. Davies for help with computing, and Mr. E.E. Green for help with experiments at Silwood Park.

The co-operation and help of the following persons and organisations has been appreciated during the field work: Mr. G. Cox, owner of the site at Ecton mine, Staffordshire; The Crown Estates, Windsor, Berkshire, particularly Mr. J.J. Taylor and Mr. D. Stickler; The Tavistock Woodlands Estate, Gulworthy, Tavistock, Devon, particularly Mr. P.A. Hutt; and The Institute of Hydrology, Crowmarsh Gifford, Wallingford, Berkshire, particularly Dr. J. Roberts.

This work was carried out while I was in receipt of a Natural Environment Research Council studentship.

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1. INTRODUCTION.

There is increasing interest in the extent and mechanisms of dispersion of metals in the environment, because certain of them can be toxic at trace levels and because their impact as pollutants has increased with industrial growth. This particularly applies to the 'heavy metals', defined as metals with a density greater than 5 $g.cm^{-3}$. Heavy metals are dispersed by a wide variety of human activities such as mining, extraction of metals from ores, burning fossil fuels and the use of agricultural chemicals. They tend to be cumulative poisons because they are not easily eliminated from biological systems and therefore accumulate in plant ecosystems and animal food chains, as well as in sewage.

Because of the concern over pollution, natural pathways of trace metal cycling tend to be overlooked. For example, several heavy metals are essential plant nutrients, and it is well established that plants absorb many elements for which they have no known nutritional requirement. The soils and rocks on which plants grow show wide variability in their contents of metals, and the distribution and performance of plant species are often restricted by mineral deficiencies and toxicities. One way in which these effects are useful is in the study of vegetation as a guide to locating economic ore deposits. Mapping the geographical distribution of plant species and communities is the basis of 'geobotany', while the chemical analysis of selected plants or plant parts is the allied science of 'biogeochemistry' (Brooks, 1972). Interest in the remote sensing of natural resources has led to the expansion of these concepts. The interpretation of aerial photographs is obviously related to geobotany, while the use of various detector systems mounted in aircraft or satellites, recording quantitative data such as spectral reflectance, is an extension of biogeochemistry. A further concept is that anomalous concentrations of trace elements may be present in the atmosphere, related to geochemical anomalies. In vegetated regions, such atmospheric aureoles would depend largely on the uptake of metals by plants and on processes influencing any dispersion into the atmosphere. If plants are capable of releasing trace elements into the atmosphere, it is also important to consider their general significance as a source of aerosol. It is towards a better understanding of these possibilities that the work presented in this thesis is directed.

1.1 Metal uptake and distribution in plants.

Release of metals from plant shoots can be expected to be influenced by the uptake of metals into plants, and their distribution on an organ or tissue level and on a sub-cellular level. Release must also depend on the chemical forms of metals within plants. The composition of plant tissues is in turn dependent, to some extent, on the essentiality of mineral elements. The major mineral elements required by green plants are N, P, K, S, Ca and Mg. The micronutrients currently recognised to be essential to all higher plants are Fe, Mn, Cu, Zn, B and Mo (of which all except B are heavy metals). Other elements may be essential to certain plants or in certain circumstances (e.g., Co, Ahmed & Evans, 1960, 1961; V, Arnon & Wessel, 1953; I, Borst Pauwells, 1961; Na, Brownell & Wood, 1957; Cl, Broyer *et al.*, 1954; Se, Trelease & Trelease, 1938; see Peterson, 1973). However, the composition of plant tissue is by no means restricted to these elements.

The concentration of every metal in soils depends on climate, the parent material from which the soil was formed, and topography. Moreover, the concentration of a metal available to plants - conceptually, the concentration in the soil solution at the root surface - is the result of an extremely complex network of interacting factors, including (1) the release from soil minerals and organic residues by weathering, strongly affected by biological activity, (2) the solubility of metal ions under different conditions, particularly pH and oxidation-reduction conditions (aeration and waterlogging), and (3) adsorption on to clay minerals and humus, and uptake by bacteria.

For many metals, including Fe, Al, Mn, Zn, Cu, Pb and Cd, there is a general increase in solubility as pH decreases (e.g. Andersson, 1975) and metal toxicities are often associated with acid soils, which includes many mine wastes (Foy et al., 1978). The situation can be complicated by metals having more than one ionic form. For example, manganese occurs in the available Mn^{2+} form in reduced (waterlogged) soils, as opposed to the insoluble Mn^{4+} ion predominating in well-drained soils, and thus Mn toxicity can occur in waterlogged alkaline soils (Gupta & Chipman, 1976). Metal availability is further complicated by the presence of natural, soluble organic chelates (DeKock & Mitchell, 1957).

Although there has been some success in correlating the uptake of some metals by plants with available levels in soils, estimated by various mild extraction procedures, plants differ enormously in their uptake in the same soil. Sometimes the variation is definable (for example red clover takes up more copper from soil than does ryegrass for a given increase in EDTA-extractable soil Cu; Mitchell, 1972) but in other cases the assessments of availability do not seem to be useful. For example, Evans et al. (1974) found that Zn uptake by maize could be predicted quite well by any of three soil extraction procedures, but that the correlations for sorghum were poor. Shewry & Peterson (1975) found that 12 methods of measuring chromium availability were all unsatisfactory. Because of problems with 'availability' and because, in most biogeochemical work, only total metal levels in soil are measured, plant uptake is often given in relation to total soil levels (see Brooks, 1972).

Listing the factors affecting elemental uptake by plants, Brooks (1972), considered the most important to be (1) type of plant, (2) organ sampled, (3) age of organ, and (4) root depth. All these factors were given higher priority than the soil factors already discussed.

The use of a plant, or plant organ, for biogeochemical prospecting requires some change in uptake in response to changing soil concentrations. Two types of response which have been found are given below (species used as examples are cited by Brooks, 1972, and Peterson, 1975):

(1) Exclusion, up to a threshold soil concentration, at which the plant metal content increases dramatically, e.g. copper and lead in *Triodia pungens*. This breakdown of the exclusion mechanism is associated with toxicity, and the plant ceases to occur on soils containing yet more metal. Exclusion of this type can be useful in providing an 'enhanced contrast' between mineralised and non-mineralised sites. It seems likely that any exclusion mechanism must break down at a high enough soil concentration, and that this may be a general explanation of toxicity. However, it is possible to envisage the margin of soil concentration between exclusion-breakdown and fatal toxicity being extremely small, or a very slight increase in the metal content of the plant being fatal, in which case the plant would not be useful in biogeochemical prospecting.

(2) Linear increase in plant content with increasing soil content, e.g. uranium in *Coprosma australis* and zinc in *Triodia pungens*. This response can often be expressed as

a constant plant/soil ratio at increasing soil metal levels, but with essential nutrients the ratio increases at low soil metal concentrations. Antonovics _et_ _al_. (1971) review evidence which tends to show that, in general, zinc uptake by plants increases in a more-or-less linear pattern with increasing soil content, whereas copper levels tend to remain remarkably constant, as in the exclusion situation above. Nevertheless, N.A.S.A. (1968) list 50 sampler plants for biogeochemical prospecting for Cu, although the number given for Zn was 120.

Metal-tolerant plants showing a biogeochemically useful response in the shoots or in a particular organ must inevitably contain 'high' concentrations of the mineralised element. If the concentration in the plant exceeds the estimated-available or total concentration in the soil, the plant can be said to be an 'accumulator', although the word is also used to refer to any unusually high concentration (Peterson, 1971). Accumulator plants have been found for a wide variety of elements all over the world and include most types of plant, although the examples given by Peterson (1971) seem particularly deficient in grasses. The same seems to be true of the species listed by N.A.S.A. (1968) as plants found to be useful in biogeochemical prospecting. A possible reason is suggested later in this section. Apart from an apparent paucity of grasses, biogeochemically useful species are taxonomically diverse, including many conifers and both woody and herbaceous angiosperms, and some lower plants. Plants with deep root systems are often preferred because they are potentially able to indicate deeply-buried ore bodies.

Accumulation of volatile elements is interesting in the context of this review. Warren _et_ _al_. (1968) found that arsenic accumulated up to 10 000 ppm (ash weight) in the growing tips of Douglas fir over sulphide mineralisations. Arsenic was thus suggested as a 'pathfinder' for other metals. Since As is volatile, there may be atmospheric despersion aureoles, partly generated by trees, over mineralisations, although I am not aware that this has ever been tested or exploited. A similar situation undoubtedly exists with regard to selenium which is accumulated by various plants and volatilised (Lewis, 1975), and may apply to mercury accumulators, e.g. Pinus contorta and Betula papyrifera (Warren et al., 1966).

The work that has been done on the physiology of metal tolerance has concentrated on grasses and a few herbaceous plants, and generally shows that metal-tolerant plants take up large quantities of metals. Exclusion from the whole plant does not normally seem to be a tolerance mechanism (Antonovics, 1975; Ernst, 1975b), although some plants seem able to restrict their Al, Mn, and Fe uptakes (Foy et al., 1978).

Two distinct patterns of root/shoot metal distribution have been found in tolerant plants. In grasses of the Agrostis genus, tolerant populations contain similar metal levels to non-tolerant plants in the shoots but accumulate excess metal in their roots (Wu & Antonovics, 1975, Cu and Zn; Peterson, 1969, Zn). Three tropical tolerant grasses also tended to show this distribution of Pb, Cu, and Zn, but the data for Stereochlaena indicated some relationship between soil and leaf levels of Cu, Pb, Zn and Mn (Reilly & Reilly, 1973). If shoot-exclusion is widespread in grasses, it could explain why they are not more widely used in biogeochemical work. The opposite pattern of leaf-accumulation is shown by non-grasses (Reilly & Reilly, 1973, Cu). Accumulation of Cu in the leaves of Becium homblei appears to be an adaptive mechanism, because the copper is largely removed from the plant by bush fires at the end of the growing season (Reilly & Stone, 1971). This suggests one route in which metals may enter the atmosphere from plants, i.e. as particles or in some cases volatile forms during bush and forest fires, particularly over mineralisations, but no direct evidence is available. Robinson & Robbins (1971) consider the worldwide particulate emissions from this source to be extremely small, on a total aerosol mass basis. Also, leaf abscission may be a general detoxification mechanism for plants which accumulate metals in their leaves.

There are various references to seasonal changes in the metal contents of plant leaves (Sampson & Samisch, 1935, oak; Lounamaa, 1956, woody plants; Davy & Taylor, 1975, Deschampsia (grass); Ernst, 1975a, tropical trees) but it is not possible to make useful generalisations. For example, Guha & Mitchell (1966) found that zinc concentra-- tions decreased during most of the growing season in sycamore and horse chestnut, rising before abscission, but showed a steady, gradual rise throughout in beech. Seasonal changes must be considered for each metal within defined limits of plant type and environment.

For a tolerant plant to absorb a metal to concentrations which would kill a non-tolerant plant, it must either prevent the metal reaching biochemically active sites (e.g. enzymes) where it would have toxic effects, or it must have evolved biochemical resistance to the toxic action, or both. There is evidence that acid phosphatase enzymes of Zn-tolerant Anthoxanthum odoratum are resistant to Zn (Cox & Thurman, 1978), and that similar enzymes of Cu-tolerant Agrostis tenuis are resistant to Cu (Wainright & Woolhouse, 1975), and the evidence below shows that zinc (at least) is also inactivated by binding to cellular, or extra-cellular, components. In Agrostis, in which the main site of accumulation is in the roots, zinc is bound to cell wall fractions (Peterson, 1969; Turner & Marshall, 1971). Mathys (1977) suggested that Zn may be stored within cells, bound to ligands which prevent it interfering with metabolism, and stored in the vacuole. He gave evidence that malate, oxalate, and mustard oils are in some way involved with Zn tolerance in four species (genera Silene, Rumex, Thlaspi, and Agrostis) and suggested that these compounds are complexing agents. Vacuolar storage would be analogous to the accumulation of salt in the vacuole by halophytes (Flowers et al., 1977). However, the hypothesis does not explain the independence of Cu and Zn tolerance, since malate would be expected to bind both metals and, furthermore, in vivo evidence of vacuolar Zn storage is lacking (Foy et al., 1978). Using centrifugation of broken cells, Ernst & Weinert (1972) showed that 50% of the Zn was associated with the vacuolar fraction of Silene and only 10% with the cell walls, but electron microscopy confirmed only Zn accumulation in the walls and not vacuolar storage. Nevertheless, it seems true that tolerance to Zn is associated with some form of immobilisation, and essentially similar mechanisms could apply to tolerance of other metals like Cu, Pb, and Cd. If the strategy of plants is thus to immobilise excess metals in insoluble form, it does not seem likely that much metal release by leaching is likely to occur while a plant or organ is living, even in metal-stress conditions. However, if fragments of tissue are lost, these could contain enhanced levels of metals.

A different situation may apply to manganese, because Mn binding or chelation does not seem to be an important mechanism for detoxifying excess levels of Mn within plants (Foy et al., 1978). Mn tolerance in certain plants has been attributed to reduced absorption, less translocation of excess Mn to plant tops, and/or greater tolerance to high Mn levels within plant tissues (Foy et al., 1978). Thus, if Mn remains mobile in plants, one can speculate that Mn removal from foliage (e.g. by leaching), could contribute to detoxification, and that the extent of Mn removal in this way could be correlated with soil Mn levels.

1.2 Metal release by plants into the atmosphere.

Beauford et al. (1975) showed that pea and bean plants labelled with ^{65}Zn absorbed through the roots released zinc from the foliage into the atmosphere. Radioactivity was collected with a 'Casella' cascade impactor, or on 0.22 µm membrane filters and in solid CO_2/methylated spirit cold fingers, and appeared to be associated with submicron particles. The rate of release depended on the level of ^{65}Zn in the foliage, on continuous uptake of ^{65}Zn, and was enhanced by light. The highest rate of Zn release found was 21.0 pg.$h^{-1}cm^{-2}$ leaf area. Similar results were reported for Pinus sylvestris. Later, Beauford et al. (1977) gave results of ^{210}Pb release from peas, showing a maximum rate of release of 0.013 pg.$h^{-1}cm^{-2}$, depending on concentration in the leaves as for ^{65}Zn. Both isotopes could be removed from leaves to a much larger extent in water leachates than in chloroform leachates. These workers also showed that labelled particles above approximately 2 µm diameter could be collected from the surface of labelled Pinus sylvestris seedlings. Isotopes used were ^{65}Zn, ^{115m}Cd, and ^{210}Pb. On a dry weight basis, particles contained between 0.65 and 1.69 times the concentration of isotope in the needles. The foliage had been kept dry throughout the experiment.

Movement of ionic salts into the atmosphere during evapotranspiration was demonstrated by Nemeryuk (1970), and assumed to involve submicron particles. The equivalent cation contents of evapotranspirates in field conditions were in the order $Ca^{++} > Na^{+} > Mg^{++} > K^{+}$ and were usually higher over vegetation than over bare soil. Release seemed greater by day than at night, and was demonstrated for a wide variety of herbaceous plants. The total ionic content of evapotranspirates was 6 to 19 parts per million, calcium comprising 0.21 to 2.74 ppm. The author ruled out the possibility of direct condensation or deposition from aerosol as an important source of contamination, but accumulated salts deposited on leaves could have been involved. However, release of endogenous Ca (0.21 to 1.78 ppm) was confirmed by using radioactive ^{45}Ca.

A wide variety of plants emit volatile hydrocarbons (terpenes) into the atmosphere, such as isoprene and α-pinene (Rasmussen, 1972; Tyson, 1974). Went (1964) showed that α-pinene forms particles by a photochemically induced process in the size range 0.01 to 1 µm, in the presence of NO_2 or I_2 as light-absorbing agents. He has used this observation as a basis of his hypothesis that vegetation is a source of natural smog. However, cities are also a very concentrated source of sub-micron particles (condensation nuclei), and Went (1964) reported 15,000 to 100,000 nuclei.cm^{-3} in city air, compared with 1,000 to 10,000 nuclei.cm^{-3} in the country. In both environments a diurnal cycle was observed which supported his hypothesis of photochemical formation of particles. There was a rapid increase in the concentrations of the smallest particles immediately after sunrise, and after about an hour concentrations of larger particles began to increase, presumably due to agglomeration. In late afternoon and at night the total concentration decreased.

It is interesting that Went _et al_. (1967) showed the same effect of small particle formation in the air, and the same diurnal cycle, in a desert region of Colorado as in an isolated mountain forest in Nevada, although only in the latter site were terpenes detectable, using gas chromatography. This suggests that condensation nuclei were produced by the soil surface, supporting Twomey's

(1960) contention that radiation heating of a dry soil surface is an even more important source of sub-micron particles than urban, marine and plant sources, and that plants can hinder particle formation. Lopez (1974), however, found that a pine forest in southwest France was an intense source of sub-micron particles, giving particle formation rates per unit ground area which were approximately 3 times that in an agricultural area of cereal crops, and about one fifth of the rate in urban Toulouse.

Arpino _et al_. (1972) obtained enough aerosol material in a remote pine forest in southwest France for chemical analysis. Air was drawn through polystyrene filters which were analysed chromatographically. It was found that the filtered material contained aliphatic hydrocarbons characteristic of pine cuticular waxes. The substances analysed were large, non-volatile alkanes (above C_{11}) whose concentration was estimated as 0.1 $\mu g.m^{-3}$ of air. This compares with Went's (1974) estimate of the amount of terpenoid 'natural smog' in country air of 2 to 20 $\mu g.m^{-3}$ of air, which indicates that photocondensation products may be more important in aerosol than solid wax particles from trees. The mechanism of non-volatile wax loss from pine trees could involve abrasion between needles, or electrical discharge effects at the tips of needles as described by Fish (1972).

Enormously variable estimates of the total production of hydrocarbons by vegetation have been made (see Rasmussen, 1972). Robinson & Robbins (1971) estimated that the annual emission rate from this source is 200 x 10^6 tons.yr^{-1} (compared with 296 x 10^6 tons.yr^{-1} from all anthropogenic hydrocarbon sources) and conclude that there is inadequate evidence for the much higher estimates of two to ten times this figure that have been made. One can only conclude that the contribution of natural hydrocarbons to aerosol is large but quantitatively uncertain.

The question arises as to what extent metal loss from plant surfaces might be associated with volatile or particulate exudates from plants. Curtin et al. (1974) collected exudates from lodgepole pine (Pinus contorta), Engelmann spruce (Picea engelmannii) and Douglas fir (Pseudotsuga menziesii) by enclosing branches, first rinsed in demineralised water, in large polythene bags for 5 to 10 days. The condensed exudates were found to contain a wide variety of elements. In particularly high concentrations in the ash of exudates relative to the ash of needles and twigs were Na, Li, Mo, Ni, Sn, Cd, Cu, Zn, Bi, Cr, Ag, Mg, and Sr. The contamination checks in this work were extremely thorough, but in my view the workers could not completely prevent the possibility of previously deposited aerosols being involved despite washing. Although the substances could have been released in association with terpenoid compounds, it is also possible that they were leached out in an aqueous phase. To provide more natural conditions, Curtin et al. (1974) enclosed a branch of lodgepole pine; air (filtered through a glass fibre filter) was drawn over the branch and exudates were condensed in refrigerated coils. Seven elements were listed as being contained in the condensates, but a control experiment did not appear to have been carried out. Luton (unpublished) found that ^{65}Zn and ^{112}Cd did not appear to be associated with cuticular waxes of pea (Pisum sativum) leaves but could be removed by leaching with water.

It is likely that most metals in the atmosphere must be associated with particulate matter, but some metal compounds, and elemental mercury, have appreciable vapour pressures at ambient temperatures. Release of gaseous mercury from aquatic reed grass (Phragmites communis) has recently been demonstrated (Kozuchowski & Johnson, 1978). Mercury release at two sites with mercury contamination in the soil was 4 times and 19 times respectively the level at a control site. Selenium (a non-metal) can be absorbed from the atmosphere or via the roots, and released to the atmosphere. Non-accumulator plants release dimethyl selenide while accumulators release dimethyl diselenide (Lewis, 1975). Several metals have volatile alkyl compounds and there is evidence that biological systems can form such compounds. In vitro methylation of inorganic mercury has been demonstrated with a protein fraction from Pisum sativum (Gay, 1975). Microbial alkylation has been demonstrated for Hg, Se, Te, As, and Sn, and postulated for Pt and Au (Jernelöv, 1975). Microbial alkylation could be significant in metal release from higher plants if the micro-organisms are present on plant surfaces.

Based on results of laboratory experiments, Schnell & Vali (1972, 1973) suggested that decomposing leaf litter might be an important worldwide source of atmospheric condensation nuclei. If so, leaf litter could contribute to heavy metals in the atmosphere because it strongly binds heavy metals (e.g. Somers, 1975; Lawrey, 1978).

Perhaps the most obvious forms of particulate production by plants are pollen and the spores of plant pathogens. While these particles are produced seasonally in enormous numbers and capable of travelling large distances, there is no evidence that they contribute significantly to atmospheric loadings of heavy metals (see Section 1.4). As biological material, their heavy metal contents would be expected to be low, but their content of Na, K, Ca, and Mg could make them significant contributors for these metals.

1.3 Foliar leaching.

It was suggested in the last section that leaching might be involved in the availability of metals at plant surfaces for release into the atmosphere. It is already well established that leaching of foliage by rain, mist, or dew is a significant factor in biogeochemical cycling (e.g. Duvigneaud & Denaeyer-de Smet, 1970) and in loss of nutrients from agricultural crops (e.g. Tukey *et al*., 1962). The great majority of work has concentrated on leaching of major nutrient elements, and trace metals have only been studied in few reports.

Tukey *et al*. (1958) used radioisotopes of eleven elements to study leaching from bean (*Phaseolus vulgaris*) and squash (*Cucurbita pepo*) leaves. Plants were labelled via the roots. Leaching for 24 h. with a mist spray of distilled water caused 25 to 45% of the ^{22}Na or ^{54}Mn in leaves to be lost. Losses of ^{45}Ca, ^{28}Mg, ^{35}S, ^{42}K, and ^{90}Sr were between 1 and 10%, while $^{55-59}$Fe, ^{65}Zn, ^{32}P, and ^{36}Cl were difficult to remove, showing leaching losses under 1%.

Beauford *et al*. (submitted to Physiol.Plant.) studied the uptake and leaching of Cd, Zn, and Hg by *Pisum sativum*, using radioisotopes. They found that usually less than 1% of the total amount of each metal in the leaves was removed by leaching for 10 minutes with water at pH 6.0, containing 0.1% 'Tween' as a wetting agent. The amounts of each metal leached were correlated with metal levels in the leaves, which in turn depended on metal concentrations in the external solution.

Research on leaching in field situations has concentrated almost entirely on trees, from which it is obviously easy to collect leachates. Some of the rain which falls on woodland evaporates from the canopy, while the remainder reaches the ground either by dripping from leaves ('throughfall') or running down the trunks ('stemflow'). Some workers have included stemflow in their measurements, using collectors similar to that described by Likens &

Eaton (1970). The contribution of stemflow to the total water volume reaching the forest floor has been reported as ranging from 1 to 20% (see Kaul & Billings, 1965), and was less than 5% under hardwoods at Hubbard Brook, U.S.A. (Leonard, 1961) and 2% under Quercus petraca in England (Carlisle et al., 1967).

A summary of the quantitative importance of foliar leaching from trees is given in Table 1.1. The only metals for which data are available are K, Na, Ca, and Mg, except for the work of Ulrich & Mayer (1972) who also measured Al, Fe, and Mn leaching (0.00, 0.64, and 3.47 $kg.ha^{-1}yr^{-1}$, respectively). The usual method of obtaining these data was to collect 'throughfall' and open-ground rainfall. Analysis of the samples enabled rates of deposition per unit ground area to be calculated in both sites, and the difference gave the deposition from the canopy. As a method of measuring leaching, the method is open to the criticism that aerosol deposited on the foliage will also be washed off and recorded as 'leachate'. However, by considering the ratio of two elements in rainfall, one can deduce more about the importance of leaching relative to aerosol-trapping. For example, the average K : Na ratio in rainfall was 2.8 : 19.3 and in throughfall 24.2 : 33.0 (Madgwick & Ovington, 1959) which means that potassium leaching at least could not be in doubt. Other work, cited by Duvigneaud & Denaeyer-de Smet (1970), supports this example.

One of the most striking features of Table 1.1 is the very high potassium leaching reported in a tropical (Ghana) and a sub-tropical (Natal) forest, perhaps suggesting an influence of temperature and/or humidity. Zamierowski (1975) found that leaves of the tree Cassiopourea malosana growing in a moist montane forest in Kenya were more susceptible to K leaching than leaves of the same species in a dry montane forest. Leaf morphology

Table 1.1. Annual removal of metals from tree canopies by rain (partly after Attiwill, 1966).
(Corrected for composition of incident rainfall)

Species	Locality	Removal ($kg.ha^{-1}yr^{-1}$)				Reference
		K	Na	Ca	Mg	
	Natal, S. Africa	320		194		see Attiwill, 1966
Hardwoods (*Nothofagus*, *Quercus*)	Bedgebury, S.E. England	25	12	14	7	Madgwick & Ovington, 1959
Larix eurolepis		25	20	21	8	
Tsuga heterophylla		14	27	19	6	
Pseudotsuga menziesii		25	12	19	5	
Pinus nigra		16	5	8	2	
Thuja plicata		11	5	9	1	
Pinus radiata	Rotorua, N.Z.	18	24	1		Will, 1959
Pseudotsuga menziesii		19	-2	2		
Oak	Voronezh, USSR	3		6	1	see Attiwill, 1966
Aspen		2		5	1	
Pinus		1		6	1	
Eucalyptus obliqua	Mt. Disappointment, S.E. Australia	12	8	6	2	Attiwill, 1966
Tropical forest	Kade, Ghana	196		26	16	see Attiwill, 1966
Quercus/*Fraxinus*	Belgium	24		11	7	Duvigneaud & Denaeyer-de Smet, 1970
Quercus petraea	U.K.	25	20	10	5	Carlisle, *et al.*, 1966
Quercus petraea		17	37	14	6	Carlisle, *et al.*, 1967
Acer/*Fagus* *Betula*	Hubbard Brook, New Hampshire, U.S.A.	30	0.3	7	2	Eaton *et al.*, 1973 June-Oct incl., only
Pinus banksiana	Ontario, Canada	8		2	1	Foster & Morrison, 1976
Mixed hardwoods	Georgia, U.S.A.	26	2	4	2	Best, 1971
Fagus sylvatica	Solling, Germany	24	6	20	2	Ulrich & Mayer, 1972

differed in the two environments, and it is possible that low leachability accompanied adaptations for restricting water loss. Ca, and to a lesser extent Mg, leaching showed the same trend but were quantitatively much smaller. Wallace (1930, cited by Tukey, H.B., Jnr., 1970) found that more than 80% of K in apple leaves could be leached in 24 h. Long et al. (1956) showed that 71% of ^{42}K in bean plants labelled through the roots could be leached from plants kept in the dark, but only 5% from plants grown in the light.

Madgwick & Ovington (1959) found seasonal trends, in metal concentrations in throughfall. While the trend for Na seemed to depend on Na concentrations in rainfall, with a peak in winter, K and Ca showed definite seasonal variations in leaching. These trends were most marked under deciduous canopies, which lost more K and Ca than evergreens in summer, but less in winter (also Henderson et al., 1977). There is evidence that leaching reaches a peak in autumn associated with leaf abscission (Eaton et al. 1973; Madgwick & Ovington, 1959; Voigt, 1960) under evergreens (which show maximum leaf fall in autumn in New Zealand; Will, 1959), as well as under deciduous trees.

Cation leaching is thought to involve ion-exchange, by which hydrogen ions in rainwater are exchanged for metal cations in leaves (Tukey et al., 1965). It follows from this hypothesis that decreasing the pH of the leaching solution should increase foliar leaching, for which there is much experimental evidence for Ca (Mecklenburg et al., 1966; Wood & Bormann, 1975; Fairfax & Lepp, 1975). For K and Mg, the mechanism did not seem to apply in Nicotiana (Fairfax & Lepp, 1975) but did apply in Phaseolus and Acer (Wood & Bormann, 1975). Blackman (1977) and Beauford et al. (submitted to Physiol.Plant.) found that decreasing the pH increased ^{65}Zn leaching from Pisum. At pH values below approximately 3.0, increases in leaching can be attributed to tissue damage (Wood & Bormann, 1975; Ferenbaugh, 1976; Evans _et_ _al_., 1977). Increases in leaching can also be caused by other forms of damage to foliage (Tukey & Morgan, 1963). The effect of pH on leaching and plant damage is of considerable environmental importance because of the phenomenon of acid rain, caused by industrial sulphate pollution (Mellanby, 1977).

The main route of cation leaching from healthy plants is through the cuticle rather than via stomata (Franke, 1967). Therefore, leaching would be expected to depend on factors affecting wettability, such as leaf shape, waxiness, and hairiness. (Wettability is usually defined in terms of the contact angle of a drop of water on the leaf surface). The main factor determining the wettability of glabrous leaves of a wide range of plants grown in a glasshouse was the chemical composition of the surface wax, though effects of surface roughness and water-repellancy in which wax was not involved were also noted (Holloway, 1969). The morphology of wax is largely determined by its chemical composition, giving rise to distinctive 'blooms' and plate-like structures (Chambers _et_ _al_., 1976), and by environmental factors such as temperature (Whitecross & Armstrong, 1972; Haas, 1977). Highly bloomed leaves are difficult to wet, but blooms are very susceptible to abrasion and consequently tend to be lost on older leaves (Eglinton & Hamilton, 1967; Martin & Juniper, 1970). While some plants (e.g. _Eucalyptus_) reform their wax rapidly if it is removed, others (e.g. _Pisum_) show virtually no recovery (see Martin & Juniper, 1970). Because of a loss of wax and an increase in general damage (Amsden & Lewis, 1966; MacKerron, 1976) wettability increases with leaf age, and leaching losses have also been shown to increase with leaf age (Tukey _et_ _al_., 1958).

Some plants have specialised excretory and secretory structures, which Esau (1965) considers to be generally responsible for removing or compartmentalising by-products of metabolism and toxic substances. These structures include hydathodes, nectaries, trichomes and glands, and the salt-glands of halophytes and xerophytes which carry out salt removal in osmotically difficult environments (Lüttge, 1971). Heavy metal excretion by such structures could occur but as yet there are no reports of such an effect. Internal secretory structures include laticifers ('latex bearers'), and one species has been found to accumulate nickel to 25% of the dry weight of latex, presumably as a detoxification mechanism (Jaffre et al., 1976).

1.4 Trace elements in the atmosphere.

Having considered various possible ways in which plants may contribute to the trace element chemistry of the atmosphere, it is now relevant to review direct evidence from atmospheric research on the sources and concentrations of trace elements in the air.

Even at extremely remote sites such as the South Pole and mid-Atlantic, the air contains filterable particles containing a wide variety of elements (Zoller et al., 1974; Duce et al., 1975). For example, air concentrations of elements at the South Pole ranged from 7.2×10^{-9} g.m^{-3} of sodium to 17×10^{-15} g.m^{-3} of europium. By calculating an enrichment factor (EF) for element 'X' relative to its average concentration in the Earth's crust or the sea, its possible origin can be seen.

$$\text{EF sea} = \frac{(\text{X} / \text{Na})\ \text{air}}{(\text{X} / \text{Na})\ \text{sea}}$$

$$\text{EF crust} = \frac{(\text{X} / \text{Al})\ \text{air}}{(\text{X} / \text{Al})\ \text{crust}}$$

(Duce et al., 1975).

EFs indicated that (apart from sodium) K, Mg, Ca and Sr originated from the sea. Sc, Fe, and Mn (and by assumption Al) seemed largely derived from crustal weathering, but progressively higher EF crust values were shown by the following series of elements:

$$\text{Fe}(\text{EF} \backsim 1) < \text{Mn} < \text{Co} < \text{V} < \text{Cr} < \text{Zn} < \text{Cu} < \text{Cd} < \text{Sb} < \text{Pb} < \text{Se}(\text{EF} \backsim 10{,}000).$$

Essentially similar results were given by Chester & Stoner (1973), who used Fe as the crustal reference element instead of Al.

The origins of enriched elements in remote aerosol are uncertain. Pollution is an obvious candidate but Duce et al. (1975) argued that pollutant particle residence times are very much shorter than interhemisphere mixing times and that enrichments at the South Pole therefore cannot be explained by pollution. These authors suggested that natural sources are involved, and it is interesting that Robinson & Robbins (1971) estimated that natural processes account for 89% of the total world mass of aerosol produced and all human activities only 11%. Therefore, natural processes seem very important in creating a global aerosol whose relative elemental composition is remarkably uniform and enriched in certain elements relative to soil and sea. Four natural processes which could be involved are considered below.

(1) Goldberg (1976) gave theoretical evidence that levels of several heavy metals in the atmosphere could be explained by rock volatility. However, Brimblecombe & Hunter (1977) considered that average temperatures at the Earth's surface

are not high enough for this mechanism to account for heavy metal concentrations in air, assuming that the metals occur as oxides. Nevertheless, other compounds, chiefly alkyls, are more volatile than oxides and could be produced microbially and by higher plants. For example, arsine (AsH_3), methyl arsine, and dimethyl arsine are all more volatile than As_2O_3.

(2) It has been shown that Cu, Fe, Zn, Ni, and Pb are enriched in the sea-surface microlayer relative to bulk seawater (Barker & Zeitlin, 1972; Piotrowicz _et al_., 1972) and that materials are concentrated by the process of bubble-bursting (MacIntyre, 1970; Blanchard & Syzdek, 1972). Therefore, larger amounts of certain elements could be derived from the sea than previous EFsea values suggest.

(3) As discussed in Section 1.2, trace element emissions by vegetation cannot yet be reliably quantified on a world scale, but the mass of particles produced is very considerable. Since plants, if one includes marine life, cover most of the Earth's surface, it is clear that they could play a very important role in the trace element chemistry of the atmosphere and in the uniformity of aerosol composition.

(4) The composition of aerosol near the Earth's surface depends not only on sources of aerosol, whether from industry, soil, oceans or vegetation, but also on the processes controlling their dispersal in the atmosphere. The lower atmosphere ('troposphere') is a zone of turbulent mixing, but the upper atmosphere ('stratosphere') is much more stable where particle residence times may typically be two years (Newell, 1971). It seems likely to me that deposition from the stratosphere must have a 'damping' effect on local variations in aerosol composition near the ground,

particularly as the concentration of aerosol ($g.g^{-1}$air) is much greater in the lower stratosphere than in the upper troposphere (Newell, 1971). The particulate content of the stratosphere is maintained by influx of natural and anthropogenic particles from the lower atmosphere, and by direct inputs from nuclear explosions (Newell, 1971), volcanoes (Dyer & Hicks, 1968; Newell, 1971), extra-terrestrial material (Perkin & Tilles, 1968), and perhaps aircraft.

Peirson et al. (1974) measured air concentrations of trace elements at rural sites in and around the U.K., and found a remarkably uniform aerosol composition, in agreement with the worldwide data already considered. Using scandium as the reference element for soil-derived material, and allowing for the marine origin of Na, Cl, and Br, they found EF soil close to unity for Al, Mn, and Fe, but considerable enrichments for Co, Cr, V, Ni, Sb, As, Zn, Se and Pb (EF soil increasing in approximately the order given). Taking the analysis further, they measured the dry deposition velocity (Vg) of each element to a filter paper surface,

$$\text{Vg (cm.sec}^{-1}\text{)} \quad = \quad \frac{\text{Rate of dry deposition } (\mu\text{g.cm}^{-2}\text{sec}^{-1})}{\text{Concentration in air } (\mu\text{g.cm}^{-3})}$$

and found that high Vg was correlated with low EFsoil and vice versa. Since fossil fuel combustion was expected to produce small particles (small Vg), whereas natural soil-derived particles would be larger (see below), this evidence supported the inference that enriched elements were derived from pollution sources. (Vg was in the range 0.1 to 1.0 $cm.sec^{-1}$).

Rain is important in removing particles from the atmosphere, and Cawse & Peirson (1972) calculated the washout factor (W) for each element.

$$W = \frac{\text{concentration in rain } (\mu g.kg^{-1})}{\text{concentration in air } (\mu g.kg^{-1})}$$

Values of W were found to range from about 400 to 3000 depending on the element.

Release of particles from a source requires energy which, in the case of natural processes, is often provided by wind. Wind-blowing of soil is most likely with dominant particle sizes between 30 and 100 µm, and minimum friction velocity of 20 $cm.sec^{-1}$, but blowing increases very rapidly with wind speeds above the threshold (see Chamberlain, 1975). The 'giant' particles (above 10 µm diameter) sediment within a short distance, but dusts with a mass median diameter of 3 µm (which is still coarser than most aerosols) have been carried from the Sahara to Britain (see Chamberlain, 1975). Similarly, aerosols with modal sizes of 20 to 40 µm, assumed to originate in St. Louis, Missouri, were found many kilometers downwind of the city, showing that in conditions of turbulent mixing, sedimentation was relatively ineffective in removing giant particles (Johnson, 1976). Atmospheric residence times tend to increase with decreasing particle size, and 1 to 10 µm particles usually remain airborne for between 1000 and 100 hours (Esmen & Corn, 1971). The energy for initial release of small particles can be provided by light, heat, or electrical charge (Aitken, 1923; Goldsmith & May, 1966; Fish, 1972). Once in the atmosphere, small particles are less subject to sedimentation than large particles and more affected by diffusion.

Most aerosol elements show an annual cycle of air concentration, with maximum concentration in winter and minimum in summer (Cawse, 1974). This tends to apply to both 'pollutant' and 'natural' elements, and can be attributed to increased fuel combustion in winter for 'pollutants', and greater occurrence of windy weather for 'natural' elements. Trace elements produced by vegetation would have been expected to show maxima in summer associated with the growing season. A study in summer of air concentrations of mine elements in urban, forest, and coastal environments in Florida always showed lowest air concentrations in forest sites (Johansson _et al._, 1976).

1.5 Deposition of aerosol on vegetation.

In studying the release of metals from vegetation in the field one has to take the ambient aerosol into account as well as _de novo_ metal release. Therefore, the factors determining the fallout burden on plants are considered below.

The method used by the Atomic Energy Research Establishment, Harwell of collecting particulate trace elements from air was to draw air through a Whatman no. 1 filter at a constant rate. The average efficiency of particulate filtration for all elements was estimated to be 97% of the aerosol mass (Cawse & Peirson, 1972). Such sampling should be reasonably independent of particle size and weather, whereas the deposition of aerosol on to vegetation depends on these factors and on properties of the deposition surface (Goodman _et al._, 1975; Clough, 1975).

Methods of measuring deposition include the dry deposit gauge (a horizontal filter paper protected from rain), the total deposition (TD) gauge (a plastic rain gauge covered by a terylene mesh), and horizontal moss bags (MB). Goodman _et al_ (1974) have shown that these three types of deposit gauge all gave mutually correlated results for seven heavy metals over several sites and monthly sampling periods in South Wales. The deposition data were less well correlated with air concentration measurements, although there was usually a relationship.

Deposit gauges are more useful than air concentration in measuring aerosol fallout on vegetation. The deposition of particles to both moss and grass surfaces in a wind-tunnel depended on particle size and wind speed (Clough, 1975). The relationship between wind speed and Vg was usually linear, while the effect of particle size on Vg is illustrated below (Figure 1.1). The deposition characteristics of both moss and grass were thus similar, but moss was more efficient at trapping particles for any given wind speed or particle size. This was attributed to the hairiness of the moss surface, increasing initial trapping and restricting blow-off. Wet moss bags were found to give an even greater trapping efficiency.

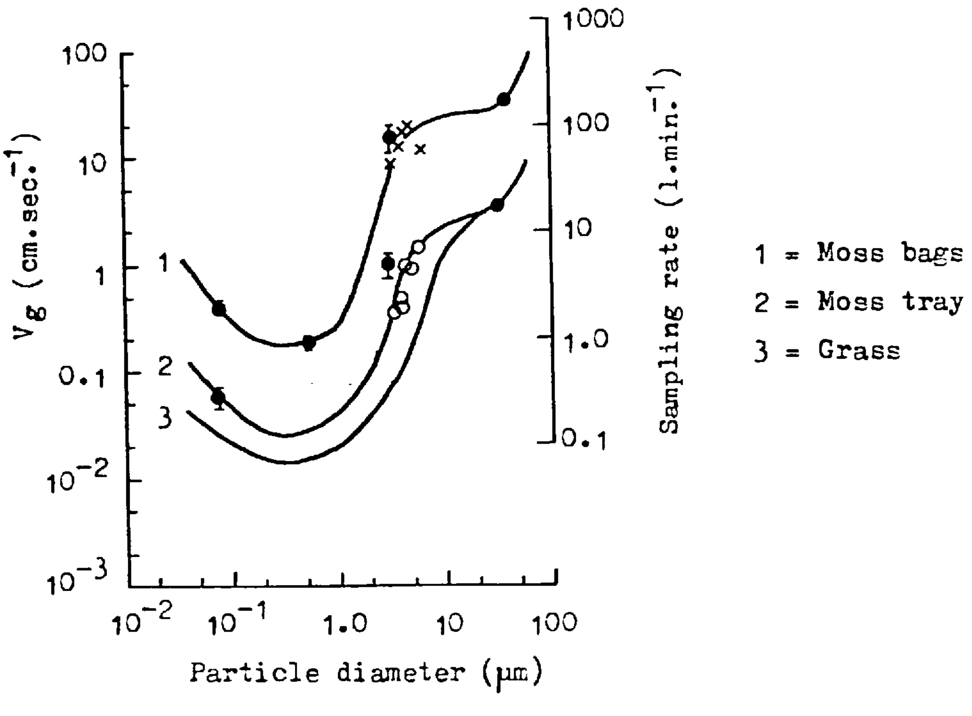


Figure 1.1. Effect of particle size on deposition to moss bags, and moss and grass trays (after Clough, 1975)

The loss of deposited particles from natural vegetation has been studied by several workers. When radioactively tagged solutions were sprayed on to grassland, about 40% of the label was initially retained by the herbage (Chadwick & Chamberlain, 1970). The subsequent 'field loss' per unit weight of herbage was exponential, after correction for radioactive decay. For example, the time taken for half the ^{85}Sr to be lost (the 'retention half life') was about 19 days in summer and 49 days in winter. The rate of field loss did not seem to depend much on the physical form of the label, but was fastest in the growing season, presumably because of growth dilution (also, Chamberlain, 1970; Milbourn & Taylor, 1965). Moorby and Squire (1963) demonstrated transfer of applied ^{89}Sr to uncontaminated plants and were able to trap it in air filters when the plants were kept in dry conditions. Normally, of course, wash-off by rain would be an important mechanism of field loss.

The deposition of aerosol particles (2 µm diameter) on to coniferous trees and their re-entrainment into the atmosphere was investigated by Rosinki & Nagamoto (1964) in wind tunnel experiments. The efficiency of a single tree at trapping aerosol particles passing through the canopy usually increased with aerosol concentration, and varied from 0.3 to 9.8%. The percentage area of the foliage covered could be varied according to dose, up to well over 100% due to multi-layer deposition. Rates of deposition and re-entrainment did not increase in a simple way with increasing wind speed; the rate of deposition on Douglas fir was maximal and re-entrainment minimal at an intermediate wind speed (280 cm.sec^{-1}).

There are numerous reports of the deposition of heavy metals on vegetation near roads, cities, and industrial sites. The bulk of the lead deposition from roads falls within about 100 metres of the road (Ward _et_ _al_., 1975; Nikiforova, 1976; McLean & Shields, 1977; Rolfe & Jennett, 1975), and roadside contamination of Cd, Ni, and Zn also occurs (Lagerwerff & Specht, 1970). The deposition from industrial sources, chiefly heavy metal smelters, is more widespread, and in the case of the Avonmouth smelter (near Bristol, U.K.) affects an area of about 10 to 15 km radius (Little & Martin, 1972; Cameron & Nickless, 1977). In Canada an area of about 260 km^2 is devoid of vegetation around the smelting complex at Sudbury, Ontario, and damage to vegetation caused by acid rain and heavy metal pollution is visible over an area of 4,700 km^2 (Hutchinson & Whitby, 1977). The amount of deposition per unit ground area falls off roughly exponentially with distance from the source until it reaches the background level (e.g. Roberts, 1975; Little & Martin, 1972; Beavington, 1977). The geographical deposition pattern depends on topography, meteorology (mainly wind speeds and directions, and rain), and strength of the emission source. Increases in the lead content of Greenland permafrost attributed to petrol usage in industrial countries illustrate that pollution has no sharp geographical boundaries (see Hall, 1972).

Atmospheric dispersion of metals in wind-blown dust from mine waste tips is of secondary importance to emissions from active industries (Roberts, 1972), but in the absence of the latter can be detected (Goodman _et al_., 1974; Johnson _et al_., 1978). Kolotov _et al_. (1965) found atmospheric dispersion aureoles of copper and tin around ore deposits, detected in rainwater, snow, and on the surface of oak leaves, but site descriptions were not sufficiently detailed to indicate whether these could have arisen from wind-blown soil or by another means.

The absorption of atmospheric particles and dissolved matter in rain is an important means by which epiphytic bryophytes and lichens obtain nutrients, and for some, e.g. Spanish moss (_Tillandsia usneoides_), must represent the only source of nutrients. Absorption depends on particle-trapping and a large cation exchange capacity (Knight et al., 1961). These organisms are consequently very susceptible to atmospheric pollution, and have been used to estimate geographical patterns of air pollution by the method of mapping lichen zones (Gilbert, 1975; Pyatt, 1970). Chemical analysis of natural populations of mosses and lichens for heavy metals and sulphur has been used successfully to show regional differences in air pollution (e.g. Nieboer et al., 1975; Ruhling & Tyler, 1971; Sheline et al., 1976; Wallin, 1976), although Laaksovirta et al. (1976) found that lichen was too efficient at taking up lead for monitoring the pollution beside roads, and that analysis of Pinus sylvestris bark was a much better indicator of traffic density (also Barnes et al., 1976). Natural mosses have been used to follow changes in atmospheric metal pollution with time (Rasmussen, 1977). The cation absorbing properties of Sphagnum and Hypnum mosses are retained after death, and suspended bags of acid washed moss have been used to map the pollution around metal works, i.e. the MB method already mentioned (also Little & Martin, 1974; Cameron & Nickless, 1977).

The foliar penetration of lead into higher plants, either as lead solution through isolated cuticles or as lead aerosol deposited on intact plants is very slight (Arvik & Zimdahl, 1974; Roberts, 1975; Little, 1973). The percentage of ^{210}Pb applied to radish or lettuce leaves that was translocated to other parts of the plants was always less than 1% (Hemphill & Rule, 1975). This evidence is consistent with the hypothesis that almost all the lead remains as a superficial coating on foliage, though perhaps incorporated into epicuticular waxes. However, Lepp & Dollard (1974) found that some lateral transport of ^{210}Pb from bark to xylem of woody plants is possible, and Lepp (1975) discussed evidence of ^{210}Pb absorption and translocation by tree leaves.

Ion (Ca^{2+}, Rb^{+}) penetration through isolated cuticles of tomato fruit depended on the ion binding capacity on the side opposite the side of entry, and permeability was greater from the outer to the inner surface than in the other direction (Yamada et al., 1964). The cuticle as a whole is negatively charged (Franke, 1967), which may account for its greater permeability to cations than anions (Wittwer et al., 1965). Nutrient cations penetrate by diffusion in ionic form, although the rate of urea penetration is enhanced 10 to 20 fold, and are retarded by chelation (Wittwer et al., 1965). In forests, it was found that inorganic nitrogen was absorbed by tree canopies from rainfall (Carlisle et al., 1966). Rb, Na, and K radioisotopes were most readily absorbed and translocated by bean leaves, followed by P, Cl, S, Zn, Cu, Mn, Fe, and Mo, which had decreasing mobility in the order given (Bukovac & Wittwer, 1957). Ca, Mg, Sr, and Ba were absorbed by leaves but not exported (Bukovac & Wittwer, 1957).

Smith (1974) categorised the effects of pollutants on temperate forest ecosystems into three classes, which are discussed here with particular reference to heavy metals. Under Class I situations (low dosage), vegetation and soils would act as a sink for atmospheric pollutants. At intermediate dosages - Class II - certain individuals or species would be subtly affected, while exposure to high dosages - Class III - would cause acute effects, starting with mortality of certain trees, leading to simplification of the ecosystem, and ultimately to barren soil.

Presumably, Class I situations occur almost everywhere since, from what has been said, all ecosystems can be assumed to be subject to some atmospheric metal fallout. Smith (1974) estimated the rates of removal of particulate metals by an Acer tree, and suggested that trees may be efficient natural filters of the atmosphere. The work of Rosinski & Nagamoto, discussed earlier, supports this.

Hill (1971) showed that vegetation is a sink for various pollutant gases.

Amongst Class II effects are included the reduction in litter decomposition rates of metal-polluted soils (Tyler, 1976), interference with stomatal function by mechanical effects (partial occlusion of stomata, Ricks & Williams, 1974) and biochemical effects (Bazzaz et al., 1974), increase in leaf temperature by 2 to 4°C caused by deposited dust (Eller, 1977), increase in disease incidence (see Saunders, 1971), and simplification of the phylloplane microflora (Gingell et al., 1976), although perhaps the latter should be considered a Class III effect. All these changes could influence the way in which forests contribute to environmental, particularly atmospheric, cycles of heavy metals, by mechanisms suggested earlier in this review. For instance, it is possible that increase in leaf temperature and partial occlusion of stomata could increase volatilisation of such elements as Hg, Se, As, and Pb.

Examples of Class III effects caused by metal pollution can be seen around many heavy metal smelters. Wood & Nash (1976) reported that most types of plant were almost entirely absent close to a copper smelter in Arizona. With increasing distance from the smelter, the density, diversity and biomass of vegetation increased (measured by no. of plants m^{-2}, no. of species, and $g.m^{-2}$, respectively). These changes were correlated with decreases in soil copper concentrations. Similar effects occur around a zinc smelter in Pennsylvania where 485 ha is sparsely vegetated or devoid of vegetation (Jordan, 1975). Jordan also noted the presence of a zinc-tolerant ecotype of Arenaria patula (Caryophyllaceae), which accumulated zinc and was restricted to contaminated soils. Class III effects create obvious environmental problems in terms of soil-erosion, gardening, farming, human health risks and so on. In addition, it is possible that the destruction of vegetation causes pollution to become more widespread because the aerosol-filtering effect of vegetation is removed. The data of Davis et al. (1976) indicate that this effect is very significant in field conditions.

1.6 Synthesis.

All the topics which have been covered in this review can be brought together in the form of an overall biogeochemical cycle. Various authors have defined the compartments and processes to be considered in the cycle, for example Hall et al. (1975) and Likens et al. (1977; see Figure 1.2 below)

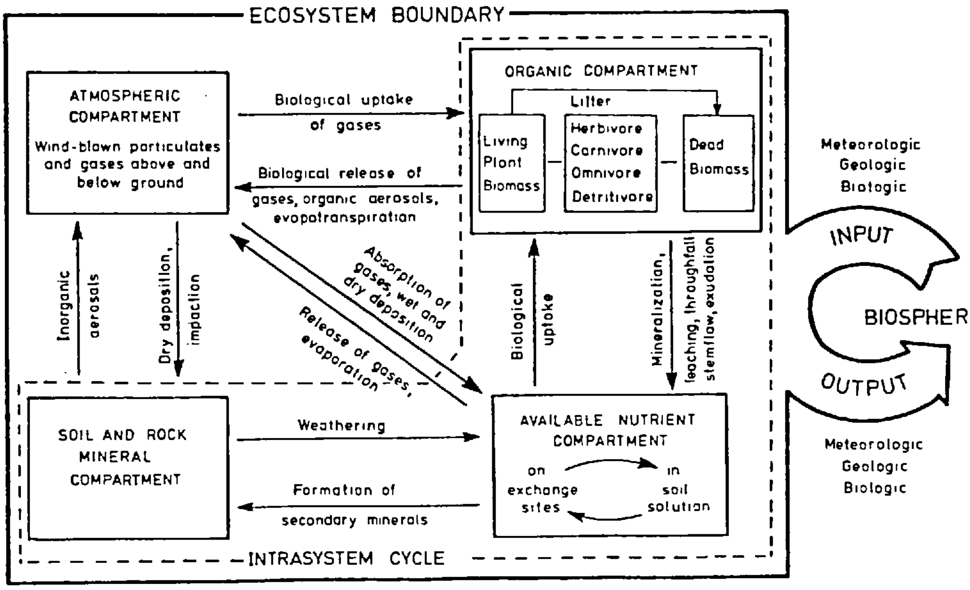


Figure 1.2. A model depicting cycling in a terrestrial ecosystem (after Likens et al., 1977; by courtesy of Springer-Verlag).

While such cycles cannot at present be quantified for heavy metals (Hall _et_ _al_., 1975; Fortescue & Marten, 1970), major nutrients have received much more attention. The Hubbard Brook ecosystem, New Hampshire, U.S.A., is perhaps the most thoroughly studied environment anywhere in the world, and the annual calcium budget for this ecosystem is given below as an example (Figure 1.3).

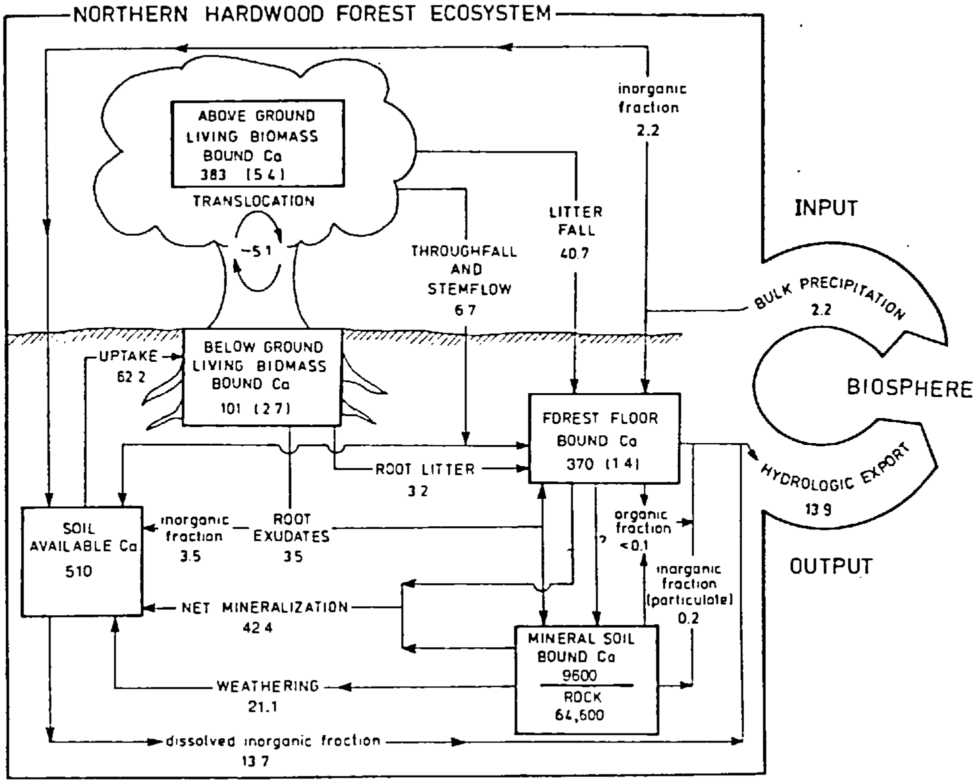


Figure 1.3. Annual calcium budget for a forested ecosystem at Hubbard Brook. Standing crop values are in $kg.ha^{-1}$ and calcium fluxes are in $kg.ha^{-1}yr^{-1}$. Values in parentheses represent annual accretion rates (after Likens _et_ _al_., 1977; by courtesy of Springer-Verlag).

Clearly, there is a need to know more about how plants affect the movement of heavy metals in the environment. I have been particularly interested in plant-atmosphere relationships, and evidence has been presented in this introduction to show that metals like Zn, Cd, Pb, and Mn do become available at plant surfaces for release into the environment by some means. It is important to know what processes occur and what significance they have in overall biogeochemical cycles.

Heavy metals are important as pollutants, but they are also of considerable interest to those engaged in mineral exploration. The concept that the atmosphere contains localised anomalous concentrations of trace elements related to ore deposits has been investigated by Barringer (1975) with very interesting results. The method was to carry out high-volume air sampling in aircraft, collecting aerosol particles by impaction on special tape. Precautions were taken to ensure that the particles were of local origin by (1) using an aerodyne at the sample intake to separate particles above and below 10 µm diameter, of which only the +10 µm fraction was impacted, and (2) using temperature-switching to separate particles carried in rising air currents ('hot spot') from those in falling air currents ('cold spot'), of which the hot spot contained the local-derived particles. The tape was analysed after a flight by vaporising each spot with a CO_2 laser and passing the vapour using argon carrier gas into a radio-frequency plasma for multi-elemental spectroscopic analysis. Examples were given of airborne metal anomalies which had been detected over mineralisations, and of a Mn/Fe ratio anomaly over an oil and gas field, confirmed by ground geochemical surveys. The use of in-flight spectroscopic analysis for mercury and hydrocarbons has also been described by Barringer (1971, 1975). The dense vegetation cover of the areas surveyed suggested that vegetation must have been an important source of the airborne particles, which was supported by tests showing that much of the particulate material had low specific gravity.

In view of the evidence that has been considered, the aim of the research described in this thesis was to gain a better understanding of the release of metals from plant surfaces into the atmosphere. The complementary approaches of radioactive labelling experiments and of fieldwork on 'natural' vegetation have been used. The object of the radioactive work was to study the release of selected metals from plant surfaces without the complication of extraneous metal sources, though in fact, unless precautions are taken, the same problem of background contamination applies to radioactive experiments as to those involving fieldwork and chemical analysis. In both types of work the release of metals in particulate and water-soluble forms from foliage has been studied. Fieldwork was carried out at a range of urban/rural and mineralised/non-mineralised locations in England, and samples were analysed by quantitative multielemental techniques and electron microprobe analysis/electron microscopy. Methods of sampling, analysis and data processing have been intended to allow the relative importance of metals released by plants and deposited by atmospheric fallout to be elucidated in field conditions.

2. MATERIALS AND METHODS.

2.1 General procedures.

2.11 Particle collections using a cyclone.

Particles associated with leaf surfaces were collected using a cyclone. This is a device through which air is sucked, creating a spiralling air stream from which particles above about 2 μm diameter sediment out. The one used (Figure 2.1) was made of hard anodised aluminium by Barringer Research Ltd (B.R.L.). Suction was provided by a Moulinex 'T800' vacuum cleaner rated at 750 watts. Samples were collected in pyrex glass tubes. The intake of the cyclone was covered by a 190 μm monofilament nylon mesh (Henry Simon Ltd.), unless another size is specified.

The method of collecting plant surface particles was to gently brush the intake over the foliage, without causing damage. Suction was switched off as necessary to allow large fragments to be removed from the intake mesh. The usual collection time was 30 minutes per sample, but this was sometimes modified according to the size of sample needed. One sample was always collected from one plant. Between taking samples, the cyclone was washed with distilled water and wiped with cotton wool and paper towels. Contamination tests with powders of known composition and multi-elemental analysis by B.R.L. showed that the cyclone added a small amount of aluminium to collected dusts, but no other metal.

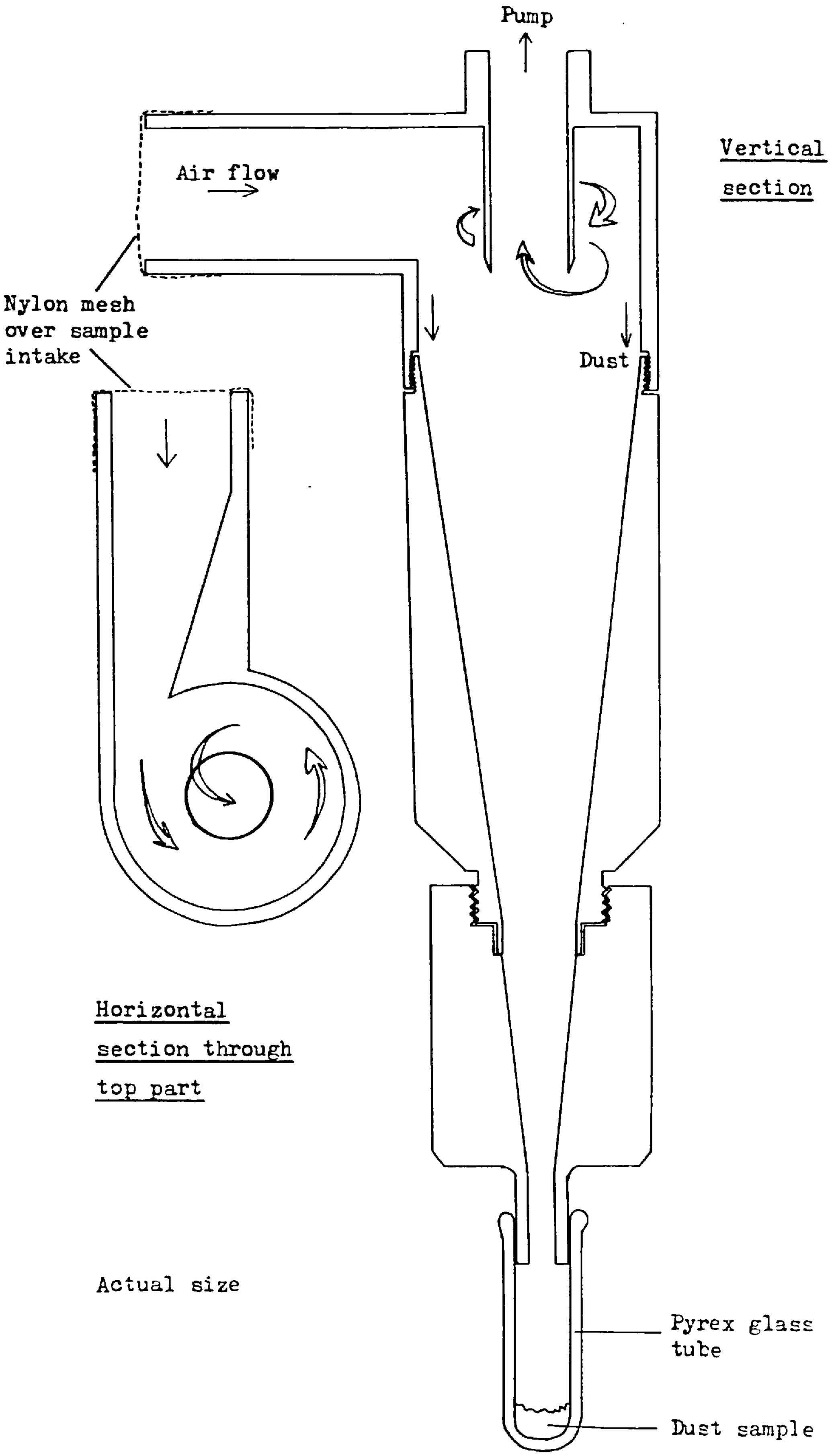


Figure 2.1 The cyclone used to collect foliar surface particles.

2.12 Leaching methods.

Leaching experiments were carried out on samples of radioactive plants and trees in the field. Before leaching, herbage was either left unwashed or washed for 10 seconds by immersion and agitation in a large beaker of distilled water. The washing was intended to remove surface particles but not cause significant leaching from the interior of leaves. Samples were placed in leaching solution without immersing the cut ends of branches, and were leached for the time stated in each experiment. The leaching solution was distilled water acidified with sulphuric acid ('Analar' grade) to pH 3.2 ± 0.1, and at least 8 blank samples in each experiment were analysed in the same way as leachates. Unless stated otherwise, leaching was carried out in 60 ml of solution in washed polypropylene bottles which could be fitted with screw-caps. Fresh weights and dry weights of leached herbage samples were recorded so that leaching losses could be expressed on a weight basis.

2.13 Herbage and soil preparation.

Elemental concentrations in plants and soils are given on a dry weight basis in this thesis except where stated. Drying temperatures could not be controlled exactly with the equipment available but were usually between 65 and 85°C for at least 72 h., which was more than enough time for constant weight to be achieved. Before analysis, the samples were ground with a pestle and mortar, sometimes using liquid nitrogen to facilitate herbage grinding, and stored in polythene tubes. Herbage samples which were analysed were unwashed as would be the case in biogeochemical surveys (though washing was used to assess amounts of surface dust as described above). Soil samples were sieved through a 1 mm nylon mesh unless other treatment is specified.

2.14 Statistical methods.

The purpose of this section is to define the parameters used in data processing. Computations were made using Hewlett Packard (H.P. 55) and Texas Instruments (SR.51.A and TI.51.III) calculators and facilities of the Imperial College Computer Centre. Programs for linear regression were based on those of Dr P. Mueller (Botany Dept., Imperial College) and Mr R.G. Davies (Davies, 1971).

n = no. of observations.
x means 'observation(s)'; $\lesssim$ means 'the sum of'.

$$\text{Mean} = \bar{x} = \frac{\lesssim x}{n}$$

$$\text{Variance} = s^2 = \frac{\lesssim(x^2) - \frac{(\lesssim x)^2}{n}}{n-1}$$

$$\text{Standard Deviation} = s = \sqrt{s^2}$$

$$\text{Standard Error of } \bar{x} = \text{S.E.} = \sqrt{\frac{s^2}{n}}$$

Confidence Interval for $\bar{x}$ = t x S.E., where t = Student's t value for n-1 degrees of freedom and probability selected.

2.141 Linear regression.

x = independent-variabe observation.
y = dependent-variable observation.

$$\text{Slope} = \frac{\lesssim(xy) - \frac{\lesssim x . \lesssim y}{n}}{\lesssim(x^2) - \frac{(\lesssim x)^2}{n}} = \frac{S_{xy}}{S_{xx}}$$

$$\text{S.E. of slope} = \sqrt{\frac{\left[\dfrac{S_{yy} - \dfrac{(S_{xy})^2}{S_{xx}}}{n-2}\right]}{S_{xx}}}$$

$$\text{where } S_{yy} = \lesssim(y^2) - \frac{(\lesssim y)^2}{n}$$

$$\text{Intercept} = \frac{\lesssim y - (\text{Slope}).\lesssim x}{n}$$

$$\text{Correlation coefficient} = r = \frac{S_{xy}}{\sqrt{S_{xx}.\ S_{yy}}}$$

2.2 Radioactive labelling experiments.

2.21 Radioisotopes and counting methods.

Radioactive materials were purchased from the Radiochemicals Centre, Amersham, U.K. The isotopes, ^{65}Zn (code ZAS.1), ^{115m}Cd (CAS.1), and ^{54}Mn (MFS.2) were each supplied as chlorides of the divalent metal ion in 0.1 M HCl.

Most samples were counted on a Nuclear Chicago end-window gas-flow counter for 100 minutes or 3000 counts. The counting efficiency for ^{115m}Cd was 27%, and for ^{65}Zn, 3%. Samples were dry and stuck securely on to 2.5 cm diameter planchets with 'Gloy' paste.

A Nuclear Enterprises solid scintillation counter was also used. Solid or liquid samples in flat-bottomed tubes or test tubes were placed in the shielded well of the detector over a sodium iodide crystal. The method was used for relatively active samples of soil, herbage, and hydroponic solution because counting efficiencies for the isotopes used were lower than on the gas flow counter. The counting efficiency of the solid scintillation counter for ^{210}Pb was 1.3%, and for ^{65}Zn varied from about 1.5 to 3% depending on the activity of the sample. With a sample of 0.17 µCi of ^{65}Zn, the solid scintillation counter was as efficient as the gas flow counter, but less efficient with lower activities.

2.22 Cupressus leylandii growing systems.

Attempts were made to fully label Cupressus leylandii plants growing in normal environmental conditions with isotopes of zinc and cadmium. The species was chosen because it is a rapidly growing tree and, being evergreen, could be sampled at all times of year. Twelve seedlings with shoots about 40 cm high were potted into 18 cm diameter pots in April 1976, using dried, sieved soil from Silwood Park. The eight pots to be treated with isotopes were only filled about three-quarters full at this stage. The lower branches were removed to give about 10 cm clearance between the top of the pot and the base of the foliage. The pots were placed in plastic bags and watered lightly before applying isotopes. They were kept in a fenced-off area at Silwood Park with 50 cm separation between pots.

0.5 mCi of ^{65}Zn in 20 ml of water were added to each of four pots, and 0.5 mCi of ^{115m}Cd in 20 ml of water to a further four (activities on date of application, 8/4/76). The pots were filled with soil, fully watered, and the necks of the plastic bags tied around the stems to prevent radioactive soil reaching the foliage externally. Watering was carried out as necessary via a plastic tube inserted through the side of each bag.

The plants began to look chlorotic in May 1976, and it was thought that root aeration could be a problem. The plastic bags were removed and replaced by polythene sheets tied around the stems and spread out to cover the pots like tent fly-sheets. Another source of stress was that the pots were exposed to solar heating, and they were therefore dug into the soil. However, during the year the plants gradually became increasingly necrotic and the experiment was terminated in September 1976 when it was apparent that recovery would not occur.

New plants were set up at Imperial College, South Kensington where closer care could be maintained. Improvements were made to the system for growing the plants (Figure 2.2) which was designed to enable metal uptake and release to be monitored over a long period of time. ^{65}Zn

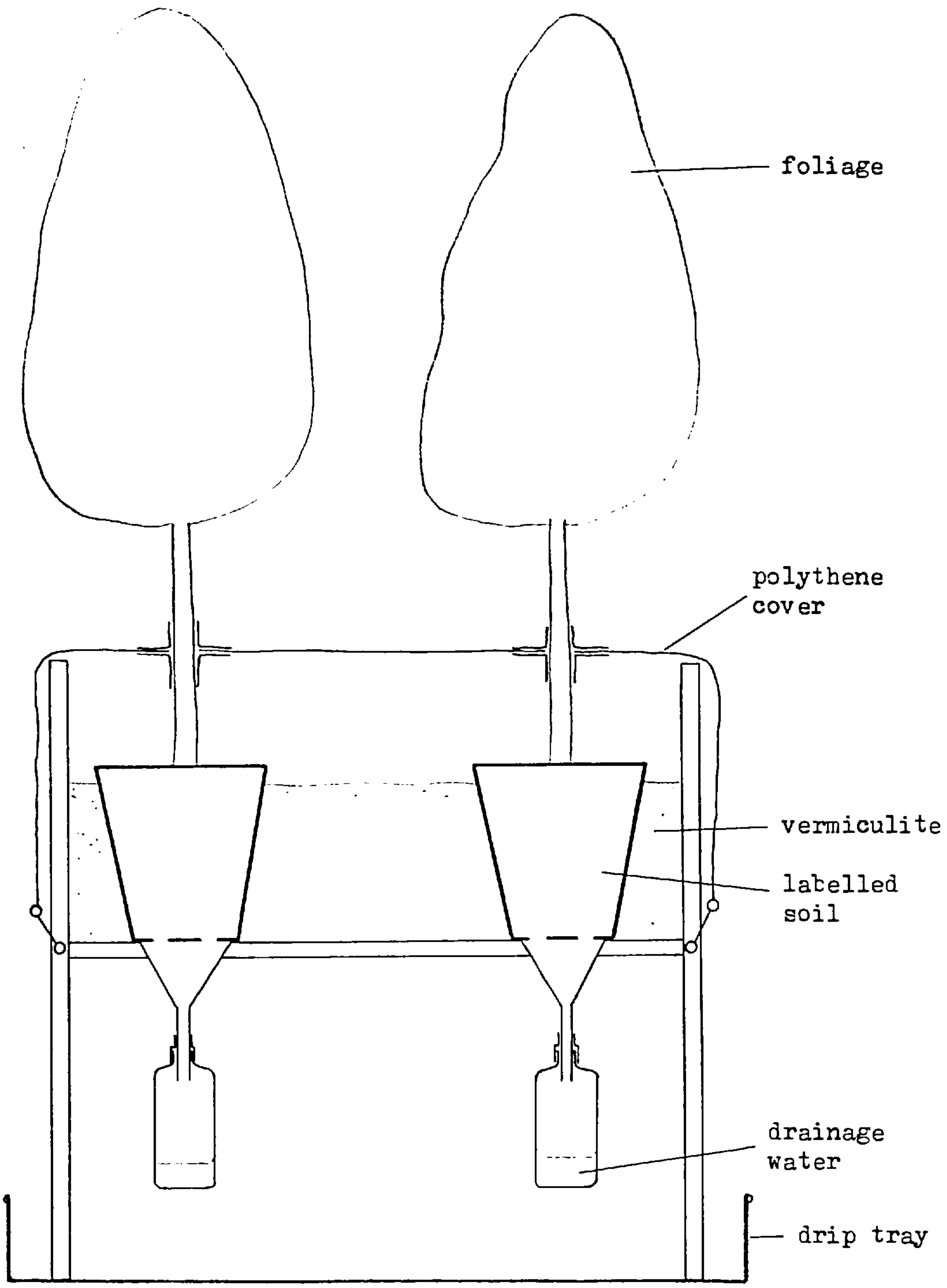


Figure 2.2 The *Cupressus leylandii* growing system at South Kensington.

was the only isotope used, having a much longer half-life (245 days) than ^{115m}Cd (44 days). The experiment comprised four labelled and four control plants.

Larger plastic pots were used than previously (25 cm diameter), and the ^{65}Zn-labelled soil from the previous experiment was transferred into them, giving an estimated ^{65}Zn activity of 0.25 mCi per pot on 3/12/76. In addition, 0.5 mCi (On 3/12/76) of ^{65}Zn per pot were poured evenly over the soil. About 5 cm depth of unlabelled soil were added to cover the isotope.

The plastic covering over the pots was designed to prevent external transfer of ^{65}Zn to the foliage, and could be lifted for watering. The vermiculite insulation around the pots protected them from extremes of temperature, and the collecting bottles underneath were used to recycle drainage water. The radioactivity in drainage water was always found to be small, using a monitor (G.M. meter, type 5.10, Mini-instruments Ltd., London).

A further application of ^{65}Zn was given to the soil on 13/5/77, of 1.0 mCi to each of plants 5, 6, and 7, and 2.0 mCi to plant 8. The diluted isotope solution (10 ml ≡ 1.0 mCi) was carefully poured into several holes spiked in the soil.

2.23 Transpiration experiments.

Transpirates were collected from radioactively labelled plants by enclosing them in cylindrical perspex chambers. The method was first used on ^{65}Zn- and ^{210}Pb-labelled plots at Silwood Park. The two 1.5 m^2 plots had been cleared of their herbaceous vegetation in spring of 1975, labelled by sprinkling isotope solution evenly over the soil surface, and left for vegetation to regrow. 2.0 mCi of ^{65}Zn and 1.0 mCi of ^{210}Pb (on 24/4/75) had been applied to the two plots respectively in large volumes of water. The same type of transpiration experiment had previously been carried out by White (1975) in summer, apparently showing release of both isotopes associated with transpiration water.

The chambers (30 cm diameter by 30 cm high) were thoroughly washed and the upper end of each was covered with plastic cling-film, weighted in the centre with a marble so that condensate would drip into a collecting vessel (Figure 2.3). Chambers were placed over vegetated and unvegetated parts of the plots. Water dripped into a filter funnel, through a Whatman no. 1 filter paper to exclude insects etc., and into a conical flask. Care was taken to ensure that foliage was not in contact with the collecting apparatus which was also raised off the soil surface to minimise contamination.

When used over Cupressus leylandii plants at South Kensington (Figure 2.4), which were washed with a hose pipe before being enclosed, 3 chambers were placed one on top of another to enclose the plants, and sealed at the joints with adhesive tape. Polythene was used to seal the bottom ends of the enlarged chambers around the stems. Water was collected in a polypropylene beaker standing on a shelf built into the uppermost section of each chamber.

Evapotranspiration samples were spotted in successive 1 ml doses on to glass fibre pads in planchets under a mercury vapour lamp to assist drying. The whole of each transpiration sample was thus accumulated on to one planchet.

2.24 Deposition experiment.

Rainwater and deposited solids were collected underneath each Cupressus canopy at South Kensington in 11.5 cm diameter polypropylene funnels and passed through

Figure 2.3. Transpiration chambers in use over herbaceous vegetation at Silwood Park.

Figure 2.4. Transpiration chamber in use over Cupressus leylandii at South Kensington.

The joints between sections have not yet been sealed and the chamber has not begun to mist up.

small columns of Amberlite IR 120 (H) ion-exchange resin (Figure 2.5). Polythene was spread under some plants so that the deposition from the whole canopy would be channelled into the funnels. During dry weather the plants were showered from a watering can fitted with a sprinkler, to wash off accumulated leachates and debris. Ion exchange columns were collected after two weeks exposure, and dried sub-samples (approximately the top third of each column) were counted in the gas flow counter.

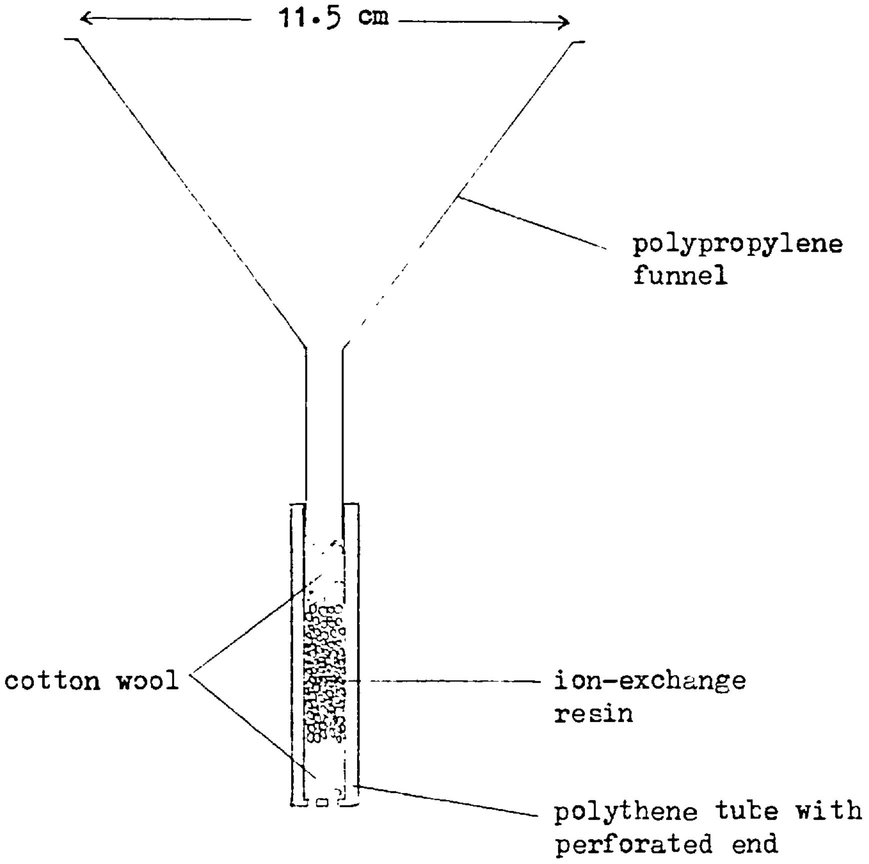


Figure 2.5. The apparatus used to collect radioactive deposition.

2.25 Scots pine hydroponic experiment.

2.251 Plant material.

One year old Scots pine (Pinus sylvestris L.) seedlings, with shoots approximately 25 cm high, were collected from sandy common land near Farnborough, Hants. on 23/2/78.

2.252 Growing conditions.

Plants were grown in a growth room at 25°C ± 2°C. Illumination was provided by a bank of 4 x 60 watt fluorescent tubes about 150 cm above the plants. The pH of the solution was 4.5. Polystyrene canisters (Stewart Plastics Ltd.) were used, each holding 1.5 litres of solution and four plants (Figure 2.6). There were eight plants (two canisters) per treatment. Aeration was continuous throughout the experiment. A single, branched aeration line served all 14 canisters, through which air was blown by a small electric pump. A cardboard cylinder was placed around the four plants in each canister to separate the foliage of plants in different treatments.

The method of hydroponic culture was based on that of Ingestad (1960). The composition of the culture solution is given in Table 2.2. All chemicals were 'Analar' grade. After carefully cleaning soil from the roots, plants were placed in 1/8 strength culture solution for one week, then in 1/4 strength for one week, and half strength for one week. They were then transferred to full strength medium including ^{65}Zn or ^{115m}Cd label. A list of treatments is given in Table 2.1. Plants were grown for four weeks in labelled solution, and the solution was changed

Table 2.1. Labelling treatments of Scots pine in hydroponic culture.

Treatment ($\mu g.\ ml^{-1}$)	Radioactivity ($\mu Ci.\ ml^{-1}$ on 23/3/78)
Control (0.02 μg Zn ml^{-1}; no Cd)	-
0.1 Zn	0.001 ^{65}Zn
1.0 Zn	0.01 ^{65}Zn
10.0 Zn	0.1 ^{65}Zn
0.01 Cd	0.0002 ^{115m}Cd
0.1 Cd	0.002 ^{115m}Cd
1.0 Cd	0.02 ^{115m}Cd

Non-radioactive Zn and Cd were supplied as acetate.

Radioactive isotopes as chlorides.

Table 2.2. Composition of culture solution used for hydroponic growth of scots pine (after Ingestad, 1960).

Ion	ppm	Salt used
Ca^{++}	40	$CaCl_2.6H_2O$
Mg^{++}	15	$MgSO_4.7H_2O$
K^+	50	KH_2PO_4, KCl
NH_4^+	25	NH_4NO_3
NO_3^-	25	NH_4NO_3
$PO_4^{\equiv}$	20	KH_2PO_4
$SO_4^{=}$	20	$MgSO_4.7H_2O$
Cl^-	1.8	Various chlorides
Fe^{+++}	0.93	$FeCl_3.6H_2O$
Mn^{++}	0.17	$MnCl_2.4H_2O$
$BO_3^{\equiv}$	0.17	H_3BO_3
Cu^{++}	0.02	$CuCl_2.2H_2O$
Zn^{++}	0.02	$ZnCl_2$
$MoO_4^{=}$	0.003	$Na_2MoO_4.2H_2O$

every week. Harvesting was carried out during the fifth week of labelling.

2.253 Harvesting.

Particles were collected using the cyclone from shoots of surviving plants in Control, 10 ppm Zn, and 1 ppm Cd treatments. The samples were dried, weighed and counted in the gas flow counter. Every healthy shoot was then cut off and placed upside down in a beaker containing 150 ml of leaching solution. Shoots were leached for three consecutive periods of $1\frac{1}{2}$ h. The leachates were boiled to 1-2 ml and then warmed gently to dryness after transferring to planchets.

Shoots were separated into needles, bark, wood, and buds. Roots were washed for 5 minutes under running tap water and separated into old roots and new roots formed during hydroponic culture. Herbage was dried and counted in the gas-flow counter.

2.26 Stem injection trial.

2.261 Plant material.

Four conifer species were used. Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco), western hemlock *Tsuga heterophylla* (Raf.) Sarg.) and western red cedar (*Thuja plicata* D.Don.) were provided by the Tavistock Woodlands Estate, Gulworthy, Tavistock, Devon, and Scots pines were obtained from Farnborough as before. Plants were all of similar size, about 50 cm high, and were

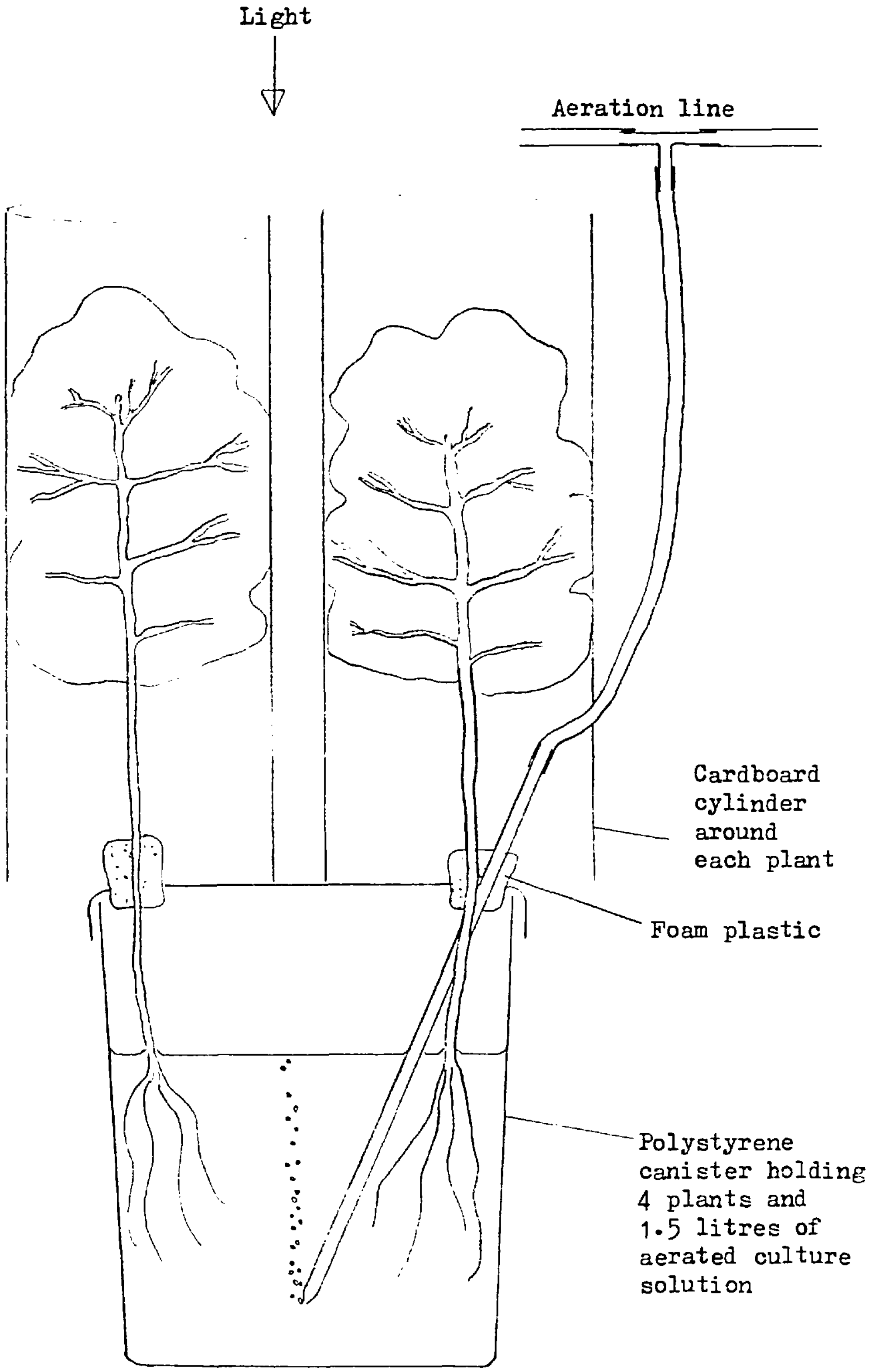


Figure 2.6 The hydroponic growing system used for *Pinus sylvestris*.

dormant when potted up in John Innes no. 2 compost at the end of January 1978.

2.262 Isotope injections.

Isotopes were injected into the base of the stems on 14/2/78, by making a downward-pointing hole with a small drill into the middle of a trunk, injecting the labelled solution, and sealing the hole with 'Romac' rubber solution. 10 μCi of ^{65}Zn were injected into one or two plants of each species and 1.7 μCi of ^{115m}Cd into others, leaving some as 'controls'. The volume of each injection was 5 μl, containing either 24.0 μg Zn or 6.4 μg Cd (stable and radioactive).

2.263 Growth conditions.

The seedlings were kept in a glasshouse under high-intensity mercury vapour lamps giving a 14 h photoperiod. The temperature varied between 21 and 32°C. All four Scots pines failed to grow and eventually died, and one of the cedars died. The Douglas firs, western hemlocks, and remaining cedars began to grow extremely vigorously. Plants were always watered over the foliage to simulate rainfall and natural leaching.

2.264 Sampling.

Herbage was sampled regularly for 4 weeks after injections by taking a few leaves or needles from all over the canopy, which were dried, weighed, and stuck on planchets for counting.

An attempt was made to monitor metal release from western hemlock plants using the apparatus shown in Figure 2.7. Air was passed over the plants in perspex chambers at the rate of 1 litre.min^{-1} and then through 1.2 µm cellulose membrane filters (Millipore) and solid CO_2 cold fingers. In run 4, cold fingers only were used, and two 150 watt tungsten filament lamps were mounted above the chambers, raising the temperature in the chambers from 20 to 26°C. Each run lasted 4 h. Runs 1 and 2 were discarded because leaks in the apparatus indicated false flow rates. Cyclone samples were also taken from western hemlock and Douglas fir plants.

2.27 Western hemlock stem injection experiment.

Materials and methods were similar to those described in Section 2.26, apart from differences set out here. Western hemlock seedlings about 120 cm high were purchased from a garden centre near Farnham, Hants. in April 1978 and were grown in soil in a glasshouse with no artificial heating or lights. After new growth was well established, plants were injected with ^{54}Mn and ^{65}Zn. Four plants were each injected with 5 µCi (on 1/6/78) of ^{54}Mn (100 µl per plant), and four more with ^{65} µCi of ^{65}Zn each (20 µl per plant). Four plants were kept as Controls.

After allowing two weeks for isotope uptake into the foliage, each plant was sampled with the cyclone for 45 minutes, and herbage samples were also taken.

Leaching experiments were carried out on washed and unwashed samples from these western hemlocks and from <u>C.leylandii</u> grown outdoors at South Kensington. Herbage samples were leached for 2 h. or 24 h. Leachates and blanks were boiled to 1 to 2 ml in conical flasks and then warmed gently to dryness on planchets. Leaf samples were taken for radioactive counting in conjunction with leaching tests. Separate samples of new leaves and old leaves from the previous year were taken from western hemlock, but the mode of growth of C.leylandii did not make this distinction possible.

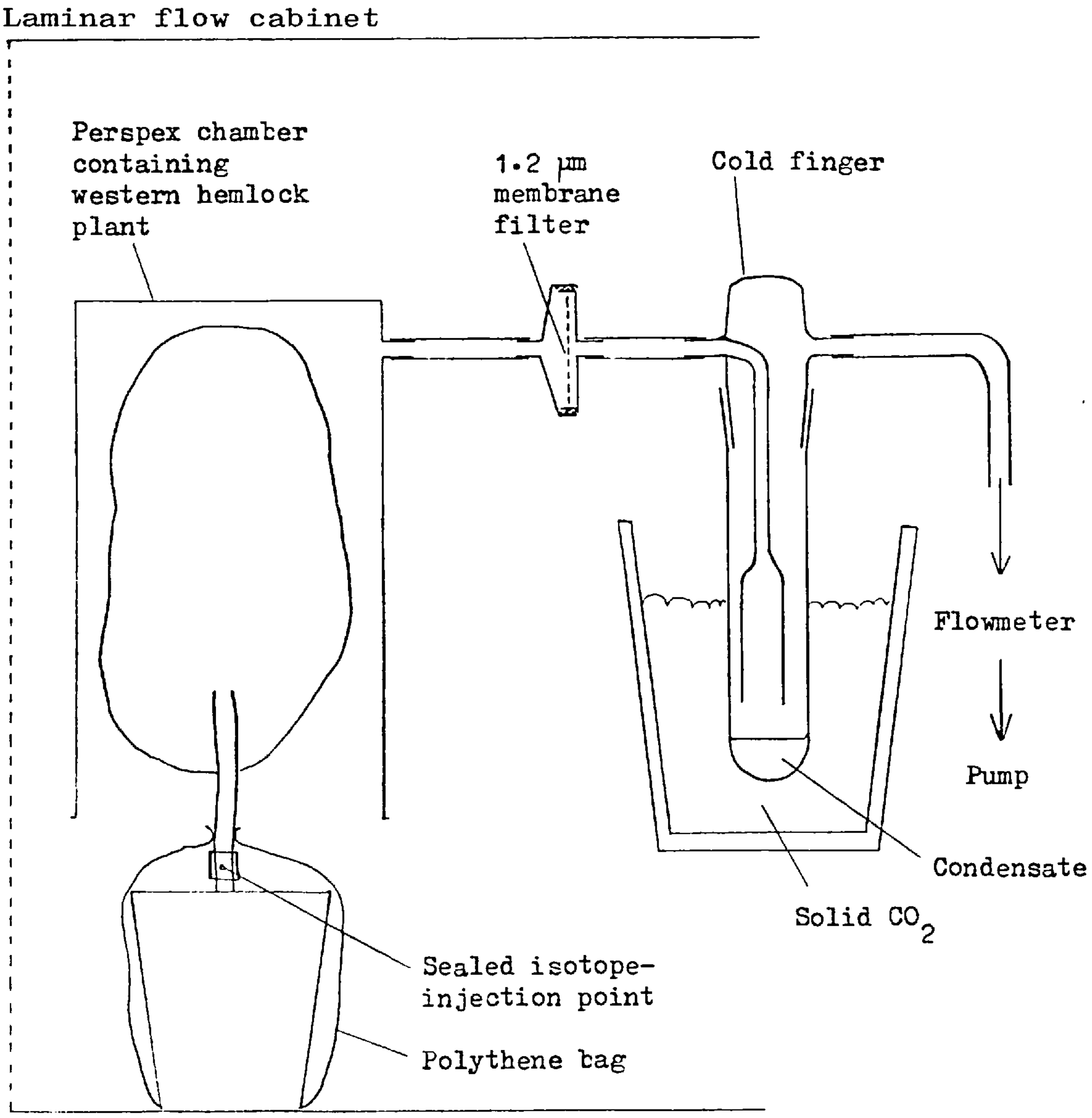


Figure 2.7 Apparatus used in experiment to detect labelled metal release from western hemlock.

2.3 Analytical methods for fieldwork.

2.31 Multielemental analysis by Barringer Research Ltd. (B.R.L.)

B.R.L. used 2 multielement analytical systems, based on Applied Research Laboratories equipment, one designed for solution analysis (ARL 2) and the other for solid sample analysis (ARL 1). Both systems utilised argon-plasma radio-frequency emission spectroscopy. About 20 elements were analysed simultaneously on each sample.

2.311 Soil and herbage digests (ARL 2).

Samples of soils, plant material, and some samples of plant surface particles were sent to B.R.L., Toronto, by air mail in washed polythene tubes. At B.R.L., 0.5 g samples were digested in a 4 : 1 mixture of HNO_3 : $HClO_4$ and made up to 5 ml in 0.5 M HCl. Samples were analysed by system ARL 2. Because of the digestion used, most major soil elements were partially extracted, potassium hardly, and trace elements almost completely. Possible spectral interferences occurred on wavelengths used for Ag, Cr, Co, and Cd determination. Lead was analysed at B.R.L. by atomic absorption spectrophotometry. Results were checked by having samples of standard kale analysed (Bowen, 1974; Table 3.10)

2.312 Solid particulate samples (ARL 1).

Particulate samples were usually sent to B.R.L. on standard adhesive tape, protected by Teflon cover tape, although samples on nylon mesh and filter paper were also analysed with corresponding blanks. Samples of about 10 µg could be analysed by system ARL 1 which was to vaporise a small disc of sample with a CO_2 laser and feed the vapour into the plasma for spectroscopic analysis.

The mass of sample vaporised was unknown and therefore its elemental composition could not be calculated absolutely. An estimate was made by assuming that the oxides of the seven major soil elements, Si, Al, Ca, Fe, Mg, Mn, and Ti constituted 90% by weight of the sample. (The system was initially calibrated with soils of known composition). Using this algorithm, the elemental composition of the sample was expressed in 'pseudo-ppm'. The method worked well for soils but less well for plant material and plant surface particles (test data provided by A. Murray, B.R.L.). Table 3.22 gives a similar impression, and shows some serious inaccuracies for plant material. Plant surface particles gave intermediate results between soils and plants.

2.32 Atomic absorption spectrophotometry.

Atomic absorption spectrophotometry was carried out in the Botany Department, Imperial College using an Instrumentation Laboratory (I.L.) 151 machine with a blue air/acetylene flame and a 3-slot Boling burner. The instrument was calibrated using chemical standards in distilled water, and usually a direct ppm readout was obtainable. If the calibration could not be made linear over the concentration range needed, readings were converted to ppm by drawing a calibration curve. A list of salts used for standards and possible interferences are given in Table 2.3. The most

Table 2.3. Atomic absorption spectrophotometry (I.L. 151)

Element	Salt used in standard	Wavelength (nm)	Possible interferences under conditions used. (Reference: 'Atomic Absorption Methods Manual', Instrumentation Laboratory, Inc., 1975).
Cu	$CuCl_2$	324.7	None
Mn	$MnCl_2$	279.5	None
Zn	$Zn(CH_3COO)_2$	213.9	No chemical interference but non-atomic species absorb strongly at this wavelength.
Pb	$Pb(NO_3)_2$	217.0	Phosphate, carbonate, iodide, fluoride and acetate suppress Pb - absorbance when their respective concentrations are approximately 10 x the Pb concentration. (Interferences decreased by 0.1 M EDTA).
Ca	$Ca(NO_3)_2$	422.7	Silicon, aluminium, phosphate and sulphate decrease Ca sensitivity, and there is a slight ionisation interference. (Controlled by lanthanum chloride, 0.1-1.0% w/v).
Mg	$MgCl_2$	285.2	Similar to Ca.
Fe	$FeCl_3$	248.3	Sensitivity decreased by HNO_3 and Ni. (Effect smallest in very lean flame).
Cd	$CdCl_2$	228.8	None.

serious interferences were probably those caused by phosphate in measuring Ca, Mg and Pb. Additives to control interferences were not used. The signal was automatically integrated over 4-second periods, and three readings in close agreement were recorded. The 'best reading' for each sample was estimated.

2.33 Electron microprobe analysis.

Plant surface particles from gorse and Scots pine were analysed to determine their elemental constituents using the electron microprobe technique. The particulate samples were placed on double-backed sellotape on zinc stubs using a small brush. The stubs were then carbon-coated to prevent charging. Blank stubs to which no sample had been added were also prepared. A Cambridge Stereoscan 2A electron microscope was used, with an 'Ortec' Si-Li detector and 'Tracor' multichannel analyser. The instrument detected all elements of atomic number 11 or greater, but data for most spectra were only accumulated in the lower half of the energy range, which meant that Zn was the heaviest detectable element. A few complete spectra were recorded, but did not show any peaks in the second half. Samples were photographed using instant-developing film so that a record could be kept of the particles analysed.

The sizes of particles were recorded, and their overall X-ray count rates were assessed as high, medium, or low. These factors were noted mainly to see if they bore any relationship to particle composition. No attempt was made to quantify either the general X-ray yields of particles or the intensities of elemental peaks. It is possible to obtain ppm data from electron probe analysis but there are problems. In the results reported here, it is not possible to take peak heights on the spectra as relative ppm values, for the following reasons: (1) the expansion factor of the y-scale is not constant, (2) X-ray yields vary for different elements, and for different samples and particles depending on their composition, surface features and orientation to the electron beam, and (3) counting times varied for different particles, depending on the time needed to give reasonable statistical counts. (The majority of particles were counted for 200 seconds.)

Provided that good counting statistics are obtained, there can be very little doubt about the elements detected, but if statistics are poor, fluctuations in the curve can produce spurious peaks or hide genuine ones. In this case it is best to record only the obvious elements. Na and Mg may have been missed in some spectra because their X-ray energies are near the low limit of detection and are on a part of the curve where the background intensity rises steeply. Si and Zn were possible contaminants, which are discussed in the Results section.

2.4 Plant surface particle sampling.

2.41 London.

2.411 Sites and species.

Dust was collected from a mixture of yew (*Taxus baccata* L.) and holm oak (*Quercus ilex* L.) vegetation growing in a cemetery on Barnes common (Ordnance survey map reference TQ 227 762). The weather had been dry for several weeks before sampling in March 1976 and there was no ground vegetation at the site, which was therefore dry and dusty. Clouds of dust could readily be shaken from the foliage.

Particles were brushed from three other species; whole branches, i.e. leaves and twigs, of ivy (*Hedera helix* L.) from Barnes common (O.S. map reference TQ 224 760), whole branches of Lebanon cedar (*Cedrus libani* A.Rich.) from Richmond Park (TQ 205 727), and leaves of rhododendron (*R.ponticum* L.) from the same site in Richmond Park.

2.412 Methods.

Particles from yew and oak were collected by shaking foliage inside a 350 μm nylon mesh bag, within a polythene bag. Both +350 μm and -350 μm fractions were analysed, after picking out any obvious plant fragments from the coarse fraction. The only likely contaminants in the dust were polythene and nylon.

Particles from the other three species were collected by brushing, using a bristle brush, because shaking did not release adequate amounts of particles.

Only particles below 350 µm diameter were kept. Handling the foliage, and the paper on which particles were collected, may have been additional sources of contamination.

After collecting particles from them, herbage samples were retained for analysis. Surface soil samples were collected from Barnes Common cemetery and under the rhododendrons in Richmond Park and were sieved into +350 µm and -350 µm fractions, after drying. All the samples were analysed by Barringer Research Ltd. by ARL 2.

Small subsamples of dust were kept for scanning electron microscopy, and fresh material was also examined. Samples were mounted on double-sided sellotape on zinc stubs and examined in a Cambridge Stereoscan microscope.

2.42 Southwest England.

2.421 Sites.

Fieldwork was carried out August 1976 during unusually hot, dry weather. Gorse (*Ulex europaeus* L.) was the only species sampled because it was ubiquitous and was often the only species on the tailings of disused mines. Five general LOCALITIES were sampled, almost entirely in Cornwall. (Sites 13 and 14 were on the Devonshire side of the Tamar river; see Figure 2.8). SITES within a locality were within a few miles on one another and had similar geology. Four sites in each locality were sampled, of which two were expected to be mineralised and two control. Pairs of sites were regarded as FIELD REPLICATES. Site descriptions are given in Table 2.4.

Figure 2.8 Map of Cornwall showing sampling sites used in August 1976. Numbers refer to sites listed in Table 2.4. Land over 500 feet, mainly granite, is shown.

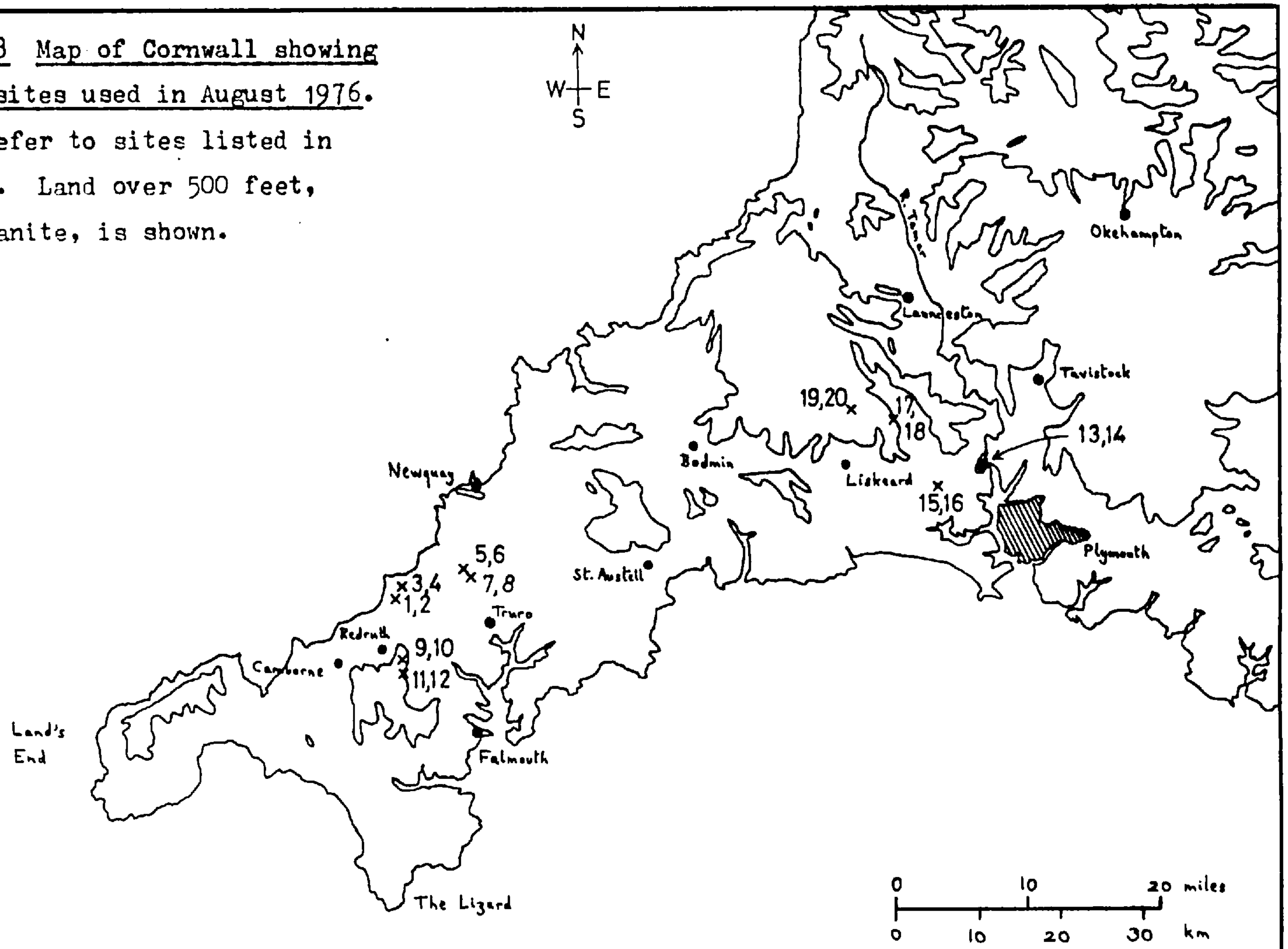


Table 2.4. Site descriptions, Cornwall, August 1976.

Site	O.S. map reference	Site Description	Locality
1	SW705469	Vegetated site near long disused mines. Expect Mn, Sn mineralisation.	Mount Hawke, N. Cornwall. Grampound Grit on metamorphic aureole. KILLAS.
2	SW707469	Site with much bare ground near old mines. Nearby ground recently disturbed by earth-movers. Expect Mn, Sn.	
3	SW714471	Hedgerows of pasture fields, about 400 yds from nearest mine workings. 'Control'.	
4	SW714471		
5	SW792508	Abandoned mine tailings, near Ventongimps. Unvegetated, but for gorse. Expect Pb, Zn, Ag.	Ventongimps, N. Cornwall. Non-metamorphosed Grampound Grit. KILLAS.
6	SW793509	As site 5, but just off the main spoil heaps, on vegetated ground, not much disturbed.	
7	SW800496	Near Killivose. Hedgerow next to pasture. 'Control'.	
8	SW801496	Close to site 7, but hedge next to farm track. 'Control'.	
9	SW719390	Well vegetated site near old Cu, Sn mine.	Redruth area. GRANITE.
10	SW719390	Similar to site 9, about 400 yds away.	
11	SW717375	Gorse in hedges between permanent pastures. 'Control'.	
12	SW717376	Similar to site 11. Adjacent field.	
13	SX414646	Hedge beside Tamar estuary. These gorse plants looked more necrotic than those elsewhere. Combined effects of drought and salinity? Expect Pb, Zn, Cu, Sn, Mn, As.	Bere Alston area. ALLUVIUM.
14	SX414646		
15	SX378618	Gorse on river Lynher bank, next to permanent pasture. 'Control'. but possibly As according to farmer.	
16	SX378618		
17	SX266722	Spoilheaps, mostly unvegetated, of disused mine. Expect Sn, Cu.	Bodmin Moor. GRANITE.
18	SX266722		
19	SX223726	Well vegetated moor, but ploughed field nearby. 'Control'.	
20	SX222726		

2.422 Sampling.

At each site, one sample of leaf surface particles, one soil sample to 10 cm depth, one sample of spinous gorse leaves, and one gorse fruits sample were collected. Particles were collected using the cyclone apparatus, powered by a 1.5 kwatt petrol generator, which was always kept downwind of the cyclone during sampling. Leaves were cut with stainless steel scissors and placed in polythene bags. Fruits were picked by hand (which may have caused sodium contamination) and put in polypropylene bottles. Small samples of bark were stripped by hand from bushes in the 'Mount Hawke' locality, but it proved very slow and difficult to remove bark without using a metal tool for scraping which it was thought might introduce contamination. (When sampling leaves, only a single scissor cut had to be made.) Therefore no more bark samples were taken.

2.423 Particle fractionation.

Particulate samples were dried, weighed and then wet-filtered through a series of three monofilament nylon meshes (Henry Simon Ltd.) held in 'Swinnex 13' filter holders (Millipore Ltd.). Mesh had been previously cut to circles of 13 mm diameter, washed in RBS 25 solution and acetone, dried and weighed. Particulate samples were suspended in 10 ml of distilled water in a syringe, and squeezed through the three filters of 45 µm, 20 µm, and 5 µm mesh sizes. The system was then washed through with another 10 ml of distilled water. The eluted liquid (20 ml) was collected in a beaker containing a weighed Whatman no. 1 5.5 cm diameter filter paper and was evaporated to dryness.

It was noticed that part of the particulate samples floated in water and therefore could not be filtered. This fraction ('float') was collected from the syringe with a glass rod (for samples in Field Replicate 1 only), and was smeared on a pre-weighed 2.5 cm diameter Whatman no. 1 filter paper.

All the dried filter fractions were reweighed to determine the weight of material on each. This information, and the appearance of each fraction, is summarised in Table 2.5. Particulate samples were analysed on the nylon or filter paper surfaces using ARL 1. +45 µm particles, however, were removed from the mesh by Barringer Research Ltd. and stuck on standard adhesive tape for analysis. Soils and herbage were analysed by ARL 2.

2.43 Ecton mine, Staffordshire.

2.431 Site description.

The site was the waste tip of Ecton Mine, Staffordshire (O.S. map reference SK 097582) which has been disused since 1858, but was previously one of the richest copper producers in England, in terms of the concentration of copper in the ore. The mine also yielded lead and zinc. The mineralisation comprised a number of veins and pipes in the limestone of Ecton Hill, and the waste material on which this sampling was carried out was strewn over the lower slopes of the west side of the hill over an area of about four acres. Further details of the mine are given by Robey & Porter (1972).

The mine waste is naturally devoid of vegetation, but several tree species were planted in 1959, in hollows 2 metres in diameter by 30 cm deep, filled with non-mineral-

Table 2.5. Weight and nature of particulate samples collected from gorse.

Fraction	Mean Weight (mg)	Range (mg)	% Recovery of original sample	Appearance
Float	1.1	<1-9	1	Bright green.
+45 µm	42	17-68	57	Fluffy, green.
+20 µm	10	2-21	14	Not fluffy, mainly particulate, grey-green.
+ 5 µm	0.9	<1-3	1	Soil-like, grey-green.
Eluate	4.0	<1-10	5	Grey-brown, no visible structure.
Total	58		79	
Original sample	74	27-159	(100)	Green, fluffy, with greenish particles.

ised soil. Usually about four trees of different species were planted in the same hollow. A nitrogen-magnesium fertiliser has been applied to the soil (Personal communication, Peak Park Joint Planning Board, Bakewell). At the time of this work the trees were between 1.5 and 4.5 metres high, and many showed discoloration of the leaves, perhaps suggesting metal toxicity.

2.432 Fieldwork, 1976.

Foliage samples were taken on 26/4/76 about 1.5 metres above the ground from trees of Scots pine (Pinus sylvestris L.), rowan (Sorbus aucuparia L.), birch (Betula pendula Roth), and other species. Samples were placed in polythene bags whose necks were knotted. The birch and rowan trees were just coming into leaf and the birches had catkins bearing pollen. Soil samples were taken of the surface microlayer of the mine waste, and of about the top 10 cm of both mine waste and imported soil used for planting trees.

2.433 Laboratory, 1976.

In the laboratory, particulate matter was collected from tree samples. For pine, the method was to brush the foliage with a bristle brush, collecting the particles in a nylon mesh of 350 µm over a sheet of clean paper. Both +350 µm and -350 µm fractions were analysed, after removing very big particles (e.g. needles) from the +350 µm fraction. Brushing proved too vigorous for the relatively delicate foliage of rowan and birch, and therefore the samples were placed inside the 350 µm mesh which was held as a bag and shaken over a sheet of paper. Only the -350 µm fraction of the deciduous trees' particles was collected. Particulate samples were placed on standard adhesive tape with a fine brush for analysis by ARL 1. In addition, enough coarse (+350 µm) pine particles were collected for one sample to be analysed by ARL 2.

After collecting particles, herbage was dried and separated into bark, leaves, and buds or floral parts. Wood was discarded because it was not a potential particle-producing material.

2.434 Fieldwork, 1978

Fieldwork was carried out on 22/5/78. Five trees of each species, Scots pine, rowan, and birch, were selected and four samples cut from each, of which two were washed and the other two left unwashed. Samples were leached for 2 h. and then placed in individual, labelled polythene bags. Very few leaves became detached in the leaching bottles but any that did were removed with a fine stainless steel needle if floating, or if sunk by pouring the leachate carefully into another bottle. The leachate bottles were fitted with screw caps. Separate herbage samples were taken for analysis, two replicates from each tree.

2.435 Laboratory, 1978.

Leaf areas, as well as fresh weights and dry weights, of leached herbage samples were recorded. Leaf areas were measured with an Eel Large Area Meter, although the value of these measurements when comparing plants of such different morphologies is doubtful. Leached herbage samples were then discarded.

1.0 g (dry weight) samples of unwashed herbage samples for analysis (leaves and twigs) were digested in conical flasks in 25 ml of 4 : 1 HNO_3(70% Analar) : $HClO_4$ (60% Lab. reagent grade). After cold digestion overnight, the liquid was boiled to about 4 ml and made up to 20 ml with distilled water. Digestion was virtually complete.

Leachates and herbage digests were filtered (Whatman no. 1) and analysed for Na and K by flame photometry and for Cu, Mn, Zn, Pb, Ca, and Mg by atomic absorption spectrophotometry. For Cu and Pb determinations on leachates, replicates 1 and 2 were combined, recording the volume (which was decreased by previous analyses), concentrated by boiling and made up to 5 ml. Data were converted back to ppm in the original leachates. Leachate concentrations were converted to µg of metal removed per g dry weight of herbage as follows:

$$\mu\text{g metal. } g^{-1} \text{ herbage} = \frac{\text{leachate ppm} \times \text{leachate vol., ml}}{\text{herbage dry wt., g}}$$

Birch leachates were noticeably yellow, due to pollen, and considerable difficulty was found in analysing samples, especially after concentrating, because the spectrophotometer kept blocking. Filtering through Whatman no. 1 paper did not make any difference.

2.5 Deposition sampling.

The chief aim was to compare metal deposition on open ground and under forests, and an urban site was included for comparison. Moss bags (MB) and total deposition collectors (TD) were at first exposed concurrently then, after two 4-week runs, TD sampling was continued alone. A third MB run was set up at Thetford in April 1978, to check unusual aspects of the deposition at Thetford. The sampling timetable is given in Table 2.6., and the replication at each site in Table 2.7.

2.51 Sites.

Sites used for both TD and MB work were Thetford forest, Norfolk (O.S. map reference TL 805836); the roof of the Zoology Department, Imperial College, South Kensington, London; Silwood Park, Ascot, Berks. (SU 944687); Swinley forest, near Ascot (SU 900671); and Blanchdown Wood, near Tavistock, Devon (SX 428735). The three forest sites are described below.

2.511 Thetford.

At Thetford the sole tree species was Scots pine. The trees were about 48 years old with an average height of about 18 metres and a density of 800 stems.ha^{-1}. The leaf area index (the ratio of total leaf area to ground area) lay within the range 9 to 12. The soil at Thetford is composed of 1-2 metres of acid eluviated sand overlying a clay- and iron-enriched illuvial front and a chalky sand till (Oliver, 1975). The site was at least 3 km from any

Table 2.6. Timetable of total deposition and moss bag sampling.

	Thetford	London	Ascot (Silwood Park & Swinley)	Tavistock
TD set up. MB run 1 set up	26 Aug 77	12 Aug 77	11 Aug 77	15 Aug 77
End of period 1 TD samples only	9 Sept 77	17 Aug 77	18 Aug 77	29 Aug 77
End of period 2 TD & MB samples MB run 2 set up	24 Sept 77	9 Sept 77	8 Sept 77	12 Sept 77
End of period 3 TD & MB samples	21 Oct 77	7 Oct 77	6 Oct 77	10 Oct 77
End of period 4 TD samples only	16 Dec 77	2 Dec 77	1 Dec 77	5 Dec 77
End of period 5 TD samples only	27 Jan 78	27 Jan 78	26 Jan 78	30 Jan 78
MB run 3 set up	22 Apr 78			
End of period 6 TD Samples. MB run 3 harvested.	20 May 78	19 May 78	18 May 78	15 May 78

Table 2.7. Replication of total deposition bottles and moss bags.

Site		Number of TD	Number of MB
Thetford	T	4	10
	F	4	10
	O	-	10
London	O	3	6
Silwood	O	3	6
Swinley	O	4	6
	F	4	6
Tavistock	O	9	15
	F	6	10

T = top of tower; O = open ground near ground level;

F = under forest canopy near ground level.

main road or village. Samples of pine needles and twigs, bracken, leaf litter/humus, and 'A' horizon soil (eluviated) were taken on 9/9/77, dried and analysed along with samples from other sites by ARL 2. The site was equipped with a 30 metre high meteorological tower. TD and MB were set up at the top of the tower (T) and under the forest (F), and in MB run 3 in a clearing (O).

2.512 Swinley.

The forest was planted to Scots pine and European larch with an estimated height of 12 metres and age of 20 years. The tree density was very much higher than at Thetford. The open site (O) was a very large clearing. Both O and F sites were about 400 metres from a main road (A332) and about 2 km from the outskirts of Bracknell. Soil, humus, and leaf litter samples were taken on 31/9/77.

2.513 Tavistock.

The forests surround the disused Devon Great Consols Mine (Cu and As) in a rural but strongly mineralised area 14 km north of Plymouth (see Booker, 1971). The areas of forest used for sampling were mixed stands of Scots pine, oak, and birch of which Scots pine was by far the most important canopy species. Aerial photographs showed that the forest had grown up within the last 27 years. Tree height and spacing were intermediate between Thetford and Swinley. Soil and tree samples were taken on 2/5/77 and 29/8/77.

Deposition samplers were set up in five blocks, with increasing distance from the main mine waste area, but all on mineralised soil. Three TD bottles and five MB were placed in each block. Block I was in the open at the edge of the forest on more-or-less bare mine waste. Blocks II and IV were in grassy clearings, of about 25 metres and 5 metres diameter respectively. Blocks III and V were under the forest about 300 metres and 500 metres respectively from the main spoil area.

2.52 Total deposition bottles.

2.521 Construction of gauges.

Each TD gauge comprised an 8.9 cm diameter polypropylene funnel, covered with 350 µm washed nylon mesh, placed in the neck of a collecting bottle and fixed with PVC tape. Initially, 500 ml washed polythene bottles were used, covered in black plastic to inhibit algal growth, but exceptionally heavy rain in the first week of sampling caused these to overflow. Subsequent samples were collected in 2.5 litre Winchesters, previously containing acids or alcohols, and washed thoroughly before use. These bottles had tinted glass which was expected to inhibit algal growth, and black plastic was also used as a covering. The bottles were placed on the ground.

2.522 Sampling procedures.

Samples of rainwater and suspended matter (well shaken) were taken at intervals, largely determined by amounts of rainfall, from August 1977 to May 1978. The final sampling interval of 15 to 18 weeks was the longest because of relatively dry weather and because large (500 ml) samples were required for more detailed analysis. Actual sampling dates are given in Table 2.6.

The usual sampling procedure was to take approximately 60 ml from each gauge after shaking the Winchester to ensure that particles were well dispersed. The total volume in each gauge was recorded and then the remainder of the rainfall was discarded. Samples were kept in polypropylene bottles (washed before use) and stored in a refrigerator. 500 ml samples were collected in washed polythene bottles.

2.523 Preparation of samples for analysis.

Na and K were first measured by flame photometry, followed by a pH determination. Samples were then concentrated for heavy metal analysis. The exact volume of each sample was recorded and samples were boiled to a few ml in Pyrex conical flasks. 1.0 ml of 5 M HCl ('Analar' grade) was added to each flask and the volume made up to 10 ml with distilled water. Blanks were prepared in the same way using 60 ml aliquots of distilled water. Samples were filtered through Whatman no. 1 paper and analysed for Cu, Mn, Zn, and Pb by atomic absorption spectrophotometry.

The 500 ml samples collected in May 1978 were boiled to 30-50 ml and acidified with 5 ml of 5 M HCl, recording the exact final volume. Otherwise, the preparation was the same as for the small samples. These samples were analysed for Cu, Mn, Zn, Pb, Ca, Mg, Cd, and Fe.

2.53 Moss bags.

2.531 Preparation of moss.

Moss bags were prepared using Sphagnum moss either bought from Rassell's Garden Centre, Earls Court Road, London or collected from Black Pond, Esher, Surrey (O.S. map reference TQ 127623). The moss was carefully sorted, selecting only green shoots of Sphagnum, rinsed three times in distilled water, and left soaking in 0.1 M 'Analar' grade HNO_3. After three 24 h. washes in 0.1 M HNO_3 the moss was again rinsed three times in distilled water, squeezed out and stored in a moist condition in polythene bags. The moss was also squeezed out between each wash or rinse to ensure as complete a change of solution as possible, and was only handled during and after washing with polythene gloves.

2.532 Making the bags.

Moss bag design was based on Goodman et al. (1974). Monofilament nylon mesh of 1550 μm pore size was used (Henry Simon Ltd., type 14 GGN). The mesh type was selected as having the largest percentage open area (63%). The bags were flat, 10 cm by 10 cm, evenly packed with about 12 g of moist moss (approximately 1.5 g dry weight). Moss bags were suspended in the middle of plastic-coated wire hoops by a thread at each corner and exposed horizontally on the top of bamboo canes 1 metre above ground level for 4 weeks (Figure 2.9).

2.533 Preparation for analysis.

After exposure, bags were placed in individual polythene bags, brought back to the laboratory and dried along with unexposed moss. The dry weight of moss in each bag was recorded. Subsamples from runs 1 and 2 were analysed by ARL 2, and lead by atomic absorption at Barringer Research Ltd. Bags from run 3 (Thetford only) were dried, weighed, digested and analysed as described in Sections 2.13 and 2.32. Digestion was virtually complete.

Figure 2.9. Moss bag, showing the method of exposure in the field. Behind the bag, a TD gauge of the type used in the first two weeks can be seen.

3. RESULTS.

3.1 Metals released from radio-labelled plants.

3.11 Transpiration experiments.

Since the object of the research programme was to measure release of metals from plants in the field, it was decided initially to try and trap metals which might be associated with evapotranpirates. The first experiments were carried out in late 1975 on plots which had regained their natural mixed herbaceous vegetation after applying isotopes to the soil surface at the start of the growing season.

Table 3.1 shows the distribution of ^{65}Zn and ^{210}Pb in the soil at the time of the experiments. While the greatest activity was still in the top 5 cm of soil, there had been appreciable penetration of both isotopes during the nine months to at least 15 cm depth, although in taking the cores there may have been some contamination of deeper layers by soil originating nearer the surface. The results for zinc are in good agreement with the migration of ^{65}Zn in soil columns reported by Abebe (1972) and Singh (1974). The distribution of total Zn and Pb as determined by atomic absorption, however, was relatively uniform with depth. Because there had not been complete isotopic mixing over depths penetrated by roots, data from these experiments have been expressed in activity (counts.sec^{-1} or counts. min^{-1}), and not converted to amounts of Zn or Pb.

There was appreciable ^{65}Zn loading in the vegetation (Table 3.2) and evidence of slightly higher levels

Table 3.1. Radioactivity in soil on ^{210}Pb and ^{65}Zn plots at Silwood Park, nine months after application of isotopes to the soil surface. (Solid scintillation counter)

Mean of 6 soil cores per plot ± standard deviation. Total Zn and Pb were determined on 2 soil cores from each plot.

Site	Depth (cm)	Activity (Counts. sec.$^{-1}$ g^{-1} dry weight, corrected for background)	Total Zn ppm dry wt.	Total Pb ppm dry wt.
^{65}Zn plot	0- 5	2.07 ± 1.31	55	59
(Background	5-10	0.74 ± 0.53	36	59
at 1.14 MeV =	10-15	0.64 ± 0.64	24	51
0.21 counts.	15-20	0.29 ± 0.21	48	56
sec^{-1})				
^{210}Pb plot	0- 5	2.42 ± 2.35	82	41
(Background	5-10	1.65 ± 1.29	83	39
at 0.10 MeV =	10-15	1.31 ± 1.32	69	43
0.03 counts.	15-20	0.34 ± 0.15	91	57
sec^{-1})				

Note: 1 count.sec.$^{-1}$ represents 1.95 ng of applied Zn or 0.03 ng of applied Pb.

Table 3.2. Radioactivity in herbage (October 1975) on ^{65}Zn and ^{210}Pb plots at Silwood Park, allowed to regrow for six months after application of isotopes to the bare soil surface (Solid scintillation counter)

	Activity (Counts.sec.$^{-1}$g^{-1} herbage, corrected for background)	
	Dry	Ash
^{65}Zn (1.14 MeV)		
^{65}Zn plot:		
Grass (living)	5.13	79.79
Grass (dead)	7.82	
Thistles (dead)	3.01	-
Control plot:		
Grass (living)	0.31	0.71
Grass (dead)	0.31	
Thistles (dead)	0.69	-
^{210}Pb (0.10 MeV)		
^{210}Pb plot:		
Grass (living)	0.15	1.86
Grass (dead)	0.28	
Thistles (dead)	0.05	-
Control plot:		
Grass (living)	0.26	0.12
Grass (dead)	0.23	
Thistles (dead)	0.05	-

Note: Grass (living + dead) contained 87 ppm Zn dry weight (std.dev. 25 ppm) and 101 ppm Pb (std.dev. 6 ppm).

on a dry weight basis in the old, dead leaves of grass relative to living material. There was however very little ^{210}Pb in the foliage, which suggested that ^{210}Pb levels in transpirates were likely to be low.

Preliminary runs with two chambers were inconclusive, and more chambers were constructed to provide replication. The results of the main series of experiments are given in Table 3.3 and show that variable amounts of radioactivity were collected, ranging from background levels to easily detectable amounts. The consistency of control samples showed that laboratory procedures, which involved accumulating the whole of each sample on to one planchet by evaporation, did not introduce contamination, and it seemed that radioactivity must have been transported from the soil by a process which did not necessarily involve the plants. Effects of rain-splash and wind-blowing were ruled out by the nature of the experiments, and the two most likely possibilities were that slight but significant contamination was sometimes introduced (1) in the process of setting up or dismantling the apparatus, although great care was taken, and/or (2) by activities of small animals such as insects in the chambers.

Because of difficulties inherent in using the plots for this type of experiment (e.g., radioactivity derived from the soil surface, the heterogeneity of the vegetation, and the problem of keeping a close watch on the experiments), a further transpiration experiment was carried out using the Cupressus leylandii system at South Kensington, whose design is described in Section 2.22. The bottoms of the chambers were sealed around the plant stems to make completely closed systems (Figure 2.4), and a permanent feature of the growing system was that the shoots were at all times protected from the radioactive soil (Figure 2.2).

About 30 ml of water were collected per plant in each 24 h. run, and more condensed on the walls of the

Table 3.3. Radioactivity in evapotranspirates on ^{65}Zn and ^{210}Pb plots at Silwood Park.

Counts.min^{-1} per sample, not corrected for background; gas flow counter.

A

Run		3 (7 - 17/11/75)		4 (17 - 28/11/75)		5 (28/11 - 12/12/75)	
Duration		241 h		264 h		334 h	
Volume dried down per sample		44 ml		41 ml		37 ml	
Site	Replicate ↓	ml	counts. min^{-1}	ml	counts. min^{-1}	ml	counts. min^{-1}
^{65}Zn plot							
Vegetation	1	52	63.81	56	14.54	50	14.46
	2	58	16.41	57	15.64	46	29.51
	3	45	31.28	53	15.36	44	14.97
Bare soil		53	13.87	65	(186.53)	59	14.81
^{210}Pb plot							
Vegetation	1	49	17.32	57	14.80	46	15.58
	2	54	15.99	42	15.49	38	23.39
Bare soil	1	53	20.91	65	14.14	52	18.20
	2	56	18.61	66	15.19	56	14.30
Laboratory control							
Distilled water	1		13.64		14.31		14.54
	2		13.84		13.90		14.08
	3		13.20		13.58		14.34
	4		13.64		14.75		14.12

B

	Mean vol. ± std.dev.	Mean counts.min^{-1} ± std.dev.
^{65}Zn Vegetation	51.2 ± 5.3	24.00 ± 16.33
^{65}Zn Bare soil	59.0 ± 6.0	14.34 ± 0.66
^{210}Pb Vegetation	47.7 ± 7.2	17.10 ± 3.19
^{210}Pb Bare soil	58.0 ± 6.0	16.89 ± 2.76
Lab. control.	-	14.00 ± 0.45

chambers, showing that transpiration was actively occurring. The ^{65}Zn activity in the herbage (plant 8) was approximately 500 times the control level (Figure 3.1). Even so, transpirates from the ^{65}Zn-labelled plant contained scarcely more radioactivity than control samples, though the possibility of a slight effect cannot be ruled out (Table 3.4).

It is possible to calculate the maximum release that could have been occurring, as follows. The whole radioactive shoot which was enclosed contained enough ^{65}Zn to give about 0.25 x 10^6 counts.min.$^{-1}$ on the gas flow counter. (Shoot activity was approximately 5 counts.min.$^{-1}$ mg^{-1} dry weight from Figure 3.1, and a shoot dry weight of 50 g is assumed; see section 3.74.) The count rate of transpirate from the labelled plant was within 0.5 counts. min.$^{-1}$ of the control level (Table 3.4). This implies that, very roughly, less than 0.0002% of ^{65}Zn activity in the shoot was collected in 24 h. Release of ^{65}Zn in the transpiration water of C.leylandii was thus extremely small, if it existed at all.

The insides of the chambers were swabbed with glass fibre pads at the end of the experiment because the condensate on the walls might have contained ^{65}Zn leached out of the foliage, at points of contact. However, Table 3.4 shows that no radioactivity could be picked up in this way. It was intended also to swab the plant surfaces to collect leachates, but the foliage was found to be dry immediately the chambers were dismantled, perhaps due to leaf temperature being slightly above ambient temperature.

3.12 Metal release to the atmosphere from radioactively labelled plots.

If metal release from plants into the atmosphere

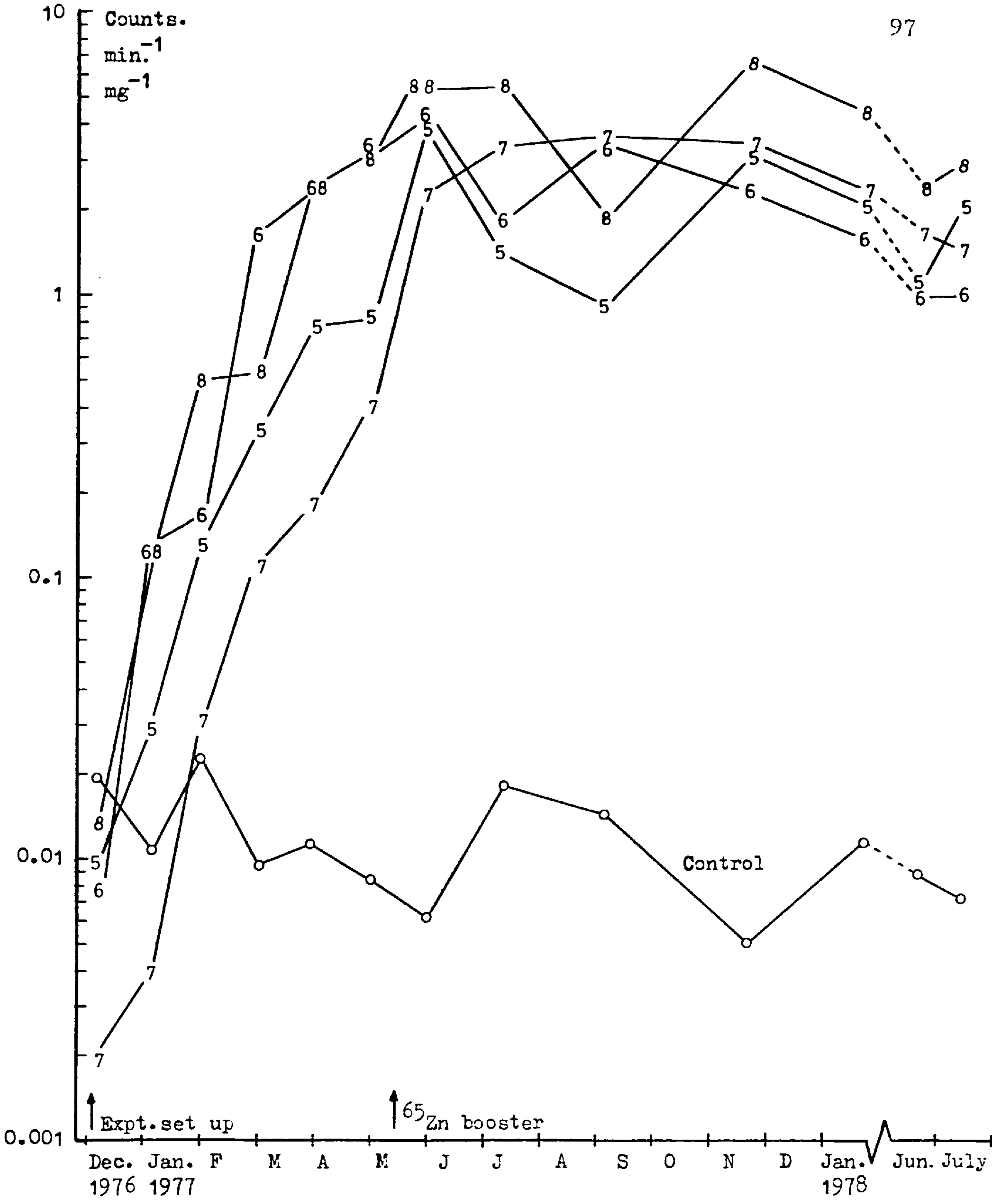


Figure 3.1 Time course for uptake of ^{65}Zn by Cupressus leylandii at South Kensington (counts. min.$^{-1}$ mg^{-1} herbage dry weight).

Gas flow counter. Counts corrected for background but not for decay. Numbers 5,6,7,8 refer to individual labelled plants. Control is mean of four plants.

Table 3.4. Radioactivity in transpiration water of Cupressus leylandii.

Counts.min^{-1} per sample, not corrected for background; gas flow counter.

Each sample was collected for 24 h. (20 to 30 ml).

Run	Transpirates		Water swabbed from inside of chambers at end of experiment (i.e., 6 reps. after run 3)	
	Control (Plant 1)	^{65}Zn (Plant 8)	Control (Plant 1)	^{65}Zn (Plant 8)
No. of replicates →	3	3	6	6
1	13.78	13.89		
2	14.24	14.36		
3	13.89	14.33		
Mean ± standard deviation	13.97 ±0.24	14.19 ±0.26	14.17 ±0.25	14.11 ±0.34

Background = 13.80 ± 0.40 counts.min^{-1}

is a significant source of aerosol, it should be possible to demonstrate this by collecting aerosol particles close to a labelled source. With this in mind, experiments were carried out on the radioactive plots already described, using 'Casella' cascade impactors.

The first approach utilised a modified transpiration chamber with an inlet and outlet hole. Air was drawn through the chamber using a suction pump, being filtered through a glass-fibre filter on the intake side, and passed through a cascade impactor at the outlet. However, it was impossible to seal the chamber at the soil surface even if it was embedded, and therefore the chamber was discarded.

Using free-standing cascade impactors (October - November 1975) to sample ambient air 0.3 metres above ground level, no differences in radioactivity could be detected between samples taken immediately downwind of the ^{65}Zn or ^{210}Pb plots and a control site 5 metres upwind of both plots. Samples were collected for up to 6 hours, which represents a filtered air volume of 6.3 m^3. Visible deposits were present on all 4 stages, covering an impacted-particle size range of approximately 0.4 µm to over 20 µm. Negative results were also obtained with labelled Cupressus leylandii seedlings in summer 1976.

3.13 Radioactivity in plant surface particles.

3.131 Cupressus leylandii at Silwood Park.

Because aerosol is such a highly dispersed material, both in terms of its concentration and its distance of travel, it seemed more practical to investigate possible release of metals from plants by collecting particles on plant surfaces. This approach was adopted at various stages in the project, using a cyclone and other methods. The cyclone did not collect particles smaller than about 2 µm, or vapours.

Sampling C.leylandii plants at Silwood Park with a cyclone did not show any detectable loading in particles from ^{65}Zn-labelled plants, but slight ^{115m}Cd release seemed to be occurring (Table 3.6). The detection limit for Zn in particulate samples was estimated to be about 11 ng per sample (or per plant), as follows:

> ^{65}Zn activity in shoot was 1.145 counts.min.$^{-1}$ mg^{-1} (Table 3.5). C.leylandii shoots were found to contain 25 ng Zn.mg^{-1} dry weight (std.dev. 6 ng.mg^{-1}; mean of 8 replicate samples, August 1978), giving a specific activity of 0.046 counts. min.$^{-1}$ng^{-1}Zn. Limit of detection was about 0.5 counts.min^{-1} above background, equivalent to 11 ng Zn.

Using a similar argument, the Cd release was estimated to be about 1 ng from each shoot about 40 cm high, weighing about 50 g dry weight:

> ^{115m}Cd activity in shoot was 4.209 counts.min.$^{-1}$ mg^{-1} (Table 3.5). C.leylandii shoots contained 0.35 (std.dev. 0.07) ng Cd.mg^{-1} dry weight, giving a specific activity of 12.03 counts.min.$^{-1}$ng^{-1} Cd. Cd release was 13.61 counts.min.$^{-1}$ (above control; Table 3.6), equivalent to 1.13 ng Cd.

An attempt was made to fractionate such particles into various sizes and a water-soluble fraction to determine the distribution of activity. However, although relatively large samples of 10 to 20 mg were obtained from each plant, any activity that may have been present was

Table 3.5. Radioactivity in herbage of Cupressus leylandii at Silwood Park.

Counts.min.$^{-1}$mg^{-1} dry weight, corrected for background; counted on gas flow counter; not corrected for decay. Mean of 4 samples ± standard deviation.

Sampling date	27/7/76	10/9/76
Counting date	9/8/76	21/9/76
Mean dry wt. of herbage per planchet (mg)	212	79
Control	0.004 ± 0.003	0.015 ± 0.003
^{65}Zn	1.145 ± 0.712	1.241 ± 0.778
^{115m}Cd	4.209 ± 3.237	3.932 ±3.037

Table 3.6. Radioactivity in foliar particles collected from *Cupressus leylandii* at Silwood Park using a cyclone.

Counts.min.$^{-1}$ per sample, not corrected for background or decay; Gas flow counter. All the plants were of uniform size and were sampled for the same length of time.
Mean ± standard deviation.

Sampling date	No. of reps.	Treatment		
		Control plants	^{65}Zn plants	^{115m}Cd plants
21/5/76	3	15.29 ± 1.84	16.85 ± 1.21	28.29 ±11.57
2/6/76	2	15.85 ± 3.78	13.20 ± 0.09	28.67 ±19.33
26/7/76	4	16.06 ± 2.57	17.17 ± 2.31	30.53 ±20.09
All	9	15.76 ± 2.29	16.18 ± 2.29	29.37 ±15.26

Background = 13.09 ± 0.48 counts.min^{-1}

diluted out in the fractionation process (Table 3.7).

3.132 Cupressus leylandii at South Kensington.

For this long-term labelling system, Cd was not used since all its isotopes have relatively short half-lives, and the experiment concentrated on achieving the highest practical ^{65}Zn loading in the foliage in a reasonably natural growing situation. The long-term uptake of ^{65}Zn into the foliage is plotted in Figure 3.1, showing that the ^{65}Zn activity in the leaves was approximately five times that obtained in the Silwood experiment (Table 3.5 cf. Figure 3.1).

Particulate samples were collected with the cyclone on several occasions summarised in Table 3.8 , and indeed marginally higher count rates than recorded in the Silwood experiment were found. However, a similar increase also applied to control plants and seemed to originate from radioactivity in aerosol fallout on the plants. It was found that enough aerosol for counting could be collected by leaving the cyclone on for several hours and that this material contained more activity per mg than particles collected from the labelled plants (Table 3.8).

It is possible to distinguish isotopes having different energies of γ-emission using a multi-channel analyser. Samples were therefore recounted for 10,000 secs. over a Ge-Li detector with a 'Laben 8000' analyser (University of London Reactor Centre). The results showed that aerosol samples had a very similar spectral composition to dust collected from the plants, but neither contained detectable ^{65}Zn. The only sample in which ^{65}Zn was detected was a check sample of labelled herbage, which gave 11.55 counts.min^{-1} (combined count over the 3 peak channels [= keV units; 1115, 1116, 1117] corrected for background). On the gas flow counter, the identical

Table 3.7. Radioactivity in foliar particles collected from Cupressus leylandii at Silwood Park using a cyclone on 28 to 30 June 1976 and wet-sieved.

Counts.min.$^{-1}$ per sample, not corrected for background; Gas flow counter. Each sample was estimated as 10 to 20 mg dry weight.
Mean of 4 replicates (plants) ± standard deviation.

Filter size (μm)	Treatment		
	Control plants	^{65}Zn plants	^{115m}Cd plants
190 (retained by)	14.05 ± 0.36	14.54 ± 0.26	14.26 ± 0.53
99	14.38 ± 0.29	14.06 ± 0.44	14.44 ± 0.41
20	14.80 ± 0.54	14.31 ± 0.45	15.25 ± 0.88
5	13.43 ± 0.50	13.87 ± 0.44	14.24 ± 0.92
0.22	13.14 ± 0.42	13.62 ± 0.69	13.70 ± 0.32
Aqueous	14.52 ± 0.38	15.31 ± 0.64	15.53 ± 1.54

Background = 13.09 ± 0.48 counts.min^{-1}

Table 3.8. Radioactivity in foliar particles collected from Cupressus leylandii at South Kensington using a cyclone. (Gas flow counter)

Sampling date	No. of replicate samples	Treatment & Sample	Activity in particles	
			(Counts. min^{-1} per sample, not corrected for background) Mean±std.dev.	(Counts.min^{-1} mg^{-1} dry weight, corrected for background) Mean±std.dev.
25/5/77	1	^{65}Zn (Plant 8)	16.63	0.34
1 - 8/6/77	4	Control plants	16.51±1.09	0.21±0.09
	4	^{65}Zn plants	16.86±1.52	0.25±0.14
11 - 15/7/77	2	Ambient aerosol	28.18±0.81	1.72±0.79
	2	^{65}Zn plants	21.86±3.66	0.70±0.09
9 - 14/1/78		Pre-treatment by enclosing plants in polythene bags for 4 to 5 days:		
	1*	Control plants	16.48	0.21
	1*	^{65}Zn plants	17.23	0.35
	* Bulked samples from 4 plants			
All	5	Control plants	16.51±0.95	0.21±0.08
	8	^{65}Zn plants	18.34±3.03	0.38±0.22
	2	Ambient aerosol	28.18±0.81	1.72±0.79

Background = 13.49 ± 0.40 counts.min^{-1}

sample gave 140.19 counts.min.$^{-1}$ (above background) indicating the superiority of the gas flow counter for low-activity samples.

A variation to the cyclone experiment was tried by first washing the plants thoroughly using a hose pipe to remove deposited dust, and then sealing the shoots in polythene bags to (1) prevent further dust being deposited and (2) create a wet micro-climate which might encourage leaching of ^{65}Zn on to the plant surface. However, samples collected with the cyclone when the bags were removed after four to five days did not reveal any measurable enhancement of metal release (Table 3.8).

3.14 Throughfall experiment on C.leylandii at South Kensington.

The importance of radioactivity deposited on these cypress plants, as opposed to any ^{65}Zn released, was further demonstrated by collecting rainwater in filter funnels underneath each canopy and passing it through ion-exchange resin which was counted after two weeks exposure (4 to 18 November 1977). The radioactivity collected did not appear to depend on the presence of ^{65}Zn in the foliage but was markedly raised by increasing the catchment area of a funnel with polythene sheeting, under control and labelled plants (plants 1 and 6 respectively, Table 3.9).

Table 3.9. Radioactivity collected beneath the foliage of Cupressus leylandii at South Kensington.

Plant	Activity	
	Counts.min.$^{-1}$ per resin sub-sample, not corrected for background.	Counts.min.$^{-1}$mg^{-1} resin dry wt., corrected for background (resin blank)
Control		
1 (Total)	21.94	2.32
2	17.12	1.35
3	14.78	0.38
4	13.72	0.09
^{65}Zn-labelled		
5	16.16	0.81
6 (Total)	29.68	5.09
7	17.83	1.18
8	16.67	0.94
Resin blank	13.41 (std.dev. 0.04, 2 replicates)	

3.2 Composition of plant surface particles in London.

One positive conclusion from the ^{65}Zn-C.*leylandii* experiments at South Kensington was that pollution was very important in an urban situation in determining the composition of plant surface particles. To assess this on a multi-elemental basis, dust was collected from plants in London and analysed along with herbage and soil at each site. All samples were analysed by the same method (ARL 2) and therefore it should be possible to compare all types of sample with one another, unlike later work where ARL 1 was used for particulate samples. Because ARL 2 required relatively large samples (at least 50 mg, and preferably 500 mg) there was no replication of dust samples from each species, but trends which are generally apparent for all four species seem likely to result from aerial pollution.

The accuracy of the analytical system was checked by having samples of Bowen's kale analysed (Bowen, 1974). The consistency of analysis seemed good, although some elemental concentrations differed from previously published values (Table 3.10).

The mixed foliar dust sample shaken from yew and holm oak at Barnes Common Cemetery was large enough for accurate analysis (about 500 mg), and was separated into coarse (+350 µm) and fine (-350 µm) fractions. The two fractions were very different in composition, the coarse particles essentially resembling herbage (ratio of columns 1:3, Table 3.11), while the fine fraction was enriched in several elements compared to plant material (ratio of columns 2:3, Table 3.11), chiefly Ni (enriched x 7), V (x 5.5), Na (x 4), and Zn, Cr, and Be (x 3). The fine foliar dust showed even less resemblance to surface soil sieved through the same mesh (ratio of columns 2:5, Table 3.11), and was enriched in Ca (x 15), Na (x 10), Zn (x 8.5), Sr (x 8), Ni (x 7), Cu (x 5), and V, Mn, and Mg (x 4). It was strongly depleted in Si (x 0.1), although Si was incompletely extracted from all samples by the digestion used. The only logical conclusion is that the chemistry of plant surface dust was strongly affected by atmospheric fallout, although one obviously cannot rule out an influence of the plants or local surface soil.

In appearance, the +350 µm dust fraction was fibrous, and under the electron microscope was seen to be mainly composed of the stellate trichomes which form a dense, white indumentum on the underside of <u>Quercus</u> <u>ilex</u> leaves. The trichomes appeared to have small particles sticking to them (Figure 3.2). The visual appearance of the -350 µm fraction in contrast was particulate and 'soil-like'. It contained irregular particles of various sizes and some stellate trichomes (Figure 3.3).

From rhododendron, cedar, and ivy (Tables 3.12, 3.13, and 3.14), dust was collected by brushing rather than shaking, but despite this more vigorous treatment it was only possible to collect relatively small samples (about 50 mg), perhaps because all the plants were glabrous. Only the -350 µm fractions were retained because it appeared that coarser, fibrous material was produced by breaking-up the leaf surface. The enrichment ratios in foliar dust: herbage were generally larger than at the cemetery, particularly for Cu, Zn, Cr, Ti, Al, Fe and Pb. This could be due to differences between methods, species, and sites, and the possibility of errors arising from analysing very small samples should also be borne in mind.

Considering all four sets of data (Table 3.15), the following elements showed no enrichment in fine surface particles compared to herbage: Ca, Mg, P, and Mn, which are all plant nutrients. Ni, Cr, and V were always strongly enriched, and usually Ti, Cu, Al, Fe, Pb, Zn, Ag, and Ba, most of which are heavy metals, often associated with pollution.

Table 3.10. Analysis of Bowen's Standard Kale by Barringer Research Limited, 18th May, 1976. Values in ppm dry weight.

Element	ppm in Kale samples			Value from Bowen, 1974
	Sample No. 21	Sample No. 41	Sample No. 50	
Ni	3.8	5.1	4.1	< 0.2
Cu	5.05	4.79	5.08	4.99(3.6-6.5)
Zn	33.4	48.9	43.9	33.2 (30-38)
Cr	3.0	4.0	3.7	0.308
Co	6.3	14.1	9.3	0.0581
Cd	2.2	3.2	2.5	0.80 (0.38-1.06)
Ag	0.8	1.8	1.2	(0.03-0.5)
Sr	82.3	84.2	88.7	98.9 (65-150)
V	1.7	2.3	2.0	0.36 (0.33-0.41)
Be	0.68	0.78	0.84	not determined
P	2,200	5,800	6,200	4,489 (4020-4810)
Ti	0.5	not detected	not detected	(0.33-3.3)
Mn	12.5	15.8	15.9	14.73 (12.6-18)
Ba	4	5	8	4.55 (4-6.4)
Al	43	37	37	38 (6-88)
Fe	98	108	108	118
Ca	18,100	38,000	41,600	40,850
Mg	1,370	1,630	1,570	1,572
Si	6.7	11.6	9.9	237
Na	2,280	2,540	2,620	2,506
Pb	1.5	0.5	2.5	2.6 (1.6-3.8)

Table 3.11. Elemental composition of yew and holm oak foliar surface dust, herbage and surface soil from Barnes Common Cemetery. (ppm dry weight)

Element	Foliar dust		Herbage	Surface Soil		Enrichment or Depletion Ratios				
	+ 350µm Coarse	− 350µm Fine		+ 350µm Coarse	− 350µm Fine					
Column	1	2	3	4	5	2/3	2/5	3/5	1/3	5/4
Ni	17	92.7	12.7	11.6	13.2	7.3	7.4	1.0	1.3	1.1
Cu	23.4	88.6	36.2	11.7	18.0	2.4	4.9	2.0	0.6	1.6
Zn	140	503	172	46.2	59.2	2.9	8.5	2.9	0.8	1.3
Cr	14	57.1	16.6	24.9	24.1	3.4	2.4	0.7	0.8	1.0
Co	14.4	16.0	9.5	8.3	9.0	1.7	1.8	1.1	1.5	1.1
Cd	2	6.0	2.7	2.5	2.6	2.2	2.3	1.1	0.7	1.0
Ag	3	2.4	1.3	1.0	1.0	1.8	2.4	1.3	2.3	1.0
Sr	18.2	79.1	29.3	7.7	9.6	2.7	8.2	3.1	0.6	1.2
V	25.8	127	22.9	27.5	31.8	5.5	4.0	0.7	1.1	1.2
Be	0.3	1.53	0.52	0.42	0.5	2.9	3.1	1.0	0.6	1.2
P	1870	1650	1338	530	650	1.2	2.5	2.1	1.4	1.2
Ti	38.2	171	108	114	194	1.6	0.9	0.6	0.4	1.7
Mn	132	249	163	58.8	61.4	1.5	4.1	2.7	0.8	1.0
Ba	25	31	40	26	35	0.8	0.9	1.1	0.6	1.3
Al	586	7620	3310	4290	5800	2.3	1.3	0.6	0.2	1.4
Fe	1830	7770	4843	10800	10500	1.6	0.7	0.5	0.4	1.0
Ca	5010	21800	12232	1090	1460	1.8	14.9	8.4	0.4	1.3
Mg	1160	2460	1124	464	566	2.2	4.3	2.0	1.0	1.2
Si	11	29.2	43	68.3	305	0.7	0.1	0.1	0.3	4.5
Na	2430	5610	1463	450	520	3.8	10.8	2.8	1.7	1.2
Pb	219	193	204	118	180	0.9	1.1	1.1	1.1	1.5

Possible contaminants in dust: nylon, polyethylene (and any substances on surface of polyethylene).

Table 3.12. Elemental composition of rhododendron leaf surface dust, leaves, and soil surface material, from Richmond Park (ppm dry wt.)

Element	Leaf Surface Dust -350 µm	Leaves	Surface Soil		Enrichment or Depletion Ratios			
			+350µm Coarse	-350µm Fine				
Column	1	2	3	4	1/2	1/4	2/4	4/3
Ni	503	8.1	14.8	31.7	62	15.9	0.3	2.1
Cu	1920	12.1	18.8	39.9	159	48	0.3	2.1
Zn	1420	31.6	59.8	125	45	11	0.3	2.1
Cr	84	5.1	27.7	53.5	16.5	1.6	0.1	1.9
Co	24.1	5.8	7.5	14.0	4.2	1.7	0.4	1.9
Cd	7	1.3	2.5	4.3	5.4	1.6	0.3	1.7
Ag	10	0.9	0.9	1.7	11.1	5.9	0.5	1.9
Sr	54.8	7.9	11.6	23.2	6.9	2.4	0.3	2.0
V	112	2.7	35.4	61.2	41	1.8	0.04	1.7
Be	1.27	0.32	0.44	0.88	4.0	1.4	0.4	2.0
P	2860	1540	730	1440	1.9	2.0	1.1	2.0
Ti	368	2.5	226	556	147	0.66	0.004	2.5
Mn	287	906	377	613	0.32	0.47	1.5	1.6
Ba	155	59	51	104	2.6	1.5	0.6	2.0
Al	6910	156	4880	10900	44	0.63	0.01	2.2
Fe	15800	358	10400	15200	44	1.0	0.02	1.5
Ca	7480	14000	1750	3570	0.53	2.1	3.9	2.0
Mg	1840	2810	718	1490	0.65	1.2	1.9	2.1
Si	35	10.3	29.2	86.6	3.4	0.40	0.1	3.0
Na	3420	660	410	810	5.2	4.2	0.8	2.0
Pb	453	11.5	113	170	39	2.7	0.07	1.5

Possible contaminants in dust: nylon, human skin.

Table 3.13. Elemental composition of cedar (Cedrus libani) twigs, needles and foliar surface dust, from Richmond Park (Dust was brushed from whole twigs).

Element	Leaf Surface Dust (-350μm)	Twigs	Needles	Enrichment or Depletion Ratios	
Column	1	2	3	1/2	1/3
Ni	77	14.5	4.4	5.3	17.5
Cu	311	139	13.6	2.2	22.9
Zn	229	57.8	39.1	4.0	5.9
Cr	28	12.9	3.9	2.2	7.2
Co	9.4	6.2	6.8	1.5	1.4
Cd	3.0	1.6	0.8	1.9	3.8
Ag	3.0	1.0	0.9	3.0	3.3
Sr	19.7	28.0	10.7	0.70	1.8
V	26.5	23.9	4.5	1.1	5.9
Be	0.40	0.47	0.19	0.85	2.1
P	890	830	1860	1.1	0.5
Ti	119	70.6	3.5	1.7	34
Mn	59.9	77.9	168	0.77	0.36
Ba	51	45	6	1.1	8.5
Al	1830	1090	268	1.7	6.8
Fe	4460	2600	367	1.7	12.2
Ca	4090	13100	6260	0.31	0.65
Mg	568	534	1000	1.06	0.57
Si	14	5.0	4.5	2.8	3.1
Na	1230	1350	2290	0.91	0.54
Pb	466	275	52.5	1.7	8.9

Possible contaminants in dust: nylon, human skin.

Table 3.14. Elemental composition of ivy (*Hedera helix*) twigs, leaves, and leaf surface dust, from Barnes Common 23/3/76. (Dust was brushed from leaves only). ppm dry weight.

Element	Leaf Surface Dust	Twigs	Leaves	Enrichment or Depletion Ratio
Column	1	2	3	1/3
Ni	72	7.0	10.1	7.1
Cu	231	40.4	15.8	14.6
Zn	365	105	269	1.4
Cr	39	4.1	6.2	6.3
Co	26	8.3	11.0	2.4
Cd	6	3.5	3.8	1.6
Ag	4	1.1	1.4	2.9
Sr	44.3	68.5	43.3	1.0
V	81.1	5.1	9.2	8.8
Be	0.90	0.44	0.58	1.6
P	2750	1470	1770	1.6
Ti	147	1.0	7.9	18.6
Mn	110	39.2	156	0.71
Ba	100	63	43	2.3
Al	2860	92	195	14.7
Fe	7790	407	732	10.6
Ca	12300	18600	22700	0.54
Mg	1630	1210	2010	0.81
Si	21	7.4	9.9	2.1
Na	3800	1750	1780	2.1
Pb	750	90	100	7.5

Possible contaminants in dust: nylon, human skin.

Table 3.15. Enrichment ratios for foliar dust (-350μm)/ herbage (leaves) at four sites.

Element	Cemetery Barnes Common	Rhododendron Richmond Park	Cedar Richmond Park	Ivy Barnes Common	Mean Ratio
Ni	7.3	62	17.5	7.1	23
Cu	2.4	159	22.9	14.6	50
Zn	2.9	45	5.9	1.4	14
Cr	3.4	16.5	7.2	6.3	8.4
Co	1.7	4.2	1.4	2.4	2.4
Cd	2.2	5.4	3.8	1.6	3.3
Ag	1.8	11.1	3.3	2.9	4.8
Sr	2.7	6.9	1.8	1.0	3.1
V	5.5	41	5.9	8.8	15.3
Be	2.9	4.0	2.1	1.6	2.7
P	1.2	1.9	0.5	1.6	1.3
Ti	1.6	147	34	18.6	50
Mn	1.5	0.32	0.36	0.71	0.72
Ba	0.8	2.6	8.5	2.3	3.6
Al	2.3	44	6.8	14.7	17
Fe	1.6	44	12.2	10.6	17
Ca	1.8	0.53	0.65	0.54	0.88
Mg	2.2	0.65	0.57	0.81	1.1
Si	0.7	3.4	3.1	2.1	2.3
Na	3.8	5.2	0.54	2.1	2.9
Pb	0.9	39	8.9	7.5	14

Figure 3.2. Particles shaken from Quercus ilex and Taxus baccata, retained by 350 µm mesh.

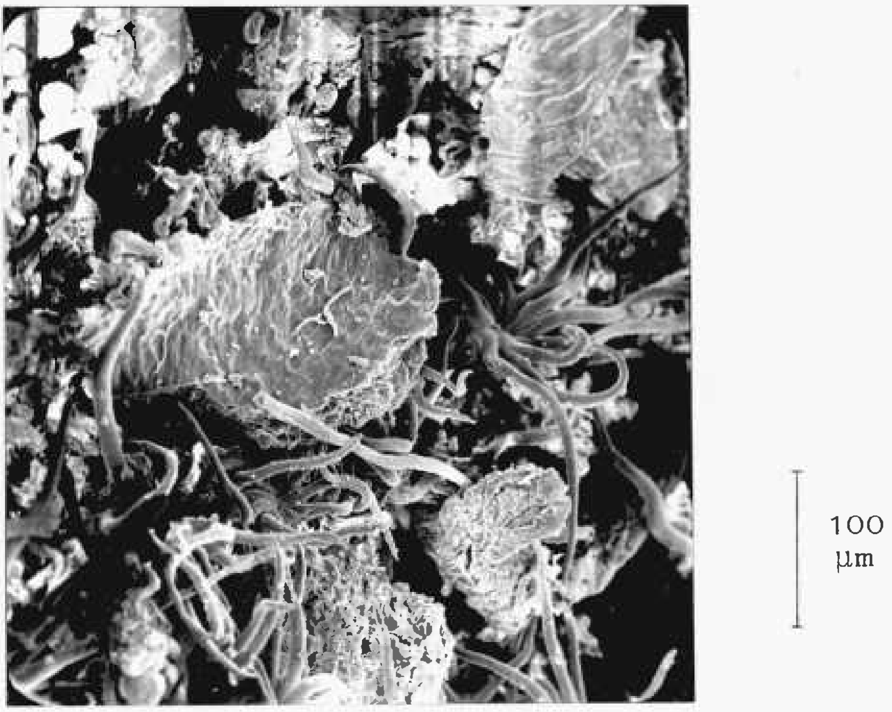


Figure 3.3. Particles shaken from Quercus ilex and Taxus baccata, released by 350 µm mesh.

3.3 Composition of surface particles of gorse in relation to geochemistry and biogeochemistry in southwest England.

Sections 3.1 and 3.2 raised the question of the significance of pollution in dominating the chemistry of plant surfaces, whereas one of the main objectives of the work was to study the usefulness of plant surface particles in geochemical exploration. For this reason, studies were made on plants growing in areas where air pollution is minimal. Under these conditions, local geochemistry may be the main factor determining metal levels at the leaf surface. This could either result from the uptake of substances by roots and their movement through the plant on to the plant surface, or from local wind-blown soil being deposited on the plant. Southwest England was particularly suitable for this work because strong local mineralisations exist for various heavy metals, and there has been little industrial activity in the areas sampled for many years. Fieldwork was carried out in August 1976 during a remarkably hot, dry summer, and these unusual conditions could obviously have had an important bearing on the uptake and release of metals by plants, and on biogeochemical cycling in general.

3.31 Geochemistry.

It was originally intended that the survey might be analysed as a factorial experiment comprising five pairs of 'mineralised' (M) and 'control' (C) sites, with replication. However, Table 3.16 , using four heavy metals as examples shows that mineralisation was not always found exactly where it was expected on the basis of geological survey maps (Institute of Geological Sciences, London),

Table 3.16. Soil copper, manganese, zinc and lead at survey sites in southwest England. (ppm dry weight).

Data are means of pairs of sites (field replicates).

Locality (see Table 2.4)	Site (see Table 2.4 and Figure 2.8)	Cu	Mn	Zn	Pb
Mounte Hawke	1, 2	228	420	289	13
	3, 4	78	2158	276	417
Ventongimps	5, 6	345	898	1337	3258
	7, 8	25	910	123	435
Redruth	9, 10	565	424	1075	37
	11, 12	22	371	109	385
Bere Alston	13, 14	64	709	212	575
	15, 16	368	2108	235	35
Bodmin Moor	17, 18	2175	769	357	25
	19, 20	13	170	48	290

Dines (1956), Booker (1971) and information from the Applied Geochemistry group, Imperial College. For example, site 13 (M), on alluvial soil by the Tamar estuary, was expected to have elevated Pb and Cu levels. In fact, my particular site was not contaminated with Cu, but did have a high level of Pb, and slightly anomalous Cd, Ni, Mg, V, Fe, and Cr. A 'control' alluvial site was selected about three miles away beside the river Lynher where there had not been much mining activity upstream according to the geological survey map. However, this 'control' site showed moderately high soil Cu and very high Mn, although normal Pb levels. The same difficulty applied at other sites, e.g. site 1 (M) had high Cu, but low Mn, levels, while site 3 (C) had elevated Mn levels but low Cu.

Therefore, regression analysis for each element selected as the best way to analyse plant and particulate elemental concentrations with respect to soil levels, and to analyse interrelationships amongst the various plant and particle fractions. Data from all the sites were analysed together, and therefore effects of geology (see Table 2.4) were not considered. Two replicates of each sample were analysed, and each regression analysis was computed with 40 pairs of observations (20 sites x 2 analytical replicates). However, the data points shown in Figures 3.5, 3.6, 3.7 and 3.8 are means of the two analytical replicates and two field replicates. 18 elements were analysed in all types of sample, but Ag is not discussed because no particular enrichments were found and the metal was not detectable in gorse tissues. All the other elements showed at least a useful spread of soil concentrations, and many had a very large range (Table 3.17). Unfortunately, K data were not available because of its incomplete digestion and the low sensitivity of the spectrometer for this element.

Table 3.17. Ranges of elemental concentrations in soils and gorse leaves and fruits. Cornwall, August 1976 (ppm dry weight)

Element	Soil	Leaves	Fruits
Ag	1 - 6	not detected	not detected
Al	34900 - 91700	163 - 418	45 - 1180
Ba	163 - 763	12 - 48	11 - 30
Be	1.8 - 8.9	0.09 - 0.22	0.09 - 0.25
Ca	840 - 13180	2340 - 5220	1820 - 5250
Cd	5 - 23	0.5 - 1.7	N.D. - 3.5
Co	6 - 62	0.5 - 1.8	N.D. - 2.0
Cr	25 - 86	6.3 - 8.6	5.5 - 8.3
Cu	13 - 2175	3.7 - 12.7	4.5 - 10.0
Fe	13000 - 96900	158 - 338	57 - 757
Mg	1955 - 4968	1323 - 3190	1280 - 2120
Mn	170 - 2158	39 - 280	16 - 252
Na	1065 - 3863	1960 - 5280	1700 - 5790
Ni	9 - 65	1.7 - 6.9	1.4 - 9.7
P	990 - 2380	933 - 1515	930 - 2670
Pb	13 - 3258	5 - 22	0.5 - 75
Sr	32 - 268	9 - 53	2.9 - 30
Ti	574 - 1171	3 - 13	0.9 - 17
V	36 - 134	0.9 - 2.0	0.4 - 2.4
Zn	48 - 1337	34 - 108	26 - 111

3.32 Biogeochemistry.

The concentrations of all elements in plant material were less variable than in soil (Table 3.17), and therefore gorse appeared to exert a degree of control over its elemental composition, within broad or narrow limits depending on the element. The concentration of Cu in gorse was remarkably constant even at total soil levels of over 0.2% dry weight (see also Figure 3.5). Since I did not measure soil concentrations available to the plant, it is not known whether physiological exclusion mechanisms were involved, but this would certainly seem likely in the case of Cu. The only elements whose concentrations in gorse were higher than in soil, on a dry weight basis, were Ca (in low-Ca soils only) and Na (in all sites).

Regression analyses between the various biogeochemical fractions are summarised in Figure 3.4. This Figure shows the results of testing the hypothesis that the slope of each regression line is zero. Table 3.18 shows the degree of association between the two variables in each regression, expressed by the correlation coefficient. The concentrations of the following elements in gorse leaves depended on total soil concentrations: Pb, Mn, Zn, Al, Mg, Be, Sr, Ba, Ni, Cd, and Co (5% probability). For gorse fruits, this was true for the same elements excluding Pb, Be, Ni, and Co, but including Ti. Other elements did not show significant relationships. The regression analyses for Cu, Mn, Zn and Pb are plotted in Figures 3.5, 3.6, 3.7 and 3.8 as examples.

3.33 Chemistry of surface particles of gorse.

Particles were analysed by system ARL 1, which was not comparable with ARL 2, used for soils and herbage,

(to page 128)

← Columns (y) Rows (x) ↓	Leaves				Fruits				Particles(+45µm)				Particles(+20µm)				Particles(+5µm)				Aqueous(-5µm)			
Soils		$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	Zn			$\underline{\text{Mn}}$	Zn		$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	Zn		$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	Zn	Cu	$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	$\underline{\text{Zn}}$		$\underline{\text{Pb}}$	*	
	Al				$\underline{\text{Al}}$				Al	Ca	*		Al	$\underline{\text{Ca}}$	Cr	$\underline{\text{Fe}}$	$\underline{\text{Al}}$	*	*	Fe	*		*	*
	$\underline{\text{Mg}}$	Be	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	Mg		$\underline{\text{Sr}}$	$\underline{\text{Ba}}$		*	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	*	Be	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	*	*	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$		Be		*
	$\underline{\text{Co}}$		Ni	$\underline{\text{Cd}}$		Ti		Cd				Cd			*	*	P			Cd		*		*
Leaves						Pb	$\underline{\text{Mn}}$	Zn		$\underline{\text{Pb}}$	$\underline{\text{Mn}}$			$\underline{\text{Pb}}$	Mn	Zn		$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	Zn		$\underline{\text{Pb}}$	*	
					$\underline{\text{Al}}$	Ca		Fe	$\underline{\text{Al}}$		*		$\underline{\text{Al}}$	*	*	*	$\underline{\text{Al}}$	Ca	Cr	*	*		*	*
					Mg		$\underline{\text{Sr}}$	$\underline{\text{Ba}}$		*	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	*	Be	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	*	*	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$		Be		$\underline{\text{Ba}}$
						$\underline{\text{Ti}}$	$\underline{\text{Ni}}$	$\underline{\text{Cd}}$		Ti		*			*	*				*		Ti		*
Fruits									$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	$\underline{\text{Zn}}$	$\underline{\text{Cu}}$	$\underline{\text{Pb}}$		$\underline{\text{Zn}}$	$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	$\underline{\text{Zn}}$	$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	*	$\underline{\text{Zn}}$
									$\underline{\text{Al}}$		Cr	Fe	Al	*	Cr	*	$\underline{\text{Al}}$	*	*	*	*		Cr	Fe
										Be	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	*	*	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	*	*	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$		*		$\underline{\text{Ba}}$
										$\underline{\text{Ti}}$		*	P	$\underline{\text{Ti}}$	*	*	$\underline{\text{P}}$	Ti		*		Ti		*
Particles (+45 µm)													$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	$\underline{\text{Zn}}$	$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	$\underline{\text{Zn}}$	$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	*	$\underline{\text{Zn}}$
													$\underline{\text{Al}}$	$\underline{\text{Ca}}$	$\underline{\text{Cr}}$	$\underline{\text{Fe}}$	$\underline{\text{Al}}$	$\underline{\text{Ca}}$	Cr	$\underline{\text{Fe}}$	*		Cr	*
													$\underline{\text{Mg}}$	*	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	$\underline{\text{Mg}}$	Be	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$		*		$\underline{\text{Ba}}$
														$\underline{\text{Ti}}$	$\underline{\text{Ni}}$	Cd		$\underline{\text{Ti}}$	$\underline{\text{Ni}}$	$\underline{\text{Cd}}$		*	$\underline{\text{Ni}}$	Cd
Particles (+20 µm)																	$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	$\underline{\text{Mn}}$	$\underline{\text{Zn}}$	$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	*	$\underline{\text{Zn}}$
																	Al	$\underline{\text{Ca}}$	$\underline{\text{Cr}}$	$\underline{\text{Fe}}$	Al		$\underline{\text{Cr}}$	*
																	Mg	Be	$\underline{\text{Sr}}$	$\underline{\text{Ba}}$	*	$\underline{\text{Be}}$		$\underline{\text{Ba}}$
																	$\underline{\text{P}}$	$\underline{\text{Ti}}$	$\underline{\text{Ni}}$	*		Ti	$\underline{\text{Ni}}$	Cd
Particles (+5 µm)																					$\underline{\text{Cu}}$	$\underline{\text{Pb}}$	*	$\underline{\text{Zn}}$
																					*	*	*	*
																					*	*	Sr	Ba
																						*	$\underline{\text{Ni}}$	*

Figure 3.4

Correlations between elemental concentrations in soils, gorse leaves and fruits, and foliar particles.

Cornwall, August 1976.

Rows show the material used as the 'x' factor in regression analysis, and columns show the 'y' factor; all regressions are of y on x. Elements which appear in a box show a significant (5 % probability) correlation between the two materials. If an element is underlined, the regression is significant at (0.1 % probability). an asterisk (*) indicates that the 'blank' analysis (of tape or filter substrate on which ARL 1 samples were analysed) exceeded the mean sample concentration for that element.

Table 3.18. Regression analysis (x on y) of biogeochemical survey, August 1976: Correlations between elemental levels in soils, plants and particle fractions.

Variables		Correlation coefficients for elements shown																
x	y	Cu	Mn	Zn	Pb	Ca	Mg	Fe	Al	Ti	Sr	Ba	Cd	Cr	Ni	P	Be	Co
1	2	0.21	0.62	0.40	0.64	0.23	0.65	0.11	0.45	0.22	0.73	0.62	0.59	0.28	0.35	-0.23	0.48	0.62
1	3	0.10	0.55	0.45	0.22	0.23	0.33	0.18	0.59	0.42	0.69	0.67	0.40	0.07	0.24	0.08	0.14	-0.09
1	4	0.07	0.75	0.33	0.56	0.54	0.02	0.29	0.41	0.16	0.73	0.54	0.37	0.05	0.11	0.02	-0.23	-
1	5	0.23	0.56	0.49	0.77	0.35	0.08	0.54	0.45	0.10	0.75	0.60	0.12	0.38	0.14	0.21	0.33	-
1	6	0.47	0.69	0.51	0.58	0.22	-0.07	0.33	0.56	0.09	0.74	0.51	0.35	0.21	0.11	0.50	0.29	-
1	7	0.07	0.05	0.23	0.73	-0.03	0.09	0.12	0.05	-0.23	0.06	0.28	0.22	0.16	0.17	-0.03	0.41	-
2	3	0.30	0.82	0.48	0.40	0.33	0.42	0.39	0.64	0.50	0.82	0.84	0.55	-0.03	0.85	0.24	0.23	-0.19
2	4	-0.04	0.66	0.29	0.58	0.10	-0.05	0.17	0.63	0.32	0.71	0.83	0.31	-0.15	-0.16	0.10	-0.04	-
2	5	0.22	0.40	0.39	0.65	0.27	0.05	0.01	0.60	0.31	0.76	0.77	0.11	-0.19	-0.21	0.10	0.38	-
2	6	0.14	0.64	0.42	0.58	0.35	0.01	-0.06	0.58	0.28	0.74	0.76	0.22	-0.37	-0.27	-0.08	0.24	-
2	7	0.06	0.05	0.22	0.69	-0.02	-0.24	-0.28	-0.01	0.32	0.08	0.57	0.05	-0.14	-0.05	0.03	0.39	-
3	4	0.68	0.53	0.88	0.89	0.16	0.24	0.42	0.55	0.59	0.70	0.69	0.19	0.40	-0.17	-0.21	-0.45	-
3	5	0.71	0.24	0.80	0.70	-0.13	0.25	0.22	0.41	0.65	0.56	0.68	0.07	0.32	-0.23	0.34	-0.12	-
3	6	0.64	0.56	0.89	0.87	-0.01	0.31	0.24	0.60	0.44	0.71	0.66	0.09	0.21	-0.24	0.56	-0.28	-
3	7	0.64	0.22	0.66	0.80	-0.15	0.04	-0.40	0.08	0.33	0.12	0.53	0.23	0.46	-0.14	-0.20	-0.02	-
4	5	0.87	0.62	0.91	0.93	0.63	0.67	0.58	0.77	0.70	0.72	0.81	0.33	0.63	0.95	0.24	0.21	-
4	6	0.84	0.70	0.95	0.96	0.51	0.56	0.56	0.68	0.64	0.66	0.73	0.51	0.43	0.87	-0.07	0.33	-
4	7	0.87	-0.10	0.82	0.94	-0.25	0.00	0.02	0.17	0.12	0.07	0.53	0.43	0.46	0.69	0.25	0.07	-
5	6	0.86	0.74	0.95	0.89	0.75	0.48	0.65	0.49	0.55	0.72	0.74	0.27	0.53	0.95	0.62	0.45	-
5	7	0.75	0.14	0.82	0.95	-0.03	-0.05	0.10	0.34	0.35	0.11	0.60	0.39	0.58	0.80	0.14	0.72	-
6	7	0.76	-0.02	0.80	0.93	-0.07	-0.12	-0.11	0.16	0.26	0.37	0.42	0.26	0.28	0.78	-0.21	0.28	-

Key to Variables: 1 = soils; 2 = gorse leaves; 3 = gorse fruits; 4 = foliar particles, + 45 µm; 5 = particles, + 20 µm; 6 = particles, + 5 µm; 7 = particles, -5 µm, and water-soluble fraction.

Significance levels of correlation coefficient: 0.31 (5%), 0.41 (1%), 0.50 (0.1%)

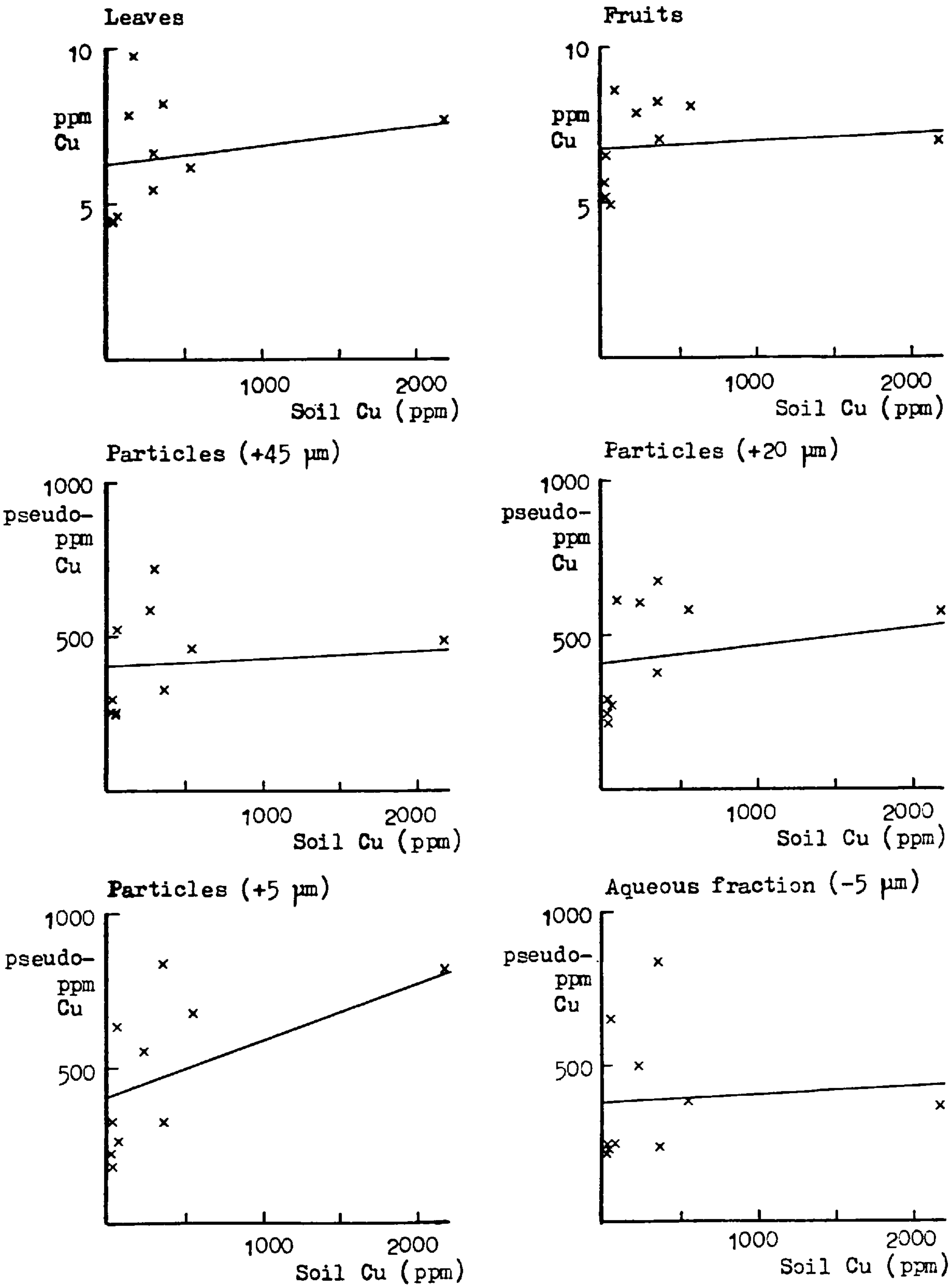


Figure 3.5 Copper in leaves, fruits and foliar particles of gorse against soil copper concentrations in Cornwall, August 1976.

Each data point is the mean of 2 field replicates and 2 analytical replicates.

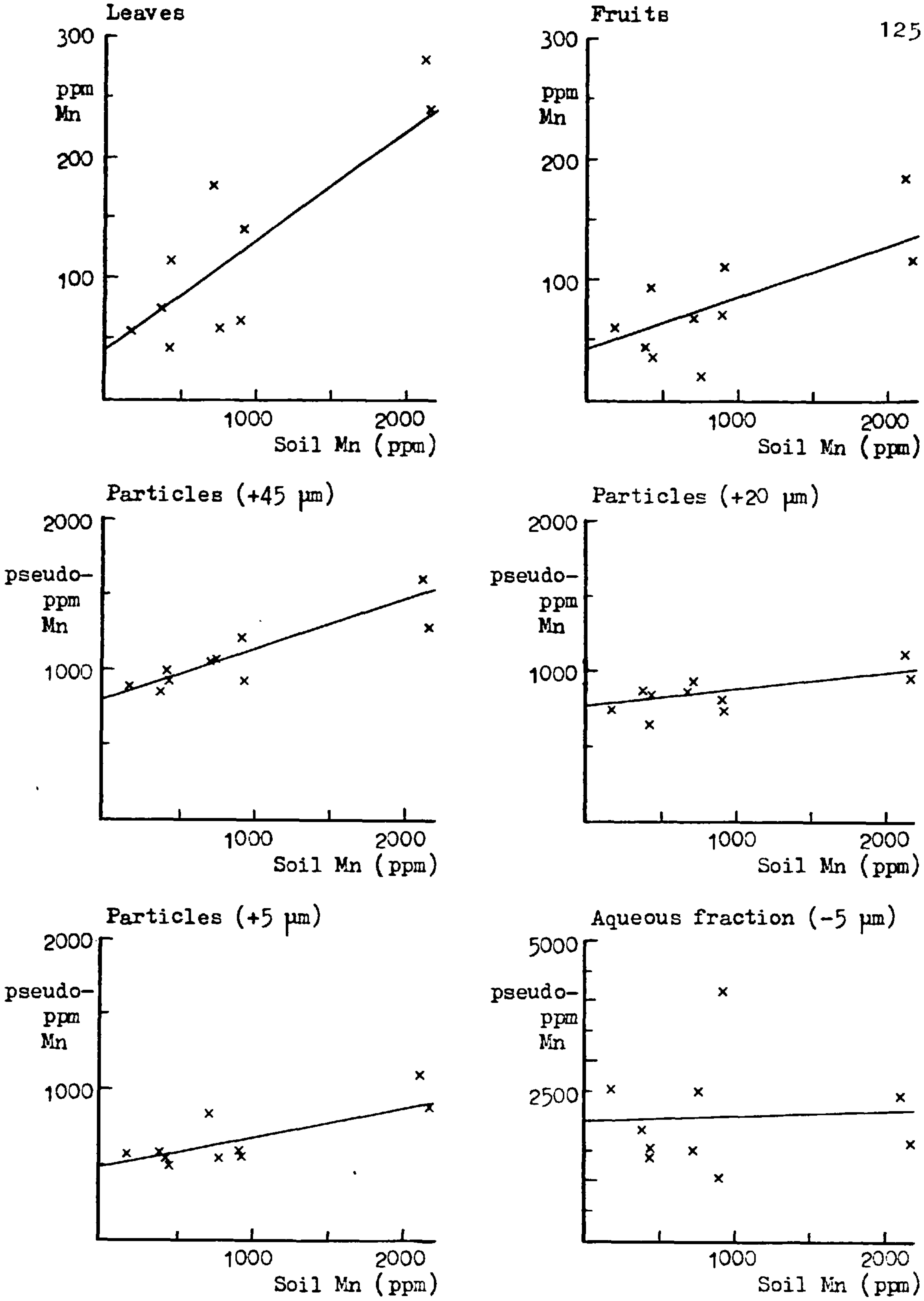


Figure 3.6 Manganese in leaves, fruits and foliar particles of gorse against soil manganese concentrations in Cornwall, August 1976. Each data point is the mean of 2 field replicates and 2 analytical replicates.

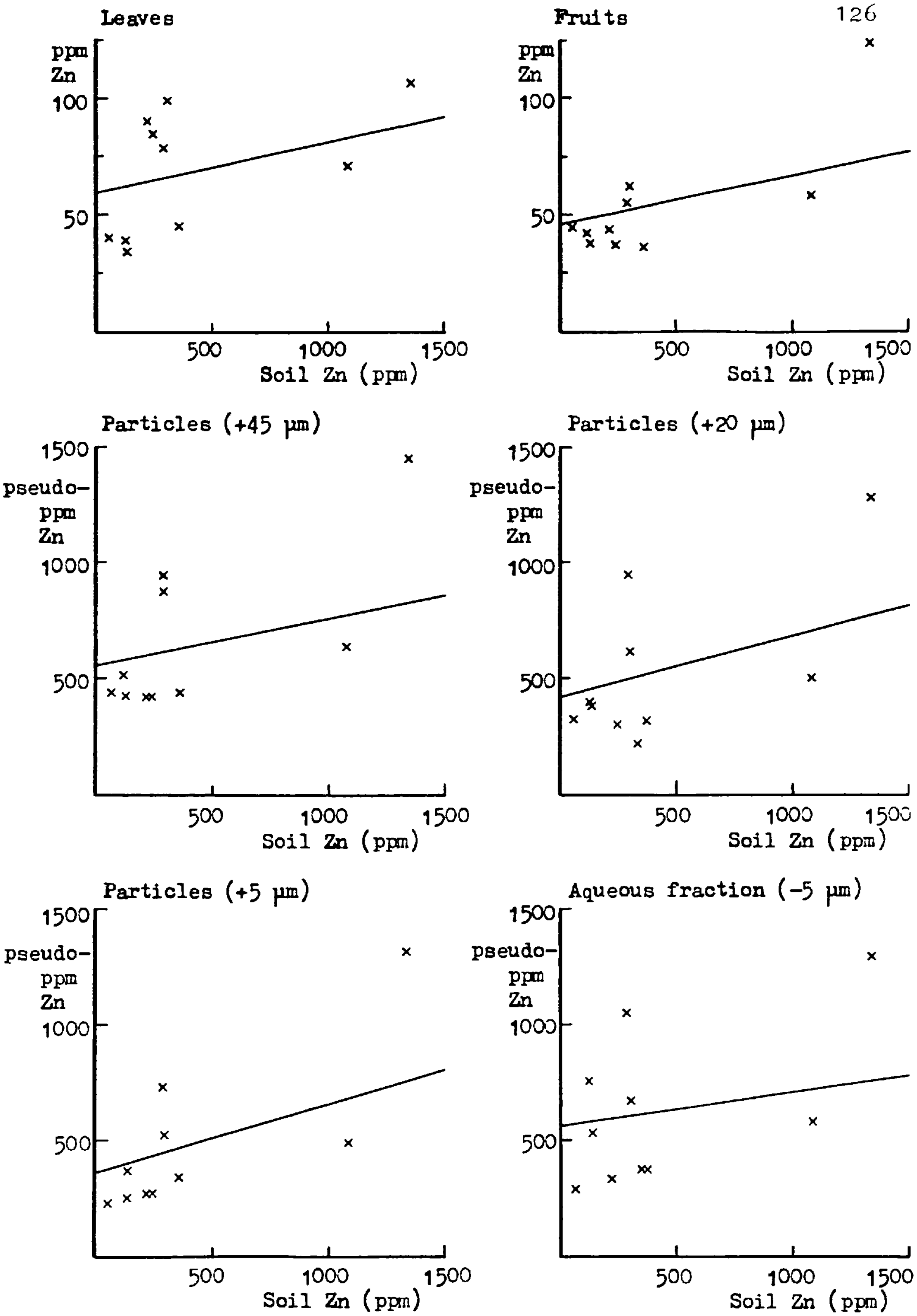


Figure 3.7 Zinc in leaves, fruits and foliar particles of gorse against soil zinc concentrations in Cornwall, August 1976.

Each data point is the mean of 2 field replicates and 2 analytical replicates.

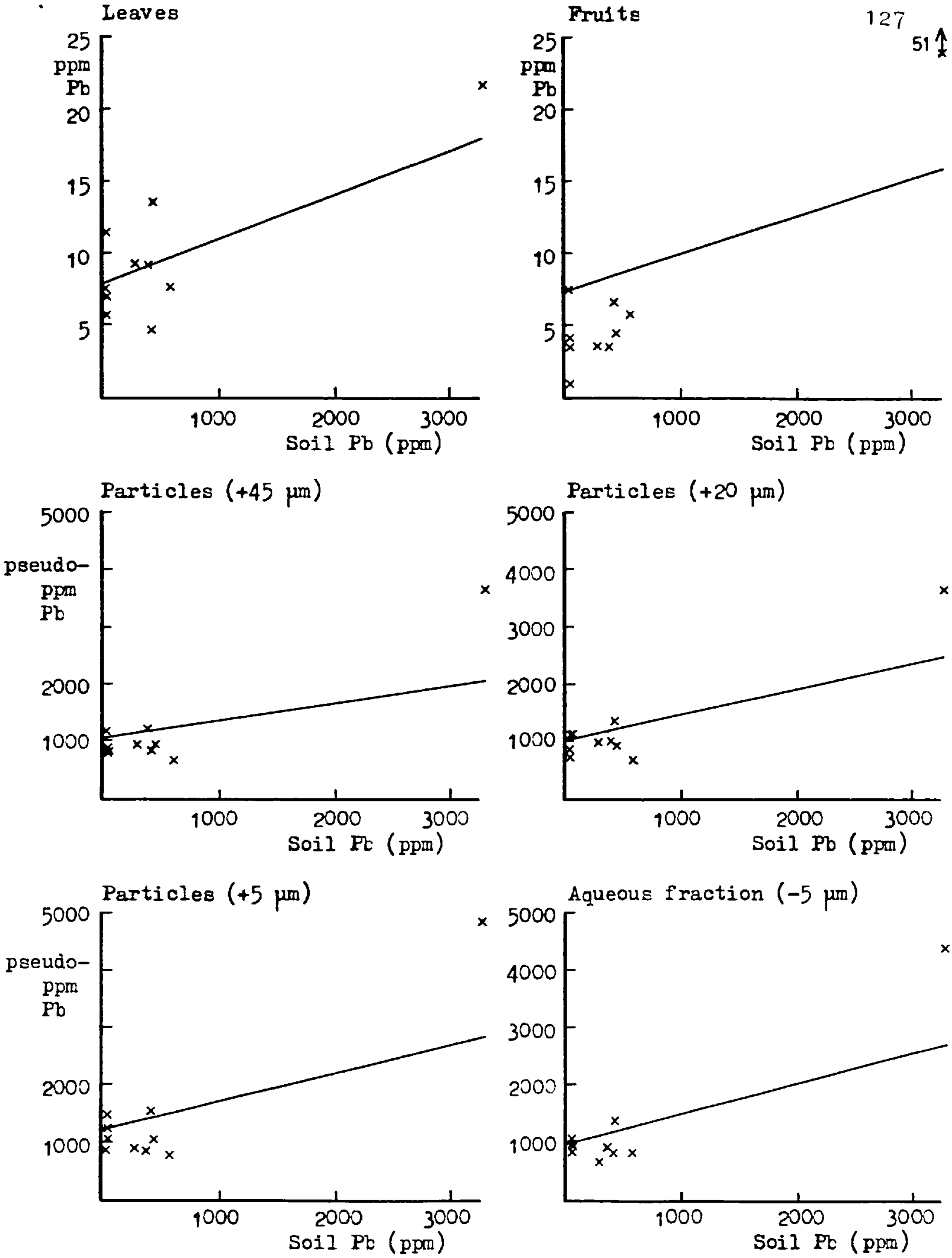


Figure 3.8 Lead in leaves, fruits and foliar particles of gorse against soil lead concentrations in Cornwall, August 1976.
Each data point is the mean of 2 field replicates and 2 analytical replicates.

on an absolute basis, but was assumed to indicate the relative concentrations of elements between sites. A comparison of ARL 1 and ARL 2 is shown in Table 3.22.

Particulate samples, except the +45 µm fraction, were presented for analysis on nylon mesh or filter paper. The squares with asterisks in Figure 3.4 indicate that the levels in blank mesh or filter paper were higher than the mean sample level. However, very erratic data were obtained for nylon blanks and I cannot be confident of blank levels. The main safeguard is the unlikelihood of producing significant, spurious regressions, certainly at the 0.1% level, from 'blank' data alone.

The composition of all particulate fractions was presumably affected by leaching of soluble components during sample preparation, and it is likely that such solutes were not adequately collected or analysed in the -5 µm fraction, for reasons discussed in Materials and Methods.

3.331 Copper.

The very strong associations between copper levels in fruits and particles show the obvious biological origin of particulate copper. Some of the copper may have been in an easily soluble form because it was found in the final "aqueous" (-5 µm) fraction. The only particulate fraction to show any correlation with soil, for copper, was +5 µm, which was the most soil-like fraction in appearance. This implies that soil particles containing copper, between 5 and 20 µm in diameter, were present on foliage.

3.332 Zinc.

For zinc, unlike copper, plant uptake into both leaves and fruits was correlated with soil levels (correlation coefficients of 0.40 and 0.45 respectively). Despite significant soil v. particle regressions, the size of correlation coefficients indicated that fruits were the main source of particulate zinc (Table 3.18). This was true for all particle sizes and it appeared that, like copper, some of the zinc was in a water-soluble form or in particles smaller than 5 µm.

3.333 Manganese and Lead.

Both these metals could be said to be 'good' biogeochemical elements from this work because highly significant correlations existed between almost all pairs of sample types. The main exception for manganese was that the -5 µm 'aqueous' fraction did not correlate with any other fraction, but because of the poor method used to isolate the -5 µm fraction, one cannot make any conclusion about this. Lead, however, in the -5 µm fraction was strongly correlated with every other fraction. The only regression not to be significant for lead was soils v. fruits. In the case of a pollutant element like lead, one possibility is that all the significant regressions arose from patterns of aerosol deposition, for example, caused by proximity to roads, but since all the sites were in rural areas well away from main roads or industry this does not seem likely.

3.334 Calcium and Magnesium.

Calcium and magnesium, on the other hand, showed few correlations between various biogeochemical fractions. Calcium levels in gorse were not correlated with soil levels. Particles above 20 µm indicated local soil calcium content, and +5 µm particles were correlated with leaf calcium, but other regressions for calcium were not significant. Although magnesium uptake by gorse depended on soil magnesium, all regressions between particulate fractions and soils or plant material were non-significant. It is possible that both metals were leached from particles during wet-filtering.

3.335 Other metals.

Iron uptake into gorse was not correlated with soil levels, and iron is thus another element with which a distinction between soil- and plant-derived material might be possible. Large particles (+45 µm) correlated with gorse fruits in iron content, while smaller particles (45 to 5 µm) correlated with soil. Aluminium, strontium and barium showed good correlations between most pairs of sample types.

3.336 Multi-elemental data.

Different elements may be dispersed in various ways and carried in different-sized particles, but useful inferences may be made by examining collective trends, with particular reference to Figure 3.4.

+45 µm dust was green and fibrous and was seen under the microscope to contain large numbers of trichomes. Regression analysis of soils v. 45 µm particles showed a remarkably similar pattern to the regressions of soils v. leaves or fruits, which suggests that the material was indeed plant-derived. The +45 µm fraction showed an additional correlation with soil calcium, which is surprising because copper and iron data suggested that only the smaller particles were partly soil-derived. A possible explanation is that only trichomes took up calcium in proportion to soil levels while the rest of the foliage accumulated calcium without regard to soil levels.

It is notable that the +45 µm fraction correlated with fruit composition for eleven elements, and with leaf composition for only six elements, at the 5% level. This suggests that fruits contributed more to the +45 µm particle fraction than did leaves, which seems tenable in view of the very hairy nature of the fruits. If the correlations for the additional five elements, Cu, Cr, Fe, Be, and Zn were due to extra soil particles being trapped among the fruit hairs, these same elements should show soil v. + 45 μm particle correlations. In fact, the only element to do this was zinc. Therefore, it seems that release of the trichomes themselves was more important than trapping of large soil particles retained in this fraction.

3.337 Floating particulate fraction.

The particulate fraction from each site which could not be filtered because it was extremely buoyant in water was analysed by ARL 1. Regression analyses were calculated for the Cu, Mn, Zn and Pb contents of this fraction against the same elements in soils, leaves and fruits (Table 3.19). The floating fraction was very strongly correlated in Pb content with soils, leaves and fruits, while its Zn content correlated only with leaves and fruits, and its Mn content only with soils. For Cu, however, the fraction was not correlated with any of these three materials. The floating fraction appeared to be biological, since it was green and partly cellular under the microscope. Apart from fragmented gorse tissue, it could contain micro-organisms living on the plant surface which would presumably introduce their own set of biogeochemical correlations into the data.

3.338 Dry-ashing.

A spare sample of unfractionated particulate material from gorse foliage from a control site was dry-ashed in a muffle furnace at 475°C for 22½ h. and the loss of weight was found to be 52% of the dry weight (after drying at 72°C for 19 h.). Therefore the ash content was 48% of the dry weight. The ash content of higher plants ranges from 0.17% to 7.7%, and Angiosperm leaves have 6.4%

Table 3.19. Regression analyses involving the floating particulate fraction from gorse: correlation coefficients

Regressions of y (floating fraction, pseudo-ppm) on x (soils, leaves or fruits, ppm).

Metal	x = soil		x = leaves		x = fruits	
Cu	0.313	NS	-0.198	NS	0.079	NS
Mn	0.520	*	0.440	NS	0.218	NS
Zn	0.327	NS	0.631	**	0.551	*
Pb	0.920	***	0.750	***	0.933	***

ash (Bowen, 1966). Herbage would have to be mixed in approximately a 1:1 ratio (w/w) with a predominantly mineral material to produce the proportion of ash in this particulate sample. The mineral material presumably comprises locally derived soil dust and deposited background aerosol.

3.34 Conclusion.

The evidence from this survey indicated that material collected from plant surfaces was useful in predicting soil chemistry for some elements, and strongly suggested that many of these correlations were due, in part at least, to uptake of these elements into the plant and their migration into surface particles, including trichomes.

It was felt that a possible approach to characterising the nature of these particles was by electron microscopy and electron microprobe analysis. By examining and analysing enough individual particles, one might be able to get statistical evidence on the relative importance of different particles types both in general terms, e.g. numbers of soil- and plant-derived particles, and by looking at types of particles carrying specific elements.

3.35 Electron microprobe analysis of surface particles from gorse.

97 spectra were accumulated using an electron microprobe analyser. 83 of these were emission spectra of discrete particles collected from plant surfaces, 7 were spectra of plant trichomes, and the remainder were spectra derived either from general scans over particulate samples

or were scans of the sellotape on which samples were mounted. 13 elements could easily be detected in the samples: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, and Zn. A few other elements were sometimes thought to have been detected, such as Cr, Co, and Cu, but these peaks may not have been significant.

The sellotape background spectrum in Figure 3.9 was recorded from the stub at a point where there did not appear to be any particles, but the spectrum could still have been affected by the sample. From completely blank stubs, three further sellotape spectra were also obtained. These showed no Al, but traces of Si, S, Cl, K, Ca, and Fe. The peak sizes were in fact smaller than on the illustrated background spectrum, but the y-axis is not quantitative. One can conclude that the sellotape will not give rise to any spurious major peaks in the spectra of particles but could be the source of small signals for the elements mentioned.

Zn peaks were present in most spectra, and could originate from the zinc stubs. Painting the stubs with polyurethane did not decrease the Zn signal. Zn results are not discussed in detail because of the possibility of contamination, unless large amounts seemed to be present.

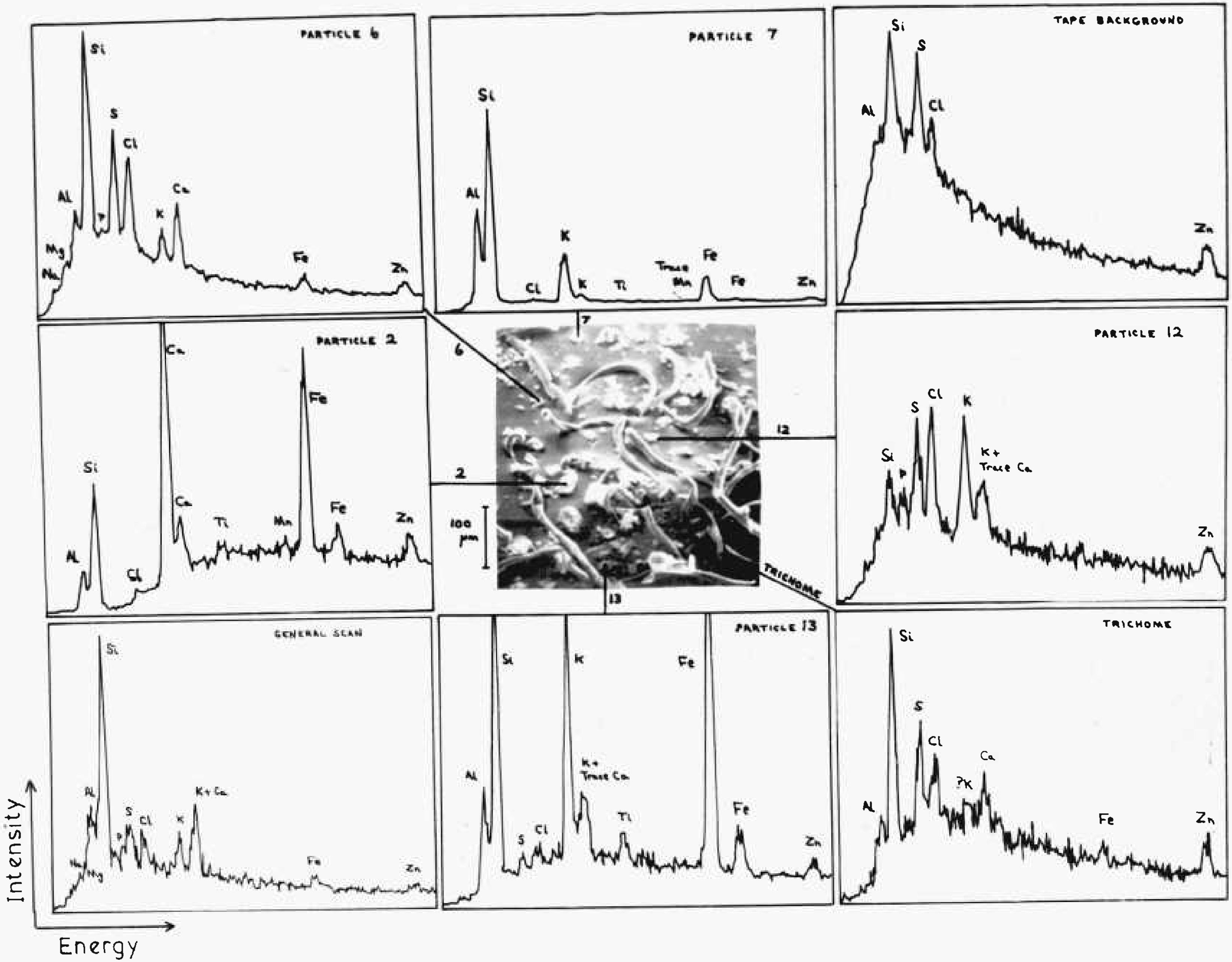
Si was the most ubiquitous element, and was detected in almost every spectrum. Si can be a contaminant from the oil used in electron microscopes, but the facts that Si was not detected in a few spectra and only gave small peaks in the sellotape blanks suggest that the large Si peaks of most spectra did not arise from contamination.

Considering the spectra from discrete particles only, Si was the most frequent element, detected in 99% of particles, followed by S (73%), K and Zn (71%), Cl (67%), Al (65%), Fe (63%), P (43%), Ca (29%), Ti (28%), Mg (16%), Na (12%) and Mn (1%).

The sample shown in Figure 3.9 was collected from

Figure 3.9 Qualitative electron microprobe analysis of particles collected from gorse (*Ulex europaeus* L.)

Facing page 135


PARTICLE 6
Si
S
Cl
Al
P
K
Ca
Mg
Na
Fe
Zn
PARTICLE 7
Si
Al
K
Cl
K
Ti
Trace
Mn
Fe
Fe
Zn
TAPE BACKGROUND
Si
S
Al
Cl
Zn
PARTICLE 2
Ca
Fe
Si
Ca
Ti
Mn
Fe
Zn
Al
Cl
7
6
12
2
100 µm
13
TRICHOME
PARTICLE 12
S
Cl
K
Si
P
K+
Trace Ca
Zn
GENERAL SCAN
Si
Al
S
Cl
K
K+Ca
P
Na
Mg
Fe
Zn
PARTICLE 13
Si
K
Fe
Al
K+
Trace Ca
Ti
S
Cl
Fe
Zn
TRICHOME
Si
S
Cl
Ca
?K
Al
Fe
Zn
Intensity
Energy

gorse at site 20 in Cornwall (see Table 2.4). This was a control site, but the electron microprobe work did not show any difference in the major-element composition of particles from mineralised and control sites. Fifteen particles were analysed in the area of sample shown in Figure 3.9, and particle identification will be considered with reference to these, as examples. A few particles could be clearly identified as minerals such as quartz, felspar, and gypsum. Particle no. 4 gave a signal only for Si, and was probably quartz, SiO_2. Particle no. 8 gave peaks only for S and Ca, and was probably calcium sulphate, anhydrite or gypsum. These very simple spectra are not illustrated. Then there were spectra of slightly greater complexity, from particles such as nos. 7 and 13, comprising predominantly Al, Si, K, and Fe, or particle no. 2, containing Al, Si, Ca, and Fe. These spectra also showed small amounts of other elements, such as S, Cl, Ti, and Mn. All these elements are typically the main components of soil minerals. Particle no. 6 gave one of the most complex spectra, with Na, Mg, Al, Si, P, S, Cl, K, Ca, and Fe all being detected. These results indicate that many of the particles collected from leaf surfaces could have been wind-blown soil, and the analyses of other samples gave similar impressions.

It is important to note, however, that the gorse trichomes could have been interpreted in the same way from spectral data alone. The spectra would have suggested that they were Si- and Ca-based minerals. This shows the problem of identifying biological particles with this electron probe. The main constituents of organic matter, C, N, O, and H, are not registered. The problem applies to the identification of soil organic matter and of organic particles derived directly from leaves. I did not find any marker elements which could be used with the available equipment to distinguish soil from plant-derived particles.

Seven gorse trichomes were analysed, and the trichome spectrum in Figure 3.9 is in fact slightly untypical, because the main peak in the other six spectra was for Ca, not Si. However, both Si and Ca always gave strong signals, with S and sometimes Cl. Mg, Al, P, K, and Fe were also detected in some trichome spectra. Of course, not all plant particles are necessarily calcified and silicified, as the gorse trichomes appeared to be, and nor is it necessarily true that metals released from plants must be in particles with an organic matrix. The metals could be present as sub-micron salt crystals, or adsorbed onto larger, possibly soil-derived, bodies.

The particles were categorised partly subjectively into those with high, medium and low count rates over the whole X-ray spectrum. This parameter may be related in some way to particle composition. The percentages of particles containing P in high, medium, and low count rate categories were 36, 61 and 68% respectively. For S, the figures were 36, 92, and 89%, and for Cl, 36, 75, and 86%. The reverse trend was indicated for Al, with figures of 76, 75, and 50% respectively. These trends imply that there were positive correlations between the presence of P, S, and Cl in particles, and negative correlations between the presence of each of these three elements and Al. In fact, a Chi-squared test showed a strong positive correlation (0.1% probability level) between the occurrence of S and Cl in particles, but the other suggested correlations were non-significant. However, trying to draw conclusions from presence-and-absence data, rather than quantitative data, is obviously a rather crude process. Since P, S, and Cl occur in higher concentration in organic than mineral matter, and Al in lower concentration (Bowen, 1966), the evidence is consistent with the hypothesis that organic particles give lower count rates than mineral particles. This effect would be expected, and evidence of it has been obtained (P. Grant, Imperial College, personal communication). Certainly, the trichomes were all in the medium and low categories.

This electron microprobe work does not give any evidence about trace metals which may be leached from the plant and adsorbed on to surface particles, for two reasons. Firstly, at the accelerating voltage of 20 kV which was used, the penetration of silica-based particles was probably about 7 µm and of organic particles about 20 µm (P. Grant, personal communication). Therefore, the structural material of the particles would have given the main analytical signal. Secondly, the sensitivity of the analysis was in the region of 0.1% or 1000 ppm (P. Grant, personal communication), and therefore it is likely that there was not enough adsorbed surface material to be detectable.

In some respects the electron microprobe work was disappointing because (1) it was not possible to analyse the low-atomic-number elements important in an organic matrix, (2) the sensitivity to detect trace elements was not available, and (3) quantitative analysis was not possible. With improved instrumentation, it is possible to analyse elements as low as atomic number 4 (Be), which includes most of the organic-matrix elements and it is possible to improve the sensitivity to trace-element levels. However, quantitative analysis of particulate samples, which by their nature are heterogeneous and present a rough surface, gives highly complex theoretical problems.

3.4 Fieldwork at Ecton Mine, Staffordshire.

3.41 Mineralisation in soils and trees.

In the first survey at Ecton mine, soil and plant samples were taken from the top, middle, and bottom of the waste tip, which is on a hillside. There were no significant differences in soil composition between any of the three positions for any element, and therefore the whole area was regarded as having a uniform soil composition for the purpose of this work.

Table 3.20 gives the elemental composition of surface mine waste (gently brushed from the ground; material which might be raised by wind), waste to 10 cm depth, and uncontaminated soil used for planting trees. The surface layer had essentially the same composition as the top 10 cm of mine waste and any differences, if statistically significant, were small. The mine waste was heavily mineralised in many elements compared with imported soil (chiefly in Cu, Zn, Pb, Cd, and Co), but contained less Ti, Mn, Ba, and Al. Apart from the heavy metal mineralisations, the mine waste also contained high levels of Ca and Mg, being derived from limestone.

Unwashed herbage samples were taken from several tree species planted on the mine waste and were separated into leaves, bark, and floral parts (or shoot buds in the case of Pinus sylvestris), which were all potentially particle-producing organs or tissues. The results of multi-elemental analysis, for three species, are shown in Figure 3.10. There were numerous examples of differences in elemental content on a dry weight basis between species and tissues. For example, elements with higher concentrations in bark than in leaves, for all three species, were V and Pb. In one or two species only, this was also true for Cu,

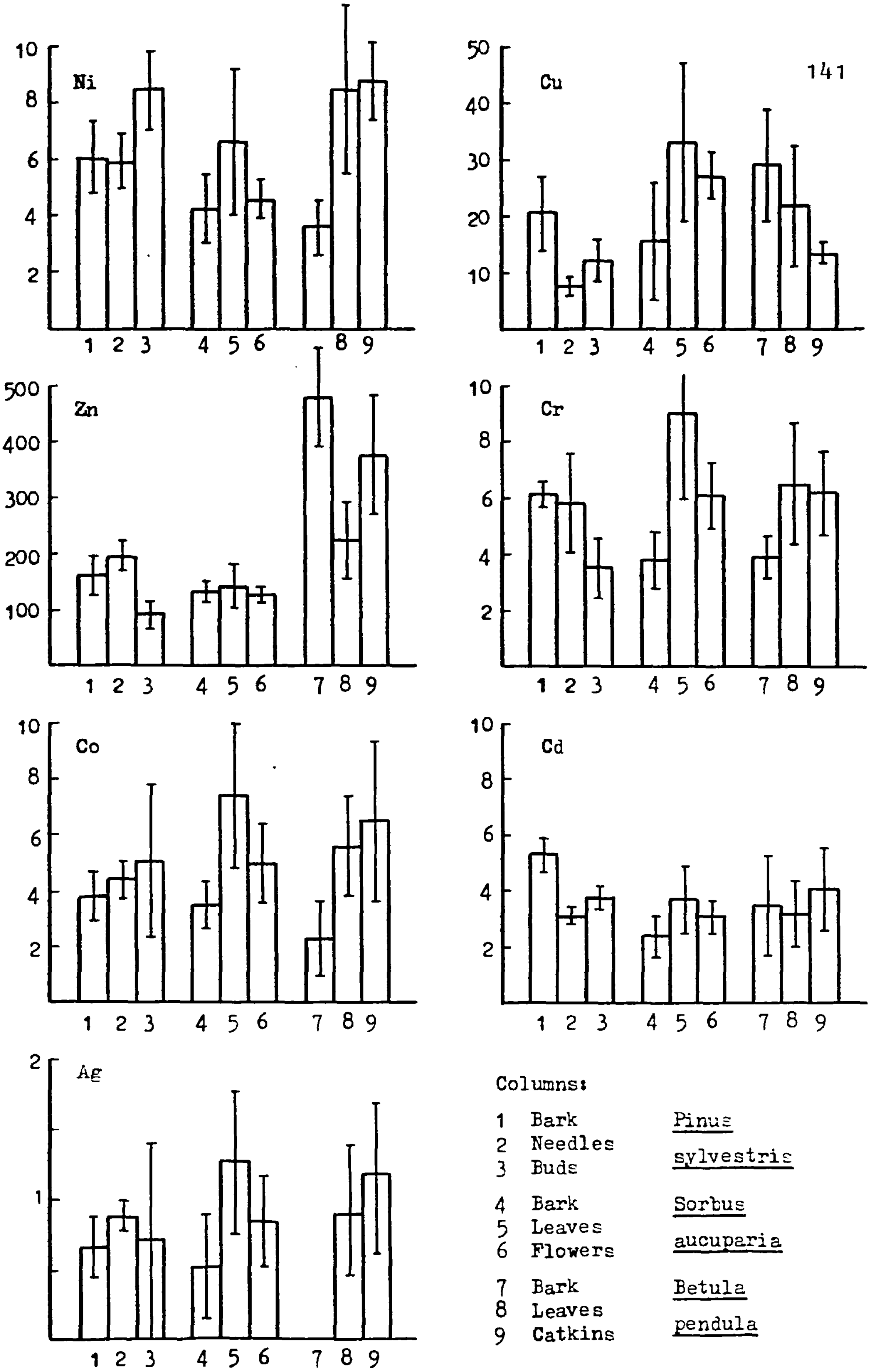
Table 3.20. Elemental levels in soils at Ecton Mine, 26th April 1976.

Parts per million dry weight

Mean ± 95% confidence interval.

Column	I		II	III	
Element	Surface layer of mine waste	Significance of difference from Col. II	Mine waste to 10 cm depth	Imported soil used for planting trees, to 10 cm depth	Significance of difference from Col. II
No. of determinations	12		10	12	
Ni	110 ± 11	NS	130 ± 28	53 ± 14	*
Cu	21375 ± 2871	NS	17969 ± 7695	382 ± 228	*
Zn	25467 ± 8121	NS	19749 ± 7330	805 ± 351	*
Cr	51 ± 3	*	66 ± 7	37 ± 8	*
Co	97 ± 15	NS	100 ± 21	19 ± 5	*
Cd	235 ± 78	NS	212 ± 72	17 ± 5	*
Ag	10 ± 1	NS	10 ± 2	ND	*
Sr	90 ± 20	NS	92 ± 24	41 ± 7	*
V	56 ± 4	NS	63 ± 9	53 ± 8	NS
Be	4.2 ± 0.5	*	5.4 ± 0.6	1.7 ± 0.4	*
P	9250 ± 933	NS	8560 ± 3486	1633 ± 344	*
Ti	136 ± 20	*	171 ± 7	420 ± 52	*(-)
Mn	1229 ± 142	*	1332 ± 300	3008 ± 856	*(-)
Ba	36 ± 9	NS	58 ± 13	885 ± 293	*(-)
Al	15900 ± 1890	NS	18100 ± 2390	30400 ± 4500	*(-)
Fe	31400 ± 4500	NS	40560 ± 18200	23300 ± 4600	NS
Ca	132000 ± 16100	NS	134140 ± 22000	4430 ± 1900	*
Mg	7380 ± 986	NS	12940 ± 5406	2630 ± 800	*
Na	4304 ± 1202	NS	3800 ± 871	658 ± 116	*
Pb	3998 ± 1565	NS	3060 ± 1283	597 ± 152	*

NS=not significant; *=significant at least at 5% probability level; (-)=imported soil 'mineralised' relative to mine waste; ND=not detected.



Columns:

1	Bark	<u>Pinus</u>
2	Needles	<u>sylvestris</u>
3	Buds	
4	Bark	<u>Sorbus</u>
5	Leaves	<u>aucuparia</u>
6	Flowers	
7	Bark	<u>Betula</u>
8	Leaves	<u>pendula</u>
9	Catkins	

<u>Figure 3.10 A</u> <u>Elemental levels in tree samples, Ecton, April 1976.</u>
ppm dry weight. 95 % confidence intervals shown.

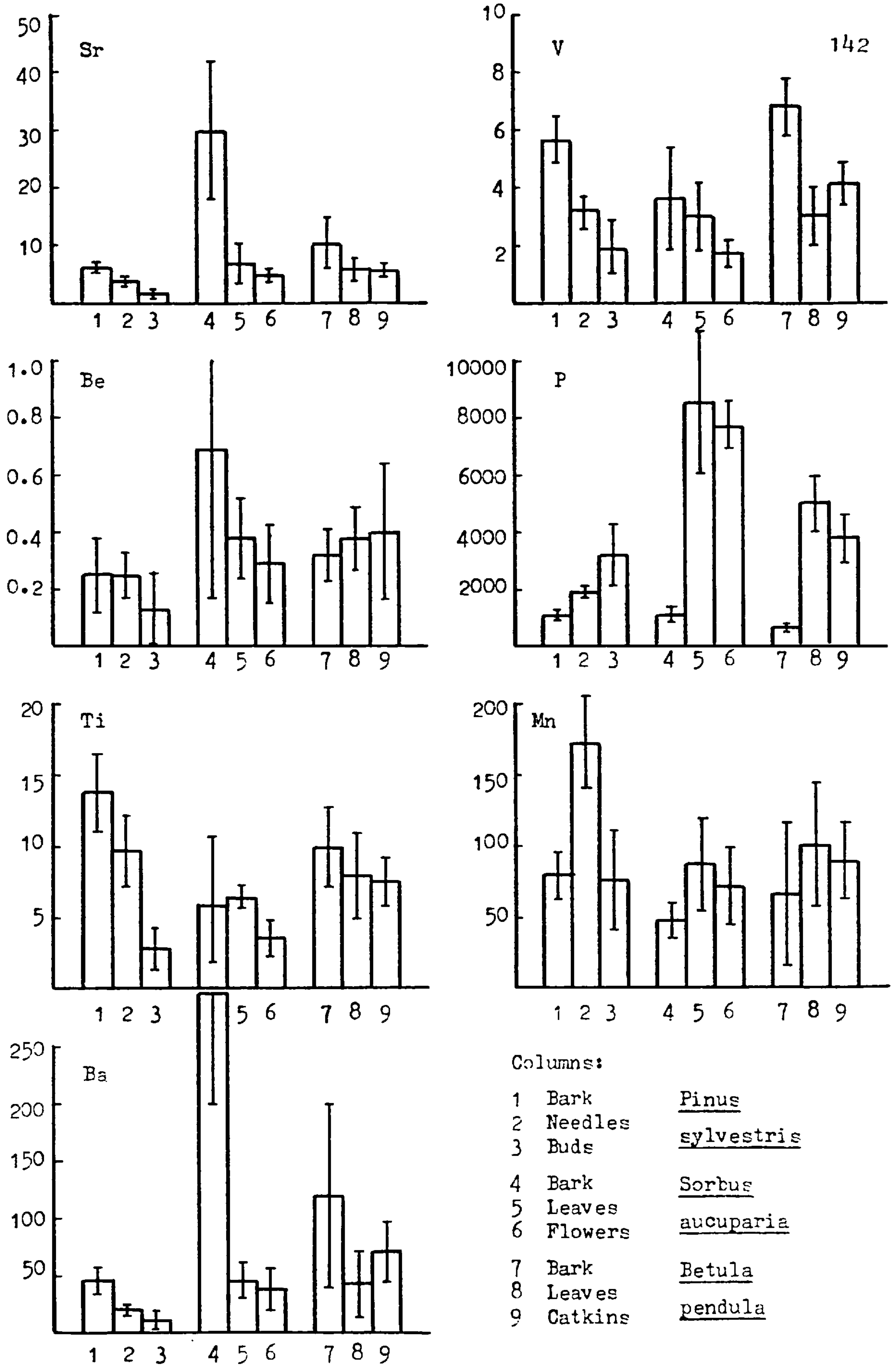


Figure 3.10 B Elemental levels in tree samples, Ecton, April 1976. ppm dry weight. 95% confidence intervals shown.

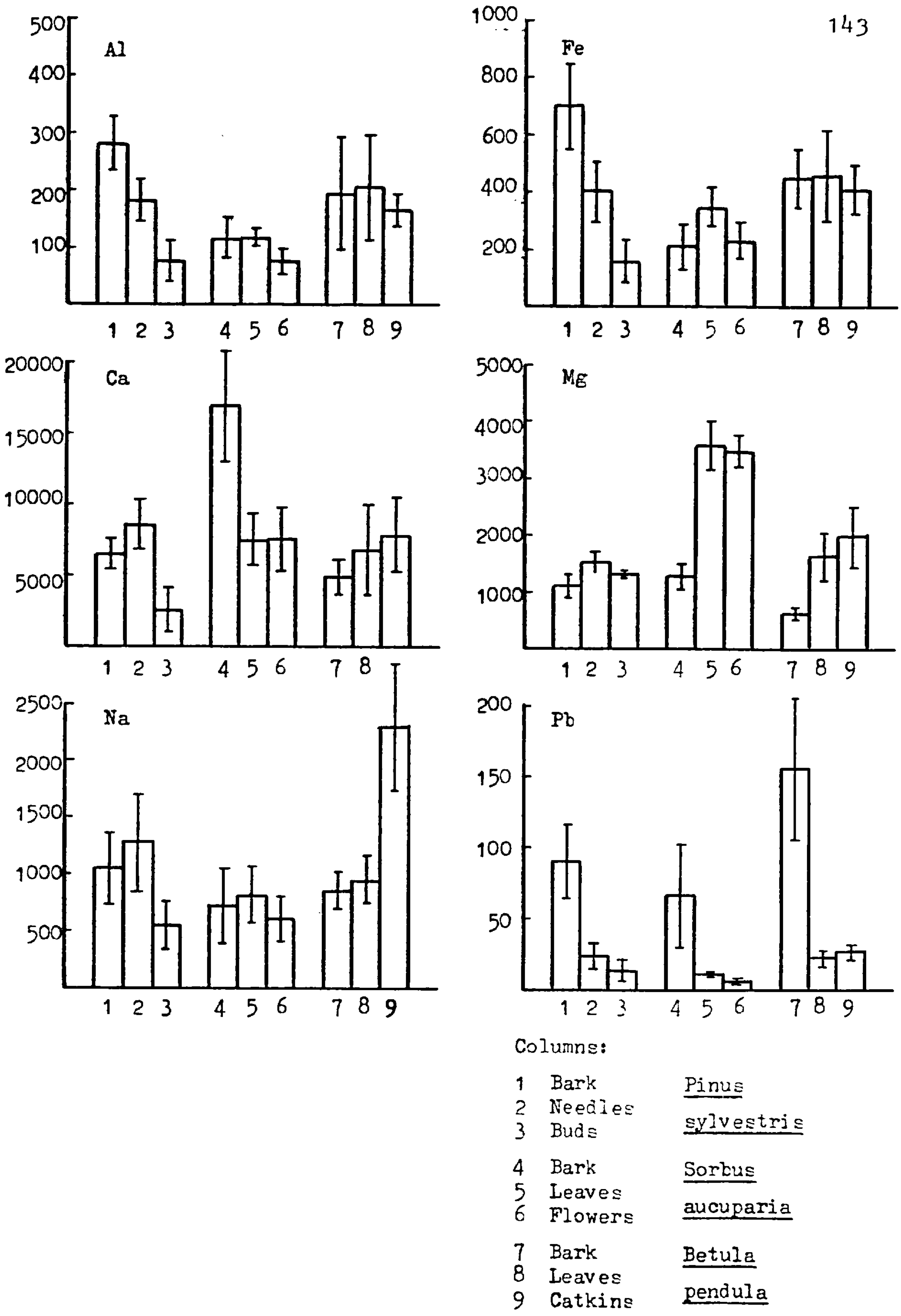


Figure 3.10 C Elemental levels in tree samples, Ecton, April 1976. ppm dry weight. 95% confidence intervals shown.

Cd, Sr, Al, Fe, Ba, Ca, and Zn. Elements with lower concentrations in bark than leaves, for at least one species, were P, Mg, Mn, Cr, Co, Ni, and Ag. There were several instances where a particular tissue had an exceptionally high elemental content, as for example, Ca, Ba, and Sr in rowan bark, Mn in pine needles, Na in birch catkins, and P and Mg in leaves and flowers of rowan. These examples indicate that the composition of particles collected from plants might depend on (1) the tissue forming most particles, (2) retention of dust particles by different species and tissues, (3) metal uptake and distribution in different species and tissues and (4) time of year, which would determine the growth phase of the plant (e.g. the presence of leaves, flowers and fruits).

A 'control' site about 200 metres away from the mine waste had anomalous levels of Pb in soil but had much lower levels, compared with the mine waste, of the other four metals shown in Table 3.21. These elements were selected because they were the chief metals mineralised at Ecton. Metal concentrations in unwashed pine foliage, however, did not seem to be greatly decreased compared to foliage of trees actually growing on the mine waste.

3.42 Particles.

Particulate samples were brushed from pine and shaken from rowan and birch samples collected at Ecton and taken to the laboratory in sealed plastic bags. Particulate samples were analysed by system ARL 1, which was not quantitatively comparable with ARL 2 (Table 3.22) but was assumed to be useful for comparing samples on a relative basis. Only one particulate sample, from pine (+350 µm), was obtained in sufficient bulk for analysis by ARL 2, and this sample indicated a heavy metal composition intermediate

Table 3.21. Metals in soils, unwashed pine tissue and foliar particles at Ecton Mine and at a less-mineralised site about 200 yards away.

	Anal. System (ARL 1 or ARL 2)	No. of Reps.	Metal ppm (ARL 2) or pseudo-ppm (ARL 1). Dry weight basis. Cu	Zn	Pb	Cd	Ni
Mineralised							
Soil	2	10	17969	19749	3060	212	130
Pine: Bark	2	10	20.7	163	90	5.3	6.1
Needles	2	14	7.6	196	24	3.1	5.9
Buds	2	6	12.3	92	14	3.8	8.4
Particles:							
Coarse	2	1	161	257	785	6	31.2
Coarse	1	63	1233	1881	12050	14.3	250
Fine	1	72	1367	1916	8020	17.0	259
Control							
Soil	2	3	790	4457	2863	50	55
Pine: Bark	2	1	7.7	179	69	4.7	5.1
Needles	2	2	8.3	137	41	2.6	4.4
Buds	2	1	8.9	122	50	4.3	13.5
Particles:							
Coarse	1	2	525	1415	3930	9.7	233
Fine	1	6	457	1322	2820	11.6	232

Table 3.22. Analytical systems comparisons: ARL 1 (laser vaporisation) and ARL 2 (acid digest)

Element Units: ppm or pseudo-ppm (x factor shown)	Talc			Soil Ecton Mine waste, surface microlayer			*Betula pendula* Catkins			*Pinus sylvestris* coarse foliar surface particles		
	ARL 2	ARL 1	RATIO 1/2	ARL 2	ARL 1	RATIO 1/2	ARL 2	ARL 1	RATIO 1/2	ARL 2	ARL 1	RATIO 1/2
No. of determinations	2	6		6	12		6	6		1	63	
Ni	0.9	16.5	18.3	112	451	4.0	8.8	277	31.5	31.2	250	8.0
Cu	0.35	11.4	32.6	17417	22048	1.3	13.5	676	50.1	161	1233	7.7
Zn	6.7	26.8	4.0	31817	29031	0.9	376	6353	16.9	257	1881	7.3
Cr	3.35	204	60.9	48.0	205	4.3	6.2	1035	166.9	51.5	332	6.4
Cd	0.3	7.69	25.6	271	341	1.3	4.1	63.2	15.4	6.0	14.3	2.4
Sr	1.16	7.10	6.1	73.6	265	3.6	5.70	370	64.9	20.1	551	27.4
Be	N.D.	0.13	-	3.59	6.29	1.8	0.40	2.59	6.5	1.16	7.10	6.1
P x 10^3	0.025	0.43	17.2	8.12	37.4	4.6	3.78	113.7	30.1	1.16	9.82	8.5
Ti	2.9	32.6	11.2	146	2011	13.8	7.5	822	109.6	222	3247	14.6
Mn	1.65	30.6	18.5	1352	1414	1.0	90	1019	11.3	106	667	6.3
Ba	5.5	1.05	0.2	31.5	146	4.6	71	101	1.4	106	113	1.1
Al x10^3	0.11	0.94	8.5	15.5	67.4	4.3	0.17	93.8	551.8	3.94	65.3	16.6
Fe x10^3	0.10	1.85	18.5	27.0	66.6	2.5	0.41	27.7	67.6	8.53	77.3	9.1
Ca x10^3	0.11	0.17	1.5	117	135	1.2	7.92	69.9	8.8	3.19	15.1	4.7
Mg x10^3	4.38	60.7	13.9	7.17	9.72	1.4	1.97	94.1	47.8	1.07	14.3	13.4
Pb	<0.5	110	-	2400	45142	18.8	26.5	1618	61.0	785	12050	15.4

between soil and herbage (Table 3.21). A comparison of the metal content of particles from pines in 'mineralised' and 'control' sites, also in Table 3.21, indicated that there may have been an extremely local wind-blown soil contribution to pine surface particles.

The +350 µm and -350 µm pine particulate fractions were very similar in elemental composition (data for seven elements are shown in Figure 3.11). The only slight differences were for Mn, Pb, and Sr which were more concentrated in the fine than in the coarse fraction. In contrast, there were marked differences in the elemental contents of particles collected from the three species, and the most notable feature was very high levels of certain elements in birch particles, especially Zn, Cd, S, P, Mn, K, Ca, Mg, and C. (Not all these elements are illustrated.) Many of these elements have high concentrations in plants, which suggests that the birch particles were largely plant-derived, and their yellow colour indicated that pollen was significant. The elements listed above generally showed similar or slightly higher concentrations in rowan than in pine particles.

In general, there did not seem to be a relationship between the composition of the plant and of particles taken from its surface, although the occasional result, e.g. Zn in birch particles, might be explicable in these terms. Thus, particles do not seem simply to be plant tissue. This implies (1) that they comprise deposited particles, and/or (2) that certain elements selectively pass through the plant to its surface to give rise to the distinctive chemistry of foliar particles. Apart from the specific mechanism of pollen production already suggested, leaching could play a general role in this phenomenon, particularly in view of the wet conditions in which the plant material was kept (in plastic bags) prior to collecting particles.

3.43 Leachates.

Ecton mine was revisited at the same time of year as for the initial work, to carry out leaching tests on site on the same three species. The amounts of eight metals removed from washed and unwashed herbage are given in Figure 3.12. Washing had a consistent effect in decreasing the amounts of metal 'leached' in 2 h. although the decrease was significant only for Ca and Mg. 61, 94, and 108 µg Ca were removed by distilled water washing from 1 g of pine, rowan and birch foliage respectively. The corresponding amounts of Mg were 10.3, 10.4, and 22.5 $\mu g.g^{-1}$ respectively. Since the area has limestone geology, these data suggest a surface coating of soil dust, and the Ca:Mg ratios are consistent with the soil analysis in Table 3.20.

Figures 3.11 and 3.12 allow a visual comparison of metals in particles and leachates from the three species, and the correlations are striking. There were marked differences between species in the amounts of metals that could be removed from foliage by leaching, and, while more Cu and Pb could be removed from pine than from birch or rowan, for other metals the two deciduous species, particularly birch, were more leachable. Corresponding trends could be seen in metal concentrations in plant surface particles.

The washing treatment probably did not remove all the plant surface particles and therefore a portion of the metals removed from washed herbage could have been 'leached' from surface contaminants rather than from within the plant. However, if one were to assume that no true leaching occurred, then one would have to suppose that pine foliage was relatively good at retaining particles containing Cu and Pb, and that deciduous species were relatively good at retaining particles containing other metals. It seems much more likely that the species differed in leachability in the order Birch > Rowan > Pine. This trend seemed

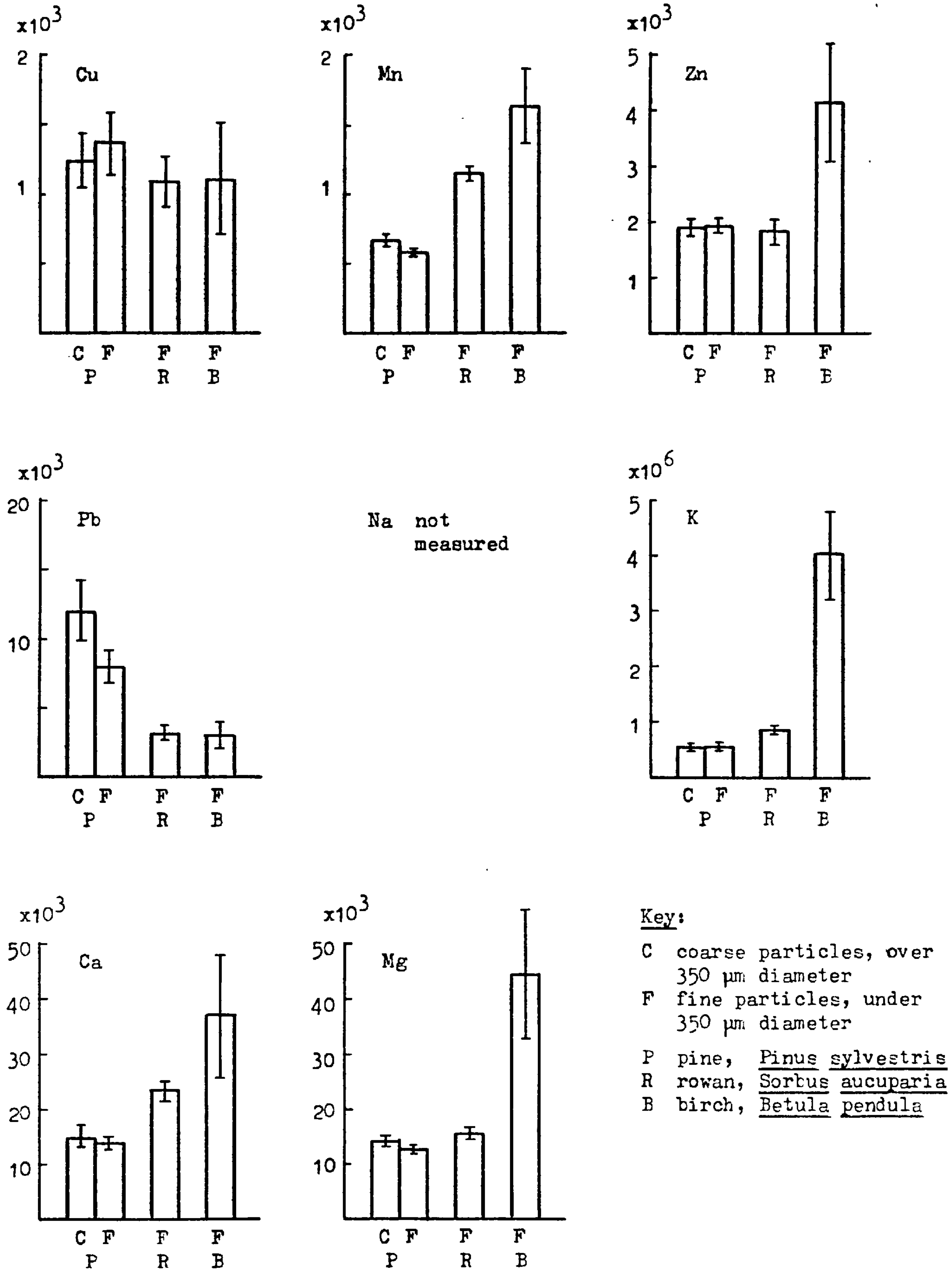


Figure 3.11 Metals in foliar particles from three species at Ecton mine. 'pseudo-ppm'. 95% confidence intervals shown.

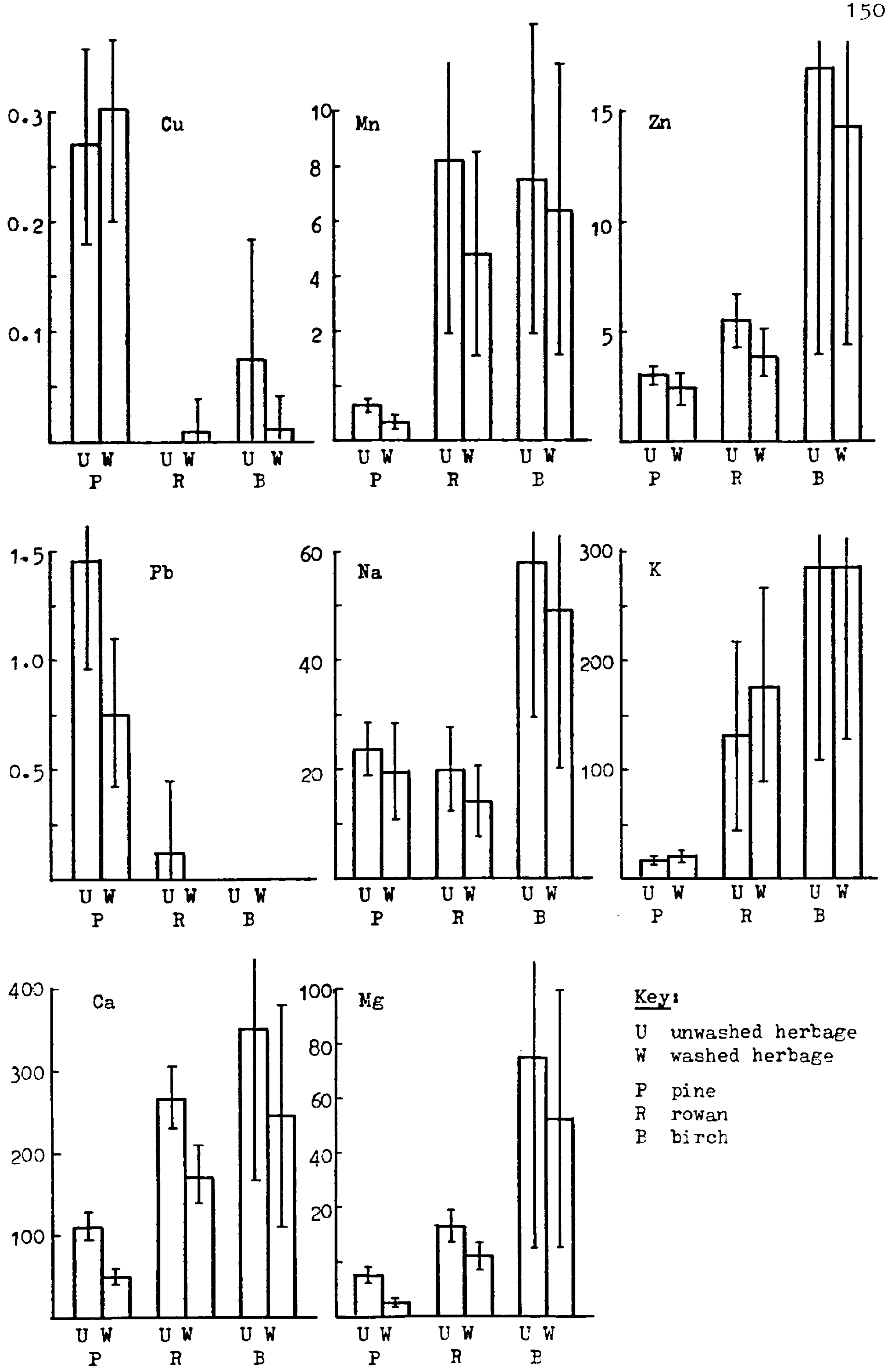


Figure 3.12 Metals leached from herbage of three species at Ecton mine. µg metal per g dry herbage. 95% confidence intervals shown.

generally applicable to the metals Mn, Zn, K, Ca, and Mg, and to Na except that Rowan $\backsimeq$ Pine (see also Table 3.23). Birch pollen was a factor in leached materials, because birch leachates were yellow and must have contained fine particulate material because they frequently blocked the spectrophotometer even after filtering.

Levels of Cu and Pb in leachates were extremely low and it was necessary to concentrate the samples ten times to obtain readings. At such low concentrations it seems quite possible that differential retention, between species, of mineralised particles was involved, and it may be relevant that Scots pine has sticky, resinous foliage. It may also be significant that Little (1973) found that much of the lead in leaf washings remained insoluble unless they were acidified in 10% acid, whereas in the present work 0.01% acid was used for leaching (to simulate rainwater) and was not further acidified prior to analysis. While this oversight does not explain differences between species, it could result in measured Pb levels being too low.

Leaching has been expressed above on a dry weight basis. Table 3.24 shows that the actual mean weights of samples used for leaching tests differed between the three species, and that the differences were exaggerated by taking a dry weight basis, as opposed to a fresh weight basis, because of differences between the species in the dry weight:fresh weight ratios. It would be more logical to use a surface area basis to express leaching but, although an attempt was made to measure surface areas (Table 3.24), it was felt that the method that was used (Section 2.435) was unlikely to give meaningful comparisons between plants with totally different morphologies.

Table 3.23. Leachability of metals from three tree species at Ecton Mine.

Means of 10 replicates. May 1978

$$\text{Leachability (\%)} = \frac{\text{Metal in leachate } (\mu g.g^{-1} \text{ dry wt. herbage}) \times 100}{\text{Metal in unwashed herbage } (\mu g.g^{-1} \text{ dry wt.})}$$

	Pine		Rowan		Birch	
	Unwashed	Washed	Unwashed	Washed	Unwashed	Washed
Cu	0.80	0.89	0.00	0.06	0.25	0.03
Mn	0.96	0.52	6.13	4.05	9.15	8.07
Zn	2.49	1.95	14.81	11.05	7.71	6.49
Pb	2.35	1.22	0.92	0.00	0.00	0.00
Na	2.83	2.33	9.95	6.97	10.23	8.66
K	0.66	0.82	2.05	2.76	6.82	6.82
Ca	5.14	2.31	2.47	1.61	6.95	4.82
Mg	1.21	0.40	1.18	0.81	4.70	3.58

Table 3.24. Leaf areas, fresh weights, and dry weights of leached herbage samples from Ecton Mine, May 1978.

Mean ± 95% confidence interval

Species	Treatment	No. of trees	Reps. per tree	Leaf area (cm^2)	Fresh wt. (g)	Dry weight (g)
Pine	Unwashed	5	2	40.7± 6.4	4.24±0.77	1.74±0.32
	Washed	5	2	40.0± 6.6	4.22±0.76	1.68±0.32
Rowan	Unwashed	5	2	46.5± 6.6	3.40±0.83	0.77±0.16
	Washed	5	2	46.6±10.8	3.64±1.12	0.80±0.22
Birch	Unwashed	5	2	43.9± 6.3	2.75±0.44	0.60±0.10
	Washed	5	2	47.5± 6.2	3.14±0.57	0.64±0.10

3.5 Total deposition from the atmosphere and forest canopies.

It seemed likely that most of the material leached from trees would be deposited directly to the ground, and therefore experiments were set up to collect deposited metals. In this section, results using total deposition (TD) bottles, similar to rain gauges, are discussed. Moss bags (MB) were used for the same purpose, but are discussed later. Figures 3.13 to 3.16 show the mean rainfall rates ($ml.wk^{-1}$), pH, and Cu, Mn, Zn, Pb, Na, and K concentrations (ppm) in TD samples at Thetford, London, Ascot (Swinley forest), and Tavistock. Data for Silwood Park are not illustrated, being very similar to Swinley (Open). At the three rural sites, Figures 3.14 to 3.16 also compare concentrations of metals collected in the open ('O'; or 'T' at Thetford) and under forests ('F'). It will be shown that it is necessary to make a distinction between the sampling position at the top of Thetford tower (T) and other sites in the open near the ground (O), but when referring to all three forests collectively, 'O' is used to mean 'O or T'.

Tables 3.27 A to 3.32 A show the calculated deposition of Cu, Mn, Zn, Pb, Na, and K in $ng.cm^{-2}$ or $\mu g.cm^{-2}$ of ground area, and ratios of F:O deposition. The Cu, Mn, Zn, and Pb data were obtained by the normal procedure of concentrating 60 ml samples approximately 5 times, but for the last sampling period, these data are compared with results for concentrating 500 ml samples approximately 10 times. The 'x 10' samples were also analysed for Ca, Mg, Cd, and Fe and these results are shown in Table 3.33.

It was found that interesting trends were obtained by using the data in Tables 3.27 A to 3.32 A to calculate regressions of F on O deposition for each element and site (Table 3.34; Figure 3.17). A significant correlation coefficient indicated that F depended on O, in other words that atmospheric fallout was the main variable factor determining deposition from the trees for the element and site in question. If the regression was significant, a slope of about 1.0 would be expected, unless foliar retention or absorption were occurring, when it would be less than 1 (possibly for Pb). A slope greater than 1 (recorded for Na) presumably indicates a process of fallout-dependent leaching, or that trees are filtering out aerosol from the atmosphere, which is then deposited to the ground. The intercept of the F on O regression theoretically indicates the deposition that would be expected from trees not subject to any atmospheric fallout, i.e. the amount of leaching. However, a standardised sampling interval is needed to make the intercept useful in this way.

The data were not ideal for this type of regression analysis because sampling periods varied from 1 to 18 weeks. It could be argued that both F and O deposition were varying independently as functions of a third factor, such as sampling period or rainwater volume. However, Tables 3.34 and 3.35 show that F deposition was better correlated with O deposition than with either rainwater volume or sampling period. Open deposition did, however, appear to depend on sampling period and rainwater volume, particularly for Mn, Zn and Pb.

As described in Materials and Methods, deposition sampling at Tavistock was carried out at different distances from the main area of mine waste. However, there were no obvious effects due to this factor, at the level of replication used, and therefore the data were combined into two groups (O and F) as at other forests.

Metal concentrations in soils and plants at the deposition sites are shown in Table 3.25. The data in Table 3.26, giving further information on the Tavistock site, were originally collected as a survey to enable me to loc-

Table 3.25. Elemental levels in soil and plant material at deposition-sampling sites ppm dry weight.

Means of at least 5 samples. September, 1977.

Element & site		Soil	Humus	Litter	Ground flora	Pine	Birch	Oak
Cu	Thetford	4.10	11.42		5.64	10.08		
	Swinley	11.38	12.80	7.40	4.40			
	Tavistock	1055.20	111.78	14.14		12.04	12.65	12.32
Mn	Thetford	89	234		656	443		
	Swinley	157	165	543	49			
	Tavistock	1080	507	1571		439	1311	2138
Zn	Thetford	15.8	60.8		40.8	65.4		
	Swinley	50.4	101.0	64.4	30.8			
	Tavistock	195.1	81.1	104.1		117.4	311.3	28.9
Pb	Thetford	ND	42.0		42.0	ND		
	Swinley	88.3	134.0	50.0				
	Tavistock	338.9	154.0	35.0		ND	ND	ND
Ca	Thetford	430	2702		6772	3328		
	Swinley	2707	2562	3952	6976			
	Tavistock	2356	1874	4490		3900	6124	4796
Mg	Thetford	451	332		1794	647		
	Swinley	4057	421	771	1398			
	Tavistock	2878	970	1307		1175	2263	1917
Na	Thetford	ND	ND		2320	940		
	Swinley	310	ND	180	ND			
	Tavistock	446	310	ND		460	640	530
Fe	Thetford	11366	3268		192	340		
	Swinley	22300	2484	642	543			
	Tavistock	66532	19715	879		317	133	136
Cd	Thetford	0.8	NOT DETECTED					
	Swinley	5.0						
	Tavistock	1.0						

Other metals showed high levels in soil at Tavistock, but were not detectable in plants.

Table 3.26. Metal levels in soils and pine needles at Devon Great Consols Mine, near Tavistock, 2nd May 1977, and regression of 'pine' on 'soil' ppm.

ppm dry weight. Means of 15 samples.

Metal	Soil Mean	Soil Range	Pine Mean	Pine Range	Correlation Coefficient (NS = not significant)
Cu	779	150- 1820	9.7	4.1-17.7	0.141 N.S.
Mn	470	110- 1020	451	155-1010	0.118 N.S.
Zn	116	54- 198	33.4	21- 52	0.382 N.S.
Pb	260	100- 525	12.5	5- 26	0.081 N.S.
Ca	1137	219- 2790	2758	1230-4700	-0.050 N.S.
Mg	2706	1180- 4450	813	580-1120	-0.027 N.S.
Na	833	680- 1140	838	470-1560	0.382 N.S.
Fe	66833	10700-246000	310	53- 627	0.339 N.S.
Cr	44.6	11.7-148.0	4.6	4.1- 5.2	0.352 N.S.
Al	42529	8330- 68900	408	188- 754	0.348 N.S.

Mineralised in soil, but not detectable in pine: Ni, Cd, Co, Ag, As.

ate the exact areas of forest which were on mineralised soil. These mineralised areas were then used for TD and MB work. The data have been used here to calculate regressions, which show that metal levels in Scots pine did not reflect soil mineralisations.

3.51 Rainfall volume and pH.

Exceptionally heavy rain during the first week of sampling in August 1977 caused all the bottles to overflow except at Thetford, and therefore elemental deposition for the first sampling period cannot be calculated exactly.

Thetford was the driest site and Tavistock the wettest (Figure 3.13). At Thetford, there was occasionally not enough rainfall for heavy metal analysis.

The volume of rainfall collected under a forest was less than in the open, except at Thetford where the amounts were similar. There are two reasons for a difference: (1) water flowing down the trunks ('stemflow'), and (2) evaporation from the canopy. At Thetford, the canopy was more open than in the other forests and probably intercepted a lower proportion of incident rainfall. One would expect that evaporation from the canopy would concentrate the solutes in rain and therefore the higher metal concentrations in 'F' than in 'O' sites, apparent from Figures 3.14 to 3.16, do not necessarily indicate leaching. Because of this, deposition was calculated in ng or $\mu g.cm^{-2}$ ground area (Tables 3.27 to 3.32).

Rainfall pH ranged from 3.3 to 6.6, both extremes occurring under the forest at Swinley. Rainfall between August and December 1977 at both Swinley forest and Silwood Park was of unusually high pH, often above 5.6, which is the pH of pure water in equilibrium with atmospheric CO_2. At other times and at other sites rainfall pH was between

3.3 and 5.3. pH at all sites tended to increase from August till about October and then decrease till May 1978 when sampling ended.

3.52 Copper.

The highest levels of Cu in any given sampling period were always recorded at South Kensington, indicating an anthropogenic origin for this metal. At Thetford, 'F' deposition was always lower than 'T', both as ppm in rainwater and as $ng.cm^{-2}$. Data from Thetford are unusual in many respects, probably because deposition at the top of the tower was greatly enhanced by the very windy conditions. At Swinley forest, Ascot, where the 'open' site was probably a better comparison to 'forest' in windiness, slightly higher deposition of Cu was recorded under the forest than in the open, with fairly consistent ratios of F:O deposition of between 1.0 and 1.3. Ratios slightly above 1 do not necessarily imply leaching from foliage, since the canopy may act as a filter or trap for ambient aerosol.

At Tavistock, ppm Cu in throughfall were sometimes above, and sometimes below, those in rainfall, and the deposition ($ng.cm^{-2}$) under the forest was usually less than in the open. Ratios of F:O deposition less than 1.0 are difficult to explain unless foliar absorption occurred, but would seem more likely to result from sampling error, for example because of stemflow and other causes of non-uniform rainfall distribution under the forest.

The 500 ml samples taken at the end of sampling period 6 (May 1978) generally indicated higher deposition than the normal sampling procedure (60 ml samples). A possible reason is that growth of filamentous algae, which was mainly taken into the 500 ml bottles, was likely to have absorbed Cu from the accumulated rainwater. Algal growth in the bottles was not seen at previous sampling times.

Regression analysis of F on O deposition indicated that F deposition of this element was mainly influenced by atmospheric fallout.

3.53 Manganese.

Mn had very low deposition rates in urban and rural sites, but the most obvious feature of the results was the enhancement of Mn deposition under forest canopies. Ratios of F:O deposition ($ng.cm^{-2}$) varied between 3.6 and 48.1 which can only be explained by leaching from foliage. At Swinley, under Scots pine and European larch, the highest deposition rates occurred from October to January. At Tavistock, peak deposition was from September to December under mainly Scots pine forest, but the peak was much less pronounced than at Swinley. A similar trend seemed to apply at Thetford, although accurate analysis during the autumn was difficult because of low rainfall volumes. The values from the 500 ml samples (concentrated x 10) corresponded quite closely to the usual sampling method (concentrated x 5).

3.54 Zinc.

Zinc deposition ($ng.cm^{-2}$) was usually highest at South Kensington, but in terms of zinc ppm in rainwater, bottles at Thetford (F and T) and at Swinley (F) often collected similar concentrations because of low rainfall volumes. There was no consistent difference in deposition rate between F and T sites at Thetford, possibly due to wind-enhanced deposition above the forest, but at Swinley, F deposition was always greater than O by a factor of 1.2

to 3.3. At Tavistock, however, O and F deposit rates were similar with F:O ratios varying from 0.4 to 1.5.

Deposition of zinc to the forest floor depended very strongly on aerial fallout at both Swinley and Tavistock, as was the case for copper. Whereas general air pollution was probably involved at Swinley, it is possible that wind-blown mineralised mine waste played a part at Tavistock.

3.55 Lead.

The pattern of Pb deposition was similar in many respects to those of Cu and Zn, but deposition in the heart of London was about an order of magnitude higher than anywhere else. Deposition at Thetford (T) was also high in the last sampling period which, incidentally, was after the petrol-engined electrical generator at the site had ceased working. It is possible that wind-enhanced deposition and exhausts from low-flying military aircraft, which are frequent in the area, were involved.

In sampling period 4, the ratio of F:T deposition at Thetford was 2.6 and, at Swinley, F:O ratios were 2.4, 2.6, and 2.3 in sampling periods 3, 4 and 5 respectively. These ratios above 1.0, occurring simultaneously at different sites, perhaps indicate that the two forests may have been acting as filters for a generally dispersed aerosol, or that seasonal leaching of Pb occurred. Regression analysis of F on O deposition supported the inference that much of the Pb reaching the forest floor was derived from the atmosphere.

3.56 Sodium.

Sodium deposition was highest at Thetford and

Tavistock which suggests the maritime origin of sodium, already well documented. Deposition ratios of F:O were fairly similar at all sites and times, between 1.4 and 5.0, which were lower than for manganese and potassium, and may reflect sodium's greater abundance in aerosol rather than lower leachability. Table 3.34 suggests that variations in 'F' deposition depended on aerosol deposited on the foliage. Regression analysis of F on O deposition at each of the three forests gave correlation coefficients of 0.95 at Thetford, 0.90 at Swinley, and 0.90 at Tavistock, all of which are significant at 5% probability. There appeared to be a seasonal influence on sodium deposition, most apparent at Tavistock, with peak deposition in winter (Figure 3.16).

3.57 Potassium.

The main points that were made about manganese apply to potassium; like manganese, potassium was not abundant in deposited aerosol or rainwater, but was leached in relatively large quantities from tree crowns. There seemed to be a seasonal pattern of leaching with a maximum in autumn, particularly under larch and pine at Swinley. This may be associated with leaf fall. Larch, of course, is deciduous, but pines also shows an autumn peak in leaf fall (Will, 1959, for radiata pine and Corsican pine).

3.58 Other metals in Total Deposition.

Ca, Mg, Cd, and Fe were only determined in the last set of samples (Table 3.33). Calcium deposition was highest in London, 10.2 $\mu g.cm^{-2}.4\ wks^{-1}$, and in the other sites between 0.1 and 0.25 $\mu g.cm^{-2}.4\ wks^{-1}$. Deposition rates under the forests were 2.3 to 2.8 times higher than in the open, which suggests that leaching losses occurred from foliage. For Mg, F:O ratios were between 1.4 and 2.3, and there was a much less pronounced urban source of Mg than was the case for Ca. F:O ratios for Fe were between 1.1 and 2.9, and the highest deposition rate was in London. Cd also showed evidence of an urban origin, and was barely detectable in rural samples.

3.59 Conclusion.

It is difficult to quantify leaching losses using field data because the extent to which trees accumulate ambient aerosol is uncertain, but with the use of a range of polluted and remote sites, sampled at regular intervals, and with such methods as F on O regression analysis, these factors could be elucidated. However, it seems clear from the data obtained that Mn, K, and Na (and probably Ca, Mg, and Fe) were leached from forest canopies. There was no consistent evidence of Cu, Zn or Pb leaching. Average 'leaching' rates, under all three forests, estimated by the difference between F and O deposition, in $\mu g.cm^{-2}.4\ wks^{-1}$, were, 0.8 (Mn), 18.1 (Na), 17.2 (K), 2.5 (Ca), 1.4 (Mg), and 0.1 (Fe). The equivalent annual rates, in $kg.ha^{-1}$ are 1.1 (Mn), 23.5 (Na), 22.4 (K), 3.3 (Ca), 1.8 (Mg), and 0.1 (Fe). In proportion to the concentration of each element in pine needles (Table 3.26; K was not measured), metal 'leachability' was in the order:

$$Na > Mn > Mg > Ca > Fe.$$

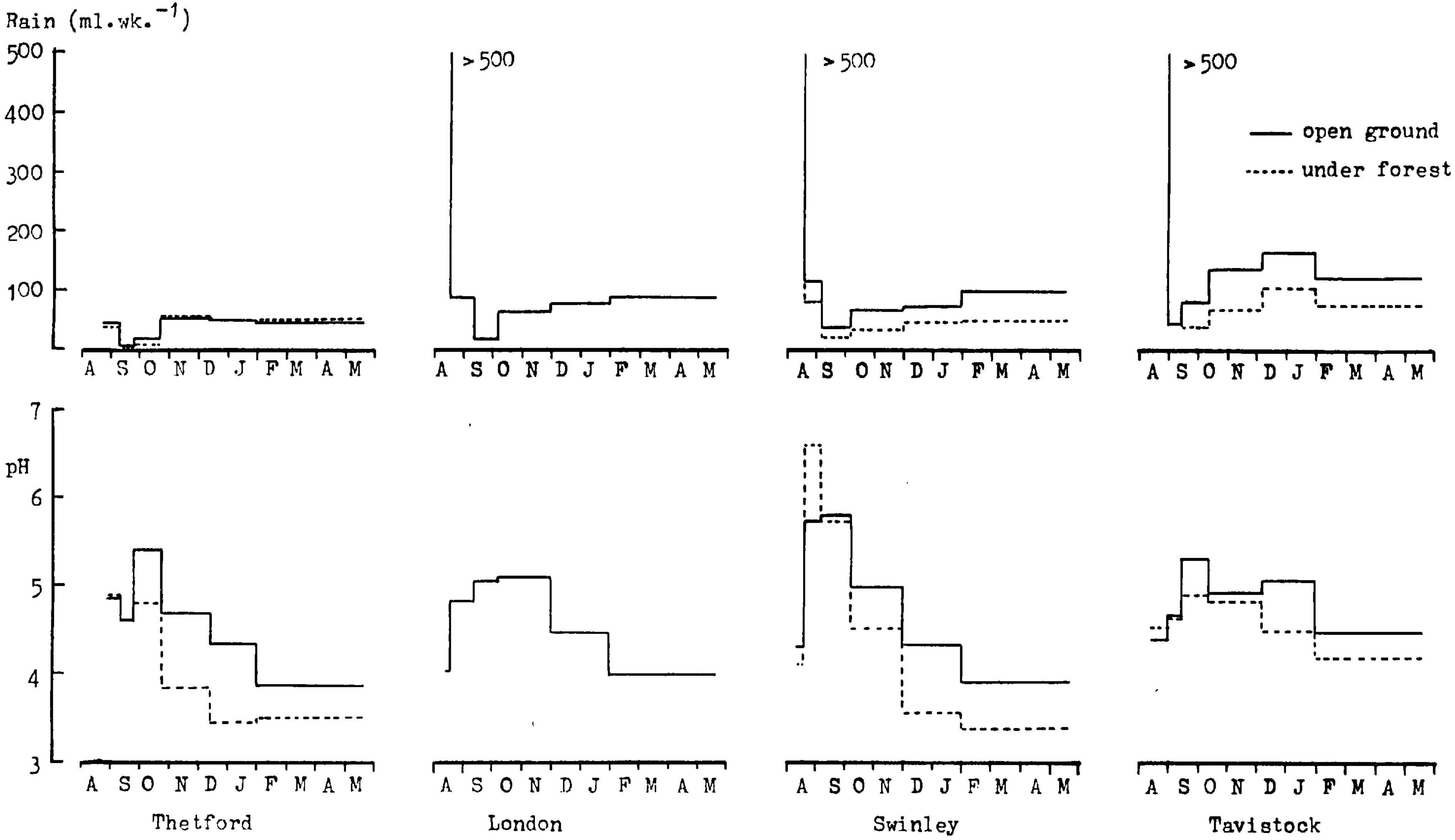


Figure 3.13 Mean rainfall rates and pH recorded by total deposition bottles, August 1977 to May 1978.

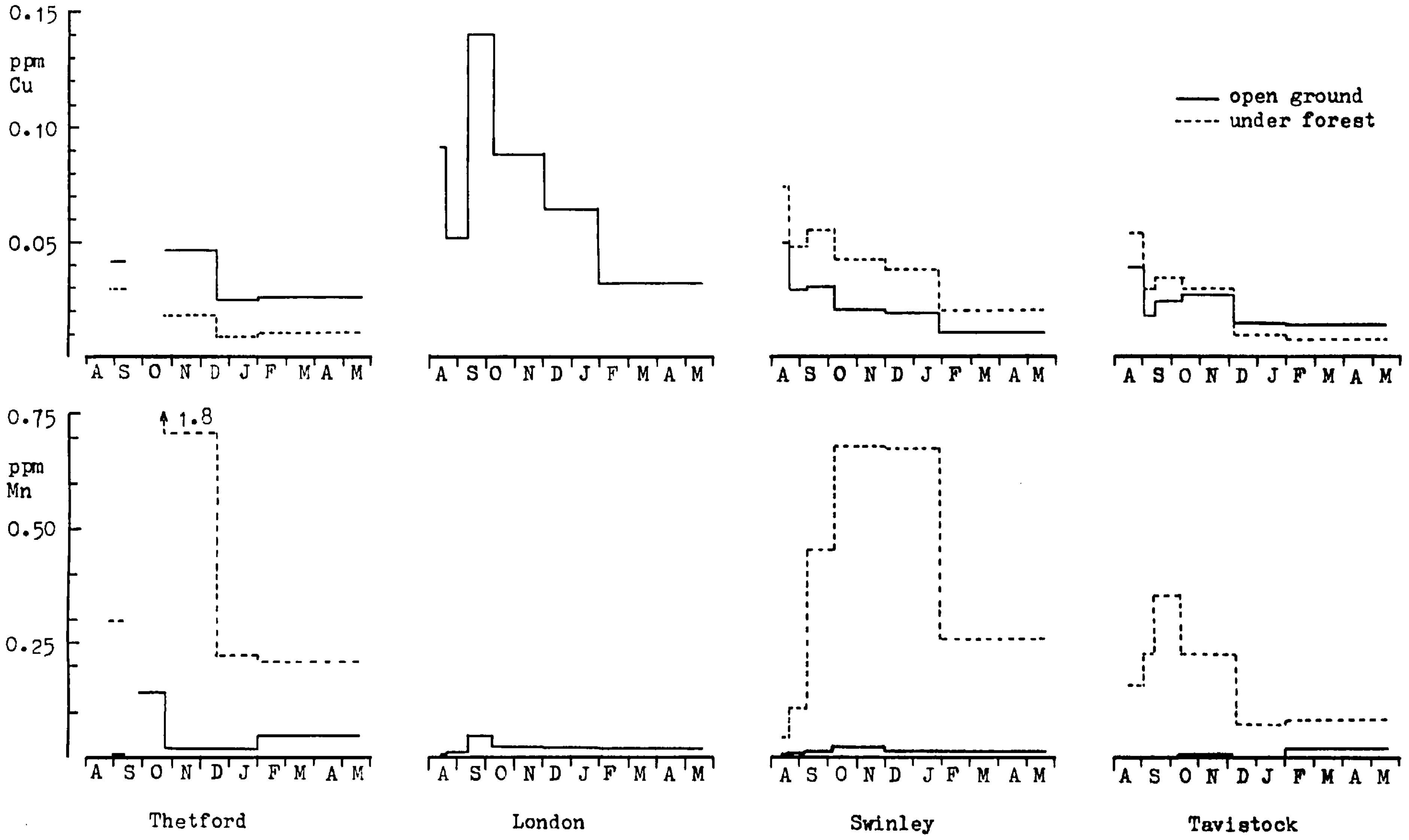


Figure 3.14 Copper and manganese in total deposition samples, August 1977 to May 1978 (parts per million).

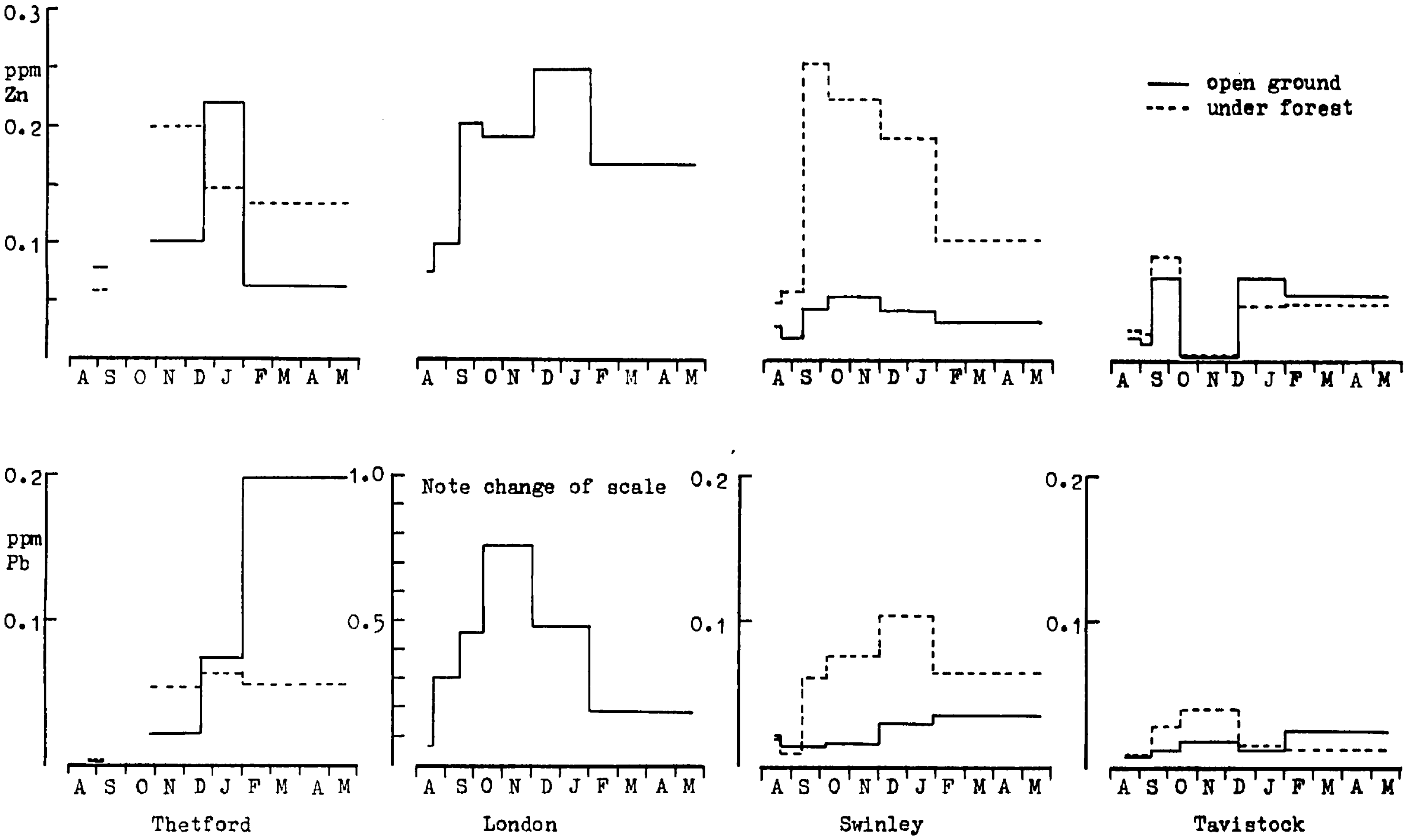


Figure 3.15 Zinc and lead in total deposition samples, August 1977 to May 1978 (parts per million).

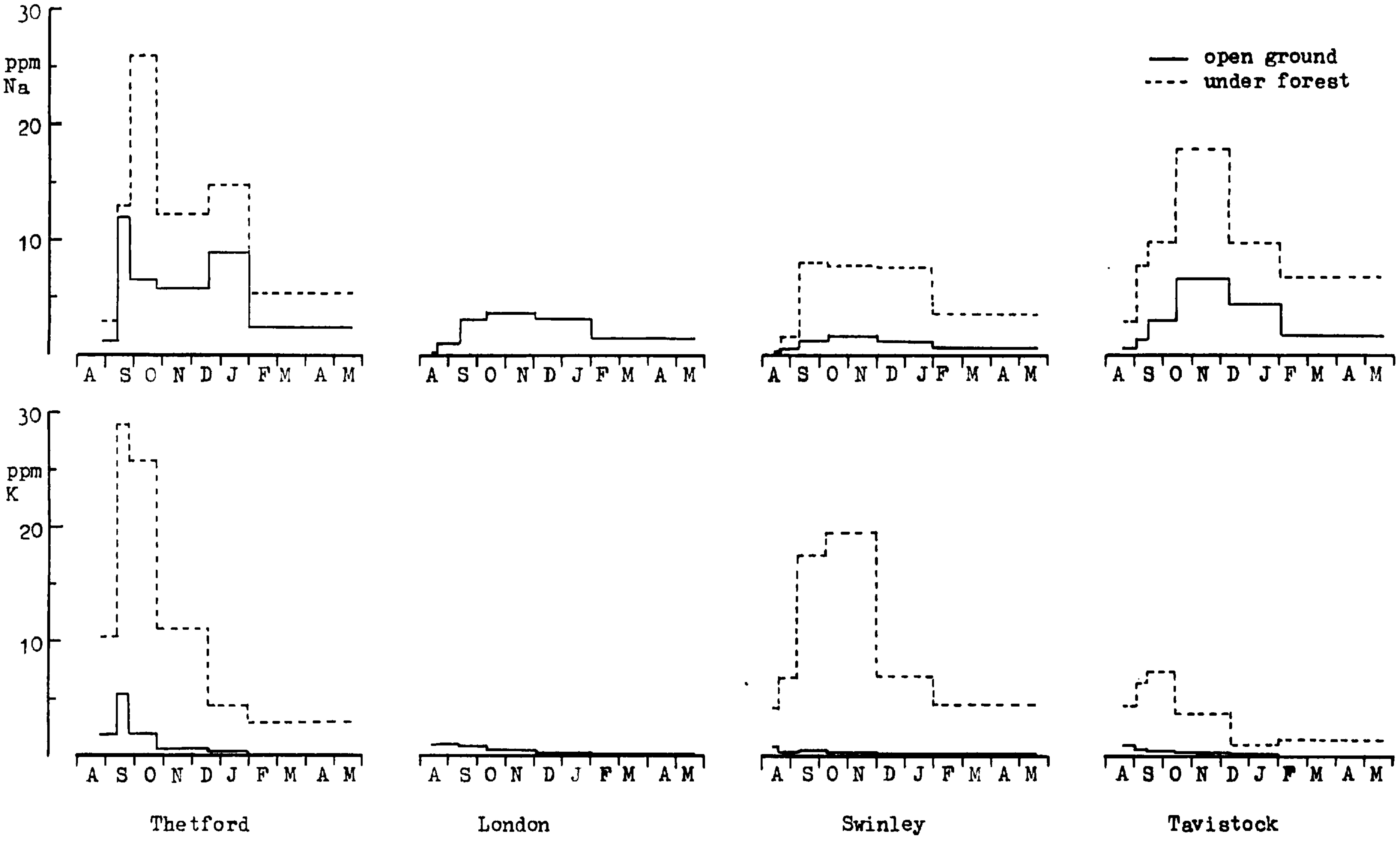


Figure 3.16 Sodium and potassium in total deposition samples, August 1977 to May 1978 (parts per million).

Tables 3.27. to 3.32. Mean deposition (ng or $\mu g.cm^{-2}$ per sampling period) at various sites, and ratios of Forest:Open deposition. Data are the means of 3 to 9 TD replicates and 6 to 15 MB; replication at each site is shown in Table 2.7.

Table 3.27. Copper ($ng.cm^{-2}$)

A. Total deposition bottles.

Sampling Period (Actual dates given in Table 2.6.)	Site										
	Thetford			London	Silwood Park	Ascot (Swinley)			Tavistock		
	Tower	Forest	F/T	Open	Open	Open	Forest	F/O	Open	Forest	F/O
1 (1-2 wks.)	59	36	0.61	>741	>586	>401	>600	-	>311	> 435	-
2 (2-3 wks.)	55	-	-	220	193	166	188	1.14	27	39	1.44
3 (4 wks.)	441	344	0.78	169	163	76	77	1.01	125	88	0.70
4 (8 wks.)	319	132	0.41	728	353	183	200	1.09	470	267	0.57
5 (6-8 wks.)	120	41	0.34	667	262	188	249	1.32	418	134	0.32
6 (15-18 wks.)	352	157	0.45	801	307	269	281	1.04	399	141	0.35
6 'x 10' samples	577	87	0.15	6312	1905	1089	1103	1.01	952	560	0.59

B. Moss Bags.

1 + 2 (4 wks.)	19	20	1.07	121	50	40	53	1.33	32	45	1.42
3 (4 wks.)	92	46	0.50	205	36	12	27	2.25	7	0	-

Table 3.28. Manganese (ng.cm^{-2})

A. Total deposition bottles.

Sampling Period	Site										
	Thetford			London	Silwood Park	Ascot (Swinley)			Tavistock		
	Tower	Forest	F/T	Open	Open	Open	Forest	F/O	Open	Forest	F/O
1 (1-2 wks.)	15	371	25.2	> 56	>30	> 19	> 370	-	> 9	>1255	-
2 (2-3 wks.)	4	-	-	61	34	37	412	11.2	6	293	48.1
3 (4 wks.)	172	938	5.5	49	28	30	629	20.8	25	907	36.6
4 (8 wks.)	176	5097	28.9	163	165	154	3184	19.3	63	1958	30.9
5 (6-8 wks.)	138	2087	15.1	184	85	111	4353	39.2	76	972	12.7
6 (15-18 wks.)	629	3065	4.9	448	267	277	3420	12.4	437	1570	3.6
6 'x 10' samples	469	2966	6.3	455	267	200	2814	14.1	163	1477	9.1

B. Moss Bags.

1 + 2 (4 wks.)	84	418	5.0	216	184	81	782	9.6	60	1001	16.7
3 (4 wks.)	162	1104	6.8	173	60	0	838	-	0	1204	-

Table 3.29. Zinc ($ng.cm^{-2}$)

A. Total deposition bottles.

Sampling Period	Site										
	Thetford			London	Silwood Park	Ascot (Swinley)			Tavistock		
	Tower	Forest	F/T	Open	Open	Open	Forest	F/O	Open	Forest	F/O
1 (1-2 wks.)	110	72	0.66	>615	>175	>252	>403	-	>159	>207	-
2 (2-3 wks.)	9	-	-	428	132	106	227	2.14	20	30	1.48
3 (4 wks.)	501	483	0.96	246	86	107	349	3.26	366	228	0.62
4 (8 wks.)	727	1441	1.98	1590	410	525	1052	2.00	635	382	0.60
5 (6-8 wks.)	1079	735	0.68	2587	256	409	1241	3.03	1495	650	0.44
6 (15-18 wks.)	1801	939	0.52	3991	622	828	1394	1.68	1633	913	0.56
6 'x 10' samples	2912	1277	0.44	5433	1350	1802	2096	1.16	2466	1760	0.71

B. Moss Bags.

1 + 2 (4 wks.)	182	140	0.77	606	275	211	254	1.21	125	144	1.16
3 (4 wks.)	275	7	0.02	287	184	35	161	0.47	0	13	-

Table 3.30. Lead (ng.cm^{-2})

A. Total deposition bottles.

Sampling Period	Site										
	Thetford			London	Silwood Park	Ascot (Swinley)			Tavistock		
	Tower	Forest	F/T	Open	Open	Open	Forest	F/O	Open	Forest	F/O
1 (1-2 wks.)	37	40	1.10	>545	>268	>173	>151	-	>65	>77	-
2 (2-3 wks.)	23	-	-	1306	190	89	39	0.43	18	13	0.74
3 (4 wks.)	248	226	0.91	553	27	34	83	2.44	64	72	1.13
4 (8 wks.)	150	387	2.58	6150	290	139	357	2.57	310	353	1.14
5 (6-8 wks.)	359	310	0.86	4972	242	293	672	2.30	257	229	0.89
6 (15-18 wks.)	2651	855	0.32	4344	676	905	866	0.96	769	238	0.31
6 'x 10' samples	995	356	0.36	5044	762	666	668	1.00	361	358	0.99

B. Moss Bags.

1 + 2 (4 wks.)	358	218	0.61	3896	593	383	296	0.77	0	454	-
3 (4 wks.)	0	0	-	2556	0	0	1684	-	0	0	-

Table 3.31. Sodium ($\mu g.cm^{-2}$).

A. Total deposition bottles.

Sampling Period	Site										
	Thetford			London	Silwood Park	Ascot (Swinley)			Tavistock		
	Tower	Forest	F/T	Open	Open	Open	Forest	F/O	Open	Forest	F/O
1 (1-2 wks.)	1.7	3.7	2.21	> 1.6	>0.8	>0.8	> 2.4	-	> 5.6	> 23.4	-
2 (2-3 wks.)	1.7	-	-	4.6	3.0	3.3	6.1	1.87	2.1	10.3	4.99
3 (4 wks.)	7.9	13.6	1.72	3.8	3.7	3.1	11.1	3.60	15.8	25.3	1.60
4 (8 wks.)	39.1	88.6	2.27	30.4	16.0	15.2	36.7	2.41	116.6	160.0	1.37
5 (6-8 wks.)	43.3	73.1	1.69	32.0	8.7	10.6	49.5	4.65	95.1	132.8	1.40
6 (15-18 wks.)	31.8	82.4	2.59	33.0	14.0	17.3	47.5	2.74	51.2	128.4	2.51

B. Moss Bags: Data were dubious because of very high initial levels of Na in moss.

Table 3.32. Potassium ($\mu g.cm^{-2}$).

A. Total deposition bottles.

Sampling Period	Site										
	Thetford			London	Silwood Park	Ascot (Swinley)			Tavistock		
	Tower	Forest	F/T	Open	Open	Open	Forest	F/O	Open	Forest	F/O
1 (1-2 wks.)	2.8	13.0	4.7	>8.9	>7.0	>6.9	>33.8	-	>8.5	>36.2	-
2 (2-3 wks.)	0.8	-	-	4.8	5.2	2.6	26.7	10.5	1.1	8.8	7.9
3 (4 wks.)	2.4	13.5	5.6	1.2	2.0	1.3	24.3	18.7	2.8	19.1	6.8
4 (8 wks.)	4.0	83.6	21.1	4.2	5.1	2.6	91.9	34.9	7.6	34.0	4.5
5 (6-8 wks.)	2.4	22.2	9.1	3.1	2.4	2.7	45.4	16.8	6.2	16.8	2.7
6 (15-18 wks.)	2.0	47.3	23.5	6.1	3.0	0.6	61.8	96.6	2.6	30.4	11.6

B. Moss Bags: K not analysed by ARL 2.

Table 3.33. Mean deposition collected by total deposition bottles, January to May 1978. (ng.cm^{-2}. 4 weeks^{-1}).

Samples were concentrated approximately 10 times.

Element	Site										
	Thetford			London	Silwood Park	Ascot (Swinley)			Tavistock		
	Tower	Forest	F/T	Open	Open	Open	Forest	F/O	Open	Forest	F/O
Cu	128	19	0.15	1578	476	272	276	1.01	254	149	0.59
Mn	104	659	6.34	114	67	50	704	14.07	43	394	9.06
Zn	647	284	0.44	1358	337	450	524	1.16	658	469	0.71
Pb	221	79	0.36	1261	191	167	167	1.00	96	95	0.99
Ca	1527	4002	2.62	10193	2485	1884	5321	2.82	1269	2936	2.31
Mg	1562	2716	1.74	2692	1036	1184	2710	2.29	2986	4372	1.46
Cd	2.1	2.0	1.0	10.0	0.5	1.9	2.0	1.0	0.0	0.5	-
Fe	540	652	1.21	986	370	368	420	1.14	51.0	145.0	2.88

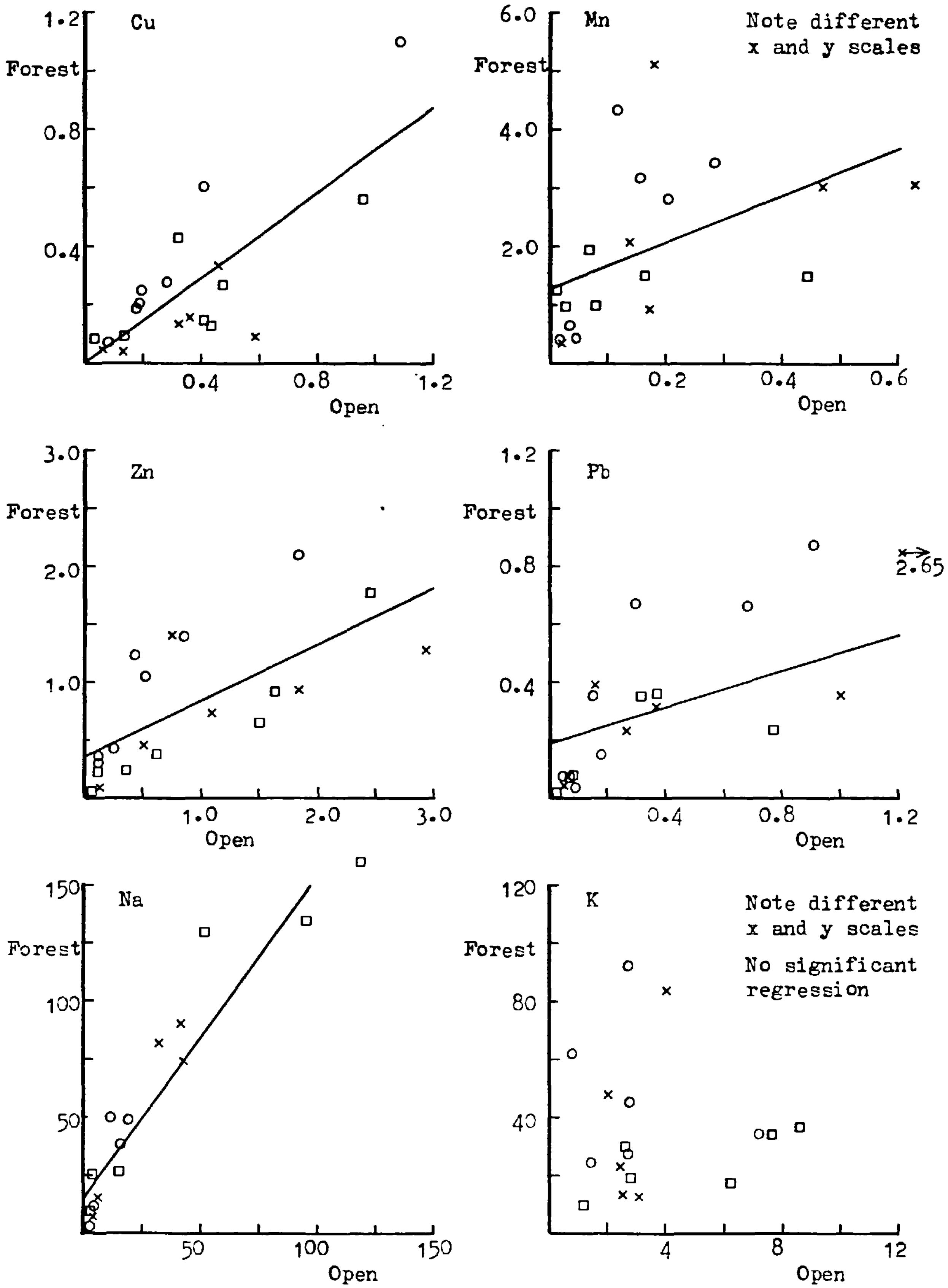


Figure 3.17 Relationship between elemental deposition to the ground under forest canopies and on open ground ($\mu g. cm^{-2}$).

Each point represents the mean of 4 to 9 TD bottles.

× Thetford, o Swinley, □ Tavistock.

Computed regression lines of F on O for all 3 sites are shown (see Table 3.34).

Table 3.34. Regressions of forest deposition on open deposition.

(µg or ng.cm^{-2} per sampling period).

Each 'observation' is the mean of between 4 and 9 TD gauges.

		No of pairs of observations	Correlation coefficient		Slope	Intercept
Cu (ng)	Thetford	6	0.524	NS	0.307	37.18
	Swinley	7	0.981	***	1.009	43.68
	Tavistock	7	0.797	*	0.519	37.23
	All sites	20	0.791	***	0.736	2.62
Mn (ng)	Thetford	6	0.407	NS	2.972	1628.71
	Swinley	7	0.749	NS	12.688	668.06
	Tavistock	7	0.445	NS	1.567	1030.21
	All sites	20	0.483	*	3.969	1270.73
Zn (ng)	Thetford	6	0.626	NS	0.312	454.37
	Swinley	7	0.926	**	1.056	358.43
	Tavistock	7	0.963	***	0.627	- 10.65
	All sites	20	0.690	***	0.483	360.43
Pb (ng)	Thetford	6	0.918	**	0.251	176.99
	Swinley	7	0.880	**	0.884	114.80
	Tavistock	7	0.631	NS	0.338	102.44
	All sites	20	0.705	***	0.310	184.61
Na (µg)	Thetford	5	0.952	*	2.043	1.686
	Swinley	6	0.905	*	2.790	2.161
	Tavistock	6	0.898	*	0.935	27.617
	All sites	17	0.941	***	1.400	14.730
K (µg)	Thetford	5	0.676	NS	26.422	- 35.949
	Swinley	6	-0.203	NS	-2.391	53.972
	Tavistock	6	0.694	NS	2.499	12.220
	All sites	17	-0.022	NS	-0.227	36.600

Significance levels: NS = not significant; * = 5%; ** = 1%; *** = 0.1%.

Table 3.35. Regressions of open and forest deposition (µg or ng.cm^{-2} per sampling period) on sampling period (weeks) and rainwater volume (ml). Correlation coefficients.

Dependent variable:	Forest deposition				Open deposition			
Independent variable:	Period		Rain Vol		Period		Rain Vol	
Cu Thetford	-0.130	NS	-0.215	NS	0.684	NS	0.659	NS
Swinley	0.455	NS	0.707	NS	0.565	NS	0.689	NS
Tavistock	0.346	NS	0.486	NS	0.773	*	0.820	*
Mn Thetford	0.555	NS	0.583	NS	0.948	**	0.933	**
Swinley	0.715	NS	0.453	NS	0.954	***	0.890	**
Tavistock	0.589	NS	0.605	NS	0.834	*	0.862	*
Zn Thetford	0.696	NS	0.692	NS	0.985	***	0.920	**
Swinley	0.927	**	0.780	*	0.858	*	0.870	*
Tavistock	0.892	**	0.863	*	0.922	**	0.928	**
Pb Thetford	0.795	NS	0.772	NS	0.815	*	0.803	*
Swinley	0.906	**	0.790	*	0.915	**	0.970	***
Tavistock	0.785	*	0.756	*	0.884	**	0.865	*
Na Thetford	0.793	NS	0.776	NS	0.722	NS	0.694	NS
Swinley	0.857	*	0.493	NS	0.911	**	0.737	NS
Tavistock	0.764	NS	0.744	NS	0.436	NS	0.673	NS
K Thetford	0.493	NS	0.572	NS	0.144	NS	0.228	NS
Swinley	0.601	NS	0.319	NS	-0.603	NS	-0.339	NS
Tavistock	0.312	NS	0.456	NS	-0.119	NS	0.179	NS

Levels of significance as in Table 3.34.

3.6 Moss bags.

3.61 MB runs 1 and 2.

Figure 3.18 shows the concentrations of 15 elements collected by Sphagnum moss exposed for 4 weeks, in ppm dry weight of moss after correction for the elemental content of unexposed moss. Two runs were carried out in August to October 1977 in conjunction with TD sampling. In Tables 3.27 B to 3.30 B, the deposition of Cu, Mn, Zn, and Pb recorded by MB is given in $ng.cm^{-2}.4\ wks^{-1}$ for comparison with TD data.

To discuss patterns of deposition in the Open sites first, most elements showed their highest deposition rates in London, and lower deposition in rural sites. This trend applied to all the elements shown in Figure 3.18, except for Mg which had highest deposition at Thetford and Tavistock, perhaps indicating a marine source (see also Table 3.33). Sodium data, which might have been expected to show the same trend, are not presented because the initial Na content of moss was very high and the results did not seem reliable.

The only element to show higher deposition in F than O sites at all three forests was Mn. At Thetford, T deposition was much greater than F for several elements, and it has already been suggested that this was due to windiness. Excluding Thetford, Ca and Mg usually also showed F:O ratios substantially greater than 1.0 (Figure 3.18). (K was not analysed in MB runs 1 and 2.)

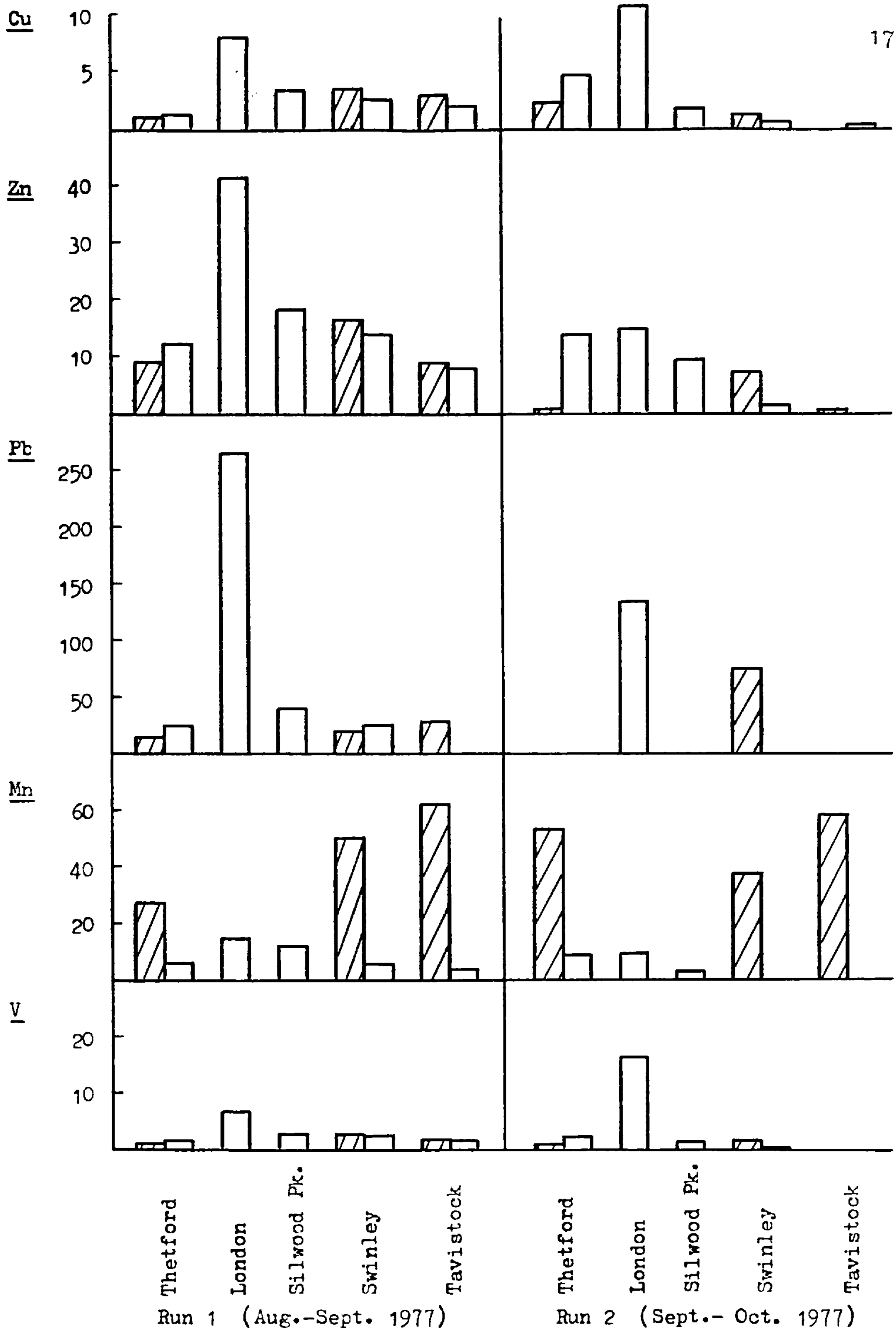


Figure 3.18 A Elemental deposition on moss bags at various sites after four weeks exposure (ppm dry weight of moss, corrected for unexposed moss). Cross-hatched columns show deposition under forests; others show deposition on open ground (O or T).

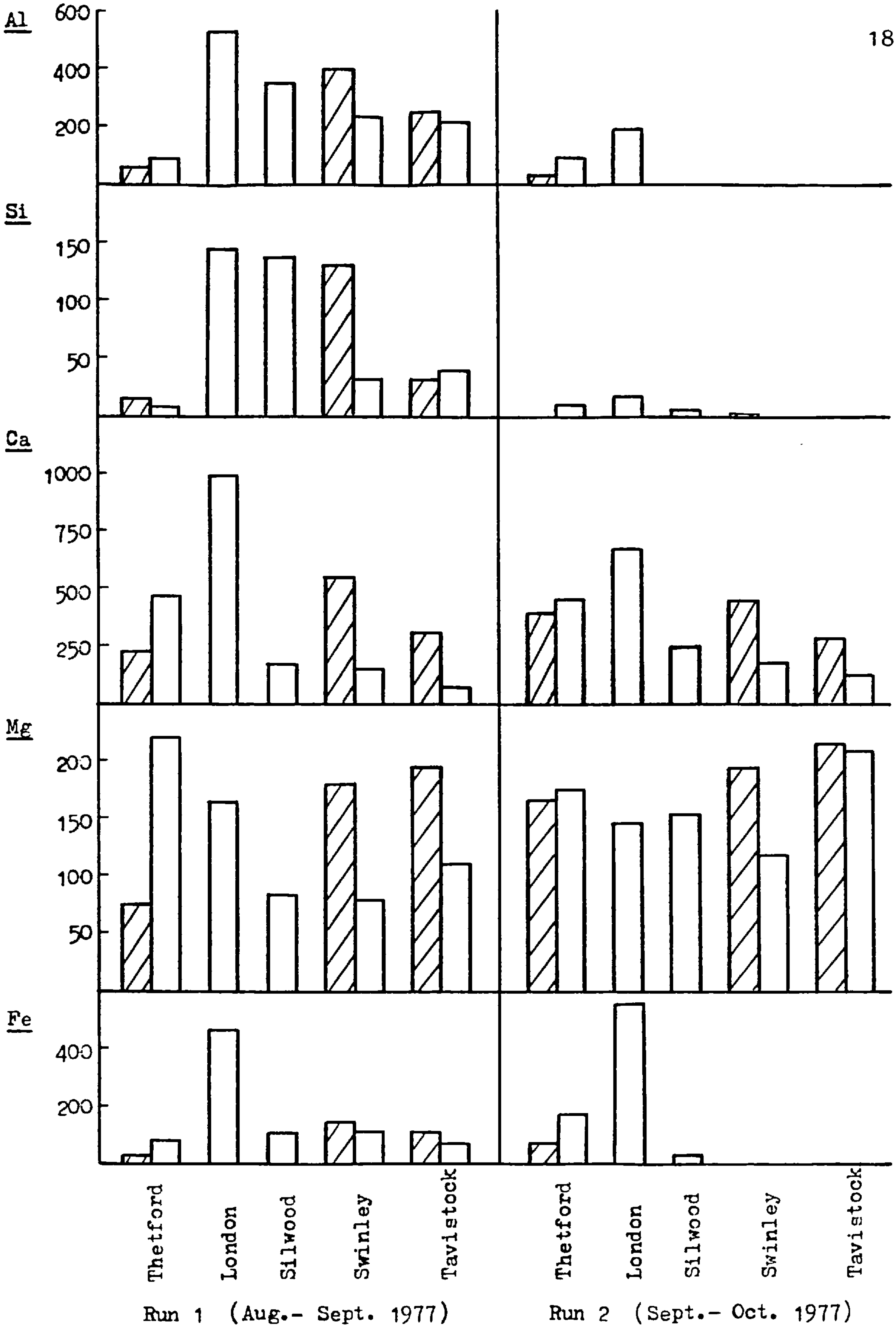


Figure 3.18 B Elemental deposition on moss bags at various sites after four weeks exposure (ppm dry weight of moss, corrected for unexposed moss). Cross-hatched columns show forest (F) deposition; others show open-ground deposition (O or T).

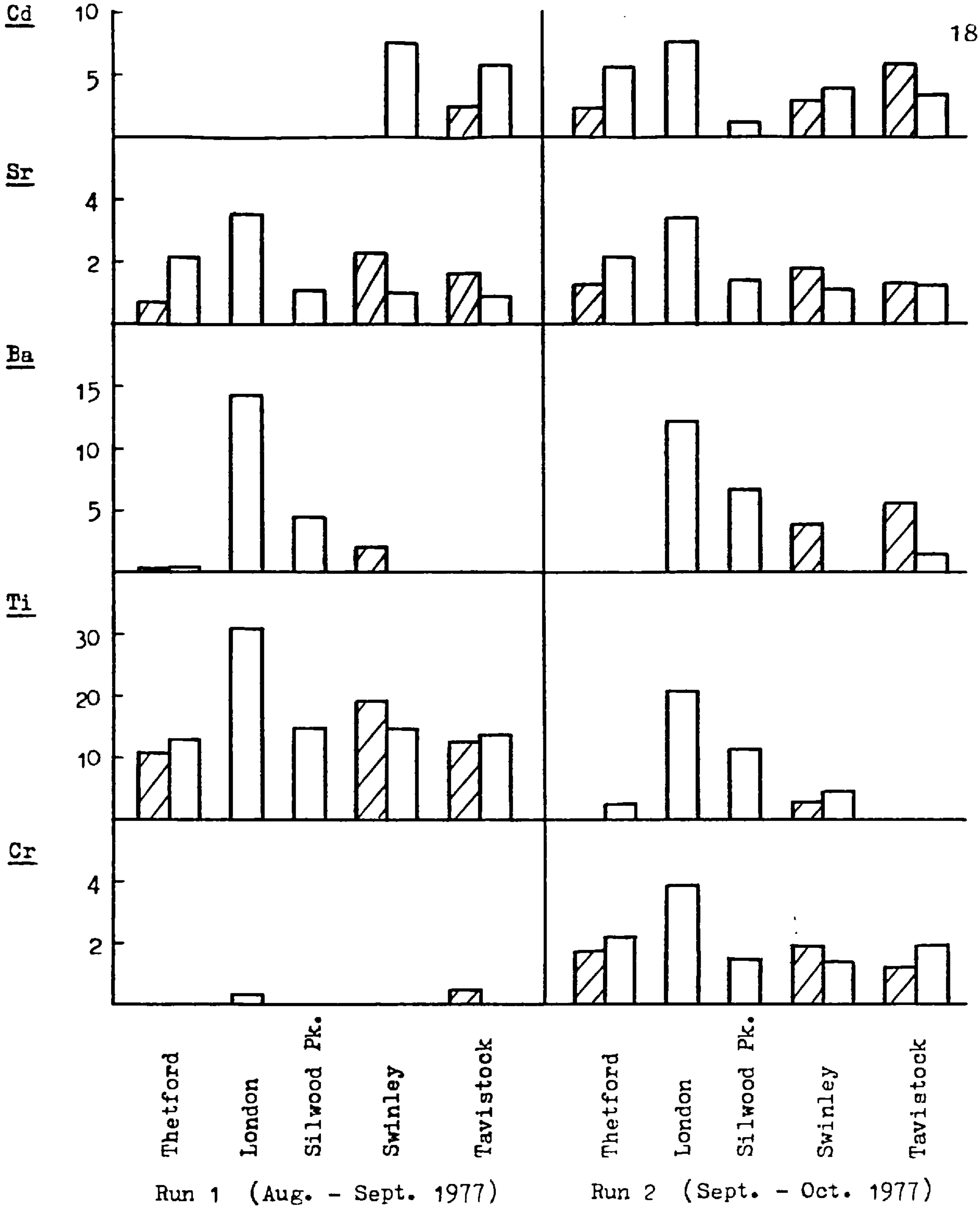


Figure 3.18 C Elemental deposition on moss bags at various sites after four weeks exposure (ppm dry weight of moss, corrected for unexposed moss). Cross-hatched columns show forest (F) deposition; others show open-ground deposition (O or T).

3.62 Comparison of MB and TD.

MB runs 1 and 2 were exactly concurrent with TD sampling periods, but because some of the TD bottles overflowed during the first week, most of the comparative data for the two methods is from MB run 2 (Table 3.36). The four metals for which comparative data were obtained were Cu, Mn, Zn, and Pb. MB collected less Cu than TD in the same situations, except in London where the MB:TD ratio was 1.2. MB also collected less Zn than TD, except at three sites: Thetford (T), London, and Silwood Park. However, MB were usually more efficient than TD at collecting Mn, though the relative differences between sites were similar to those for Zn. The only available MB:TD ratios for Pb were considerably above 1, but there was a problem in that some of the batches of unexposed moss gave rather high Pb readings, and thus Pb deposition was not recorded at several sites. The MB:TD ratios generally indicated that the two methods had different relative efficiencies for different metals and different sites.

In general, however, MB results were consistent with TD findings when comparing sites. MB seemed to fulfil the requirements of this work, which involved measurements in relatively unpolluted environments. Previously, the use of MB has only been reported for monitoring heavily polluted areas.

3.63 Moss Bags run 3.

Because of the unusually high deposition of many elements found at the top of Thetford tower, a third MB run was set up at Thetford, using the two original locations at the top of the tower (T) and under the forest (F), and in addition an open site at ground level (O). There was no

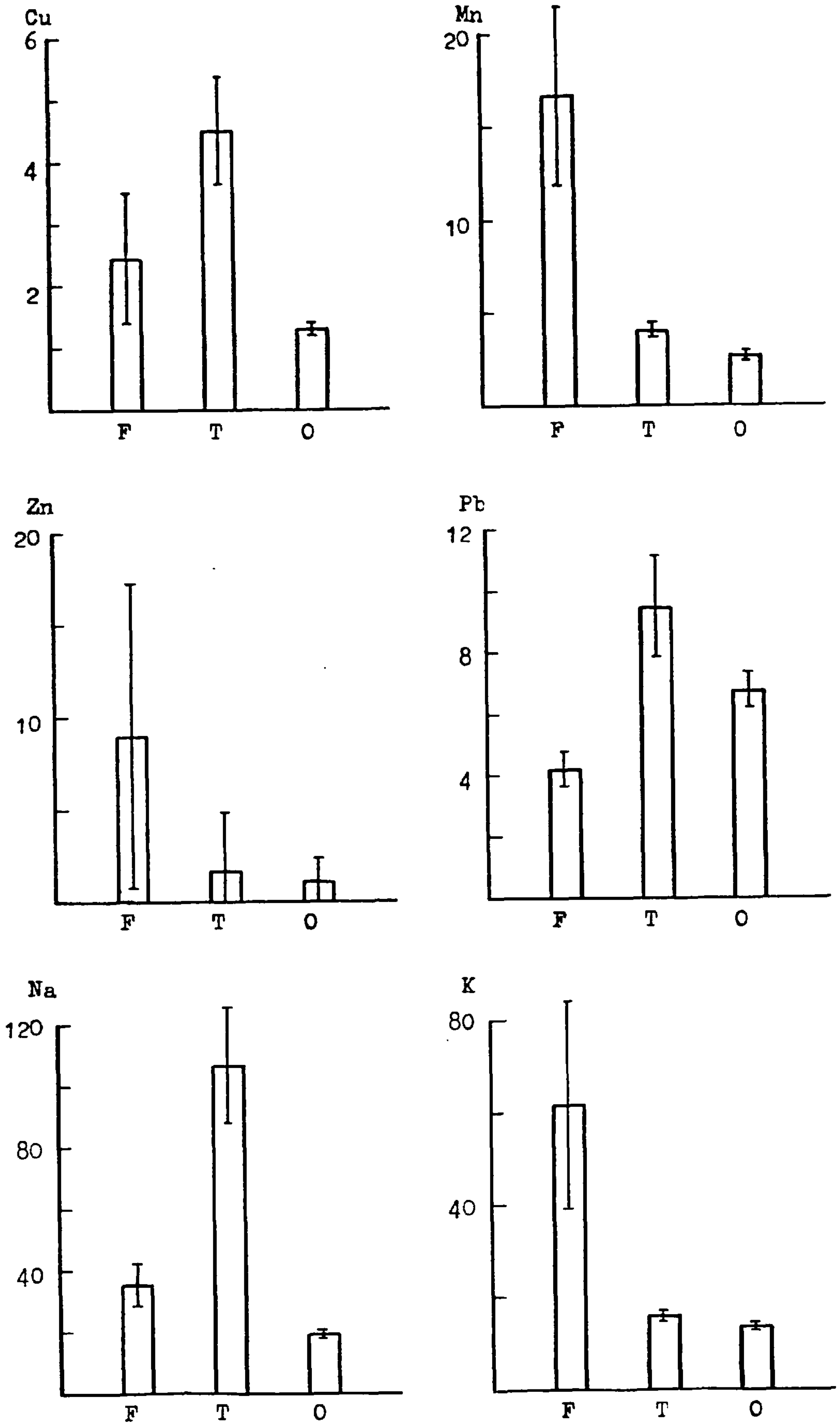
Table 3.36. Ratios of deposition collected by moss bags: total deposition bottles during two 4-week sampling periods August - October 1977. MB/TD

Element	Sampling Period	Site							
		Thetford		London	Silwood Park	Ascot		Tavistock	
		T	F	O	O	O	F	O	F
Cu	1 + 2 (4 wks.)	0.17							
	3 (4 wks.)	0.21	0.13	1.21	0.22	0.16	0.35	0.06	-
Mn	1 + 2	4.40							
	3	0.94	1.18	3.53	2.14	-	1.33	-	1.33
Zn	1 + 2	1.53							
	3	0.55	0.01	1.17	2.14	0.33	0.46	-	0.06
Pb	1 + 2	9.76							
	3	-	-	4.62	-	-	20.29	-	-

suitable clearing, except where forestry operations were taking place, and so the 'O' site was beside a forest track. The nearest tree canopy was at least 2 metres away (vertical projection from the edge of the canopy to ground level). Previous sampling at Tavistock showed that a clearing of this size was in fact typical of an 'Open' site. The main error was probably not deposition from trees, but from vehicles passing along the track, as the Pb analysis suggested (Figure 3.19).

The moss was analysed for Cu, Mn, Zn, Pb, Na, and K, and the results showed that the tower site (T) indicated unusually high rates of Cu, Pb and Na deposition and should therefore not be used for comparison with F. Even Mn, whose deposition rates were low, was deposited at a higher rate at the top of the tower (T) than near the gound (O), and K and Zn showed a non-significant trend in this direction.

The results provided clear confirmation of Mn and K removal from trees. The same effect was indicated for Cu and Na (comparing F and O), but the high depositions of these elements collected at the top of the tower suggest an alternative explanation, i.e. that the forest was acting as a 'filter' or 'sponge' for aerosol. It was not clear in which category Zn could be placed, as there were no significant differences between any of the three positions.



<u>Figure 3.19</u> <u>Elemental deposition on moss bags, Thetford, April-May 1978 (ng. cm^{-2}. 4 weeks^{-1}).</u>

Means of 10 bags, corrected for unexposed moss. 95% confidence intervals shown.
F = under forest, T = tower above forest, O = open ground near ground level.

3.7 Uptake of ^{65}Zn and ^{115m}Cd by Scots pine grown hydroponically.

Fieldwork had indicated that Scots pine, apparently growing in strongly mineralised soil, did not contain elevated metal concentrations in the foliage when compared with Scots pine growing in non-mineralised soils (Tables 3.21, 3.25 and 3.26). Possible reasons were that (1) the trees excluded metals from foliage, (2) metals were not freely available in soil, or (3) the trees were only absorbing nutrients from pockets of non-mineralised soil. Since Scots pine was the most dominant species in the TD and MB work, it seemed important to find out whether it would take up heavy metals which were freely available to the roots, and to what extent these metals could reach the plant surface and be available for release.

Replication, which should have been 8 plants per treatment, suffered badly because of plant mortality. Survival depended on production of new roots which occurred in only 18 out of the 56 plants. All the plants had seemed healthy at the start of the experiment and many did not become necrotic until they had been grown hydroponically for nearly two months. The only plants harvested were those with new root growth.

Because of the lack of replication, which made standard errors very large, the results are presented as scatter diagrams (Figures 3.20 and 3.21) for zinc and cadmium respectively. Straight lines were drawn to connect each treatment mean. Mean uptake of ^{65}Zn and ^{115m}Cd into various plant parts is shown in Tables 3.37 and 3.38, and regressions were calculated of log. plant uptake on log. external solution concentration (Tables 3.39 and 3.40).

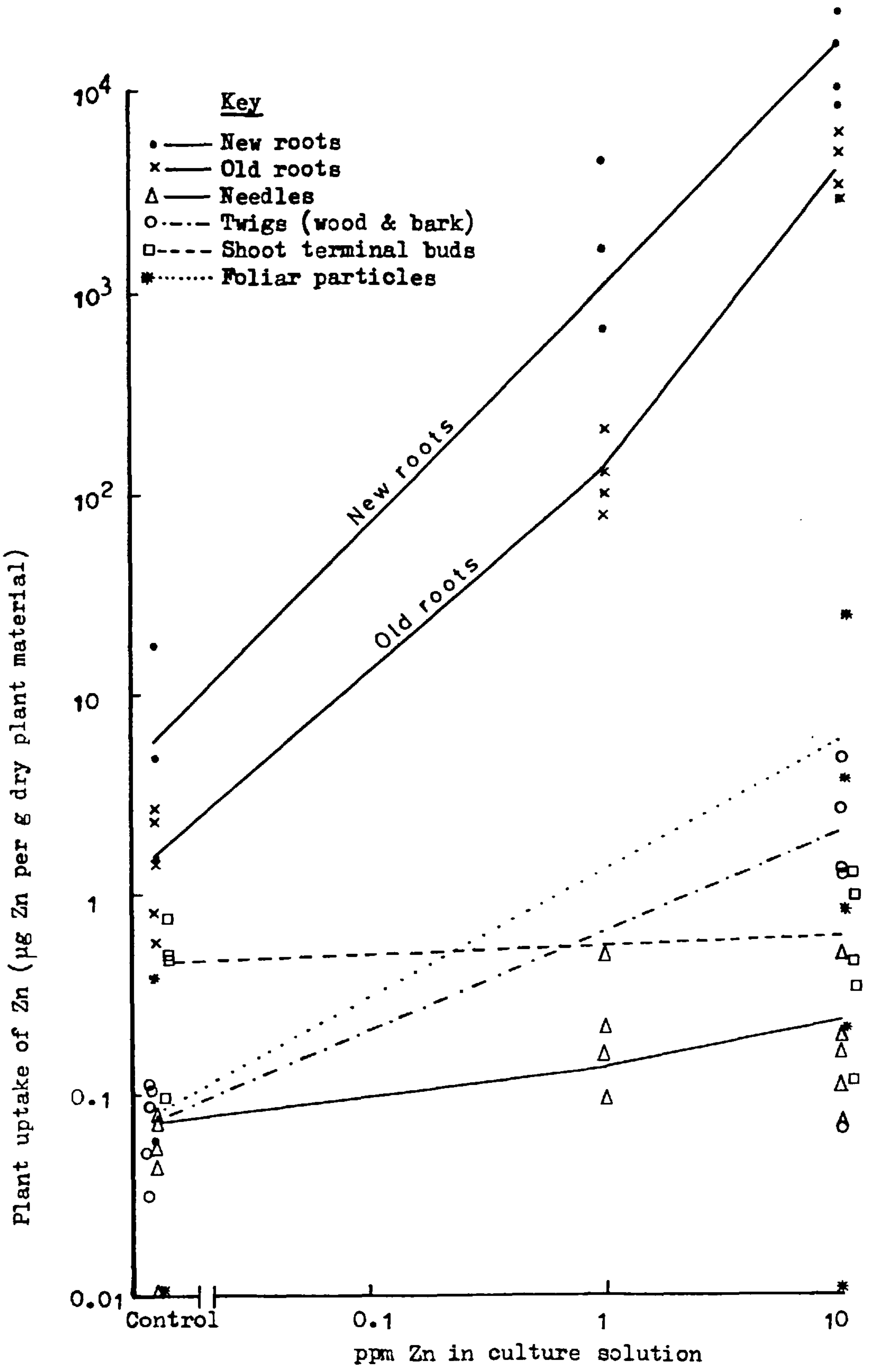


Figure 3.20 Uptake of zinc by *Pinus sylvestris* after four weeks in hydroponic culture.

Each point represents a sample from one plant. Lines connect treatment means.

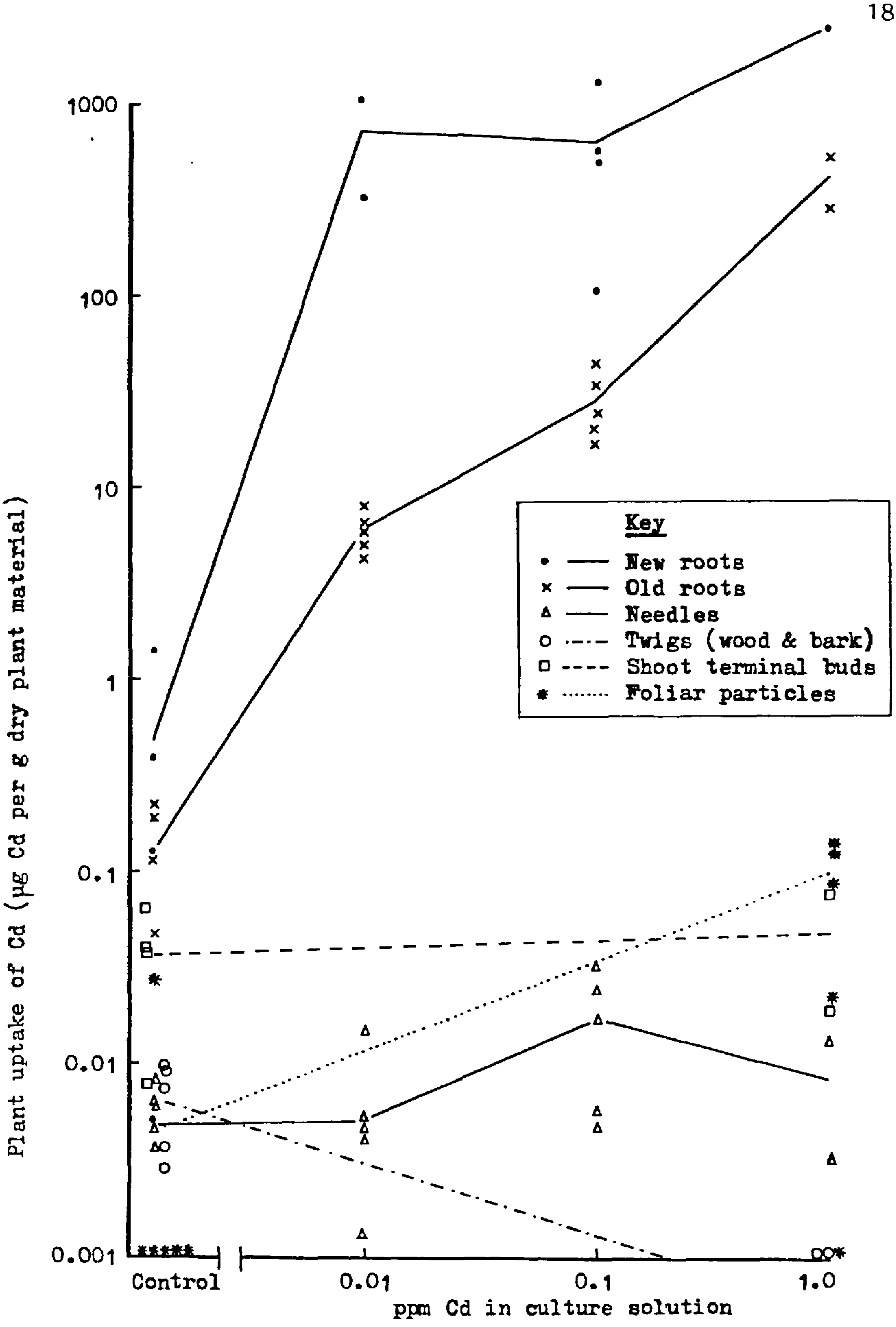


Figure 3.21 Cadmium uptake by Pinus sylvestris after four weeks in hydroponic culture.

Each point represents a sample from one plant. Lines connect treatment means.

Table 3.37. Mean Zn uptake by Pinus sylvestris grown hydroponically. (ppm Zn dry weight)

	ppm Zn in solution			
Plant part	Control	0.1	1.0	10.0
New roots	5.88_{abcd}	-	1060.95_{e}	17706.59_{f}
Old roots	1.57_{c}	-	129.58_{d}	4051.53_{e}
Twigs (bark & wood)	0.07_{ab}	-	-	2.01_{bc}
Needles	0.07_{a}	-	0.13_{ab}	0.21_{ab}
Shoot buds	0.45_{abc}	-	-	0.61_{bc}
Foliar particles	0.06_{ab}	-	-	5.79_{abc}

Table 3.38. Mean Cd uptake by pines, grown hydroponically. (ppm Cd dry weight)

	ppm Cd in solution			
Plant part	Control	0.01	0.1	1.0
New roots	0.48_{abcde}	718.41_{defgh}	638.17_{h}	2565.98
Old roots	0.13_{cd}	6.04_{ef}	29.01_{g}	435.27_{fgh}
Twigs (bark & wood)	0.01_{a}	-	-	0.00_{ab}
Needles	0.01_{a}	0.01_{a}	0.02_{ab}	$0.01_{abcdefg}$
Shoot buds	0.04_{abc}	-	-	$0.05_{abcdefgh}$
Foliar particles	0.00	-	-	0.10_{bcd}

Notes (Tables 3.37 and 3.38).

(1) Data were converted to $\log_{10}$(ppm) for statistical analysis.

(2) Figures followed by the same letter are not significantly different at 5% probability.

Table 3.39. Regression analysis of ^{65}Zn and ^{115m}Cd uptake from hydroponic solution by pine.

$x = \log_{10}$ (metal concentration in hydroponic solution), both radioactive and stable isotopes, ppm.

$y = \log_{10}$ (metal concentration in plant), both radioactive and stable isotopes, ppm dry weight.

Control treatment is excluded from regression analysis because $\log_{10}$ (zero) is not calculable.

Samples counted on gas flow counter.

Isotope & plant part	Slope (Figs. 3.20. and 3.21)	Standard error of slope	Probability level of difference of slope from zero	Correlation coefficient	Probability level of correlation of x and y
^{65}Zn					
New roots	1.213	0.145	< 0.1%	0.966	< 0.1%
Old roots	1.504	0.111	< 0.1%	0.982	< 0.1%
Needles	0.159	0.198	N.S.	0.291	N.S.
^{115m}Cd					
New roots	0.230	0.272	N.S.	0.354	N.S.
Old roots	0.872	0.077	< 0.1%	0.964	< 0.1%
Needles	0.161	0.167	N.S.	0.292	N.S.

Table 3.40. Regression analysis of ^{65}Zn and ^{115m}Cd in new roots of pine against solution concentration.

x = $\log_{10}$ (metal ppm in hydroponic solution), radioactive and stable.

y = $\log_{10}$ (counts.min.$^{-1}$mg^{-1} herbage dry weight), corrected for background, counted on solid scintillation counter.

Isotope	Slope	Standard error of slope	Probability level of difference of slope from zero	Correlation coefficient	Probability level of correlation of x and y
^{65}Zn	1.242	0.157	$< 0.1\%$	0.962	$< 0.1\%$
^{115m}Cd	0.293	0.282	N.S.	0.422	N.S.

3.71 Root uptake.

Results were similar for Zn and Cd. Both metals showed very strong uptake into washed new roots, formed since the start of the experiment, and strong uptake also into washed old roots, though not as much as into new roots. Uptake into roots depended directly on external solution concentration when both were plotted on log.scales. Uptake seemed to be linear (with both axes on log. scales) up to 10 ppm Zn and 1.0 ppm Cd external concentration. The only non-significant regression for root uptake was Cd in new roots, which could be an artifact from lack of replication or could represent a saturation or exclusion effect.

3.72 Shoot uptake and release.

In contrast to the striking uptake into roots, there was no significant uptake of either metal into any part of the shoot. This effect was maintained even at the highest levels of external loading. Any apparent trends in uptake below about 1 μg Zn.g^{-1} dry weight or 0.1 μg Cd.g^{-1} dry weight were subject to too much uncertainty to be considered.

Two particulate samples collected with the cyclone from Zn-labelled plants had above-background labelling (Figure 3.20), but the variations in the radioactivity of particulate samples and the lack of shoot uptake suggest that some radioisotope must have reached the shoot surface by an external means, e.g. splashing while changing culture solution or by insect activity.

Leaching experiments were carried out but gave no useful results because of the lack of shoot uptake.

3.73 Conclusion.

The significance of this experiment in relation to field work is that Scots pine is capable of growing in media containing very high levels of available zinc or cadmium, and therefore there is no reason to suppose that the trees at Tavistock were not actually rooting in mineralised soil. However, Scots pine excludes excess zinc and cadmium from its shoots, against very strong concentration gradients where necessary. Sampling in the field indicated that such exclusion probably also applies to Cu, Mn, Pb and Fe (Table 3.25). The lack of shoot uptake did not allow studies of metal release from foliage.

Because zinc, at least, is required as a micronutrient, it should be possible to label foliage for the purpose of studying metal release, provided that the labelling period is long enough and that the plants are growing. Studies along these lines on Cupressus leylandii were discussed in Section 3.1, and the distribution of ^{65}Zn in these plants is given below.

3.74 ^{65}Zn distribution in Cupressus leylandii.

Two C.leylandii plants grown in ^{65}Zn-labelled soil for 20 months were harvested to determine the distribution of isotope within the plants (Table 3.41). Roots were labelled to approximately the same extent as soil, per unit dry weight. If one takes the relative loading of ^{65}Zn in roots, per unit dry weight, as 100, the level of ^{65}Zn in xylem of stem was 3, in phloem and bark was 41, and in leaves was 25. Actual counts.min^{-1}.g^{-1} dry weight at the time of harvesting are given in Table 3.41. These results show that considerable activity was present in the shoots of C.leylandii, in contrast to the experiment with Pinus sylvestris.

Two further C.leylandii plants were harvested to determine the total shoot dry weights. Separation of leaves from stems was attempted, but the growth form of the plants did not enable a clear distinction to be made. Total leaf dry weights were 58 and 51 g respectively, and of wood and bark 25 and 41 g respectively.

Table 3.41. Uptake of ^{65}Zn by Cupressus leylandii grown for 20 months in labelled soil.

Means of 3 replicates.

Counts. $min.^{-1}g^{-1}$dry weight, corrected for background. Counted on solid scintillation counter.

Plant part	^{65}Zn-labelled		Control	
	Plant 5	Plant 6	Plant 1	Plant 2
Soil	4420	2331	0	0
Roots	2780	5788	1	3
Xylem of stem	96	176	2	0
Phloem and bark of stem	1748	1763	5	0
Leaves	1148	961	2	3

3.8 Uptake of stem-injected radioisotopes by conifers.

3.81 Preliminary trial using four species.

Injection of isotopes into xylem at the base of tree stems has been used as a method of assessing translocation rates (Kline *et al.*, 1972; Leyton, 1972), of studying nutrient uptake and cycling (Thomas, 1969) and of correcting micronutrient deficiency in trees (Chandler, 1937). In this case, the aim was to obtain high levels of radioactivity (^{65}Zn, ^{115m}Cd) in the foliage, which is essential in experiments on metal release, by by-passing any root barrier to metal uptake and thus avoiding the need for a prolonged labelling period. It is recognised that the artificiality of this approach will have to be considered when interpreting the results. However, the total amounts of Zn and Cd injected into each plant (24 μg and 6.4 μg respectively) were estimated to have only raised the total concentrations of these metals in the shoots by about 1.0 ppm Zn and 0.3 ppm Cd (dry weight basis).

An initial trial was carried out using four species of conifer, including Scots pine studied previously. The other three species, Douglas fir, western hemlock, and western red cedar, were listed by N.A.S.A. (1968) as useful plants in biogeochemical prospecting for Cu, Zn, Fe, and Mn, indicating that they were capable of absorbing above-background levels of metals into the shoots. All the plants were dormant when collected from the field but most of them began active growth soon after transfer to a glasshouse. All Scots pine plants eventually died but, as in the hydroponic experiment, did not show signs of mortality for several weeks.

For both isotopes (^{65}Zn and ^{115m}Cd), uptake was greatest by western hemlock, giving rise to much higher activities (counts.min^{-1}.mg^{-1} dry wt.) in foliage than in previous experiments (Figures 3.22 and 3.23). Uptake by the other species was moderate (subject to survival), giving activities of 1 to 15 counts.min^{-1}.mg^{-1} dry wt. for ^{65}Zn and 1 to 35 counts.min^{-1}.mg^{-1} dry wt. for ^{115m}Cd.

The western hemlock plants were used in an experiment to try and detect metal release from the foliage in aerosol form. Three perspex chambers were set up in a laminar-flow cabinet to exclude external contamination, and contained a ^{65}Zn-labelled plant, a ^{115m}Cd-labelled plant, and a control respectively. Air was drawn over the plants and then through membrane filters and cold fingers. The experiment was carried out under bright lights and in warm temperatures (20 to 26°C) which were expected to provide favourable conditions for metal release (Beauford et al., 1975). Nevertheless, there was no detectable metal release from the plants (Table 3.42). Because of the very high levels of radioactivity in the foliage, the negative result at this stage suggested that further experiments of a similar type would not be constructive.

Collections of plant surface particles with the cyclone, however, were slightly more encouraging. Table 3.43 shows that slight but detectable amounts of radioactivity were present in particles collected from western hemlock and Douglas fir labelled with either ^{65}Zn or ^{115m}Cd, though the levels of radioactivity in particles were always less than in herbage, on a dry weight basis.

3.82 ^{65}Zn and ^{54}Mn uptake and release by western hemlock.

The preliminary work above suggested that it was possible to demonstrate metal availability in particulate

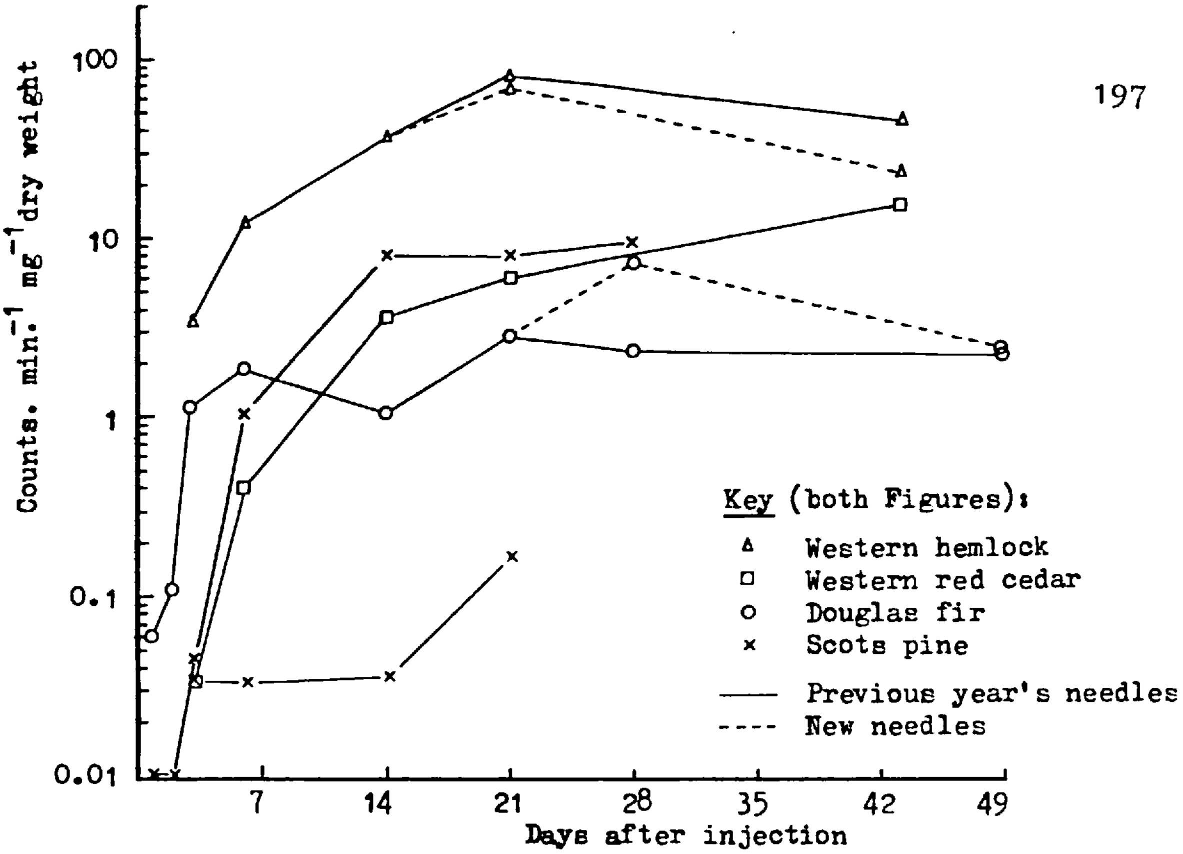


Figure 3.22 Time course for uptake of ^{65}Zn into leaves of conifers after injection into the stem base.

Both Figures are corrected for background but not for radioactive decay.

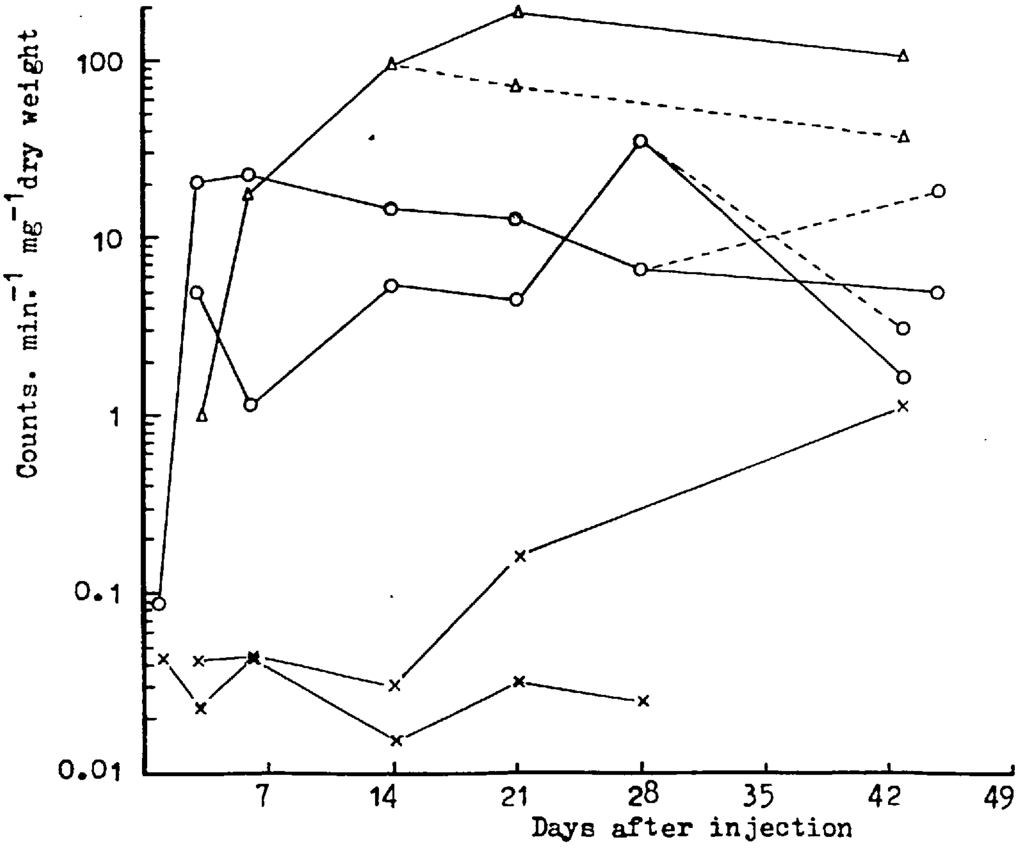


Figure 3.23 Time course for uptake of ^{115m}Cd into leaves of conifers after injection into the stem base.

Table 3.42. ^{65}Zn and ^{115m}Cd release by western hemlock; radioactivity collected by 1.2 μm membrane filters and cold fingers.

Each run lasted 4 h. at a flow rate of 1.0 litre.min^{-1}. Runs 1 and 2 were discarded because of leaks in the apparatus. About 2 ml of water were collected in each cold finger per run.

Sampled 19 & 21/3/78.

Counts.min.$^{-1}$ per sample (not corrected for background).

Plant/Treatment	Run 3		Run 4
	1.2 μm filter	Cold finger	Cold finger (no filter used)
^{65}Zn	14.90	20.38	16.87
^{115m}Cd	17.03	17.67	16.68
Control	16.53	16.72	17.10
Background	16.25, 16.65, 17.05, 17.10. Mean 16.76		

Radioactivity in leaves on 15/3/78:

^{65}Zn	79.72	counts.min.$^{-1}$mg^{-1} dry weight (not corrected for background).
^{115m}Cd	129.62	

Herbage contained 31.9 (±std.dev. 8.2) ppm Zn, dry weight and 0.55 (±0.20) ppm Cd, dry weight.

Table 3.43. ^{65}Zn and ^{115m}Cd collected with the cyclone from western hemlock and Douglas fir. Stem injection experiment, sampled 30 & 31/3/78.

Counts were corrected for background.

Plant and Treatment	Herbage	Particles (Cyclone)	
	Counts. min^{-1}. mg^{-1} dry wt.	Weight (mg)	Counts. min^{-1}. mg^{-1} dry wt.
Western Hemlock			
^{65}Zn	32.91	3.8	3.32
^{115m}Cd	66.59	5.1	0.74
Control	0.00	20.4	0.18
Douglas Fir			
^{65}Zn	2.37	7.1	0.93
^{115m}Cd (plant 1)	11.15	6.8	0.82
^{115m}Cd (plant 2; fungal infection)	2.24	11.6	1.36
Control	0.00	10.3	0.21

form at plant surfaces provided that high enough specific activity was obtained in the foliage. However, it was desirable to have more replication and, on the basis of the previous trial, western hemlock was selected as suitable species for a further experiment. The two isotopes (^{65}Zn and ^{54}Mn) were chosen to provide a contrast, as fieldwork had indicated that manganese, unlike zinc, was relatively easy to remove from foliage.

The plants were about three times taller than those used previously, to provide a larger surface area for particulate sampling. To counteract this, the ^{65}Zn dose was increased from 10 µCi to 65 µCi per plant but, even so, the ^{65}Zn activity in foliage was much lower than before (cf. Figure 3.22 and Table 3.45). Probably as a result of this factor, radioactivity was not detectable in particulate samples (Table 3.44).

Leaching experiments were then carried out to determine how much of the two metals could be removed from samples of the foliage. Leaching for 2 h. did not give detectable release of either metal, but leaching for 24 h. caused loss of both ^{54}Mn and ^{65}Zn from foliage (Table 3.45). Approximately 8% of the ^{54}Mn in herbage was leached in 24 h., and less than 2% of ^{65}Zn (apart from one replicate). In contrast to the work at Ecton mine, washing the foliage did not affect the amount of either isotope leached indicating that, in this experiment, deposited dust was not a major contaminant, probably because the plants were kept in a glasshouse and the foliage was washed frequently during watering.

Metals could have been lost from damaged areas of foliage as well as via 'genuine' routes of leaching. Care was taken not to choose injured foliage for leaching experiments and not to cause damage during the experiments, but the possible effect of small lesions on variability between replicates cannot be ruled out.

Table 3.44. ^{65}Zn and ^{54}Mn in foliar particles collected from western hemlock using a cyclone. Stem injection; sampled 18/6/78).

Means of 4 plants ± standard deviation.

Counts were corrected for background. Gas flow counter.

Treatment	Leaves (Counts.min.$^{-1}$mg^{-1} dry wt)		Particles (Counts.min^{-1}. mg^{-1}.dry wt. particles)
	Last year's	This year's	
^{65}Zn	3.82 ± 2.56	4.95 ± 5.27	0.15 ± 0.13
^{54}Mn	0.89 ± 0.61	1.77 ± 1.05	0.19 ± 0.06
Control	0.02 ± 0.02	0.04 ± 0.03	0.31 ± 0.21

Table 3.45. ^{65}Zn and ^{54}Mn in herbage and leachates of western hemlock (Tsuga heterophylla).

24 h. leaching, July 1978 (Run 3).

Treatment	Plant	^{54}Mn or ^{65}Zn in leaves (unwashed) (Counts.min.$^{-1}$ g^{-1} dry wt.)		^{54}Mn or ^{65}Zn in leachates (Counts.min.$^{-1}$ g^{-1} dry wt.)		^{54}Mn or ^{65}Zn leached as % of isotope in leaves.	
		Last year's leaves	This year's leaves	Un-washed herbage	Washed herbage	Un-washed herbage	Washed herbage
^{54}Mn	1	1086	2747	19	50	0.98	2.59
	2	1145	12144	890	608	13.40	9.15
	3	1363	3257	154	522	6.65	22.59
	4	1104	4400	214	102	7.77	3.70
	Mean	1175	5637	319	320	7.20	9.51
^{65}Zn	5	330	1988	3	183	0.29	(15.79)
	6	15000	9240	15	138	0.12	1.14
	7	6100	4987	30	87	0.55	1.56
	8	4002	9922	127	21	1.83	0.29
	Mean	6358	6534	44	107	0.70	1.00
Control	9	19	0	1	2	-	-
	10	0	44	0	0	-	-
	11	11	48	1	2	-	-
	12	21	0	0	0	-	-
	Mean	13	23	0	1		

Unwashed herbage contained 31.9 (±std.dev. 8.2) ppm Zn, dry wt., and 201 (± 58) ppm Mn, dry wt.

Cupressus leylandii plants grown outdoors in ^{65}Zn-labelled soil at South Kensington were included in these leaching experiments. Table 3.46 shows that always less than 1%, usually about 0.1%, of the ^{65}Zn in leaves was removable by 24 h. leaching, which was less than from western hemlock.

Because of large variations in isotope uptake between plants, it was found that differences between treatments could be shown most clearly when activities were converted to $\log_{10}$ (activity), (Figure 3.24). Standard deviations and 95% confidence intervals were calculated on the log-transformed data in the same way as for untransformed data.

Table 3.46. ^{65}Zn in herbage and leachates of Cupressus leylandii.

24 h. leaching, July 1978. Mean of 2 runs.

Treatment	Plant	^{65}Zn in unwashed herbage (Counts. min^{-1}. g^{-1} dry wt.)	^{65}Zn in leachates (Counts.min^{-1}. g^{-1} dry weight herbage)		% of ^{65}Zn leached	
			Unwashed herbage	Washed herbage	Unwashed herbage	Washed herbage
^{65}Zn	5	2046	0.7	2.0	0.03	0.10
	6	962	6.3	0.8	0.65	0.08
	7	1435	1.3	1.4	0.09	0.10
	8	2949	1.5	2.9	0.05	0.10
	Mean	1848	2.4	1.8	0.21	0.09
Control	1	9	0.7	3.2	-	-
	2	6	0.2	0.7	-	-
	3	7	0.6	1.0	-	-
	4	7	2.7	3.0	-	-
	Mean	7	1.1	2.0	-	-

Unwashed herbage contained 25.4 (± std.dev. 6.1) ppm Zn, dry weight.

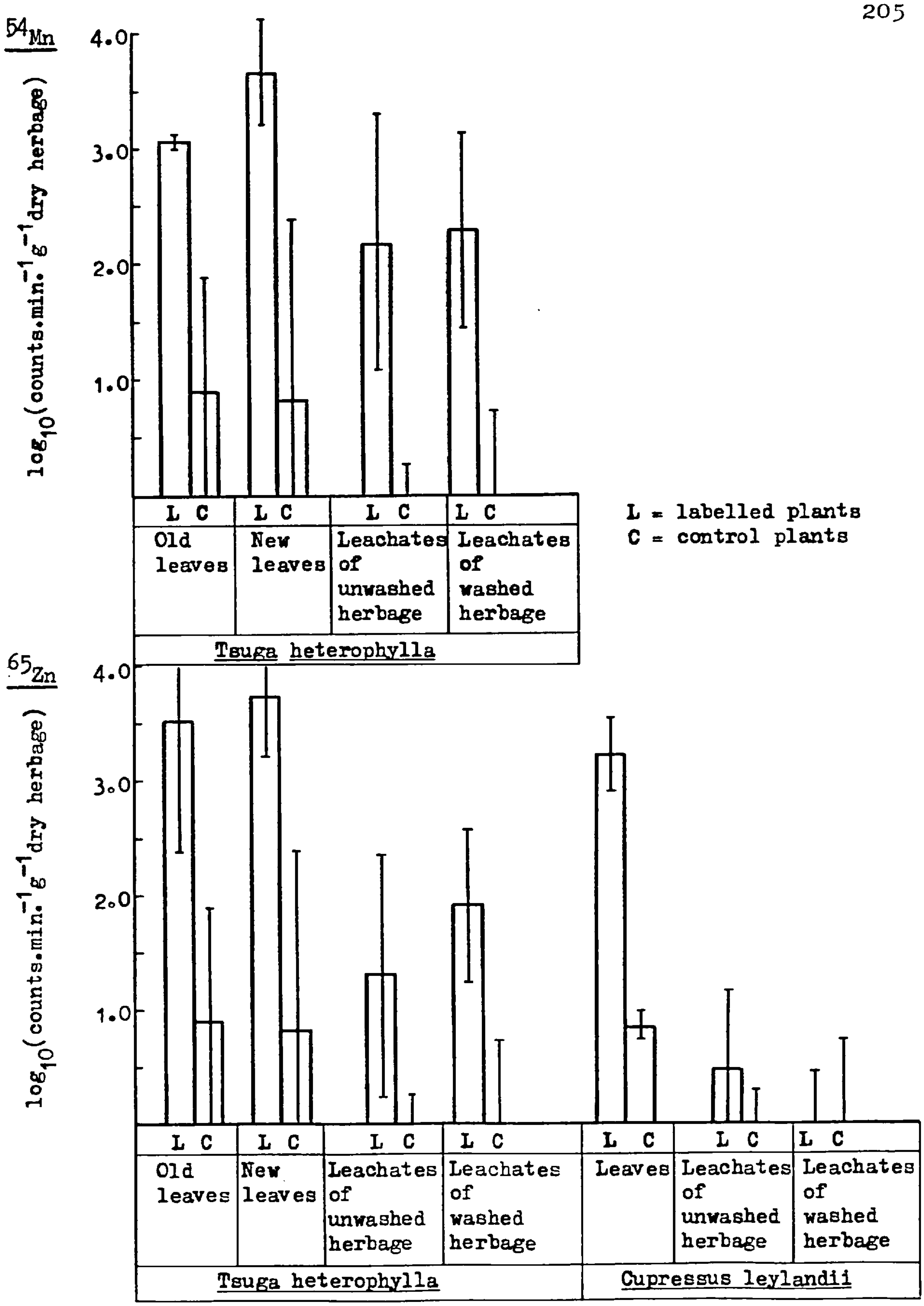


Figure 3.24 ^{65}Zn and ^{54}Mn in herbage and leachates of *Tsuga* and *Cupressus*.

Means of 4 plants. 95% confidence intervals shown.

4. DISCUSSION.

A considerable body of evidence has been accumulating to show that plants lose metal-containing material from their foliage. These are continual, everyday processes as distinct from such evident features of plant biology as leaf-fall, and pollen and seed dispersal. A number of different mechanisms are involved, of which the most obvious is perhaps foliar leaching, but volatile emissions, release of sub-micron particles and loss of larger tissue fragments also occur.

It is my aim here to put this evidence into contexts which are relevant in the natural environment. Firstly, plants may act as significant sources of atmospheric trace elements on a worldwide scale and, secondly, they may give rise to localised atmospheric metal anomalies related to ore bodies, which can be utilised in mineral prospecting. The cycling of trace elements in natural ecosystems is poorly understood, and it is unfortunate that such pathways are only investigated after it is apparent that human activities have already brought about changes.

I would first like to discuss my work in relation to atmospheric metal cycles in woodlands. There is little published information on the loss of trace metals from tree foliage, although foliar leaching is recognised to be an important factor in the cycling of major nutrient elements. There is also a need to know more about the role of forests as a 'sink' for particulate heavy metals in the air. I carried out field work to determine amounts of metals lost from tree canopies, assuming that most of the material would be deposited directly on the ground, mainly in rain (Section 3.5). To assess the background fallout from the atmosphere, deposition was recorded near ground level on open ground, and in one forest (Thetford) above the forest canopy.

The results of this deposition sampling showed that rates of manganese and potassium deposition (mass per unit ground area per unit time) were enhanced approximately ten times under Scots pine forest canopies compared with the atmospheric deposition on open ground. Such a striking effect resulted from low concentrations in ambient aerosol combined with high leachability of these two elements. If one assumes that any ratio of Forest: Open deposition (F:O ratio) greater than 1 represents foliar leaching, then Na, Mg, Ca and Fe were also leached. However, there was no consistent evidence on this basis of Zn, Cu or Pb leaching. This suggested series of elemental leachability is in agreement with the results of Tukey et al. (1958), and I have demonstrated that Mn is more leachable than Zn from western hemlock, using radioisotopes.

However, forest canopies undoubtedly filter out atmospheric aerosol to a certain extent, and thereby concentrate the fallout per unit ground area without leaching necessarily being involved. In my work, the F:O ratios for Zn, Cu and Pb were usually around 1, and only occasionally as high as 3, indicating that the deposition rate under forests was not greatly enhanced by either aerosol filtering or leaching. Forest deposition showed a close relationship to the aerial fallout on open ground for these three metals.

It is not necessarily valid to assume that a forest has the same ability to filter out different elements from aerosol, because the filtration efficiency by impaction depends on particle size (and density), and different elements are carried in particles having different size distributions (Johannson et al., 1976). Therefore, a forest would be expected to filter out 'natural' large particles showing high deposition velocity (Vg, defined in Section 1.4), like those which contain Na, Ca and Fe, with greater efficiency than 'pollutant' small particles with low Vg, containing elements such as Cu, Zn and Pb (Vg data from Cawse & Peirson, 1972). The efficiency of small-particle trapping depends largely on surface roughness (Chamberlain, 1967), but the importance of this factor in field situations can only be determined by experiment. The problem outlined above could be resolved by using a range of forests of the same species exposed to different aerosol burdens (or by sampling over a long enough period to build up data for a range of aerosol burdens at the same site) to characterise the canopy retention and leaching responses as a function of aerosol deposition for each element.

The deposition sampling in this work was carried out in the middle of forests, where the aerosol-filtering effect is presumably much less than at the edge of a stand of trees. This 'edge-effect' was noted by White & Turner (1970). Trees which are growing sufficiently far apart to be considered as individuals also show a marked ability to filter out aerosol. The ratios of the deposition in throughfall under the windward side of Pinus radiata trees to deposition on open ground were 8 (Na), 6 (K), 12 (Mg), and 4 (Ca) for trees growing close to the sea (Potts, 1978). White & Turner (1970) studied aerosol trapping to estimate the nutrient income into woodland from aerosol. Particles were trapped on filter paper discs mounted in apparatus so that the filter paper surface was held perpendicular to the wind. The monthly catch of elements (Ca, Mg, Na, K and P) depended on the average windspeed or run of wind in that month. The efficiency of branches of oak, ash, birch and hazel at catching NaCl mist droplets depended on species (presumably because of surface features) and branch diameter. This type of work provides a useful complement to deposition monitoring (MB and TD) if woodlands of different species are to be studied.

Using a simple approach to calculate the net deposition under forest canopies (i.e., F - O) my data give the average figures (in $kg.ha^{-1}.yr^{-1}$) of 23.5 for Na, 22.4 for K, 3.3 for Ca, and 1.8 for Mg, which are within the published range for similar forests (Table 1.1). My estimates of net deposition rates of Fe and Mn of 0.1 and 1.1 $kg.ha^{-1}.yr^{-1}$, respectively, compare with Ulrich & Mayer's (1972) figures of 0.6 and 3.5 $kg.ha^{-1}.yr^{-1}$, respectively, under a Fagus sylvatica forest in Germany, and with McColl & Bush's (1978) estimates of 0.1 and 0.4 $kg.ha^{-1}.yr^{-1}$, respectively, under Eucalyptus globulus in California, measured during the rainy season only (Dec. to April).

It is obviously desirable in this type of work to continue measurements for as long as possible. Because seasonal effects seemed to be apparent from my results, there is likely to be an intrinsic error in my estimates of annual deposition rates since sampling was not carried out for a full year. It is also preferable to sample for two or more years to identify any variations from year to year. Regular sampling using TD may be difficult if rainfall is highly irregular, but the problem can be lessened if bottles are designed to collect and store a much larger volume than the size of sample required. Alternatively, samples can be taken at intervals of constant rainwater volume. Bottles should be poisoned to inhibit algal growth using a substance that does not interfere with the analyses (e.g., methyl mercury could have been used in the present work), and stemflow measurements should also be included in any complete study of deposition to the forest floor.

Deposition collectors, including MB and TD, give results which depend on environmental factors and on their own properties, but the results from different types of collectors are closely correlated with one another (Goodman et al., 1975). Therefore, although MB have not previously been used for the type of experiments described in this work, there is no intrinsic reason why they should be less useful than the more commonly used TD. However, MB do have a drawback in measuring major nutrient element fluxes in forests because they already contain high concentrations of these elements, and a further disadvantage is that they have to be replaced at each sampling time whereas TD are permanent.

There are certain procedures which could be used to make deposition measurements less subject to bias caused by properties of the device used. Since all deposit gauges are affected by wind, it would be desirable to measure the total run of wind in each sampling period (as well as wind directions) and to normalise the results, based on wind tunnel studies of the effect of wind speed on the deposition recorded by the exact type of collector used. MB results could also be corrected depending on the number of wet days in each sampling period because deposition depends on whether MB are dry or wet (Clough, 1975). The results in the present work suggested that there were differences in the relative collecting efficiency of MB and TD for different elements, and this type of bias should be investigated further by reference to fixed-flow-rate aerosol sampling. In fact, comparative data of this type have already been obtained in an environmental study in south Wales (Goodman _et_ _al_., 1975), but the results were not presented in a way which allowed comparisons to be made for individual elements, although this data is presumably available.

Two different conventions appear to have grown up in expressing rates of deposition on the ground. The unit of $kg.ha^{-1}.yr^{-1}$ seems to have been adopted as standard by workers interested in nutrient cycling within forests, while the unit of $\mu g.cm^{-2}.yr^{-1}$ (or other unit of time) has been used by those studying pollutant deposition, this being numerically 10 times larger than $kg.ha^{-1}.yr^{-1}$. The difference is perhaps justified because deposition can change very rapidly with distance from a source, and thus the hectare is an unrealistically large unit of area for pollution work.

Also, the year is sometimes an unreasonably long period considering the rapid changes that can occur, and workers studying pollution often use daily or monthly intervals. The deposition rates which I recorded on open ground are similar to those given at the same types of sites by other workers using MB or TD (Little & Martin, 1972; Goodman et al., 1975; Pattendon, 1975; Cawse, 1975; Beavington, 1977; Johnson et al., 1978). In my work, the presence of mineralised mine waste tips did not have any obvious impact on local deposition rates, and therefore the results have not been presented separately for different sampling blocks at Tavistock. However, Johnson et al. (1978) showed that low levels of local airborne pollution from such sources can be demonstrated.

If leaching from plants affects the composition of aerosol, the process has to occur in two stages. The first is the movement of metals from the leaf interior on to the surface, and the second is the physical removal of metals from the leaf surface. While heavy rain carries out both stages of metal release and washes leachates to the ground, light rain, mist or dew which forms a film of water on foliage and then evaporates is expected to leave a residue of metal-enriched particles on the leaf surface. To enter the atmosphere, such particles have to overcome the boundary layer at the leaf surface and the energy for this would presumably come from mechanical buffeting caused by wind as well as from thermal gradients or electrostatic effects (see Introduction). Once in the atmosphere, particle movements are governed by forces of turbulence (horizontal wind and vertical plumes caused by solar heating of the ground), diffusion (mainly for very small particles), and sedimentation. Therefore, the most favourable meteorological conditions for the release of metal-containing particles from plants to the atmosphere are expected to be an alternating cycle of dew formation by night and dry, sunny, hot and somewhat windy weather by day. Such conditions are by no means uncommon for months at a time in many parts of the World.

On the basis of my results, the most significant contributions to aerosol from this source are likely to be for the metals potassium and manganese. Aerosol sampling by other workers has indicated that Mn and K are largely derived from a natural terrestrial source, which is usually assumed to mean soil (Chester & Stoner, 1973; Zoller et al., 1974; Duce et al., 1975; Peirson et al., 1973, 1974; Johannson et al., 1976). A proportion of K is also derived from the sea (Zoller et al., 1974; Potts, 1978). Mn has an enrichment factor compared to soil (EF soil, see Section 1.4) consistently above 1 (between 1 and 3) at a range of sites, and Vg indicated that this enrichment may be due to pollution (Peirson et al., 1974; these workers did not measure K). However, in my data there was virtually no evidence of an urban source of Mn or K, and it is suggested that leaching of these metals on to the surface of plant foliage and their release into the atmosphere could make a significant contribution to their concentrations in aerosol. The same argument applies in principle to other leachable elements, particularly sodium (Tukey et al., 1958), but because Na is one of the most abundant elements in aerosol (derived from the sea) the proportional contribution of plant-leached Na would be smaller. However, leaching of metals could contribute in general to background aerosol concentrations.

Experimental evidence for the sort of process postulated above (i.e., leaching of metals on to the plant surface and their association with surface particles, perhaps involving cation exchange) was provided by Beauford (unpublished), who showed that the amount of ^{65}Zn which could be collected with a cyclone from labelled bean plants (Phaseolus vulgaris) was increased 5 to 10 times if the plants were first subjected to artificial dew formation or a fine mist spray, and then allowed to dry. In this experiment the plants were dusted with ZnS powder to make it easier to collect surface material with the cyclone. The amount of ^{65}Zn collected was increased 17 times, compared with plants kept dry, if the plants were exposed to three wetting and drying cycles over 72 hours before sampling, in this case using bentonite (a clay mineral) as the externally applied dust. A similar trend was also apparent on undusted plants. It can be argued that the use of an externally applied dust corresponds to natural conditions, since plants in the field are subject to deposits of extraneous material.

I have not been able to demonstrate a similar effect with conifers (Cupressus leylandii, Tsuga heterophylla) because of the lower leachability of Zn from these plants, compared with beans. In the above experiments of Beauford, the particles collected from undusted bean plants were enriched in ^{65}Zn compared with herbage, on a dry weight basis, by 25 times (plants kept dry) or 50 times (plants previously wetted). In my experiments with conifers (also undusted), the concentrations of ^{65}Zn in surface particles were always much less than in the plant (dry weight basis). It was only possible to demonstrate very low levels of ^{65}Zn and ^{115m}Cd release by achieving very high specific activity in the foliage of conifers (Table 3.43) or with considerable replication (Table 3.7).

Trees were used for much of my experimental work because it was felt that they provided the greatest potential for metal release under natural conditions, because of their large size and surface area and their ecological importance as the dominant vegetation type over vast land areas. However, the metal release from Scots pine, which was largely used in fieldwork, may not be as great as from other plants, for two reasons. (1) Leaching experiments at Ecton mine showed that smaller amounts of several metals were removed from Scots pine per unit dry weight of herbage than from Rowan (Sorbus aucuparia) or birch (Betula pendula). If my interpretation of the results, in Section 3.43, is correct, these were genuine differences in leachability or in loss of plant derived particles rather than differences in retention of soil dust, for most elements. (2) Both fieldwork and a hydroponic experiment (Table 3.26 and Section 3.7) showed that Scots pine does not take up metals into the shoot in proportion to soil metal levels, and therefore an increase in metal leaching controlled by geochemistry does not occur with this species. Leaching effects from plants which do show geochemically correlated variations in metal content may prove more interesting in field situations.

Apart from the effects of leaching discussed above, amounts of metals available on plant surfaces are also partly determined by the presence of tissue fragments and soil dust on the foliage. In my biogeochemical survey of gorse (Ulex europaeus; Section 3.3), it was apparent during the fieldwork and from the analytical data, including electron microscopy and electron microprobe analysis, that the material collected with the cyclone largely comprised these two types of particle. In this survey, most of the evidence that was obtained by particulate sampling was also obtainable by a conventional biogeochemical survey (sampling the leaves). Both methods of sampling indicated the relative soil composition at different sites for the elements Pb, Mn, Zn, Al, Be, Sr, Ba and Cd. However, particles gave information on soil levels of Cu, Ca, Cr and Fe which were not obtained by leaf analysis. On the other hand, leaf analysis showed correlations with soil Mg, Co and Ni which were not evident from analysis of particles after they had been subjected to the method of fractionation used.

The various processes which give rise to particle release from plants in field conditions arise from stresses (in a broad sense) to which plants are exposed in nature.

These include wind action, abrasion, moisture and temperature cycles, and microbiological activity. The action of such forces - which, incidentally, are all well recognised as agents of geological weathering - must increase the release of metal-containing particles from plants above the levels found in laboratory conditions. For example, Beauford et al. (1975, 1977) measured the release of ^{65}Zn and ^{210}Pb from labelled pea plants (*Pisum sativum*) in perspex chambers by passing a stream of dry air over the foliage at a low flow rate, and assaying the radioactivity trapped by membrane filters and cold fingers. It is remarkable that under these very mild conditions labelled particles were released, and electron microscopy indicated the involvement of crystalline submicron particles.

Bearing in mind that these rates of metal release are likely to be much lower than in the field, these experiments do enable release rates to be calculated, since the leaf areas of the plants were measured. The maximum rate of zinc release was 21.0 pg.h^{-1}.cm^{-2} leaf area, and of lead was 0.013 pg.h^{-1}.cm^{-2} leaf area (Beauford *et al.*, 1977). Assuming a leaf area index (ratio of leaf area to ground area) of 10, applicable to a mature Scots pine forest (Oliver, 1975), the equivalent rates of metal release would be 1.84 (Zn) and 0.0011 (Pb) µg.yr^{-1}.cm^{-2} ground area. These rates alone are in fact not sufficient to account for atmospheric levels of these two metals in rural areas because Cawse (1975) estimated their deposition as 3.6 (Zn) and 1.6 (Pb) µg.yr^{-1}.cm^{-2} ground area at Plynlimon, Powys, Wales (Zn) and Leiston, Suffolk or Collafirth, Shetland (Pb). These were the sites giving the lowest deposition of zinc and lead in the U.K., but levels of Pb deposition 14 times lower than this have been recorded from marine-derived mountain air in California (Schlesinger *et al.*, 1974).

Although I believe that the mechanism of this plant metal release is of minor importance in the field, it is interesting to compare the results of Beauford et al. (1977) with those of Nemeryuk (1970), who measured the loss of Ca^{++} and other ions in association with transpiration water using methods similar to those described in Section 3.11. Nemeryuk demonstrated release of submicron particles of salts of major elements Na, K, Ca and Mg during transpiration from various plants in the field and the laboratory. In both the reports of Beauford et al. and Nemeryuk, the release was greater in light than in darkness, depended on conditions favourable for rapid water and solute uptake by the plants, and was quantitatively comparable. The release of calcium, for example, recorded by Nemeryuk gave approximately a 2 ppm solution in transpiration condensate, confirmed with radioactive ^{45}Ca. If the data of Beauford et al. are expressed as ppm Zn in transpiration water, the highest Zn concentration would be 0.002 ppm. The level of Zn in these plants was given as 0.9 ppm fresh weight, and if one assumes a plant concentration of 1000 ppm Ca fresh weight (based on my own analyses of plant material because the Ca concentrations in Nemeryuk's plants were not given) the proportional release of both metals is seen to be highly comparable. The proportional release of Pb was much smaller.

While it is obviously difficult to determine the contributions made by vegetation to concentrations of trace elements in aerosol in the field, in the final analysis the only way to do this is by aerosol sampling, bearing in mind that ambient concentrations of some elements from external sources may exceed vegetational release. It would be necessary to select an extremely remote rural area containing various types of vegetation and to carry out continuous aerosol sampling at a network of sites. The area would require at least one meteorological station recording wind speed, wind direction, precipitation, temperature and solar radiation. Aerosol sampling requires powered equipment and therefore some degree of maintenance and supervision. The aim of the project would be to identify aerosol inputs into the study area from outside, and aerosol originating from components of the study ecosystem. Techniques for the characterisation of aerosol and identification of sources could include correlations with wind-rose data (run of wind in each compass sector, e.g. Little & Martin, 1974), microscopic identification of pollen, spores and plant tissue fragments, and determinations of elemental and isotopic ratios which could be compared with those of plant surface particles from the different plant communities and with marine, soil and industrial sources. Apart from the involvement of aerosol in the dispersal of trace elements, aerosol has an important function in initiating rain, and it is the submicron particles which are involved here. Various work mentioned in the Introduction has implied that plants are sources of such particles, and therefore it would be a useful part of the programme above to monitor vegetational sources of rain nuclei.

The facilities needed to make a proper study on these lines would be extensive and require support, both in terms of manpower and finance, in excess of that available for this present work. Nevertheless, my work has given a feeling for the type of effects that may occur and hopefully will form the foundation for any further and more detailed programme designed to investigate the contribution that plants make to the chemical composition of the atmosphere.

The purposes for which most studies of heavy metals in the environment are undertaken can be grouped in two broad categories, although this division is not meant to be treated too rigidly. One aspect is the study of heavy metals as potentially toxic environmental contaminants ('pollution' studies) while the other category is concerned with metals as valuable and vital natural resources ('exploration' studies). While I do not underestimate the importance of pollution or the need for its study, I feel that the interest which has been generated in it in recent years will mean that the importance of pollution declines as people become more pollution-conscious, and indeed this trend is desirable. On the other hand, the increasing demand for heavy metals as raw materials, including new demands for rare but vital strategic metals such as cobalt and uranium, coupled with the depletion of known sources, will mean that advanced techniques of exploration become of increasing importance. Therefore, in conclusion, I would like to critically assess the significance of my work in relation to mineral exploration and to speculate on future developments.

The concept that particulate material in the atmosphere or on soil and plant surfaces can be used in exploration has been developed by Barringer Research Ltd. in the 'airtrace' and 'surtrace' systems. The sampling equipment for both systems can be carried in aircraft (for which airtrace was primarily designed) or used on the ground and, in the case of surtrace, can be carried as a backpack. In airtrace, air is scooped in at very high volumes through intakes mounted on the aircraft, and particles are impacted on special tape (Barringer, 1975; Section 1.6). The surtrace system is a further development in which soil or plant dust is collected using a flexible tube. When the equipment is carried in a helicopter, the tube is dangled along the ground, brushing the soil surface and vegetation. The sample spots on tape from an airtrace or surtrace survey are analysed by ARL 1 on a high-speed, automated basis since a survey may contain several thousand spots.

ARL 1 was thus developed as an integral part of these exploration systems to overcome the problems of rapid multi-elemental analysis of extremely small amounts of material. With this analytical facility, the time needed to collect each sample in the field is kept very small, of the order of 10 seconds. However, the technical problems involved in the analysis are considerable and partly arise from the fact that the mass of sample vaporised and analysed is unknown. The data from ARL 1 reported in this thesis were computed using an algorithm which assumed that the seven major elements in soil (Si, Al, Fe, Ca, Mg, Mn and Ti, assumed to be present as oxides) constituted 90% by weight of each sample. This worked well for mineral soils but not for organic dusts (my results and B.R.L. data). A more sophisticated algorithm including an additional nine elements has been developed to take account of the different matrix of elements which composes biological material, but does not appear to solve all the problems associated with biologically-derived particles. Further attempts have been made to decrease these 'matrix effects' by crushing and partially dry-ashing the samples prior to analysis, and the problem is still under investigation. Nevertheless, it is a very fine achievement to have produced an analytical technique which can give useful data on about twenty elements simultaneously, many in the ppm range of concentration, from a solid sample of about 10 µg, and to have combined this with rapid through-put of samples.

In these approaches to mineral exploration, one is primarily interested in detecting a reliable 'signal' indicating an ore-body, which can be distinguished from the background 'noise'. The absolute units in which the signal is expressed are not necessarily important, although obviously a scale of relative sizes is needed. The signal in this case is based on elemental concentrations in particles in the atmosphere or associated with soil and plant surfaces.

Since these concentrations must depend on numerous factors (such as the amount and composition of background aerosol, current meteorological conditions and recent weather history, and vegetation types) it is difficult to imagine a quantitative calibration between airtrace or surtrace data and geochemistry (and ultimately ore-grade) being possible. Therefore, the difficulties (which arise from the mass of sample vaporised being unknown) in producing absolute ppm values using ARL 1 are not crucial in this respect. However, the analytical system should be able to give elemental concentrations in soil and plant matrices with the same accuracy.

In other analytical applications, such as monitoring heavy metals in air, water, sewage and food, where statutory limits often have to be observed, the absolute accuracy of analysis is of great importance. The chemical species of heavy metals present are also very important in determining their roles as pollutants and their toxicology. It is disturbing that there can be large discrepancies between laboratories in the total metal analysis of standard samples, even using such a long-established technique as atomic absorption spectrophotometry, and the situation has been described as 'chaotic' by van Loon (1975). This is not to say that reliable data cannot be obtained, and the problem is partly a failure to appreciate the complex nature of interferences in atomic spectroscopy (Willis, 1975; Kopp, 1975). I have probably been guilty of a too-uncritical approach to atomic absorption spectroscopy. Rather than using external chemical standards, it would have been more rigorous to divide samples into an aliquot for each element to be analysed, using the standard-addition technique of calibration (avoiding the misuses described by Willis, 1975), adding releasing agents (e.g., lanthanum chloride) for Ca and Mg analyses, and using other procedures where appropriate to control interferences.

The airtrace results given by Barringer (1975) and my own surtrace-type data (Section 3.3) show that it is feasible to use particulate material for geochemical purposes. The surtrace method of exploration would seem more useful than airtrace from a logical view-point. Firstly, the concentrations of +10 µm particles in aerosol are extremely small whereas these particles are easy to collect from soil and plant surfaces and, secondly, sampling is not dependent on meteorological conditions favourable for vertical atmospheric mixing. These points do not apply if vapours are to be analysed, or atmospheric particles on which vapours released by soils and plants have been adsorbed.

In my geochemical survey of gorse, both soil- and plant-derived particles were implicated in the correlations between particles and soil chemistry. The surtrace approach therefore seems capable of combining the advantages of geochemical and biogeochemical prospecting. The combined benefits may be particularly applicable in semi-arid regions where plants are likely to have deep root systems which enable buried mineralisations to be detected biogeochemically (Brooks, 1972) and because anomalies are also present in surface soil (Barringer, 1975). In densely vegetated regions where local soil dust cannot be blown or deposited on foliage, surtrace is expected to be purely an extension of normal biogeochemistry and thus would depend on the occurrence of biogeochemically useful responses in vegetation.

It would be useful to build up a more comprehensive picture of the relationships of plant surface particles to geochemistry and biogeochemistry by using several species and by repeating the work under various meteorological conditions and at different times of year. In a study of surface wax and trichomes of gorse, Zabkiewics & Gaskin (1978) found seasonal variations in amounts of surface wax under New Zealand conditions, and this type of effect could lead to variations in metal release. It would also be constructive to change the rather messy wet-filtering system that was used in the gorse survey, perhaps by carrying out particle size separations during sample collection, and to compare the results with unfractionated samples.

Despite the encouraging surtrace-type results in my field study of gorse, some of my laboratory results have been rather negative. It is therefore relevant to point out some of the problems, in terms of ecology and plant physiology, which may limit the usefulness of surtrace in densely vegetated regions. In utilising plant-derived particles, the basic premise is that the metals of interest are taken up into the plant from the soil in amounts which reflect soil concentrations, and are present on the surface of foliage or are lost to the atmosphere.

The first difficulty is that plant species show wide variability in the extent to which they take up any given metal into their tissues. Some plants such as *Pinus sylvestris* show a marked ability to exclude above-normal concentrations of heavy metals from their foliage (Section 3.7), while others such as *Pisum sativum* grown under similar conditions take up these same metals (Zn and Cd) in proportion to their availability in the external medium (Beauford *et al*., submitted to Physiol.Plant.). Other plants show an ability to accumulate heavy metals to very high concentrations (Peterson, 1971). The dependence of plant uptake on available (rather than total) metal concentrations in soil is a further potential complication in the field.

Secondly, many heavy metals, such as Cu, Zn and Pb, are relatively immobile in plants and are not easily leached on to the leaf surface (Sections 3.5 and 3.8; Tukey *et al*., 1958). While this is irrelevant if tissue fragments are collected, it was undoubtedly important in my results on labelled plants (Sections 3.1 and 3.8). In these experiments, leaching was the only mechanism by which appreciable metal loss from foliage was demonstrated, even though in the conifer species used the heavy metal leachability was small by comparison with other, herbaceous plants (Tukey _et al._, 1958; Beauford _et al._, submitted). Another factor influencing the small amounts of metals lost from the experimental _Cupressus_ and _Tsuga_ plants was that they had relatively smooth foliage with few hairs, from which tissue fragments were not readily lost. Unlike natural perennial vegetation, they were too young to have accumulated any dead tissue amongst the foliage. Such material appeared to contribute significantly to the particles collected from gorse in the field. Therefore, the levels of radioactivity (^{65}Zn, ^{115m}Cd, ^{54}Mn) in particles present on the surface of these labelled conifers at any one time were always very small.

Thirdly, plants are exposed to aerial fallout which unfortunately is enriched in many of the heavy metals which are of interest (Section 3.2; Cawse, 1975). This is not a serious problem in sufficiently isolated areas, but investigators should always be aware of possible sources of pollution in each local situation.

While these drawbacks do not negate the exploration methods discussed, they may limit their usefulness. The problems arise because the techniques, although superficially involving remote sensing, depend on analysis of the metals themselves and therefore on pathways of metal movement. An alternative approach would be to utilise optical properties of vegetation in exploration. It is often apparent that vegetation growing in metal-stress conditions is discoloured and it is therefore also possible that more subtle effects occur, which can be detected with suitable equipment. For example, there are indications that trees show thermal manifestations of metal stress (Canney _et al._, 1972) and changes in reflectance at certain wavelengths (Birnie & Dykstra, 1978). With further research on plant responses and on suitable instrumentation it may be possible to use sophisticated techniques to indicate mineralisations and other resources, through effects on vegetation. Such optical effects are easily applicable to air-borne and in some cases space-borne scanning systems.

In mineral exploration, there is no single technique which provides all the answers, but results are often obtained by a combination of approaches. It makes commercial sense to use a wide range of instrumentation in each survey. Therefore, approaches which involve the vegetation cover will in practice be combined with geophysical sensors such as magetometers and radiophase equipment (see Barringer, 1971). Although gross effects of metal toxicity on vegetation have long been used in exploration, there are great potential benefits in developing advanced exploration techniques, utilising the vegetation cover, for surveying naturally vegetated regions of the World. It is hoped that in this way vegetation will prove to be an asset rather than a hindrance in the reconnaissance of natural resources.

5. BIBLIOGRAPHY.

Abebe, M. (1972). Movement of ^{65}Zn into soils from surface application of zinc sulphate in columns. In: Isotopes and radiation in soil-plant relationships including forestry: Proc.Symp., Vienna, Dec. 1971, I.A.E.A. 507-515.

Ahmed, S. & Evans, H.J. (1960). Cobalt: a micronutrient element for the growth of soybean plants under symbiotic conditions. Soil Sci. 90, 205-210.

Ahmed, S. & Evans, H.J. (1961). The essentiality of cobalt for soybean plants grown under symbiotic conditions. Proc.nat.Acad.Sci.U.S.A. 47, 24-36.

Aitken, J. (1923). Collected scientific papers. Cambridge University Press.

Amsden, R.C. & Lewis, C.P. (1966). Assessment of wettability of leaves by dipping in crystal violet. World Rev. Pest Control 5, 187-194.

Andersson, A. (1975). Relative efficiency of nine different soil extractants. Swedish J.agric.Res. 5, 125-135.

Antonovics, J. (1975). Metal tolerance in plants: perfecting an evolutionary paradigm. Proc.int.Conf.Heavy Metals in the Environment, Toronto, Oct. 1975, 2 (1), 169-186.

Antonovics, J., Bradshaw, A.D., & Turner, R.G. (1971). Heavy metal tolerance in plants. Adv.ecol.Res. 7, 1-85.

Arnon, D.E. & Wessel, G. (1953). Vanadium as an essential element for green plants. Nature 172, 1039-1040.

Arpino, P., van Dorsselaer, A., Sevier, K.D., Ourisson, G. (1972). Cires aeriennes dans une foret de Pins. C.R. Acad.Sci. Paris, t275, Series D, 2837-2840.

Arvik, J.H. & Zimdahl, R.L. (1974). Barriers to the foliar uptake of lead. J.environ.Qual. 3, 369-373.

Attiwill, P.M. (1966). The chemical composition of rainwater in relation to cycling of nutrients in mature eucalyptus forest. Plant and Soil 24, 390-406.

Barker, D.R. & Zeitlin, H. (1972). Metal-ion concentrations in sea-surface microlayer and size-separated atmospheric aerosol samples in Hawaii. J.geophys.Res. 77, 5076-5086.

Barnes, D., Hanadah, M.A. & Ottaway, J.M. (1976). The lead, copper and zinc content of tree rings and bark. A measurement of local metallic pollution. Sci.tot. Environ. 5, 63-67.

Barringer, A.R. (1971). Airborne exploration. Mining magazine 124 (3), 1-6.

Barringer, A.R. (1975). Airtrace - an airborne geochemical technique. Pre-print of a paper presented at the 1st William Pecora Memorial Symposium, Sioux Falls, S. Dakota, October 1975.

Bazzaz, F.A., Carlson, R.W., & Rolfe, G.L. (1974). The effect of heavy metals on plants. I. Inhibition of gas exchange in sunflower by Pb, Cd, Ni and Tl. Environ.Pollut. 7, 241-246.

Beauford, W., Barber, J., & Barringer, A.R. (1975). Heavy metal release from plants into the atmosphere. Nature 256, 35-37.

Beauford, W., Barber, J., & Barringer, A.R. (1977). Release of particles containing metals from vegetation into the atomosphere. Science 195, 571-573.

Beauford, W., Luton, M.T., Barber, J. & Barringer, A.R. (Submitted for publication, 1978). The uptake and foliar leaching of heavy metals by Pisum sativum. Physiol.Plant.

Beavington, F. (1977). Trace elements in rainwater and dry deposition around a smelting complex. Environ. Pollut. 13, 127-131.

Best, G.R. (1971). Potassium, sodium, calcium and magnesium flux in a mature hardwood forest watershed and an eastern white pine forest watershed at Coweeta. Masters Thesis, Univ. of Georgia, U.S.A.

Birnie, R.W. & Dykstra, J.D. (1978). Application of remote sensing to reconnaissance geologic mapping and mineral exploration. Proc. 12th int.Symp. Remote Sensing of Environment, Manila, April, 1978.

Blackman, R.A. (1977). The leaching of trace metals from leaves and their exchange across plant cuticles. M.Sc. thesis, Univ. of London.

Blanchard, D.C. & Syzdek, L.D. (1972). Concentration of bacteria in jet drops from bursting bubbles. J.geophys. Res. 77, 5087-5099.

Booker, F. (1971). The industrial archaeology of the Tamar Valley. David & Charles, Newton Abbott, Devon, U.K.

Borst Pauwels, G.W.F.H. (1961). Iodine as a micronutrient for plants. Plant and Soil 14, 377-392.

Bowen, H.J.M. (1966). Trace elements in biochemistry. Academic Press.

Bowen, H.J.M. (1974). Problems in the elementary analysis of standard biological materials. J.radioanal.Chem. 19, 215-226.

Brimblecombe, P. & Hunter, K.A. (1977). Rock volatility and aerosol composition. Nature 265, 761-762.

Brooks, R.R. (1972). Geobotany and biogeochemistry in mineral exploration. Harper & Row.

Brownell, P.F. & Wood, J.G. (1957). Sodium as an essential micronutrient element of Atriplex vesicaria, Heward. Nature 179, 635-636.

Broyer, T.C., Carlton, A.B., Johnson, C.M. & Stout, P.R. (1954). Chlorine, a micronutrient element for higher plants. Plant Physiol. 29, 562-532.

Bukovac, M.J. & Wittwer, S.H. (1957). Absorption and mobility of foliar applied nutrients. Plant Physiol. 32, 428-435.

Cameron, A.J. & Nickless, G. (1977). Uses of mosses as collectors of airborne heavy metals near a smelting complex. Water, Air and Soil Pollut. 7, 117-126.

Canney, F.C., Hessin, T.D. & Burge, W.G. (1972). Analysis of thermal patterns of geochemically stressed trees at Catheart Mountain, Maine. 4th Annual Earth Resources Programme Review, N.A.S.A., Houston, Texas.

Carlisle, A., Brown, A.H.F., & White, E.J. (1966). The organic matter and nutrient elements in the precipitation beneath a sessile oak (Quercus petraea) canopy. J.Ecol. 54, 87-98.

Carlisle, A., Brown, A.H.F., & White, E.J. (1967). The nutrient content of tree stem flow and ground flora litter and leachates in a sessile oak (Quercus petraea) woodland. J.Ecol. 55, 615-627.

Cawse, P.A. (1974). A survey of atmospheric trace elements in the U.K. (1972-73). Atomic Energy Research Establishment, Harwell, U.K. Report R7669. H.M.S.O.

Cawse, P.A. (1975). A survey of atmospheric trace elements in the U.K. Results for 1974. Atomic Energy Research Establishment, Harwell, U.K., Report R8038. H.M.S.O.

Cawse, P.A. & Peirson, D. (1972). An analytical study of trace elements in the atmospheric environment. Atomic Energy Research Establishment, Harwell, U.K., Report R7134, H.M.S.O.

Chadwick, R.C. & Chamberlain, A.C. (1970). Field loss of radionuclides from grass. Atmos.Environ. 4, 51-56.

Chamberlain, A.C. (1967). Transport of Lycopodium spores and other small particles to rough surfaces. Proc.roy. Soc. A 296, 45-70.

Chamberlain, A.C. (1970). Interception and retention of radioactive aerosols by vegetation. Atmos.Environ. 4, 57-78.

Chamberlain, A.C. (1975). The movement of particles in plant communities. In: Vegetation and the Atmosphere. Volume 1. Principles. ed. J.L. Monteith. Academic Press.

Chambers, T.C., Ritchie, I.M., & Booth, M.A.,(1976). Chemical models for plant wax morphogenesis. New Phytol. 77, 43-49.

Chandler, W.H. (1937). Zinc as a nutrient for plants. Bot.Gaz. 98, 625-646.

Chester, R. & Stoner, J.H. (1973). Average trace element composition of low level marine atmospheric particulates. Nature 246, 138-139.

Clough, W.S. (1975). The deposition of particles on moss and grass surfaces. Atmos.Environ. 9, 1113-1119.

Cox, R.M. & Thurman, D.A. (1978). Inhibition by zinc of soluble and cell wall acid phosphatases of zinc-tolerant and non-tolerant clones of Anthoxanthum odoratum. New Phytol. 80, 17-22.

Curtin, G.C., King, H.D., & Mosier, E.L. (1974). Movement of elements into the atmosphere from coniferous trees in subalpine forests of Colorado and Idaho. J.geochem. Explor. 3, 245-263.

Davies, R.G. (1971). Computer programming in quantitative biology. Academic Press.

Davis, B.L., Blair, D.N., Johnson, L.R. & Haggard, S.J. (1976). A study of the green area effect in the Black Hills of South Dakota. Atmos.Environ. 10, 363-370.

Davy, A.J. & Taylor, K. (1975). Seasonal changes in the inorganic nutrient concentrations in Deschampsia caespitosa (L.) Beauv. in relation to its tolerance of contrasting soils in the Chiltern hills. J.Ecol. 63, 27-39.

DeKock, P.C. & Mitchell, R.L. (1957). Uptake of chelated metals by plants. Soil Sci. 84, 55-62.

Dines, H.G. (1956). The metalliferous mining region of south-west England. Two volumes. H.M.S.O.

Duce, R.A., Hoffman, G.L. & Zoller, W.H. (1975). Atmospheric trace metals at remote Northern and Southern Hemisphere sites: pollution or natural? Science 187, 59-61.

Duvigneaud, P. & Denaeyer-de-Smet, S. (1970). Biological cycling of minerals in temperate deciduous forests. In: Analysis of temperate forest ecosystems, ed. D.E. Reichle. Chapman and Hall.

Dyer, A.J. & Hicks, B.B. (1968). Global spread of volcanic dust from the Bali eruption of 1963. Quart.J.roy. meteorol.Soc. 94, 545-554.

Eaton, J.S., Likens, G.E. & Bormann, F.H. (1973). Throughfall and stemflow chemistry in a northern hardwood forest. J.Ecol. 61, 495-508.

Eglinton, G. & Hamilton, R.J. (1967). Leaf epicuticular waxes. Science 156, 1322-1335.

Eller, B.M. (1977). Road dust induced increase of leaf temperature. Environ.Pollut. 13, 99-107.

Ernst, W. (1975a). Variation in the mineral contents of leaves of trees in miombo woodland in south central Africa. J.Ecol. 63, 801-807.

Ernst, W. (1975b). Physiology of heavy metal resistance in plants. Proc.Conf.Heavy Metals in the Environment, Toronto, Oct. 1975, 2 (1), 121-136.

Ernst, W. & Weinert, H. (1972). Lokalisation von Zink in den Blättern von Silene cucubalus Wib. Z.Pflanzenphysiol. 66, 258-264.

Esau, K. (1965). Plant anatomy. Second edition. Wiley-Toppan.

Esmen, N.A. & Corn, M. (1971). Residence times of particles in urban air. Atmos.Environ. 5, 571-578.

Evans, C.E., Wear, J.I., Hajek, B.F., & Cope, J.T., Jnr. (1974). The relationship of soil zinc removed by 3 extractants to zinc uptake by corn and sorghum in medium- to fine-textured soils. Commun.in Soil Sci. and Plant Analysis 5, 105-113.

Evans, L.S., Gmur, N.F., & Da Costa, F. (1977). Leaf surface and histological perturbations of leaves of Phaseolus vulgaris and Helianthus annuus after exposure to simulated acid rain. Am.J.Bot. 64, 903-913.

Fairfax, J.A.W., & Lepp, N.W. (1975). Effect of simulated "acid rain" on cation loss from leaves. Nature 255, 324-325.

Ferenbaugh, R.W. (1976). Effects of simulated acid rain on Phaseolus vulgaris L. (Fabeaceae). Am.J.Bot. 63, 283-288.

Fish, B.R. (1972). Electrical generation of natural aerosols from vegetation. Science 175, 1239-1240.

Flowers, T.J., Troke, P.F., & Yeo, A.R. (1977). The mechanism of salt tolerance in halophytes. Annu.Rev.Plant Physiol. 28, 89-121.

Fortescue, J.A.C. & Marten, G.G. (1970). Micronutrients: forest ecology and systems analysis. In: Ecological Studies I: Analysis of temperate forest ecosystems, ed. D.E. Reichle. Chapman & Hall.

Foster, N.W. & Morrison, I.K. (1976). Distribution and cycling of nutrients in a natural Pinus banksiana ecosystem. Ecology, 57, 110-120.

Foy, C.D., Chaney, R.L., & White, M.C. (1978). The physiology of metal toxicity in plants. Annu.Rev.Plant Physiol. 29, 511-566.

Franke, W. (1967). Mechanisms of foliar penetration of solutions. Annu.Rev.Plant Physiol. 18, 281-300.

Gay, D.D. (1975). Biotransformation and chemical form of mercury in plants. Proc.int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 2 (1), 87-95.

Gilbert, O.L. (1974). An air pollution survey by school children. Environ.Pollut. 6, 175-180.

Gingell, S.M., Campbell, R., & Martin, M.H. (1976). The effect of zinc, lead, and cadmium pollution on the leaf surface microflora. Environ.Pollut. 11, 25-37.

Goldberg, E.D. (1976). Rock volatility and aerosol composition. Nature 260, 128-129.

Goldsmith, P. & May, F.G. (1966). Diffusiophoresis and thermophoresis in water vapour systems. In: Aerosol Science, ed. C.N. Davies. Academic Press.

Goodman, G.T., Smith, S., Parry, G.D.R., & Inskip, M.J. (1974). The use of moss-bags as deposition gauges for airborne metals. Proc. 41st annu.Conf., Nat.Soc. for Clean Air, Cardiff, Oct. 1974.

Goodman, G.T., Smith, S., & Inskip, M.J. (1975). Moss bags as indicators of airborne metals-an evaluation. In: Report of a collaborative study on certain elements in air, soil, plants, animals and humans in the Swansea-Neath-Port Talbot area, together with a moss bag study of atmospheric pollution across south Wales. Welsh Office.

Guha, M.M. & Mitchell, R.L. (1966). The trace and major element composition of the leaves of some deciduous trees. II. Seasonal changes. Plant and Soil 24, 90-112.

Gupta, U. & Chipman, E.W. (1976). Influence of iron and pH on the yield and iron, manganese, zinc and sulphur concentrations of carrots grown on Sphagnum peat soil. Plant and Soil 44, 559-566.

Haas, K. (1977). Influence of temperature and leaf age on cuticular wax of Hedera helix. Biochemie und Physiologie der Pflanzen 171, 25-31.

Hall, C., Hughes, M.K., Lepp, N.W., & Dollard, G.J. (1975). Cycling of heavy metals in woodland ecosystems. Proc. int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 2 (1), 227-245.

Hall, S.K. (1972). Pollution and Poisoning. Environ. Sci. and Technol. 6, 31-35.

Hemphill, D.D. & Rule, J. (1975). Foliar uptake and translocation of ^{210}Pb and ^{109}Cd. Proc.int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 2 (1), 77-86.

Henderson, G.S., Harris, W.F., Todd, D.E., Jr., & Grizzard, T. (1977). Quantity and chemistry of throughfall as influenced by forest-type and season. J.Ecol. 65, 365-374.

Hill, A.C. (1971). Vegetation: a sink for atmospheric pollutants. J.Air Pollut.Control Assoc. 21, 341-6.

Holloway, P.J. (1969). The effects of superficial wax on leaf wettability. Ann.appl.Biol. 63, 145-153.

Hutchinson, T.C., & Whitby, L.M. (1977). The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. Water, Air and Soil Pollut. 7, 421-438.

Ingestad, T. (1960). Studies on the nutrition of forest tree seedlings III. Mineral nutrition of pine. Physiol. Plant. 13, 513-533.

Jaffre, T., Brooks, R.R., Lee, J., & Reeves, R.D. (1976). *Sebertia acuminata*: a hyperaccumulator of nickel from New Caledonia. Science 193, 579-580.

Jernelöv, A. (1975). Microbial alkylation of heavy metals. Proc.Conf. Heavy Metals in the Environment, Toronto, Oct., 1975, 2 (2), 845-859.

Johansson, T.B., van Grieken, R.E., & Winchester, J.W. (1976). Elemental abundance variation with particle size in north Florida aerosols. J.geophys.Res. 81, 1039-1046.

Johnson, D.B. (1976). Ultragiant urban aerosol particles. Science 194, 941-942.

Johnson, M., Roberts, D., & Firth, N. (1978). Lead and zinc in the terrestrial environment around derelict metalliferous mines in Wales (U.K.). Sci.tot.Environ. 10, 61-78.

Jordan, M.J. (1975). Effects of zinc smelter emissions and fire on a chestnut-oak woodland. Ecology 56, 78-91.

Kaul, O.N. & Billings, W.D. (1965). Cation content of stemflow in some forest trees in North Carolina. Indian Forester 91, 367-370.

Kline, J.R., Stewart, M.L., Jordan, C.F., & Kovac, P. (1972). Use of tritiated water for determination of plant transpiration and biomass under field conditions. In: Isotopes and radiation in soil-plant relationships including forestry: Proc.Symp., Vienna, Dec. 1971, I.A.E.A., 419-437.

Knight, A.H., Crooke, W.M., & Inkson, R.M.E. (1961). Cation exchange capacities of tissues of higher and lower plants and their related uronic acid contents. Nature, 192, 142-143.

Kolotov, B.A., Kiseleva, Ye.A., & Rubeykin, V.Z. (1965). On the secondary dispersion aureoles in the vicinity of ore deposits. English translation of [Geokhimiya 7, 878-879], 675-677.

Kopp, J.F. (1975). Current status of analytical methodology for trace metals. Proc.int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 1, 261-274.

Kozuchowski, J. & Johnson, D. (1978). Gaseous emissions of mercury from an aquatic vascular plant. Nature 274, 468-469.

Laaksovirta, K., Olkkonen, H. & Alakuijala, P. (1976). Observations on the lead content of lichen and bark adjacent to a highway in southern Finland. Environ. Pollut. 11, 247-255.

Lagerwerff, J.V. & Specht, A.W. (1970). Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc. Environ.Sci. and Technol. 4, 583-586.

Lawrey, J.D. (1978). Trace metal dynamics in decomposing leaf litter in habitats variously influenced by coal strip mining. Can.J.Bot. 56, 953-962.

Leonard, R.E. (1961). Interception of precipitation by northern hardwoods. Northeastern Forest Experiment Station, paper 159, 16 pages.

Lepp, N.W. (1975). The potential of tree-ring analysis for monitoring heavy metal pollution patterns. Environ. Pollut. 9, 49-61.

Lepp, N.W. & Dollard, G.J. (1974). Studies on lateral movement of ^{210}Pb in woody stems. Patterns observed in dormant and non-dormant stems. Oecologia 16, 179-184.

Lewis, B.-A., G. (1975). Selenium in biological systems, and pathways for its volatilization in higher plants. In: Environmental Biogeochemistry Vol. 1: Proc. 2nd int.Symp.Environmental Biogeochemistry, ed. Nriagu, J.O., Ann Arbor Science. 389-409.

Leyton, L. (1972). Use of isotopes in tree physiological research. In: Isotopes and radiation in soil-plant relationships including forestry: Proc.Symp., Vienna, Dec. 1971, I.A.E.A., 263-276.

Likens, G.E., & Eaton, J.S. (1970). A polyurethane stemflow collector for trees and shrubs. Ecology 51, 938-939.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S. & Johnson, N.M. (1977). Biogeochemistry of a forested ecosystem. Springer-Verlag.

Little, P. (1973). A study of heavy metal contamination of leaf surfaces. Environ.Pollut. 5, 159-172.

Little, P. & Martin, M.H. (1972). A survey of zinc, lead and cadmium in soil and natural vegetation around a smelting complex. Environ.Pollut. 3, 241-254.

Little, P. & Martin, M.H. (1974). Biological monitoring of heavy metal pollution. Environ.Pollut. 6, 1-19.

Long, W.G., Swell, D.V., & Tukey, H.B. (1956). Loss of nutrients from foliage by leaching as indicated by radio-isotopes. Science 123, 1039-1040.

Lopez, A. (1974). Contribution a l'étude de l'aerosol atmospherique. Ph.D. thesis, Paul Sabatier University, Toulouse, France.

Lounamaa, K.J. (1956). Trace elements in plants growing wild on different rocks in Finland. A semi-quantitative spectrographic survey. Annals bot.Soc.zool.-bot., fennicae Vanamo 29, 1-196.

Luton, M.T. (unpublished). Ph.D. thesis in preparation. Univ. of London.

Lüttge, U. (1971). Structure and function of plant glands. Annu.Rev.Plant Physiol. 22, 23-44.

MacIntyre, F. (1970). Geochemical fractionation during mass transfer from sea to air by breaking bubbles. Tellus 22, 451-461.

MacKerron, D.K.L. (1976). Wind damage to the surface of strawberry leaves. Ann.Bot. 40, 351-354.

Madgwick, H.A.I. & Ovington, J.D. (1959). The chemical composition of precipitation in adjacent forest and open plots. Forestry 32, 14-22.

Martin, J.T. & Juniper, B.E. (1970). The cuticles of plants. Arnold.

Mathys, W. (1977). The role of malate, oxalate, and mustard oil glucosides in the evolution of zinc-resistance in herbage plants. Physiol.Plant. 40, 130-136.

McColl, J.G. & Bush, D.S. (1978). Precipitation and throughfall chemistry in the San Fransisco bay area. J.environ.Qual. 7, 352-357.

McLean, R.O. & Shields, B. (1977). A study of factors causing changes in the lead levels of crops growing beside roadways. Environ.Pollut. 14, 267-273.

Mecklenburg, R.A., Tukey, H.B., Jnr., & Morgan, J.V. (1966). A mechanism for the leaching of calcium from foliage. Plant Physiol. 41, 610-613.

Mellanby, K. (1977). Acid rain. Nature 268, 99.

Milbourn, G.M. & Taylor, R. (1965). The contamination of grassland with radioactive strontium. I. Initial retention and loss. Radiation Botany 5, 337-347.

Mitchell, R.L. (1972). Trace elements in soils and factors that affect their availability. Geol.Soc.Am.Bull. 83, 1069-1076.

Moorby, J. & Squire, H.M. (1963). The loss of radioactive isotopes from the leaves of plants in dry conditions. Radiation Botany 3, 163-167.

N.A.S.A. (1968). Application of biogeochemistry to mineral exploration. Special Publication 5056. 133 pages.

Nemeryuk, G.E. (1970). Salt migration into atmosphere during transpiration. Soviet Plant Physiol. 17, 673-679. English abstract only.

Newell, R.E. (1971). The global circulation of atmospheric pollutants. Scientific American 224, 32-42.

Nieboer, E., Puckett, K.J., Richardson, D.H.S., Tomassini, F.D. & Grace, B. (1975). Ecological and physiochemical aspects of the accumulation of heavy metals and sulphur in lichens. Proc.int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 2 (1), 331-351.

Nikiforova, Ye.M. (1976). Lead pollution of the environment from automotive exhaust gases. Soviet Geography: Review and Translation 17, 324-333.

Oliver, H.R. (1975). Ventilation in a forest. Agric. Meteorol. 14, 347-355.

Pattendon, N.J. (1975). Atmospheric concentrations and deposition rates of some trace elements measured in the Swansea-Neath-Port Talbot area. In: Report of a collaborative study on certain elements in air, soil, plants, animals and humans in the Swansea-Neath-Port Talbot area, together with a moss bag study of atmospheric pollution across south Wales. Welsh Office.

Peirson, D.H., Cawse, P.A., Salmon, L. & Cambray, R.S. (1973). Trace elements in the atmospheric environment. Nature 241, 252-256.

Peirson, D.H., Cawse, P.A., & Cambray, R.S. (1974). Chemical uniformity of airborne particulate material and a maritime effect. Nature 251, 675-679.

Perkin, D.W. & Tilles, D. (1968). Influx measurements of extraterrestrial material. Science 159, 936-946.

Peterson, P.J. (1969). The distribution of ^{65}Zn in *Agrostis tenuis* Sibth. and *A.stolonifera* L. tissues. J.exp.Bot. 20, 863-875.

Peterson, P.J. (1971). Unusual accumulation of elements by plants and animals. Science Progress, Oxford 59, 505-526.

Peterson, P.J. (1973). Minerals and Life-a study of excess and essentiality. Biol.J.Linn.Soc. 5, 357. Abstract only.

Peterson, P.J. (1975). Element accumulation by plants and their tolerance of toxic mineral soils. Proc.int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 2 (1), 39-54.

Piotrowicz, S.R., Ray, B.J., Hoffman, G.L. & Duce, R.A. (1972). Trace metal enrichment in the sea-surface microlayer. J.geophys.Res. 77, 5243-5254.

Potts, M.J. (1978). Deposition of air-borne salt on Pinus radiata and the underlying soil. J.appl.Ecol. 15, 543-550.

Pyatt, F.B. (1970). Lichens as indicators of air pollution in a steel producing town in south Wales. Environ. Pollut. 1, 45-56.

Rasmussen, L. (1977). Epiphytic bryophytes as indicators of the changes in the background levels of airborne metals from 1951-75. Environ.Pollut. 14, 37-45.

Rasmussen, R.A. (1972). What do the hydrocarbons from trees contribute to air pollution? J.Air Pollut. Control Assoc. 22, 537-543.

Reilly, A. & Reilly, C. (1973). Zinc, lead and copper tolerance in the grass Stereochlaena cameronii (Stapf.) Clayton. New Phytol. 72, 1041-1046.

Reilly, C. & Stone, J. (1971). Copper tolerance in Becium homblei. Nature 230, 403.

Ricks, G.R. & Williams, R.J.H. (1974). Effects of atmospheric pollution on deciduous woodland. II. Effects of particulate matter upon stomatal diffusion resistance in leaves of Quercus petraea (Mathuschka) Leibl. Environ. Pollut. 6, 87-109.

Roberts, T.M. (1972). Spread and accumulation in the environment of toxic non-ferrous metals from urban and industrial sources. Ph.D. thesis, University College of Wales, Swansea.

Roberts, T.M. (1975). A review of some biological effects of lead emissions from primary and secondary smelters. Proc.int.Conf. Heavy Metals in the Environment 2 (2), 503-532.

Robey, J.A. & Porter, L. (1972). The copper and lead mines of Ecton Hill, Staffordshire. Moorland Publ. Co., Leek, Staffs. & Peak District Mines Historical Soc., Bakewell, Derbys.

Robinson, E. & Robbins, R.C. (1971). Emission, concentration and fate of particulate atmospheric pollutants. Final Report, S.R.I. Project SCC-8507. Stanford Research Institute, Menlo Park, California, U.S.A.

Rolfe, G.L. & Jennett, J.C. (1975). Environmental lead distribution in relation to automobile and mine and smelter sources. Proc.int.Conf. Heavy Metals in the Aquatic Environ., Nashville, Tennessee, Dec. 1973, ed. P.A. Krenkel. Pergamon Press. 231-241.

Rosinski, J. & Nagamoto, C.T. (1964). Particle deposition on and re-entrainment from coniferous trees. I. Experiments with trees. Kolloid-Zeitschrift und Zeitschrift für Polymere, 204, 111-119.

Rühling, A & Tyler, G. (1971). Regional differences in the deposition of heavy metals over Scandinavia. J.appl. Ecol. 8, 497-507.

Sampson, A.W. & Samisch, R. (1935). Growth and seasonal changes in composition of oak leaves. Plant Physiol. 10, 739-751.

Saunders, P.J.W. (1971). Modification of the leaf surface and its environment by pollution. In: Ecology of leaf surface microorganisms, ed. T.F. Preece & C.H. Dickinson, Academic Press.

Schlesinger, W.H., Reiners, W.A., & Knopman, D.S. (1974). Heavy metal concentrations and deposition in bulk precipitation in montane ecosystems of New Hampshire, U.S.A. Environ.Pollut. 6, 39-47.

Schnell, R.C. & Vali, G. (1972). Atmospheric ice nuclei from decomposing vegetation. Nature 236, 163-165.

Schnell, R.C. & Vali, G. (1973). World-wide source of leaf-derived freezing nuclei. Nature 246, 212-213.

Sheline, J., Akselsson, R., & Winchester, J.W. (1976). Trace element similarity groups in north Florida spanish moss: evidence for direct uptake of aerosol particles. J.geophys.Res. 81, 1047-1050.

Shewry, P.R. & Peterson, P.J. (1975). Distribution of chromium and nickel in plants and soil from serpentine and other sites. J.Ecol. 64, 195-212.

Singh, B.R. (1974). Migration of ions in soils. I. Movement of ^{65}Zn from surface application of zinc sulphate in soil columns. Plant and Soil 41, 619-628.

Smith, W.H. (1974). Air pollution-effects on the structure and function of the temperate forest ecosystem. Environ. Pollut. 6, 111-129.

Somers, G.F. (1975). The role of plant residues in the retention of cadmium in ecosystems. Completion Report, Delaware University, Newark, Department of Biological Sciences, 27 pages.

Thomas, W.A. (1969). Accumulation and cycling of calcium by dogwood trees. Ecol.Monogr. 39, 101-120.

Trelease, S.F. & Trelease, H.M. (1938). Selenium as a stimulating and possibly essential element for indicator plants. Am.J.Bot. 25, 372-380.

Tukey, H.B., Jnr. (1970). The leaching of substances from plants. Annu.Rev.Plant Physiol. 21, 305-324.

Tukey, H.B., Jnr., & Morgan, J.V. (1963). Injury to foliage and its effect upon the leaching of nutrients from above-ground plant parts. Physiol.Plant. 16, 557-564.

Tukey, H.B., Jnr., Tukey, H.B. & Wittwer, S.H. (1958). Loss of nutrients by foliar leaching as determined by radioisotopes. Proc.Am.Soc.hort.Sci. 71, 496-506.

Tukey, H.B., Wittwer, S.H., & Bukovac, M.J. (1962). The uptake and loss of materials by leaves and other above-ground plant parts with special reference to plant nutrition. Agrochimica 7, 1-28.

Tukey, H.B., Jnr., Mecklenburg, R.A. & Morgan, J.V. (1965). A mechanism for the leaching of metabolites from foliage. In: Isotopes and radiation in soil-plant nutrition studies, I.A.E.A., Vienna, 371-385.

Turner, R.G. & Marshall, C. (1971). Accumulation of ^{65}Zn by root homogenates of zinc-tolerant and non-tolerant clones of Agrostis tenuis Sibth. New Phytol. 70, 539-545.

Twomey, S. (1969). On the nature and origin of natural cloud nuclei. Bulletin de l'Observatoire du Puy de Dome no. 1, 1-19.

Tyler, G. (1976). Heavy metal pollution, phosphatase activity and mineralisation of organic phosphorus in forest soils. Soil Biology and Biochemistry 8, 327-332.

Tyson, J.B. (1974). Volatilisation of terpenes from Salvia mellifera. Nature 252, 119-120.

Ulrich, B. & Mayer, R. (1972). Systems analysis of mineral cycling in forest ecosystems. In: Isotopes & radiation in soil-plant relationships including forestry: Proc. Symp., Vienna, Dec. 1971, I.A.E.A., 329-339.

Van Loon, J.C. (1975). How useful are environmental chemical data? Proc.int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 1, 349-355.

Voigt, G.K. (1960). Alteration of the composition of rainwater by trees. Am.Midl.Nat. 63, 321-326.

Wainwright, S.J. & Woolhouse, H.W. (1975). Physiological mechanisms of heavy metal tolerance. In: The ecology of resource degradation and renewal, ed. M.J. Chadwick & G.T. Goodman: Brit.ecol.Soc.Symp. No. 15. Blackwell Scientific Publications, Oxford.

Wallin, T. (1976). Deposition of airborne mercury from six Swedish chlor-alkali plants surveyed by moss analysis. Environ.Pollut. 10, 101-114.

Ward, N.I., Reeves, R.D. & Brooks, R.R. (1975). Lead in soil and vegetation along a New Zealand state highway with low traffic volume. Environ.Pollut. 9, 243-251.

Warren, H.V., Delavault, R.E. & Barakso, J. (1966). Some observations on the geochemistry of mercury as applied to prospecting. Econ.Geol. 61, 1010-1028.

Warren, H.V., Delavault, R.E. & Barakso, J. (1968). The arsenic content of Douglas Fir as a guide to some gold, silver, and base metal deposits. Bull.Can.Min.Metall. 61, 860-866.

Went, F.W. (1964). The nature of Aitken condensation nuclei in the atmosphere. Proc.nat.Acad.Sci. U.S.A. 51, 1259-1267.

Went, F.W. (1974). Natural smog in nature. Annu.Rev. Plant Physiol. 25, 20-24.

Went, F.W., Slemmons, D.B., & Mozingo, H.N. (1967). The organic nature of atmospheric condensation nuclei. Proc. nat.Acad.Sci.U.S.A. 58, 69-74.

White, E.J. & Turner, F. (1970). A method of estimating income of nutrients in a catch of airborne particles by a woodland canopy. J.appl.Ecol. 7, 441-461.

White, H. (1975). Lead uptake by higher plants and its release into the atmosphere. M.Sc. thesis, University of London.

Whitecross, M.I. & Armstrong, D.J. (1972). Environmental effects on epicuticular waxes of Brassica napus L. Aust. J.Bot. 20, 87-95.

Will, G.M. (1959). Nutrient return in litter and rainfall under some exotic conifer stands in New Zealand. N.Z. J.agric.Res. 2, 719-734.

Willis, J.B. (1975). Atomic spectroscopy in environmental studies. Fact and artefact. Proc.int.Conf. Heavy Metals in the Environment, Toronto, Oct. 1975, 1, 69-91.

Wittwer, S.H., Jyung, W.H., Yamada, Y., Bukovac, M.J., De, R., Kannan, S., Rasmussen, H.P. & Haile Mariam, S.N. (1965). Pathways and mechanisms for foliar absorption of mineral nutrients as revealed by radioisotopes. In: Isotopes and radiation in soil-plant nutrition studies, I.A.E.A., Vienna, 387-403.

Wood, C.W., Hr. & Nash, T.N. III (1976). Copper smelter effluents on Sonoran Desert vegetation. Ecology 57, 1311-1316.

Wood, T. & Bormann, F.H. (1975). Increases in foliar leaching caused by acidification of an artificial mist. Ambio 4, 169-171.

Wu, L. & Antonovics, J. (1975). Zinc and copper uptake by *Agrostis stolonifera*, tolerant to both zinc and copper. New Phytol. 75, 231-237.

Yamada, Y., Bukovac, M.J., & Wittwer, S.H. (1964). Penetration of ions through isolated cuticles. Plant Physiol. 39, 28-32.

Zabkiewics, J.A. & Gaskin, R.E. (1978). Seasonal variation of gorse (*Ulex europaeus* L.) surface wax and trichomes. New Phytol. 81, 367-373.

Zamierowski, E.E. (1975). Leaching losses of minerals from leaves of trees in montane forest in Kenya. J.Ecol. 63, 679-687.

Zoller, W.H., Gladney, E.S., & Duce, R.A. (1974). Atmospheric concentrations and sources of trace metals at the South Pole. Science 183, 198-200.