HEAVY METAL POLLUTION IN THE

NEW ZEALAND ENVIRONMENT

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"Dalton.... for fifty-seven years... walked out of Manchester every day; he measured the rainfall, the temperature....... of all that mass of data, nothing whatever came. But of the one searching, almost childlike question about the weights that enter the construction of these simple molecules - out of that came modern atomic theory. That is the essence of science: ask an impertinent question, and you are on the way to the pertinent answer."

— p153: The Hidden Structure:
The Assent of Man
J. Bronowski.

ABSTRACT

Section I: The optimum conditions for the determination of
cadmium, chromium, copper, lead, nickel, silver and zinc by
flame atomic absorption spectrophotometry (part B) were
investigated. Elemental concentrations were determined in
samples of animal organs (organs, muscle tissue, bone and wool),
soils and plants (pasture species, natural vegetation and
bryophytes).

The historical development of non-flame atomic absorption
spectrophotometry (part C) was reviewed. Analytical methods
using the carbon rod atomizer for the determination of elemental
concentrations in natural water and tree ring-core samples were
investigated.

The analytical technique used for the determination of lead
in whole blood involved dilution with 5% Triton X-100 followed
by sample application (1 µl) to the carbon rod atomizer. A
detection limit of < 0.01 µg/ml Pb could be reached with a R.S.D.
$\sim \pm 3\%$. The effect of additives EDTA and heparin, on signal
profiles and analytical absorption curves was studied. Inter-
ferences and background absorption were also discussed.

Section II: Lead levels in whole blood of New Zealand domestic
animals using the carbon rod atomizer were investigated. Cats,
dogs and sheep showed no significant differences in lead levels
according to age whereas cattle ($t=4.67$ for 250 d.f.) and horses
($t=5.81$ for 256 d.f.) showed a very-highly significant ($P \leq 0.001$)
difference between those animals younger than 18 months compared
with all other age groups.

Generally there was little evidence for sex differentiation
for the lead content in all animal groups investigated (although
cattle showed a very-highly significant difference between male
and female - neutered animals).

Detectable differences of blood lead levels among different
breeds were only found in dogs and cattle. Sheep dogs from rural
areas showed a very-highly significant difference ($t=3.1$ for
80 d.f.) compared with pedigree dogs from city areas. It is

suggested that this is a reflection of the reduced contact with lead pollution, predominantly from motor vehicle exhaust emissions, industrial smelter fumes and service station pollutants.

The whole-blood lead concentrations of specific dogs, cattle and horses with suspected lead poisoning were also investigated.

Section III: The lead content of whole blood of 62 sheep grazed continuously for 6 months near a major highway was 0.90 µg/ml compared with 0.20 µg/ml for 38 sheep from a nearby uncomtaminated area. Accumulation of lead was observed in livers (maximum concentration of 20.0 ± 6.0 µg/g wet weight), kidneys (cortex : 154 .0 $\pm$ 34.0 µg/g w.w.) and bones (36.5 ± 4.6 µg/g w.w.) of these sheep. Edible muscle tissue showed only slight accumulation of lead.

Four sheep from the contaminated area were placed in an uncontaminated paddock and the lead content of the whole blood decreased rapidly during the first 10 days and thereafter more slowly. After 185 days, the whole-blood lead levels had still not quite reached normal levels. Similar observations were noted in the lead content of soft organs which had approached but not reached background levels. The lead content of bones had not changed appreciably in this time.

Animals from an uncontaminated area showed an immediate rise in the whole-blood lead level when placed near a major high-way.

Sheep placed in a concrete pen away from motor vehicle exhaust emissions showed a rise in lead levels of whole-blood, livers, kidney (cortex) and bones when fed with forage cut from the verges of a busy highway. Sheep placed near a highway and fed with forage from an uncontaminated area showed an increase of lead levels in the whole blood, liver, kidney cortex and bones, comparable to that of the previous experiment. High lead levels were also observed in lung tissue.

There was no evidence to suggest that lead is 'excreted' from the body organs or blood into the wool. Although washing removes a significant percentage of lead from the wool of sheep

exposed to motor vehicle emissions, lead particulates adhere and become incorporated into the wool fibres, especially in the outer 2-4cm of wool.

The lead content of the outer 2cm of wool showed a very highly significant ($P \leqslant 0.001$) correlation with the whole-blood lead content. This suggests that it is apparently possible to use easily sampled wool material in place of whole blood to assess the lead burden of sheep.

It was concluded that lead uptake by ingestion of polluted forage and by inhalation of airborne particulates are both mechanisms responsible for enhanced lead levels in sheep whole blood, livers, kidneys (cortex), bones and to some degree lungs.

Section IV: Concentrations of cadmium, chromium, copper, lead, nickel and zinc were measured in soils and pasture species along a major motorway in New Zealand. Enhanced levels of all elements were found and correlated well with traffic densities.

Concentrations in soil profiles decreased with depth and showed that the source of pollution was aerial deposition from motor vehicles. About a third of the aerial burden of each element was removable by washing of vegetation species. Highest accumulations of heavy metals were usually found on white clover and the lowest in paspalum grass. Elemental concentrations in pasture species were usually well correlated with traffic densities, particularly in the case of the grass, yorkshire fog.

Plant/soil correlations for individual heavy metals were in general poorer than for relationships involving traffic densities and concentrations in plants or soils. It is considered that apart from lead build up of copper and cadmium should give the most concern because of their toxicity and high concentrations compared with background.

Section V:

The seasonal variation in lead content of <u>Lolium perenne</u> L.

(perennial ryegrass) and <u>Trifolium</u> <u>repens</u> L. (white clover) leaves and roots at various distances along a transect across a moderately busy (less than 5000 motorvehicle/24 hours) New Zealand State Highway, north of Bulls was investigated. The influence of the particular seasonal wind direction upon the distribution of lead was indicated by the exponential decrease of lead content in soils and pasture species, resulting in elevated lead levels to a distance of at least 30 meters on either side of the highway. Significant lead accumulation occurred to a depth of 10cm. Generally the lead content of the leaves exceeded that of the roots with onethird of the lead burden being removed by washing of the aerial parts of the plant. It was also observed that agricultural activities such as ploughing may prevent the accumulation of high lead levels in the upper most 5cm of soil and thereby reducing the availability of lead to the supported pasture.

Section VI: Cadmium, copper and zinc concentrations in vegetation, soils, water and stream sediments (part B), were measured in the vicinity of the Tui Mine, Te Aroha, New Zealand. Elemental levels in leaves of <u>Beilschmiedia</u> <u>tawa</u> (Benth.& Hook f.) tawa, reflected dispersion of windborne material around an ore treatment plant. Vegetation growing over an ore body showed very high concentrations of all 3 metals accumulated by the root systems. This mode of uptake could be easily differentiated from airborne deposition by the much lower proportion of the metal burden which was removable by washing. Analysis of tree ring-core sections showed again a dissimilar pattern between airborne deposition and accumulation of metals via the root system. With airborne accumulation, tree-cores showed a significant increase of levels towards the outside of the trunk. When elements were accumulated via the root system concentrations were appreciably uniform through the entire tree trunk. Stream

sediments and waters showed very high base metal concentrations
in the immediate vicinity of the mine.

Soils and pasture species in a paddock adjacent to the
former ore treatment plant associated with the base metal mine
at Te Aroha, were analysed for cadmium, copper, lead, and zinc
at the time of closure of the mine and then 12 months later
(part C). Elevated levels of all four elements, particularly at
the end of the pasture nearest to the source of contamination,
had decreased considerably after 12 months. Analysis of
elemental concentrations in soil profiles and in pasture species
indicated loss of pollutants partly by leaching down the soil
profile and by downslope leaching along the surface.

Section VII: A comparison was made of the lead pollution
derived from a New Zealand battery factory and smelter, and from
motor vehicle emissions from a nearby major thoroughfare. Very
elevated lead levels occurred to a depth of 12cm in soils
situated near the industrial complex. Lower lead levels, found
to a depth of only 5cm, and within 30m of the thoroughfare, were
derived from motor vehicle emissions.

Elevated lead concentrations in pasture species indicated
the widespread distribution of lead particulates from the complex.
The higher lead content of leaves compared with roots reflected
the overall efficiency of atmospheric deposition of lead
compared with the alternative pathway via the soil and root
systems. The proportion of lead removable by washing from the
various pasture species organs was always higher near the
industrial complex than for those obtained from near the thorough-
fare. It is suggested that this is related to the physical
and/or chemical forms of lead at the two locations or to super-
saturation of the soil by emissions from the industrial complex.

Section VIII: The effect of lead on seedlings of Lolium
perenne L. (perennial ryegrass) and Trifolium repens L. (white
clover) was investigated by a series of pot trials involving
a sterile silica sand substrate with varying amounts of added

lead. Limiting amounts of lead were found after 14 weeks in all organs of both species for substrates containing over 1000 µg/g lead. These values were about 60 µg/g and 100 µg/g (dry weight basis)for leaves and roots of ryegrass. For clover, values of 80 µg/g, 85 µg/g and 100 µg/g were found in leaves,stolons and roots respectively. In both cases, significant uptake did not occur until 12 weeks after germination.

High lead levels in the substrate reduced plant height. A content of 500 µg/g was sufficient to cause a 50% reduction in height.

Germination of seeds of both species was retarded by high lead levels in the substrate. After 35 days, germination was 100% for lead-free substrates and only 20% and 10% for seeds of ryegrass and clover for substrates containing 1000 µg/g lead. When applied to the situation of pasture species growing adjacent to busy thoroughfares, the data indicates that ryegrass has a greater tolerance to lead than clover. Difficulties in maintaining the clover component in pastures adjacent to busy road-ways can therefore be anticipated.

Section IX: An investigation was made of the silver content of soils, stream sediments, waters and vegetation near a silver mine and treatment plant at Maratoto, New Zealand. Silver in soils showed elevated levels near the treatment plant (due to aerial fallout), and also in natural vegetation growing over the ore deposits.

Pasture soils showed silver contamination derived partly from deposition from ore trucks and partly from flooding by mineralized stream sediments. Silver in pasture species reflected the same pattern.

Silver levels in leaves and tree trunks of <u>Beilschmiedia tawa</u> (Benth. & Hook.f.) showed distinctly different mechanisms of uptake from aerial fallout and natural uptake by root systems. The silver content of stream waters and sediments,though anomalous near the deposits and treatment plant, showed a progressive decrease with increasing distance from the source.

Section X: Cadmium, copper, lead, silver and zinc were determined in bryophytes from two mining areas in New Zealand. Background concentrations of all except copper in Hypnum cupressiforme (Hedw.) were lower than in the lowest background values obtained for Swedish specimens of this species. Near the 'dusty' treatment plant at Te Aroha, all bryophytes had high metal concentrations compared with the substrate, and indicated foliar uptake of airborne contaminants compared with uptake by bryophytes in mineralized areas due presumably to passive ion-exchange at the rhizoid-soil interface.

Uptake of silver near a treatment plant at Maratoto, and uptake of heavy metals by the aquatic bryophyte Fissidens rigidulus (Hook.f.et. Wils.) were also investigated.

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GENERAL INTRODUCTION.

During the last 70 years, industrial activities have augmented the natural levels of some metals to such an extent that some are now present in the environment in quantities which may prove toxic to a whole range of animals and plants. Since the mid-1950's concern about the release of some elements, in the form of residues from industrial processes or as components of domestic wastes and consumables, has been focused on the heavy metals lead and mercury. Examination of Chemical Abstracts and other review material reveals that in the period 1950-1973, nearly 10,000 scientific papers were published concerning the biological effects of lead and lead pollution. (Brooks, 1977). In addition, essential micronutrients (copper and zinc) have attracted attention where they are found in abnormally high concentrations as have other elements such as cadmium, chromium, nickel and silver.

The discovery of increasing lead levels in Greenland snow, (Murozumi et. al., 1969), the "survey of lead in the atmosphere of three urban communities" (U.S.H. .W., 1965), and the reported high blood lead level of a control group of Manchester children (Gordon et. al., 1967), catalyzed interest in lead concentrations in air, water, food, soil, and blood.

The natural levels of cadmium, chromium, copper, lead, nickel, silver, and zinc in the environment are shown in Table 0.1. Since lead is the major element investigated in this work most of the discussion will be centred on the presence of lead in the environment.

Lead is a relatively minor constituent of the earth's crust, occurring at levels of about 15 $\mu g/g$ (igneous rocks). In its natural state, lead is found mainly as galena (PbS.) However, since lead compounds are generally insoluble and therefore poorly transferred from one phase to another (Stubbs, 1972), the concentration in natural waters is extremely low— between 0.001 and 0.01 $\mu g/g$.

As a consequence of its presence in soil and water, lead enters the food chain and becomes incorporated into plant and animal tissue. The natural lead level in vegetation (expressed

Table 0.1.
Natural Levels of Various Heavy Metals in the Environment.

Concentration in:	Heavy Metals						
	Ag	Cd	Cr	Cu	Ni	Pb	Zn
Igneous rocks (µg/g)	0.20	0.13	117	70	100	15	80
Soil (µg/g dry weight)	1.0	0.06-0.5	200	20	40	10	50
Vegetation (µg/g dry weight)	0.06	0.01	0.2	14	<5	<6	120
Fresh water (µg/ml)	0.00013	<0.08	0.00018	0.01	0.01	0.001	0.01
Marine Water (µg/ml)	0.0003	0.00011	0.00005	0.003	0.0054	0.001	0.01
Air (µg/m^3)	*	*	<0.002	<0.02	<0.002	0.8	0.7
Blood (µg/ml)	0.024	0.0074	*	1.07	*	0.2-0.4	6.5
Toxicity to plants.	Severe	moderate	Severe	Severe	Severe	Severe	Moderate

* Normal background levels not quoted as most work has been centred on anomolously high levels as a result of pollution studies.

References: Bowen (1966); Brooks (1972).

on a dry weight basis) averages around 2-3 μg/g or 70 μg/g on an ash weight basis (Brooks, 1972).

Throughout history, lead has been well known and widely used by mankind (Grandjean, 1975) and so over a long period has been dispersed by man into the environment. Furthermore, Murozumi et. al. (1969) reported very great increases in the lead concentration of snow and ice from locations in northern Greenland and the Antarctic during the past 30 years. Another geochemical indication of increasing contamination is based upon the analysis of seawater from different depths by Patterson (1971) who showed that about 1.3×10^{10}g of discharged lead entered the oceans per year, several million years ago, whilst measurement of lead in river water shows that some 2.4×10^{11}g of lead are currently entering the oceans. Analysis of lead concentration profiles showed that young waters in the Pacific and Mediterranean Oceans contain an excess of lead compared with deep older layers (Tatsumoto and Patterson, 1963) and this is due to the washout of lead aerosols with rainwater (Chow and Patterson, 1966).

Similar studies showing the increased contamination by lead have been reported by Schroeder & Balassa (1961); Ward et. al. (1974b) using tree ring-core samples, and Rühling & Tyler (1968) who analysed moss samples of up to 100 years of age from Swedish herbaria.

It is estimated that about 180,000 tonnes of lead are mobilised naturally each year throughout the World as a result of weathering processes. (Bryce-Smith, 1971). Probably 10% of this total is lost in treatment of the ore to produce the concentrate and a further 10% is lost in making pig lead (Brooks, 1977).

There are two major sources of lead pollution: industrial (including mining activities, smelters, refining lead scrap and battery factories), and emission from motor vehicle exhausts (as a result of lead alkyl additives to petrol).

The amount of lead discharged into the environment from smelters, mining activities and similar industries has only

in recent years been recognised as a major source of pollution. Lead ores average about 2% - 20% lead from which a concentrate averaging 60% - 80% is produced by a flotation process. The concentrate is roasted to remove sulphur and the lead is then smelted. The World's largest base metal smelter is situated at Avonmouth, near Bristol, England. The major investigations of heavy metal pollution from this source (Abdullah et. al., 1972; Burkitt et. al. 1972; Butterworth et. al., 1972; Little and Marton, 1972) have shown that measurable effects of heavy metal pollution in soils extended to at least 10km from the smelter and that the pattern was strongly linked with the prevailing wind direction. Similar lead patterns in the leaves could be detected up to nearly 40 km away from the source. Washing procedures removed 85% of the lead burden from elm leaves, indicating the airborne nature of the lead pollution. Particle sizes of metallurgical dusts and fumes from smelters can range from 0.001 to 100 μm. Other investigations near industrial smelters at Swansea, South Wales and Cockle Creek, Newcastle, Australia (Goodman and Roberts, 1971; Mayman, 1972) showed similar elevated lead levels in soil and air samples within distances of 16km from the source.

Lead pollution from mining activities has been studied to a lesser degree than for smelters. Several investigations on soils, grass, vegetables and drinking water from lead - rich environments (Crudgington et al, 1970; Chisnall and Markland, 1971; Markland and Vallance, 1971; Page et. al. 1971; Brooks, 1972; Ward et al, 1976), showed lead levels of up to 2-5 μg/g (drinking water), 250-6680 μg/g (soil), 4 μg/g (vegetables) and 200 μg/g (grass : dry weight basis). Such mining activities do not directly appear to present such a large problem as other sources of lead pollution due to the absence of a gaseous component and the fact that operations are restricted to areas well away from population centres. However, dust from opencast operations and ore treatment plants could scatter from the mining area, large amounts of lead as well as other heavy metals such as cadmuim, copper, silver and zinc, thus presenting a

pollution problem.

Emission from motor vehicle exhausts is by far the most serious source of lead pollution. Antiknock lead alkyls in the form of tetraethyl lead (TEL) and tetramethyl lead (TML) are added to petroleum spirit in the range of 2-4g of TEL per gallon. During driving, 25% to 75% of the lead is emitted into the atmosphere as airborne particulates, depending on driving conditions (Habibi, 1973; Cunningham et. al., 1974; Huntzicker et. al., 1975). Ter Haar et. al. (1972) reported that 18% of the lead consumed is exhausted as particles of less than 5µ mean maximal diameter. It has been estimated that more than half the lead exhausted in city driving is less than 8µ, 40% is less than 2µ with an increase in the proportion of particles of large diameter emitted with high speed driving (Hirschler et. al., 1957; Mueller et. al., 1963; Hirschler and Gilbert, 1974). As a result of this lead particulate emission, measurements in Stockholm (Laveskog, 1971) showed that aerial tetraalkyl lead is present in concentrations exceeding $0.5µg/m^3$ in the rush hours while otherwise it is around $0.1 µg/m^3$. Cities like Los Angeles have a lead value of about $5 µg/m^3$ (Hall, 1972) in the atmosphere although lead levels of $71.3 µg/m^3$ have been recorded during peak traffic periods on Los Angeles freeways (U.S.HEW, 1966).

The extensive literature devoted to lead pollution of the atmosphere, soils and vegetation along major highways as a result of motor vehicle exhaust emissions, generally concludes that wind direction and general traffic movement patterns along the highway influences the lead levels measured (Warren and Delavault, 1960; Cannon and Bowles, 1962; Atkins 1969; Singer and Hanson, 1969; Chow, 1970; Smith, 1971). The distribution and degree of accumulated lead from motor vehicle emissions in the New Zealand environment has been reported by Ward (1974a).

Although lead pollution is directly related to either industrial or motor vehicle emissions, other sources worthy of mentioning are : the release of soluble lead from glazed earthenware surfaces into the liquids contained in the vessel,

(Gilfillan, 1965; Klein et. al., 1970) and lead poisoning
(particularly in children) from lead in paint pigments (Copeland, 1971).

It is clear that Man's efforts have seriously upset the
natural cycle of lead in the environment as shown in Figure 0.1.
and as a result of the continuing discharge of lead compounds
into the environment, serious consideration has been given to the
effect of present lead levels in Man which are closer to the
threshold of potential clinical poisoning than those for any
other toxic chemical pollutant (Bryce-Smith, 1971 a, b).
Patterson (1965) calculated the natural daily intake of lead,
both from the diet, through food and drinking water, and from
the atmosphere, concluding that an estimate of the natural body
burden is 2 mg lead / day / 70 kg of body weight.

Lead may be taken into the body by inhalation, ingestion or
through the skin. The uptake of any inhaled particulate mater-
ial is a function of its size and solubility. The size of the
particle will determine the fraction which is deposited in the
lung. Percentage deposition increases with particle size from a
minimum of 25 percent for particles approximately 0.5μ in
diameter to a maximum of almost 100 percent for particles
greater than 25μ. These particle sizes are within the limits of
those associated with motor vehicle exhaust emission particulates
(Robinson et. al., 1967).

Inorganic lead (Pb^{2+}) is a general metabolic poison which
may accumulate in a number of body tissues such as erythrocytes,
liver, and kidneys. It inhibits enzyme systems (delta-amino.
levulinic acid (ALA) dehydrogenase) necessary for the formation
in bone marrow of haem, the pigment which combines with protein
to make haemoglobin. Young children are particularly affected
and can suffer mental retardation and semi-permanent brain
damage (Vigliana and Zurlo, 1951; Harrison et at., 1969;
Catton et. al., 1970). This susceptibility by children to lead
poisoning is recognized in the assessment of the toxic level in
the blood which for adults is regarded as 0.8 µg/l but for
children only 0.25 µg/l (Zielhuis, 1972). Symptoms of lead

Figure 0.1.

Cycle of lead in the environment.

1. Contamination of water by lead pipes.

2. Contaminated water drunk by humans.

3. Lead enters water via weathering processes.

4. Mining operations.

5. Lead smelting.

6. Uptake of lead by plants via root systems.

7. Smelter fumes pollute air.

8. Contaminated plant food eaten by humans.

9. Polluted air, deposits lead on vegetation.

10. Lead pollutes air via motor vehicle exhausts.

11. Contaminated vegetables eaten by food animals.

12. Food animals eaten by humans.

13. Children injest lead from paint flakes.

14. Lead glazes contaminate foodstuffs eaten by humans.
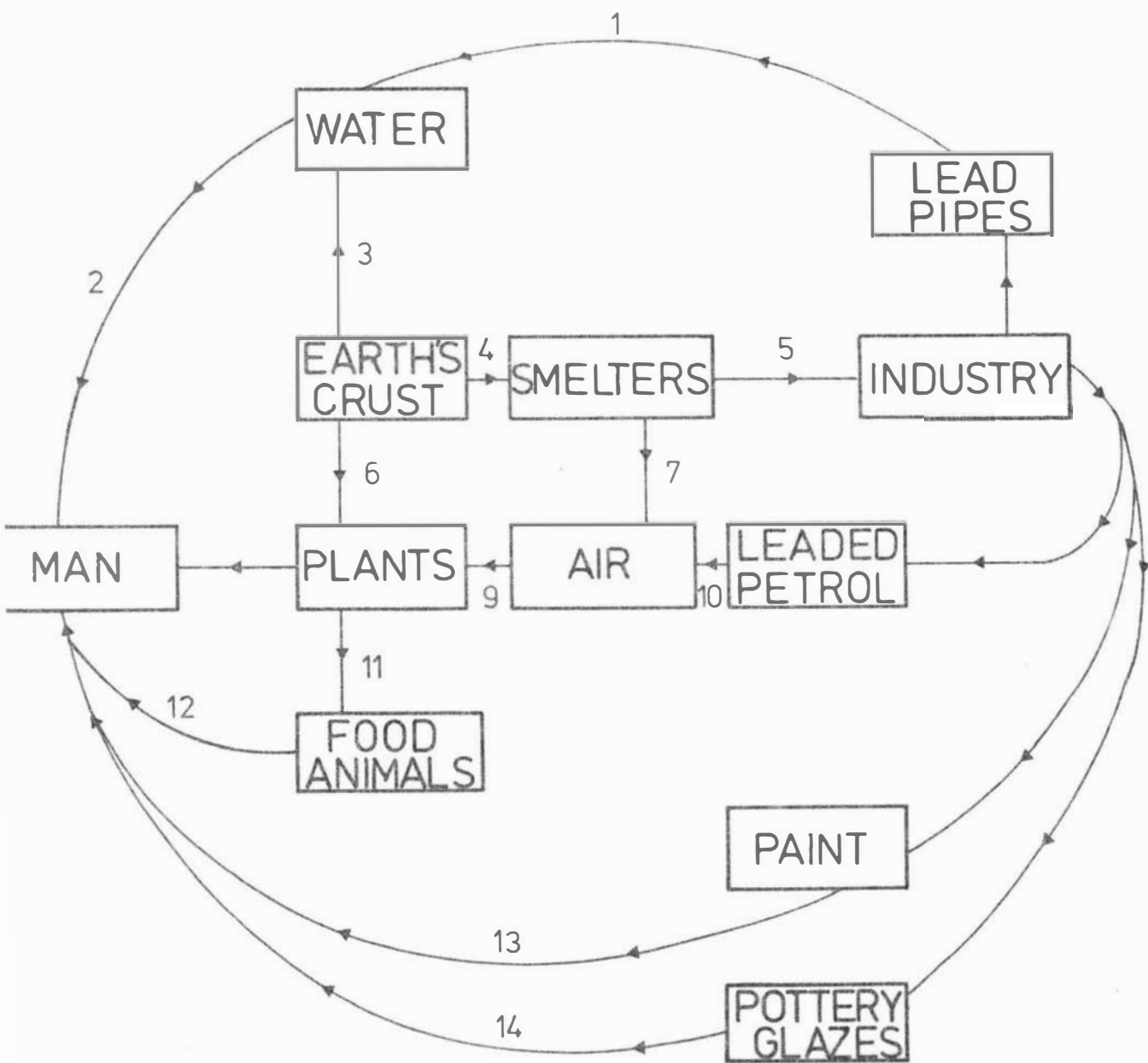
poisoning range from mild (headache, fatigue, constipation, mild anaemia) to severe (nephritis, encephalopathy). The most insidious effect of inorganic lead is its ability to replace calcium in bones and remain there to form a semi-permanent reservoir for long term release long after the initial absorption. The metabolism and pathological effects of lead are reviewed by Waldron & Stofen (1974).

Organic lead as TEL or TML is even more poisonous than inorganic lead. Lead as the triethyl-lead ion (Et_3Pb+) formed in the liver from TEL has a special affinity for lipoid and nerve tissue especially in the brain at greater concentrations (Bryce-Smith, 1971). As a result, the earliest symptoms of lead poisoning from this source are psychical, such as excitement, depression and irritability. (Hunter, 1969).

Average blood levels in adults are reported to range from 0.2 to 0.8 $\mu g/g$ lead. (Kehoe et. al.,1940; Goldwater and Hoover, 1967). Many investigations have shown blood levels exceeding these values in suburban and large city communities such as Manchester (Gordon et. al.,1967), Philadelphia (Ludwig et. al., 1965) and Tokyo (Tsuchiya et. al., 1975). Other methods of evaluating lead poisoning other than by blood are by using hair or urine samples (Kopito et. al., 1967; Kehoe, 1969; Reeves et. al., 1975). Renshaw et. al. (1972) found that analysing hair segments adjacent to the scalp after thorough washing was the best measure of the body pool of lead and concluded that the concentration of lead increased with the distance from the hair root.

Some cases of mild lead poisoning can be treated by "chelation" using ethylenediamine tetra acetate (EDTA). Unfortunately, this procedure does not cure permanent brain damage which may have occurred.

It should be pointed out however that although this study is centred mainly on the levels of lead in biological samples, some mention of the toxicity of cadmium, chromium, copper, nickel, silver and zinc should be made.

The ability of plants to absorb and concentrate cadmium means that it is a real danger to herbivores and a potential danger to carnivores. Fortunately retention is very low (1-2%) and accumulation is necessarily very slow. However, atmospheric cadmium from industrial environments (ore treatment plants and smelters in particular) can account for larger quantities of cadmium being retained by the body. Exposure to high environmental cadmium levels can result in permanent hypertension, cirrhosis of the liver and lung damage. Similarly, copper, chromium and nickel are severely toxic to plants at very high concentrations.

Zinc is an essential micronutrient for micro-organisms, plants and animals. In high concentrations, zinc is normally toxic to living systems, although there is evidence that some plants accumulate as much as 15% of their dry weight as zinc and are unaffected (Higgins and Burns, 1975).

Silver is very toxic to plants (Brooks, 1972). A man weighing 70kg, consuming 750g/day dry weight diet would have to exceed 60 mg silver/day to reach the toxic limit. Normal silver levels are 0.06 - 0.08mg/day (Sax, 1975). Absorption of silver results in a generalised greyish pigmentation of the skin and mucous membranes (argyria) and deposition of silver in the blood vessel walls, kidneys and pituitary glands. A comprehensive review on silver is presented by Boyle (1976).

In view of the extensive evidence of pollution from heavy metals in other countries it was considered that further surveys of the effect of such heavy metals (particularly lead) upon the New Zealand environment was of some urgency.

Lead as an environmental pollutant in New Zealand is associated mainly with industrial operations (mining activities, battery factories and smelting) and as motor vehicle exhaust emissions.

Cadmium, copper, lead and zinc were first mined in the Coromandel region of New Zealand near Te Aroha in 1884 with a view to supplying flux for smelting the Wairongomai ores, but as the ore was found to contain not only lead but also zinc, it was unsuitable for this purpose. In 1897 the area was taken over by the Tui Company as a base metal proposition. There are two reefs known as the Champion and Raukaka. An average assay of the primary ore (Williams, 1965) showed levels of 0.62% copper, 7.01% lead and 16.68% zinc. From 1964 the Tui Mine was under the management of the Norpac Mining Company, until 1974 (when the mine was closed), ore from the two lodes was being mined at the rate of 120 tonnes per day (Wodzicki and Weissberg, 1970). Geological investigations (Henderson and Bartrum, 1913; Cochrane, 1969; Weissberg and Wodzicki, 1970) have shown that the metallic lode body is basically quartz-pyrite, sphalerite, chalcopyrite and galena. Quartz is the main gangue material.

The base metal ore mined in the two lodes was crushed prior to separation procedures. The dust from such operations presents a serious problem of lead dispersion within the immediate environment composed of forest (large Beilschmiedia tawa trees) and a dense thicket of understorey and secondary growth species such as Melicytus ramiflorus, Hedycarya arborea, Brachyglottis repanda and Schefflera digitata.

An aerial view of the Tui Mine, Te Aroha, is shown in Plate 0.1. Reference positions are shown in Figure IV.1. and on the acetate film positioned over the plate.

Following the crushing procedure, the base metal ores were concentrated by a flotation process into copper and lead-zinc concentrations. These concentrates were then exported for smelting since no such industry has been established in New Zealand. The flotation process used may also present a major source of environmental dispersion of cadmium, copper and zinc in the form of soluble metals in the water.

A view of the Tui Mine ore treatment plant, settling pond (in fore-ground) and the immediate environment at Te Aroha is shown in Plate 0.2.

Plate O.1.
Aerial view of the Tui Mine, Te Aroha.
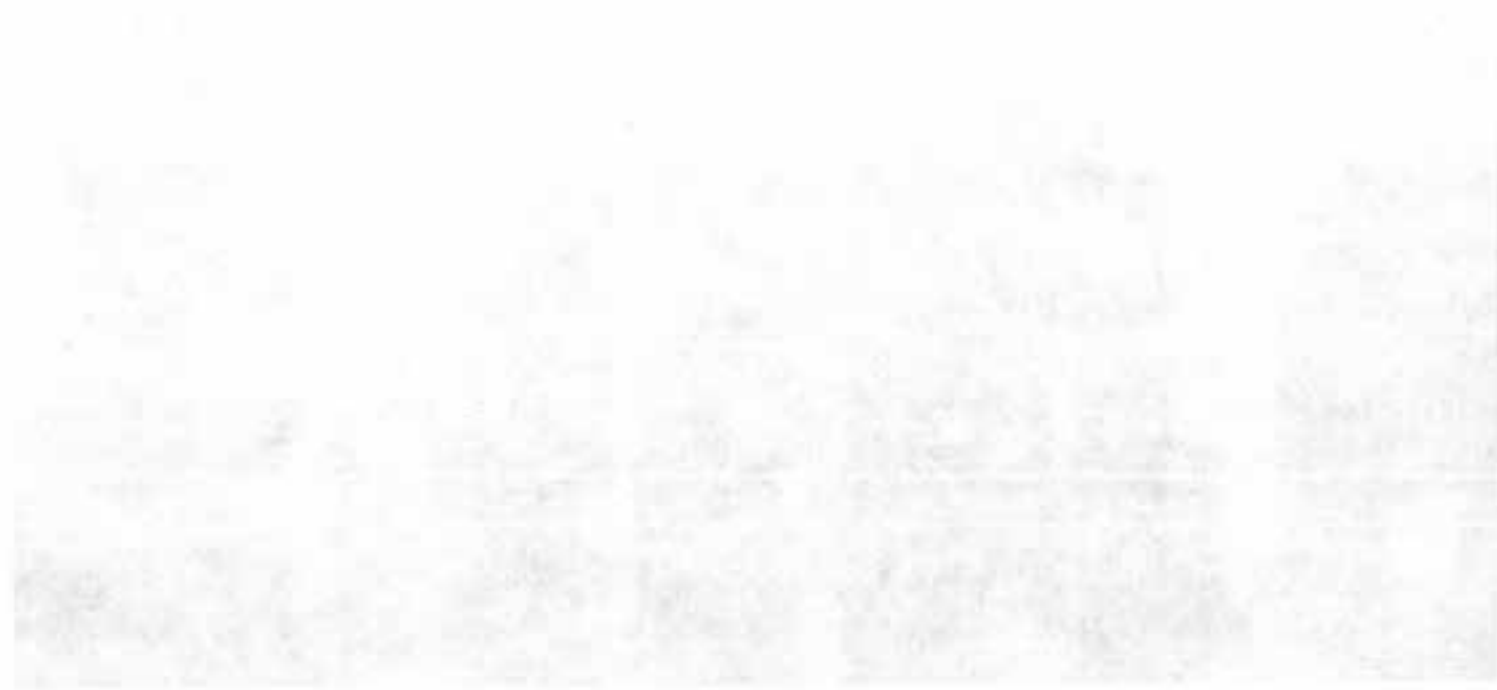
Mine
opening

Treatment plant

Raukaka lode

Mineralised
outcrop

R

Settling pond

Champion lode

Plate O.2.

A view of the Tui Mine treatment plant, settling pond and the immediate environment, Te Aroha.

In contrast to a study of cadmium, copper and zinc levels in soils and vegetation as a result of the airborne exposure from the Tui Mine ore treatment plant, experiments were proposed to determine the cadmium, copper and zinc uptake and accumulation in vegetation ($\underline{B}$. $\underline{tawa}$) growing over a base metal deposit at Te Aroha (the Raukaka lode). The results of these investigations are reported in Section IV B. In Section IV. C. there is an assessment of the accumulation of cadmium, copper, lead and zinc in the local environment, caused largely by air-borne particulates from the ore treatment plant falling upon vegetation and soils in a nearby pasture over a period of time (at closure of the ore treatment plant and 6 months later).

Because of the known toxicity of silver towards animal and plant life (Sax, 1975), and because of the virtual absence of studies on pollution from this element in the vicinity of industrial establishments and mines, a study was made of the total aerial silver burden in soils and vegetation derived from a mine and treatment plant at Maratoto, which is 36 km N. of the Tui Base Mine.

The first discovery at Maratoto was made in 1887 when a specimen was found with a reported yield of 80 oz gold and 2,146 oz silver per ton (Williams, 1965). The history of mining in Maratoto (Bell and Fraser, 1912) was one of repeated failures, partly owing to the high cost of treating relatively low-grade argentiferous ore, and partly because the ore was found to give place in certain of the low-level adits to barren calcitic veinstone. The rocks of the area are largely Tertiary calc-alkaline volcanics that range in composition from andesite to rhyolite (Weissberg and Wodzicki, 1970). The main economic zone is centred around the Silver Queen Reef which consists mainly of cavernous quartoze replacements after calcite, with minor ribs of massive quartz, the whole being stained rusty brown and black with iron and manganese oxides. Certain lenses of the vein-stones carry argentite (Ag_2S) and hessite (Ag_2Te).

An aerial view of the Maratoto mining area is shown in Plate 0.3. The acetate film cover illustrates particular points

Silver Queen Reef — S.Q.R

Mining area

Treatment plant acess road

Treatment plant

Pasture transect

Maratoto stream
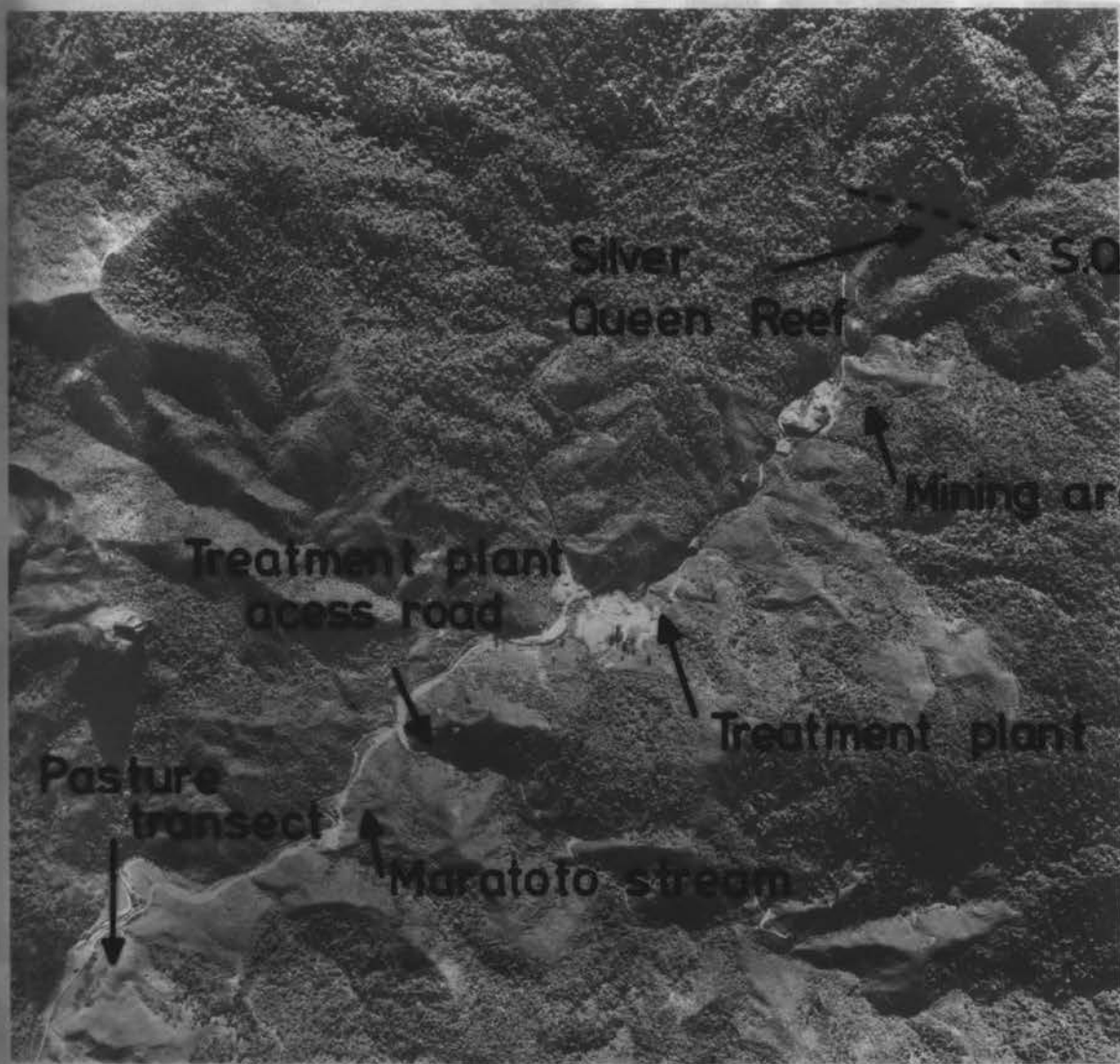
corresponding to Figure IX.1. Plate 0.4. shows the immediate
area surrounding the Maratoto ore treatment plant (above), and
the Silver Queen Reef area (below).

The surrounding environment is principally secondary growth
with a collection of Beilschmiedia tawa. Mining operations are
very similar to those of the Tui Mine, Te Aroha, where ore
crushing and conversion to a finely divided concentrate enables
large amounts of silver to be dispersed from the vicinity of the
ore treatment plant. The pattern of silver distribution in
pastures and soils resulting from fallout from ore trucks was
compared with that derived from the treatment plant. The results
of these investigations are reported in Section IX.

The assessment of background levels for heavy metals in
bryophytes is of considerable importance especially in many
countries in industrial Europe, since as a result of extensive
heavy metal contamination from mining activities, industrial
complexes etc. (Ruhling and Tyler, 1969) the overall heavy metal
content of background samples has increased. True background
values are easily obtained in the New Zealand environment (as a
result of the reduced presence of industrial contamination)
allowing for comparison with those heavy metal concentrations
derived from mining activities at Te Aroha and Maratoto.
Particular interest was given to the bryophyte Hypnum cupressi-
forme (Hedw.) as various studies on heavy metal uptake by this
bryophyte have been reported overseas. The conclusions of this
investigation are presented in Section X.

Finally, mention should be made of the two major sites of
urban lead pollution in New Zealand that were investigated in
this study.

The distribution of lead from industrial activities such as
battery factories and smelters is surveyed in Section VII. The
Te Papapa battery factory and smelter is situated in the industrial
region of Auckland City, at the intersection of two major
suburban thoroughfares. The smelter associated with the battery
factory is a secondary smelter (i.e. processing scrap from old
batteries). The main chimney is approximately 30m high, giving

Plate O.4.

A view of the immediate area surrounding the Maratoto
ore treatment plant (above) and the Silver Queen Reef
area (below), Coromandel.

a direct source for lead fallout and distribution to considerable distances from the battery factory area.

An aerial view of the Te Papapabattery factory and smelter is shown in Plate 0.5. The acetate film cover illustrates the sampling sites associated with Figure VII.1.

The magnitude and distribution of lead particulate pollution from motor vehicle emissions is best illustrated by the Auckland Motorway (having a maximum traffic density of 63,500 vehicles/24 hours). Apart from lead, very little attention has been paid to the possibility of pollution from other heavy metals derived from motor vehicles (such as cadmium, chromium, copper, nickel and zinc). The results of these investigations are reported in Section IV. A view of the sampling sites on the median strip of the Auckland Motorway is shown in Plate 0.6.

Overall, the work presented in this thesis can be divided into the following aspects of heavy metal pollution in New Zealand:

(i)   the development of atomic absorption techniques (flame and non-flame) to study lead in animal whole blood and heavy metals in general in vegetation, natural water, soils, stream sediments, wool and animal tissues (Section I),

(ii) a study of the general lead levels in domestic animals (cattle, cats, dogs, horses and sheep) as a function of age, sex and breed, and special cases of general lead poisoning in cattle, dogs and horses associated with exposure to lead from water transported by lead piping and service station areas (Section II),

(iii) a study of the contribution of airborne lead particulate distributions from motor vehicle emissions to the levels measured in sheep whole blood, organs, muscle tissue, bones, and wool as a result of exposure to lead either by ingestion or inhalation (Section III),

Plate O.5.

Aerial view of the Te Papapa battery factory and smelter, Auckland.

Major thoroughfare

Battery storage area

Battery factory

Smelter

Plate 0.6.

A view of the sampling area in the middle of the
Auckland Motorway, Auckland.
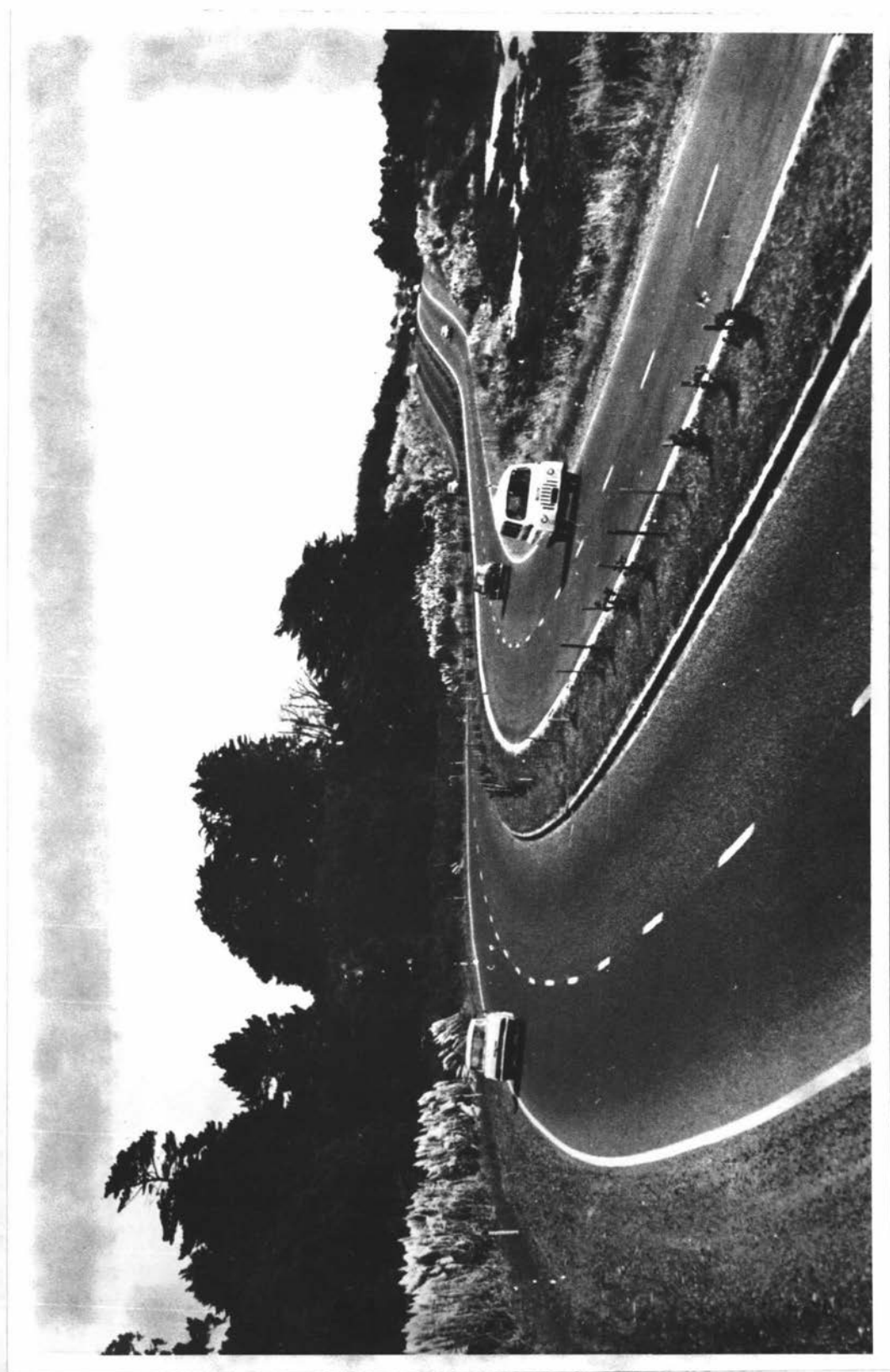
(iv)   a study of the associated levels of cadmium, chromium, copper, lead, nickel and zinc from motor vehicle emissions in relation to traffic density; pasture species and soil depth along the Auckland Motorway (Section IV); and the distribution and accumulation of lead from motor vehicle emissions in roadside pasture and soils with respect to individual pasture species and to study the seasonal variation in lead levels (Section V),

(v)   to study the influence of lead distribution and accumulation from industrial activities such as the Te Aroha base metal mine and ore-crushing treatment plant (Section VI) including the environmental levels of cadmium, copper and zinc: and from the Te Papapa (Auckland) battery factory and smelter (Section VII),

(vi)   to investigate the mode of uptake of lead by seedlings of *Lolium perenne* L., and *Trifolium repens* L. in order to determine the relative importance of lead absorption either via the root system or by airborne particulate deposition in the real situation (Section VIII),

(vii)   to study the distribution and deposition of silver as a result of mining activities at Maratoto (Section IX) and to combine this with an assessment of natural background and anomalous levels (from mining activities) of cadmium, copper, lead, silver and zinc in various New Zealand bryophytes, in particular *Hypnum cupressiforme* (Section X).

SECTION I
ANALYTICAL METHODS.

A. INTRODUCTION

In recent years the tremendous progress made in environmental chemistry has been a direct result of the development of atomic absorption spectrophotometric methods (using flame and non-flame devices), direct-reading emission spectrometry, and anodic stripping voltammetry (ASV). Although there are many possible analytical techniques that can be used to determine such elements as cadmium, copper, lead, silver, and zinc in various environmental, biological and industrial matrices only colorimetry (to some degree), emission spectrometry, polarography, ASV, and AAS have any likelihood of fulfilling the requirements of speed, sensitivity and reproducibility.

The main colorimetric method used for the determination of such elements as lead, is based on a dithizone extraction (Stanton, 1966). Dithizone is a reagent of more than adequate sensitivity and, provided that certain complexing agents are present, is of reasonable selectivity. Solutions of lead dithizonate in carbon tetrachloride have a maximum absorption at a wavelength of 520nm and obey the Beer-Lambert law up to about 3 µg/g Pb. However, if the steps involving the buffering of the solution to pH 9 for the subsequent extraction of lead are not carried out as rapidly as possible, samples containing significant amounts of calcium and phosphate (especially silicate rocks and soil, and whole blood samples) may give some precipitation of calcium phosphate that may occlude lead and cause low recovery values. A particular disadvantage of the dithizone method is interference from copper, iron and zinc (Thompson and Nakagawa, 1960), which although not reacting with dithizone in ammoniacal citrate medium at a pH value greater than 8.5 when cyanide is present (whereas lead dithizonate is readily formed), give coloured compounds which inhibit the absorption value of the lead complex.

Anodic stripping voltammetry has proved to be a very versatile technique for the determination of trace elements in the concentration range of $10^{-6} - 10^{-10}$M. The application, sensitivity and limitations of this technique are summarized by Shain (1962),

Barendrecht (1967) and Ellis (1973). Early applications of ASV were carried out by Ross et al. (1956), De Mars et. al. (1957) and Martin & Shain (1958). with successful determination of trace metals in such complex media as brines (Ariel and Eisner, 1963), fresh water (Harrison et al., 1971) and blood Matson et al.(1970) Bloom & Noller (1976).

The major advantage of ASV is the increased sensitivity associated with the decreased cost of instrumentation. Searle et al. (1973) reported a technique requiring 50 µl of blood for lead analysis by ASV whereas the basic polarographic procedure of Nylander & Holmquist (1954) required 5 ml of blood with its precision being rather low and the technique lengthy and complex. In general, the best resolution and highest sensitivity for ASV are attained with a small amplitude excitation (sinusoidal or pulse) at a mercury film electrode (Copeland et al.,1973 a,b). Colovos et al. (1973) determined trace amounts of zinc, cadmium, lead and copper in airborne particulate matter by ASV and reported coefficients of variation of 3.5%, 2.5%, 2.0% and 3.0% respect- ively for the following concentration ranges (µg/15ml): cadmium (0.01-0.05), copper (0.1-0.5), lead (0.5-2.5), zinc (0.1-0.5).

As in most trace methods, sample preparation is often more troublesome than the actual measurement and usually accounts for most of the error. Two important considerations involved in the use of ASV are the interference from other chemical substances and the requirement of chemical pretreatment so that the sample is in the Pb^{2+} ion state and not in a combined, complex state (Kozlovskii and Zebreva, 1972; Neiman and Brainina, 1973).

Although direct-reading emission spectrometry affords a rapid and sensitive method for analysis of trace constituents in environmental material, the equipment is extremely expensive and as with ASV, the appropriate instrumentation is absent from our laboratory. Therefore, the availability of the carbon rod atomizer and its well-established capabilities provided the basis for this analytical method being adopted throughout most of this study.

Atomic absorption spectrophotometry has proved to be an eminently suitable method for determining lead (and most other heavy metals), especially for rapid determination of low concentrations of the metal.

Ward (1974a) reported on the development of analytical techniques associated with the determination of lead by AAS, in particular in the field of sample preparation, (including preliminary treatment: washing, ashing and acid digestion of samples). In this section the advantages and disadvantages of flame atomic absorption devices are discussed with particular emphasis on non-flame devices, in particular the carbon rod atomizer.

Of major interest in this study is the determination of lead in whole blood samples. Table I.2. in Part C of this section summaries the major contributions by various authors to the different analytical techniques such as optical emission spectroscopy, polarography, colorimetry, atomic fluorescence as well as those methods already mentioned in this introduction. Special attention is given to the volume of whole blood required for analysis, the detection limits and any particular experimental procedures used.

The main disadvantage of flame AAS is the volume of the blood required for each analysis; - a 4 ml. sample of whole blood may contain less than 1.0 µg lead and so to determine the whole-blood lead content using conventional AAS methods requires the instrument to be operated at or near its extreme detection limit of the element. Although whole-blood lead can be pre-concentrated by chelation and extraction into an organic solvent, this introduces the possibility of reagent blank interference. Therefore it is necessary to develop a technique for whole-blood lead determination using CRA methods. The analytical and medical advantages of this technique are also discussed in this section.

B. FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY.

1. General Introduction.

The development and use of atomic absorption spectrophotometry (AAS) since its inception by Walsh (1955) has been extremely rapid. Briefly, "atomic absorption spectrometry is a spectrochemical process whereby a free atom absorbs radiation of the same wavelength which it emits when it is in a state of excitation." Measurement of the extent of radiation absorbed enables the concentration of the element to be determined.

Any literature survey of AAS would be rather extensive. Brooks & Symthe (1975) reviewed the progress of AAS for the period 1955-1971, discussing the following topics: the volume of literature, countries in which research was carried out and the language in which the work was published, the identity of the principal journals which publish atomic absorption papers, broad categories of research, and the economic benefit of the technique.

The application of flame AAS is extensively outlined by Margoshes & Scribner (1966, 1968); Kirkbright (1971); Winefordner and Vickers (1970, 1972, 1974); & Hiefije et. al. (1976). This series of Analytical Chemistry reviews gives a detailed account of publications developing the various instrumental applications and methods of flame cells. It is not the aim of this study to conduct a detailed review of the already well established techniques of flame AAS. Instead, flame and non-flame methods will be compared and their respective advantages and disadvantages reviewed.

The advantages of flame AAS atom cells can be generally outlined as follows:

(i)   they are convenient to use, reliable and relatively free from a tendency to memory effects. Most flames in common use can be made virtually noiseless and safe to operate,

(ii) most burner systems are small, durable and inexpensive sample solutions are fairly easily and rapidly handled by the use of relatively simple nebuliser assemblies;

(iii)   a wide variety of flames are available to allow the selection of optimum conditions for many different analytical purposes;

(iv)   the signal-to-background and signal-to-noise ratios obtainable are sufficiently high to allow adequate sensitivity and precision to be obtained in a wide range of analyses at different wavelengths between 200 and 800nm.

Although most of these advantages of flame AAS facilitate routine analysis of many elements and sample matrices, a detailed review of the disadvantages of flame AAS will be given in Section I. C. in order to place it in perspective against flameless AAS.

2. Instrumentation.

Essentially an atomic absorption spectrophotometer consists of:-

(i)   a stable radiation source emitting atomic spectra including resonance lines,

(ii)   an atomizing device producing an atomic vapour (usually a flame),

(iii)   a monochromator to isolate the resonance line,

(iv)   a radiation detector (usually a photomultiplier), coupled to amplification and readout facilities.

Analyses were carried out on a Varian Techtron AA5 atomic absorption spectrophotometer with an air-acetylene flame and Varian Techtron hollow cathode lamps.

The fuel/oxidant mixture of air-acetylene is particularly suitable for lead which does form highly refractory oxides. This flame also gives an approximate temperature of $2450^{\circ}K$ which is important in the production of free Pb^{2+} atoms and reduces the chemical effects of radicals and other substances present in the flame.

Correction for non-atomic absorption or background absorption (see section I. C. 6b) is achieved by means of the hydrogen continuum source with a spectral range including the same wavelength as the analyte. For routine analysis a Varian Techtron BG 6 background corrector fitted to the spectrophotometer was used.

3. Preparation of standards.

A stock solution was prepared which contained 1000 µg/ml of the analyte being investigated, from which working standards were prepared freshly for each day's analysis by successive dilutions to give standards over the range of 1-100 µg/ml. All the chemicals used were of analytical grade purity.

All potential sources of contamination of the standard solutions were examined. All containers and equipment were thoroughly cleaned and solutions were stored in polypropylene bottles to avoid contamination and to reduce the danger of absorption of lead on to the walls of the container.

4. Preparation of samples.

Samples analysed by flame AAS were prepared by the following methods:

(a) Animal organ samples.

(i) organs, muscle tissue and bones.

All animal organs, muscle tissue and bones were prepared by ashing 1.0g (wet weight) at 450°C in a muffle-furnace and re-dissolving in 2M. hydrochloric acid (prepared from a redistilled reagent) for analysis.

The alternative method is to use $HClO_4$ which is rather expensive and dangerous (Stanton, 1966). The variation in lead recovery as a result of ashing and acid digestion of the sample was reported by Ward (1974a).

(ii) wool.

10cm lengths of sheep's wool (noting which was the inside end) were divided into washed and unwashed groups and then cut into 2cm lengths. Washing was performed by placing the wool in polythene bottles with 150ml of 0.2% detergent solution. The bottles were shaken for 30 minutes with a mechanical shaker. Samples were extracted and washed with 100ml of deionized water, placed on a Büchner funnel and washed with eight further 100ml portions of deionized water. During preliminary trials, lead was undetectable (< 0.05 mg/l) in the detergent solution before the washing procedure. After drying for 3 hours at 110°C samples of 0.5-2.0g were ashed at 450°C and redissolved in 2M hydrochloric

acid.

(b) <u>Soil samples.</u>

Soil profile samples were collected by means of a core extractor with a diameter of 2.5 cm. Each core was divided into 1.0cm lengths. Soil samples and stream sediments were dried for 3 days at 60°C and sieved to -60 mesh. Digestion of 0.1g samples was carried out with 10ml of a 1:1 mixture of concentrated nitric and hydrofluoric acids contained in 50ml polypropylene squat beakers. The solutions were taken to dryness over a water-bath and the residues redissolved in 2M hydrochloric acid (1.0 to 10.0ml depending upon the elemental concentrations of the sample being analysed). Further dilution was necessary in some cases (eg. samples from the Te Papapa battery factory - Section VII).

(c) <u>Plant (pasture, natural vegetation and bryophyte)samples</u>

(i) pasture and natural vegetation samples.

Pasture and vegetation samples were divided (in most cases) into washed and unwashed portions for analysis, the washing being carried out by agitation in slowly-running tap water followed by rinsing in distilled water. Pasture species were also divided into leaves, roots, stolons etc. Samples (5-10g) were dried at 60°C and ashed at 450°C. Subsamples of ash were dissolved in appropriate volumes of 2M hydrochloric acid.

(ii) bark and twig samples

Samples of <u>Beilschmiedia tawa</u> (Te Aroha mining area -Section VI and the Maratoto silver mining area -Section IX), were collected at heights of approximately 2-3 m   and washed in distilled water to remove any surface contamination. Preparation was then carried out as above for pasture and natural vegetation samples.

Tree ring-core samples are so small that dissolved ashed samples have cadmium and silver concentrations at the lower detection limit for flame AAS. Therefore tree ring-core samples were analysed by use of CRA (Section I. C4) for cadmium and silver. Copper and zinc levels were determined by normal flame AAS methods as for pasture and natural vegetation samples.

(iii) bryophyte samples.

The growth form of many bryophytes tends to encourage accumulation of considerable debris that is very difficult to separate from the plant material. This problem has been extensively discussed by Shacklette (1965). Unless the material is carefully cleansed, contamination of the sample will occur, yielding highly variable and unusually large ash values.

All bryophyte samples were oven dried at 60°C for three days. Using procedures recommended by Shacklette (1965), the material was teased, placed in a -60 mesh sieve and the majority of the soil or substrate particles removed by blasts of compressed air. Samples were then washed with high pressure tap water for twenty minutes. The wash was terminated after agitation for 2hr. in distilled water. The samples were then oven dried at 60°C, ashed at 450°C and dissolved in 2M hydrochloric acid at a ratio of 0.05g ash to 10ml of acid.

5. Detection limits and instrumental operating conditions.

(a) The analysis line, sensitivity and detection limits.

The most sensitive analysis lines (nm) for cadmium, chromium, copper, lead, nickel, silver and zinc are shown in Table I.1. together with their sensitivity (μg/ml for 1% absorption)in an air-acetylene flame.

The limits of detection for this study, in general, are not important, for the samples investigated had elemental concentrations in solution which were in most cases 10- fold higher than normal environmental (background) values. Where the elemental concentration in solution approached the lower limits of detection, flame AAS methods were replaced by CRA. This is particularly necessary for cadmium and silver analysis of water and tree ring-core samples and lead in whole blood samples. This is reviewed in more detail in Section I. C.4a.

(b) Instrumental operating conditions.

Table I.1. gives the instrumental operating conditions for cadmium, chromium, copper, lead, nickel, silver and zinc using conventional flame AAS.

Table I.1.

Spectrographic Operating Conditions

	Element						
	Ag	Cd	Cr	Cu	Ni	Pb	Zn
Fill gas	neon	"	"	"	"	"	"
Window	pyrex	quartz	pyrex	quartz	"	"	"
Operating current (mA)	3	3	5	3	5	5	5
Strike voltage (V)	280	300	280	280	300	290	300
Operating voltage (V)	190	220	180	200	180	200	170
Spectral band width (nm)	0.5	0.5	0.2	0.5	0.2	1.0	0.5
Sensitivity* (air-acetylene flame)	0.029	0.011	0.055	0.040	0.050	0.110	0.009
Analysis line. (nm)	328.1	228.8	357.9	324.8	232.2	217.0	213.9

*ug/ml

(c) Interferences.

There are relatively few interferences in an air-acetylene flame for cadmium, chromium, copper, lead, nickel, silver and zinc. It is considered unnecessary to review any effects of interference using flame AAS as this is covered in detail in the literature.

The effects of scatter by incident light being deflected without being absorbed with the resulting spurious increase in the absorption signal, was compensated for by use of the continuous spectrum of the hydrogen lamp at the same wavelength as the absorbing line. (refer to Section I.C6b.).

6. Conclusion.

The various instrumental, sample and standard preparations associated with conventional flame AAS have been described in this subsection. Although the methods described for the analysis of cadmium, chromium, copper, lead, silver and zinc are quite adequate in various sample matrices, the application of the carbon rod atomizer was necessary for water, tree ring-core and whole blood analysis. The disadvantages of flame AAS methods as the basis for developing and investigating the use of a non-flame AAS technique for these sample matrices is described in the next subsection.

C. FLAMELESS ATOMIC ABSORPTION TECHNIQUE.

1. General introduction.

In the past, atomic absorption spectroscopy (AAS) has been widely used as the main technique for inorganic trace analysis. As such, the requirement to produce a population of free atoms within a well-defined optical path must involve an atomization method that is simple, fast, reproducible and efficient. In order to increase the sensitivity of AAS, several workers have endeavoured to increase the efficiency of the atom reservoir by using more efficient nebulizers (Hell et. al., 1968: Veillon and Margoshes, 1968), slotted burners (Russell et. al., 1957) and reducing high temperature flames (Willis, 1965; Amos and Willis, 1966; Mossotti and Duggan, 1968; Pickett and Koirtyohann, 1968).

Although there are many advantages in using flame cells (as outlined in Section I, B1.) in particular the ease and rapidity of operation, recent studies in AAS have been centred on the development of non-flame cells in an attempt to overcome some of the disadvantages of flame cells. The disadvantages of flame cells can be generally outlined as follows:

(a) the efficiency of pneumatic nebulizer spray chamber systems is low; only 10-20% of the analyte solution reaches the flame using indirect nebulizers,

(b) flame cells are only rarely able to atomize solid samples directly,

(c) the amount of sample finally reaching the flame and hence the production of atoms in the ground state, is governed by many variables such as flame temperature, interactions between flame gases, matrix components and analyte, chemical interferences, and the extent to which the analyte molecular species are dissociated. As the zone of the flame in which absorption actually occurs is only a small section of the whole flame, (combined with the overall effect of (a)), the number of atoms contributing to the analytical signal is small compared with the total amount of element aspirated,

(d)   flame gases also produce background absorption and emission bands at the wavelength of the resonance line of the analyte element. This gives rise to an unacceptable signal noise with a consequent loss of precision,

(e)   precise control over the chemical environment of the analyte and concomitant atoms in flame cells is not possible. The degree of control of chemical composition that can be obtained by variation of the fuel-to-oxidant concentration ratio is accompanied by simultaneous changes in the flame temperature and its spectral absorption characteristics.

The advent of flameless atomization has greatly reduced the limitations imposed by flame atomization processes. In particular it has increased the efficiency of atomization and reduced the undesirable influence of variable physico-chemical properties of solutions. The basic advantages of flameless AAS (in particular for the graphite furnace or carbon rod atomizer) can be outlined as follows:

(a) Pulse vaporization of the element achieved by raising the temperature under controlled conditions produces a denser population of ground state atoms, in a confined space in contrast to the low density population of the flame. This enables a higher order of sensitivity and lower detection limits along with pre-concentration of the sample on the rod,

(b)   a smaller sample size is required : less than 20 μl (0.020 ml) of sample is required for a carbon rod atomizer determination whereas a flame analysis requires about 5ml of sample,

(c)   whereas extensive sample dilution is often required for flame analysis, most liquid samples (including organic solvents and liquids with a high dissolved solid content which cannot be aspirated into a flame) can be analyzed directly by flameless cells,

(d)   prior chemical pretreatment of the sample is minimized thereby reducing the amount of sample handling. The sample can be ashed in seconds by electrical heating,

(e)   the rapid reduction of oxygen-containing components is ensured by the presence of incandescent carbon.

2. (a)   Historical development of flameless A.S.

The application in AAS of non-flame devices is extensively outlined by Kirkbright (1971); Winefordner & Vickers (1972, 1974); and Hiefije et. al. (1976). The number of publications covering this topic is far too large to review in depth, but for the sake of completeness a brief summary of the historical development of non-flame devices will be given here.

The major non-flame atomization methods that have been investigated comprise four distinct groups : furnaces, filaments, cups and rods, and other devices (cathode-sputtering cells, d.c. electric arc, induction coupled plasma etc).

As early as 1873, Champion et. al., who developed the first flame emission spectrometer, introduced samples into a flame on a mounted platinum wire. A similar approach was originated by Ramage (1929) for semi-quantitative analysis; powdered sample was rolled into filter paper and introduced into a diffusion flame. The Pt-wire procedure was extended and considerably refined by Ramsay and co-workers (1950, 51, 53) and applied to the determination of sodium and potassium in micro-volumes of insect fluids. Although there have been many extensions using platinum loops, wires and boats (Haljamae and Larsson, 1968; Katz, 1968; Nesterov and Naumov, 1969); most require samples to be dried on the device and inserted into a flame. The use of this type of micro-sampling technique in AAS was developed by Delves (1970) who accurately determined concentrations of lead in 10 μl samples of whole blood after partial oxidation with H_2O_2 in micro crucibles made from nickel foil. The samples were volatilised by using an air-acetylene flame and the product was fed into a nickel absorption tube situated in the flame. The "Delves sampling cup" technique has been developed by many more workers (Fernandez and Kahn, 1971; Fernandez, 1973; Hicks et.al. 1973) as will be explained in more depth later.

(i)   furnaces

The first basic non-flame furnace atomizer was developed by King (1929). In 1959, L'vov and co-workers adapted the King graphite-type furnace to study its potential as a source of atomic vapours for atomic absorption. In a series of publications (1961-65) the potential of this crucible was extended to the analysis of nearly forty elements. The instrument consisted of a tube of graphite 5cm long, 0.25 to 0.5cm i.d. lined with tantalum foil and placed in an inert atmosphere. Initially heating was effected by a spark between an auxiliary electrode and the furnace, but later work used a simple resistive heating of the furnace.

Further non-flame devices were investigated by Vidale (1960), Mislan (1963), Choong et. al. (1964), Hudson (1964), and Tomkins & Ercoli (1967). These basically were either silica tubes or stainless-steel absorption cells heated by a resistance wire.

L'vov's graphite furnace was further developed by Massmann (1967, 1968) who described a graphite cuvette device with a micro-sample which was pipetted directly into the furnace followed by a three-stage heating programme of drying, charring and atomization. Correction for non-selective background absorption in AAS was reported using a two-channel spectrometer and monitoring the absorption of a nearby elemental non-resonance line. The "Massmann-type" graphite furnace used by Manning & Fernandez (1970) to determine copper and strontium in milk was commercially produced as a heated graphite atomizer manufactured by the Perkin Elmer Corporation. A furnace on a much larger scale and developed by Woodriff and co-workers (1968) was resistively-heated, but the sample was placed into the tube by means of a small carbon cup.

Recent developments using non-flame furnace devices have been reported by Headridge & Smith (1971) who constructed a simple induction furnace for determining volatile elements in solutions and volatile matrices by AAS. Omang (1971) determined lead in air using a graphite tube furnace with a sensitivity of 9.7 $\mu g/m^3$. High frequency induction graphite furnaces were used for the determinations of lead and cadmium in pulp and paper (Langmyhr

et. al., 1974 a), and dental material (Langmyhr et. al. 1974 b).
Similar studies have centred on the analysis of coal and coal ash
(Block, 1975), Steel (Frech, 1975, 1976 a,b) and hair (Alder et.
al., 1976).

A dual chamber furnace was developed to demonstrate the use
of the Zeeman effect for background correction in the determin-
ation of lead in 3% salt water solutions and bovine liver without
the usual drying and ashing steps. (Hadeishi and McLaughlin,
1976). The lower limit of detection was 50pg of lead.

(ii) filaments

The original work by Bunsen (1859) introduced atomization.
techniques in which a wire loop or a sample boat carrying the
sample was introduced into the hot flame gases. Several recent
non-flame devices use an electrically heated filament or boat.
Ufvarson (1967), Brandenburger & Bader (1967, 1968) measured
nanogram amounts of mercury by amalgamating it on a wire and then
heating the wire to vaporize the mercury. A platinum loop was
used by Bratzel et. al. (1969) to atomize elements from a thin
film obtained by immersion of the loop into the sample solution.

West & Williams (1969) atomized several elements using a
heated carbon filament 5 cm long and 0.6 cm in diameter with
samples being micro-pipetted into an indentation on the top of the
rod. Other applications similar to that by West were made by
Amos et. al. (1971). Kapur & West (1974) using a 3.2mm diameter
carbon filament which could accommodate a 5-μl sample drop, .
determined lead in "instant" coffee and tea powders down to 0.02
μg/g.

(iii) cups, rods and tantalum boats/strips.

The development of the "Delves-cup" technique was followed
by investigations using a graphite cup (Dolinsek and Stupar, 1973),
gold plated graphite cups (Lech et. al. 1974), and graphite discs
(Robinson et. al., 1975).

Brodie & Matoušek (1974) determined cadmium in air by
placing cut filter discs into a graphite sampling cup. The
particulate matter from samples was collected on the filter by

drawing the air through the cup with a portable pump. The cups
were then clamped between supporting rods and subjected to a
drying, ashing and atomization cycle.

The predominent advancement of non-flame devices has been in
the use of carbon rod atomizer cells (Brodie and Matoušek, 1971;
Matoušek and Stevens, 1971; Bratzel et. al., 1972). The
applications of the carbon rod atomizer will be covered in more
depth in Section II.B.2b.

Another non-graphite atomizer was Donega & Burgess's tantalum
boat (1970) which allowed larger volume samples to be used for
direct drying, ashing and atomizations. Other boat devices have
been investigated by Kahn & Sebestyen (1970); Delves (1970) and
Hwang et. al., (1971).

(iv) other non-flame devices.

Other non-flame methods of atomization which have been
investigated include cathode - sputtering cells in which atom-
ization is produced by a sputtering action similar to that of a
hollow cathode lamp. Extensions of this idea have been invest-
igated by Walsh (1962), Goleb & Brody (1963) and Massmann(1970).

The use of the d.c. arc for sample atomization in AAS has
been described by several workers (Marinkovic et. al., 1967:
Kantor and Erdey, 1969). Spark sources to atomize the sample
were reported by Robinson (1962 a,b). Similar devices include the
use of RF or microwave plasma sources (Wendtl & Fassel, 1965,
1966; Friend and Diefenderfer, 1966).

The use of lasers offers the possibility of direct atomization
for the examination of solid surfaces by AAS. The heat produced
at the solid when a focussed laser beam strikes it, may vaporize
the solid material over a small area of surface. (Rasberry et. al.
1967).

Finally, Venghiattis (1967) proposed a technique for the
direct conversion of solid samples into atomic vapour, in which
the powdered sample is mixed with a solid - propellant powder:
the mixture is then compressed and ignited.

Research is still continuing into the development of new methods and the performance of existing methods of non-flame atomization. The most promising and widely used non-flame atomizers are variously designed graphite furnaces and in particular carbon rod atomizers.

2. (b) Review of techniques for whole blood analysis.

The literature of analytical techniques in use for the determination of lead in chemical and biological systems can be divided into : optical emission spectroscopy, anodic stripping voltammetry, polarography, colorimetry, atomic absorption (flame and non-flame) and atomic fluorescence. A general review of the major workers in each of these fields is outlined in Table I.2. together with the volume of blood used, detection limits and relevant notes.

Optical emission spectroscopy, anodic stripping voltammetry and polarography generally demand high skill, are somewhat time-consuming, require a larger sample than can be generally obtained and in the case of emission spectroscopy necessitates very expensive equipment.

The main colorimetric method used for the determination of lead is based on a dithizone extraction (Berman, 1961; Stanton, 1966). Dithizone is a reagent of adequate sensitivity and provided that certain complexing agents are present is of reasonable selectivity. The main disadvantage of the dithizone technique is that it is non-specific unless the pH is rigidly controlled. Another major factor against colorimetric methods is the requirement of large samples of blood and extensive analysis times.

The anticoagulant versenate (EDTA), a common chelating agent used for the treatment of lead poisoning, interferes with most extraction or colorimetric methods requiring samples containing it to be pre-ashed before analysis.

Although AAS using flame cells has proved to be a potentially adequate method for the determination of lead in whole blood, blood pretreatment is usually required. This is because whole

Table I.2.

Review of Techniques for Whole Blood Lead Analysis

Analytical Methods	(Reference)	Volume of Blood used (ml)	Detection Limits ($\mu g/ml$)	Notes
Optical Emission Spectroscopy				
Cholak	1935	1.00	10-20	Direct spectrographic determination.
Wells & Seidner	1965	1.00	10-20	TCA precipitation of blood, supernatant placed on electrode.
Anodic Stripping Voltammetry				
Horiuchi et. al.	1968	0.20	0-50	Acid digestion, ash dissolved in HCl and run. RSD 12%
Searle et. al.	1973	0.05	0-25	Perchloric acid addition heated dist. H_2O added and lead ions concentrated on electrode (-800mv) before "stripping" in $N_2(O_2$-free) atmosphere.
Morrell & Giridhar	1976	0.10	0-05	Blood sonicated, diluted with a Met, exchange reagent, plated and stripped -no digestion step.
Polarography				
Nylander & Holmquist	1954	5.00	0-20	Nitric acid digestion, dithizone extraction in H_2O/HCl.

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Analytical Methods	(Reference)	Volume of Blood Used (ml)	Detection Limits ($\mu g/ml$)	Notes.
Sandell	1959	20.00	0.20	Acid digestion, dithizone extraction,
Keenan et. al.	1963	20.00	0.20	back extraction in NH_4Cl.
Colorimetry				
Berman	1961	1.00	0.20	TCA digestion, dithizone extraction, lead-dithizone complex, read in spectrophotometer at λ, 520nm.
Atomic Absorption : Flame.				
Berman	1964	5.00	0.20	Protein precipitation, extraction into MIBK with APDC and aspiration of organic layer.
Slavin & Sprague	1964	5.00	< 0.34	TCA digestion, chelated with NaoIt and Ketone.
Sprague & Slavin	1966	1.00	0.10	TCA precipitation, centrifugation; no chelation or extraction.
Berman et. al.	1968	0.25	0.50	as above for Berman (1964) but smaller volume for aspiration.
Hessel	1968	1.00	0.20	Protein precipitation with $HClO_4$, supernatant filtered and aspirated.

Analytical Methods	(Reference)	Volume of Blood Used (ml)	Detection Limits ($\mu g/ml$)	Notes.
Donovan & Feely	1969	25.00	0.08	Ashing, direct extraction with APDC/MIBK.
Farrelly & Pybus	1969	2.50	0.05	Direct extraction with APDC/MIBK aspiration.
Westerlund-Helmerson	1970	11.00	—	Extraction with Triton X-100, APDC/MIBK direct analysis of supernatant into flame.
Delves et. al.	1971	2.00	0.10	Acid digestion, followed by MIBK extraction (multiple element analysis technique).
Lyons & Quinn	1971	5-10.00	0.05	Lead concentrated on anion-exchange resin and aspirated.
Zinterhofer et. al.	1971	6.00	0.05	Triton X-100, APDC complex with MIBK extraction.
Mitchell et. al.	1972	1.00	0.05	" " " "
Amore	1974	5.00	0.08	" " " "
Atomic Absorption : Delves Cup. Delves	1970	0.01	0.01	Direct analysis, sample dried, ashed with H_2O_2 in nickel crucible, vaporized.
Fernandez & Kahn	1971	0.01	0.02	Sample dried in nickel crucible, redissolved in H_2O_2, dried and vaporised.

Analytical Methods.	(Reference)	Volume of Blood used (ml)	Detection Limits ($\mu g/ml$)	Notes.
Ediger & Coleman	1972	0.01	<0.05	Standard Delves procedure, background correction.
Joselow & Bogden	1972	0.01-0.05	0.02	Filter paper spot, analysed directly on Delves cup.
Olsen & Jatlow	1972	0.01	0.02	Albumin-coated cups, H_2O_2 digestion, dried and vaporized.
Fernandez	1973	0.01	0.01	Evaluation of techniques using Delves cup method, background absorption.
Hicks et. al.	1973	0.01	0.01	Standard Delves technique.
Rose & Willden	1973	0.01	0.04	Wet ashing with aqua regia, analysis direct in modified Delves absorption tube.

Atomic Absorption : Sampling Boat.

Kahn & Sebestyen	1970	0.020	0.001	Saline dilution, dried in sampling boat, vaporised.
Hilderbrand et. al.	1970	0.10	0.002	Protein precipitation, supernatant placed on Tantalum boat dried and vaporized.

Analytical Methods	(Reference)	Volume of Blood Used (ml)	Detection Limits ($\mu g/ml$)	Notes
Hwang et. al.	1971	0.10	700ng	Direct extraction with Saponin, formamide and APDC re-extracted in MIBK, vaporized on Ta boat.
Hauser et. al.	1972	0.50	0.002	Ta sampling boat, vacuum dried, ashed and flamed in AAS apparatus.
Hwang et. al.	1973	0.025	0.5ng	Water diluted, placed on Ta ribbon dried, ashed, atomized on ribbon in H_2 atmosphere.
Atomic Absorption : Furnace and Cuvette				
Norval & Butler	1972	0.04	0.5ng	Dilution by weight add to cuvette, dried, diluted with H_2O_2, dried and ashed on cuvette.
Ealy et. al.	1974	0.50	0.10	Diluted dist. H_2O, 10ul applied to furnace and directly dried, ashed and atomized.
Fernandez	1975	0.05	0.001	Dilution with Triton X-100, direct application to HGA-2100 graphite furnace.
Kilroe-Smith	1975	0.05	0.001	Blood extraction in HCl (10 mol / litre) and extraction in perchloric TCA and H_2O.

Analytical Methods	(Reference)	Volume of Blood Used (ml)	Detection Limits (μg/ml)	Notes.
Kilroe-Smith	1976	0.05	< 1 ng	Three different matrices; Hcl, HNO_3 and a mixture of perchloric, TCA, water. Syringed into cuvette.
Atomic Absorption : Tubes, cups and carbon rods.				
Matoušek & Stevens	1971	0.0005	10ug	Xylene added to prevent standards from soaking into rod, deuterum lamp used for background absorption.
Kubasik et. al.	1972	0.001	< 0.20	Dilution in Triton X-100 and direct analysis after background correction applied.
Kubasik & Volosin	1972	0.05	< 0.07	Dilution in Triton X-100 and direct analysis.
Rosen & Trinidad	1972	0.0005	0.005	Treated with xylene and injected in CRA and subsequently dried, ashed and atomized.
Posma et. al.	1975	0.050	0.015	Blood treated with HNO_3 in carbon-tube and subjected to dry ash and atomization cycles.
Koizumi & Yasuda	1976	0.010	0.002	Dilution with Sodium citrate and analysis on a modified Massmann type carbon atom-izer.

Analytical Methods	(Reference)	Volume of Blood Used (ml)	Detection Limits (µg/ml)	Notes.
Atomic Absorption : Solid Phase Sampler.				Direct extraction with APDC/MIBK organic
Hwang et. al.	1970	0.5	0.001	layer placed on boat dried vaporized.
Atomic Absorption : Paper filter discs.				Blood is spread on paper discs, dried,
Cernik & Sayers	1971	(Volume based)	< 0.004	vaporised on carbon cup background correction.
Cernik	1973	"	< 0.004	" " "
Atomic Fluoresence : Flameless.				
Amos et. al.	1971	0.002	0.005	Direct analysis after dilution signal measured at one wavelength, background at another, using carbon rod.
Human & Norval	1974	2-5	0.0012	Dilution with distilled H_2O and nebulised.
EVALUATION OF ATOMIC ABSORPTION SYSTEMS:				Interlaboratory determinations of EDTA,
Kepper et. al.	1970	"pooled 800ml"	----	pooled blood allowing evaluation of various methods.
Anderson et. al.	1974	< 50µl	----	Investigated AAS flame, Delves nickel cup, graphite rod, electrically heated Ta ribbon and filter paper disc.

Analytical Methods.	(Reference)	Volume of Blood Used (ml)	Detection Limits (µg/ml)	Notes
Kopito et. al.	1974	2-4ml	—	Variations in extraction procedures using TCA with APDC/MIBK,perchloric acid, HNO$_3$ system, followed by aspiration.
Baily of Kilroe-Smith	1975	0.5ml	—	Comparison of 7 different ways of preparing blood samples : with application to graphite tubes and Massmann-cuvette w
Volosin et. al.	1975	0.5ul	—	Comparison of 5 methods : a simple dilution; with Trton x-100 direct analysis with no sample preparation; and a stand- ard chelation extraction procedure.

blood, even if diluted, cannot be aspirated directly into the burner. Most procedures described in the literature generally involve a step in which blood proteins are precipitated using trichloroacetic acid (TCA), perchloric or nitric acid, or chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into methyl isobutyl ketone (MIBK) with the organic phase being aspirated directly into the flame. A good description of these techniques is given by Hassel (1968). Apart from direct solvent extraction of lead from blood samples following protein precipitation, other methods described involve time-consuming wet or dry-ashing procedures. The major disadvantage in all these procedures is the need for large sample volumes.

Most of the methods currently being used involve flameless atomic absorption devices. The main advantages are simpler sample pretreatment and the need for a lesser quantity of sample. This latter point is extremely important in cases such as the removal of blood from children. These micro-techniques require only 1-50μl whereas generally >5 ml was required for other methods previously described. One difficulty which has been investigated is that which concerns the pipetting or weighing of very small blood samples. Cernik & Sayers (1971) proposed a technique involving spotting blood on to filter papers, allowing it to dry and punching out discs of a precise diameter (with a blood volume <±7%). The discs were then directly analysed by a non-flame device.

An evaluation of non-flame atomizers for determining blood lead levels has been made by Anderson et. al. (1974), Kopito et. al. (1974), Bailey & Kilroe-Smith (1975) and Volosin et. al. (1975). The major advantage compared with AAS using flame cells, is the improvement in detection limits from 0.05-1.00 μg/ml to 0.001-0.002 μg/ml lead for non-flame devices. With the use of carbon rod or furnace techniques, selective temperatures can be used to control the combustion of organic material, prior to the atomization of the lead. This provides better precision than can be obtained with a flame.

Therefore, in this work, the carbon rod atomizer was used for the determination of lead in whole blood. In order to

achieve rapid routine analyses by this method various aspects of the experimental procedure and methods were investigated as outlined in the next subsection.

3. Instrumentation

(a) Carbon rod atomizer assembly.

A Varian Techtron AA$_5$ Atomic Absorption Spectrophotometer as outlined in Section I.33. was used throughout all experiments.

The burner (used for air-acetylene flame work) was replaced by the workhead of the Model 63 CRA : Carbon Rod Atomizer (Varian Techtron) for flameless atomization (Plate I.1.)

Power was supplied to the workhead by the CRA power pack at three different variable voltages;[*] dry 0-1.8V, ash 0.4-4V and atomize 2-9V, for varying lengths of time (5-60s, 5-60s and 0-10 seconds, respectively).

An inert atmosphere was provided for the rod by supplying argon to the workhead via a gas flow meter. Argon was allowed to flow (3.8 litres/min. for all experiments) throughout the entire cycle but hydrogen (supporting a hydrogen diffusion flame) was permitted to flow by means of a solenoid switch only during the ashing and atomization portions of the cycle (H_2 flow rate was 2.2 litres/min.) Water as a coolant flowed at a rate of 0.5 litre/min.

The recorder used was a Rikadenki Kogyo fast response (0.35s f.s.d.) Model B161. This was coupled to the A.C. amplifier readout to give a full-scale deflection with a 10mV signal. The attenuation was varied when amplification of the signal was required. The recorder was of the null-balance-point zero type which prevented base-line drift during continuious operation. Chart speeds used were between 4cm/hr and 10cm/hr.

[*] NOTE:- these voltages are actual voltages and do not correspond to the range of voltage control settings which are represented by a linear 0-10 scale on the instrument.

Plate I.1.

The workhead of the Model 63, Carbon Rod Atomizer
(Varian Techtron).
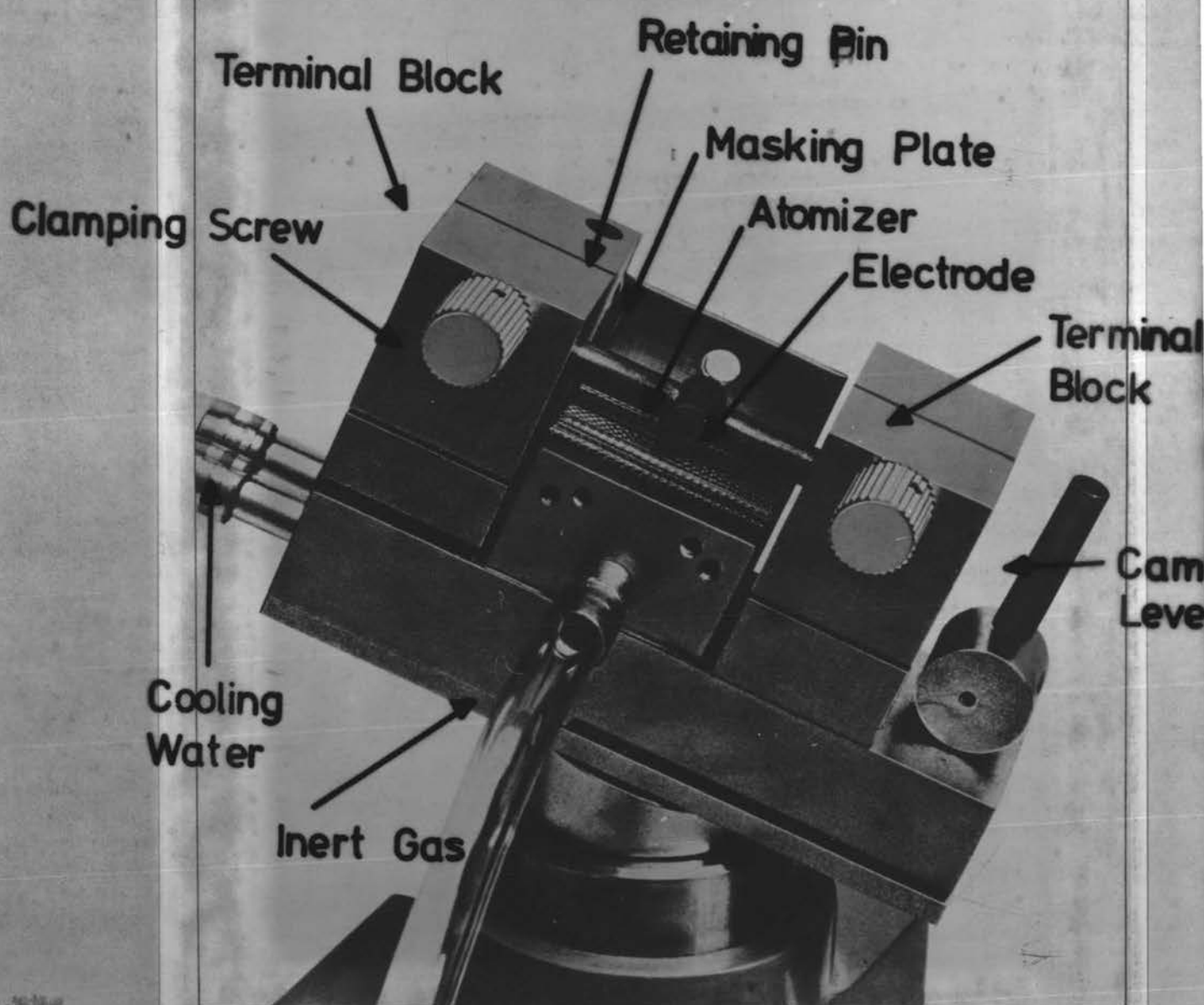
Figure 3.1.3.

The electrode system consisted of a 55mm length of Poco FX9I (Poco Graphite Inc., Decatur, Texas, U.S.A.) 4.5mm in diameter with a machined plateau 12-15mm long in the centre of the rod reducing the thickness in this portion to approximately 2.2mm, in order to localize the heating. An indentation 1.5mm deep and 3.5mm in diameter drilled into the top of the plateau allows 1-5 ul of solution to be retained on the rod.

(b) Experimental procedure.

The solutions required for each study were prepared in 5ml polypropylene vials immediately prior to analysis. In most cases a 1 µl sample of the solution was micropipetted on to the rod by means of an Excalibur set-volume pipette equipped with disposable teflon tips. These tips were replaced when the volume dispensed was not reproducible as when the tips were damaged in any way (for water analysis) and after every application (for whole blood analysis).

Decontamination of the rod was effected by heating it to a temperature above the optimum atomization temperature of the element involved and repeating the process until no more atomic vapour could be detected by the instrument. This process is required at the beginning of every series of concentration standards (especially containing high lead levels) with new rods and with excess carbonization during whole blood analysis.

Prior to a particular series of elemental determinations, a temperature-voltage programme was chosen which suited the variables of drying the sample without sputtering, ashing the sample without causing loss of the element and then atomizing the sample efficiently. The chosen atomizing temperature was high enough to avoid memory effects but not so high as to reduce appreciably the life of the rod. Each rod had an average life of about 300 determinations.

After each sample the rod was allowed to cool before placing another sample on to it. The effect this cooling time had upon signal profiles (analytical absorption curves) is described in Section I.C.5.e.

All absorption signals were recorded using the % trans-
mission mode of the amplifier unit. In every case, a minimum of
three absorption peaks were used for any one result. If reprod-
ucibility was good (R.S.D.~ᴛ 3%), then three peaks were used but
usually five or more peaks were necessary to give a reasonable
level of confidence to the results. The absorption peaks were
then read (to the nearest 0.1%), averaged, and were then converted
to absorbance values by tables.

4. Preparation of standards and samples.

(a) Water analysis

The use of CRA techniques for water analysis were necessary
for cadmium, lead and silver during the course of study outlined
in this work. The detection limits for flame AAS for cadmium,
lead and silver are 0.0006 μg/ml Cd, 0.02 μg/ml Pb and 0.002 μg/ml
Ag respectively (Parker, 1972). For a 5μl sample, the detection
limits for CRA techniques are less than 0.00002 μg/ml Cd, 0.0002
μg/ml Pb and 0.00004 μg/ml Ag (Parker, 1972). These limits may
be lowered by increasing the sample volume or preconcentrating the
sample on the rod.

Water samples were collected in 100ml polypropylene bottles
and analysed immediately on return to the laboratory. West et.
al. (1966) reported on the losses of silver due to its absorption
on container surfaces especially after 10 days storage. Although
silver is adsorbed on to borosilicate glass -, flint-,polyethylene-
and silicone-coated containers, experiments have shown that
sodium thiosulphate prevents silver losses. Therefore there is a
real need to analyse water samples immediately after collection.

Stock standard solutions were prepared by dissolving the
appropriate amount of analyte (in the form of the compound
containing the anion of interest) in distilled double-deionized
water to give a solution 1000 μg/ml with respect to the added
ion. All the chemicals used were of analytical grade purity.
The more dilute solutions required were then obtained by success-
ive dilutions with the purified water. The stock solutions were
stored in polypropylene bottles while the weaker solutions were

freshly prepared prior to analysis.

After the determination of a temperature - voltage programme standard calibration curves were obtained which obeyed Beer's law in the concentration ranges of 0.1 to 1.0 µg/ml using the absorption lines 228.8 nm Cd, 217.0 nm Pb and 328.1 nm Ag. As a result of the sample matrix not being composed of the same matrix as the standard solution, accuracy was controlled by using the standard additions method for calibration curves. Water samples were then analysed directly without any prior chemical pretreatment.

(b) Tree ring-core analysis.

Tree ring-core samples of Beilschmiedia tawa (Benth. & Hook f.) have ash samples which in solution approach the concentration limits of detection for cadmium, and silver. Therefore, to obtain accurate and more precise elemental levels for tree ring-core samples, CAA was necessary. Standard calibration curves were obtained as explained above for water analysis.

Copper and zinc levels were determined by using the flame AAS procedure outlined in part B.4c. (Section 1).

(c) Whole blood analysis - for lead.

The measurement of lead in whole blood by use of CAA has been reviewed using many different methods of sample preparation. In a review by Baily & Kilroe-Smith (1975), seven methods of sample preparation are described. Of numerous suggested, there are three major methods :

(i)   simple dilution (where one volume of whole blood is diluted with 1-5 volumes of surfactant solution);

(ii)   direct analysis of whole blood (no sample preparation).

(iii) a standard chelation extraction procedure in which sodium diethyl dithiocarbamate and methyl isobutyl ketone (isopropylacetone) are used.

Volosin et. al. (1975) in a review of these three methods,

concluded that method (i) using Triton X-100 as the surfactant solution had the most advantages for routine blood-lead analysis in a clinical laboratory.

Originally Hessel (1968) added 5% Triton X-100 (an alkyl-phenoxy polyethoxy derivative of ethanol) to blood to give solutions directly, removing the need to carry out preliminary protein precipitation. Kubasik & Volosin (1974) also described the direct determination of lead in whole blood using CRA. An evaluation of the micro-technique involving Triton X-100 for lead in whole blood has been recently reported by Koller & Bloom (1975).

The technique adopted in this work for the determination of lead in whole blood is that involving Triton X-100. A stock solution of Triton X-100 (Rohm and Haas, Philadelphia, Pa), 5% by volume in distilled water was prepared. Lead standards based on a stock 1000 µg/ml anal. grade lead nitrate in distilled water, were diluted with equal volumes of 5% Triton X-100 solution and added to 'pooled' whole blood in the ratio 1:1 by volume* to give working standards corresponding to 0-1.0 µg/ml Pb. These values represent 'added lead' only. Since the method of additions was used in preparing calibration curves, the original lead content of the 'pooled' whole blood ($\sim$0.20 µg/ml) was corrected for. The working standards were stored in polypropylene bottles and made fresh prior to every group of analyses.

Whole blood samples being analysed were also diluted (ratio 1:1 by volume) with Triton X-100 and applied to the carbon rod atomizer (1 µl). Determination of the true lead content from the calibration curve was obtained using the standard additions method for calibration.

An evaluation of this micro-technique for lead in whole blood using Triton X-100 is described in the next subsection.

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* NOTE: "pooled" whole blood was obtained by adding various normal whole blood samples collected from a Veterinary Clinic.

5. <u>Development of analytical techniques for the determin-
ation of lead in natural waters and whole blood.</u>

(a) <u>Introduction</u>.

In order to develop a routine method for the determination
of lead in natural waters and whole blood samples using CRA an
evaluation of the effects of various additives and matrix inter-
ferents on the absorption signal for lead was made. The influ-
ence on absorption signals and analytical (absorbance) profiles
through variation in instrumental settings was also investigated.

(b) <u>Analytical (absorbance) curves</u>.

(i) lead in natural waters.

Optimum parameters for the dry, ash and atomize cycles of
the Model 63 CRA were determined by altering the time and voltage
settings until smooth curves were obtained. The ash and atomize
voltage settings which are the most critical, were adjusted to
give the best absorbance reading for lead using background corr-
ection for non-atomic absorption (molecular absorption and light
scattering effects). Long dry time settings were found to give
more reproducible results.

In order to determine the optimum CRA parameters for deter-
mining lead in natural waters, an initial study of the dry, ash
and atomize cycles for lead as (Pb (NO_3)$_2$) in distilled water
solutions were investigated. The variation in absorbance obtained
from 1 μl samples of these aqueous lead standards atomized on the
rod using several different ashing and atomizing voltages are
shown in Figure I.1.

The optimum instrumental parameters for lead analysis in
distilled water using the wavelength 217.0nm, slit width 150μ,
and slit height 4nm over a lead concentration range of 1-5 μg/ml
are 5.0v (ashing) and 4.0v (atomize). Because of the low
volatility of lead, voltage settings below these respective
values for each cycle were inefficient in producing maximum
absorbance. This is a direct result of incomplete ashing of
matrix components during the ash stage (which is shown by a slow,

Figure I.1.

Analytical (absorbance) curves obtained from 1µl samples of lead (as $Pb(NO_3)_2$) atomized on the rod using several different ashing (above) and atomizing (below) voltages. The standards were prepared in distilled water and had a lead concentration range of 1-5 µg/ml.
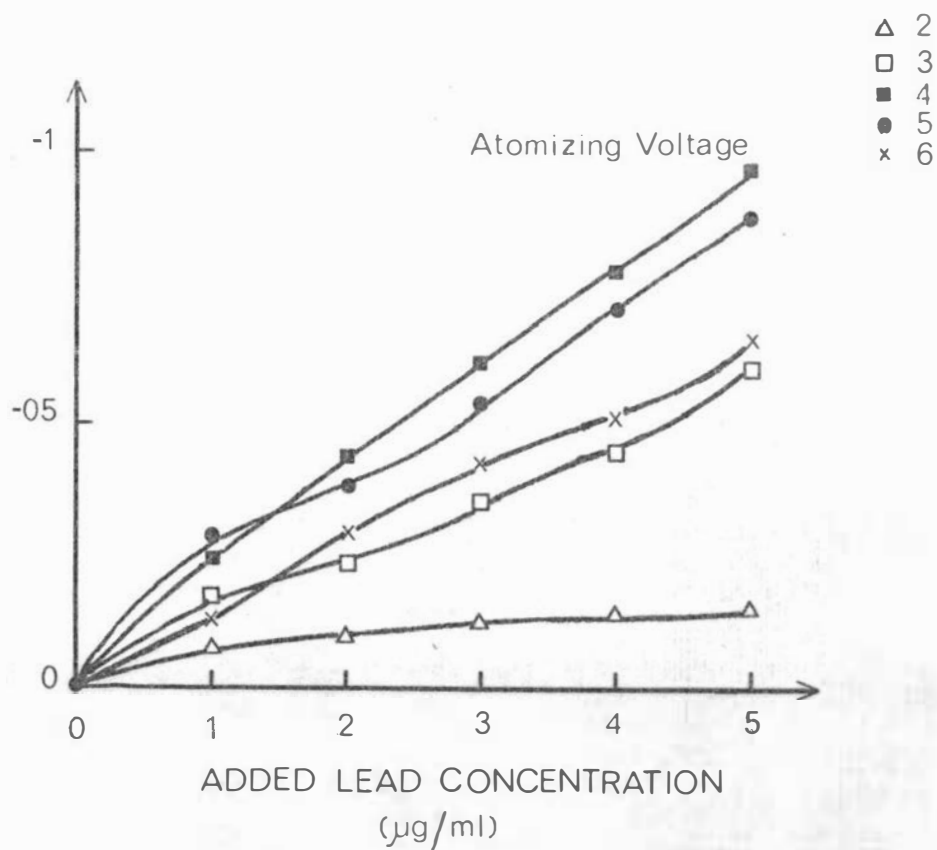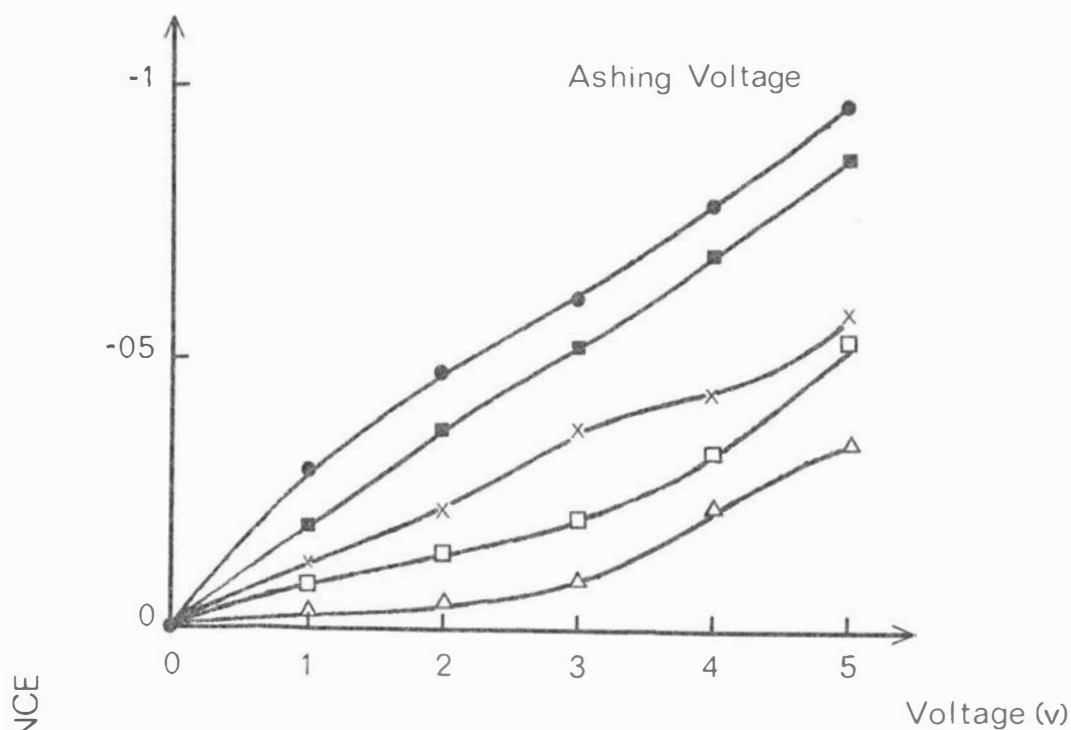
broad ash and atomize peak on the recorder signals.)

Similarly, voltage settings approaching 6.0v cause the solvent to evaporate rapidly followed by resulting sputtering and reduction of absorbance. This is usually shown by a 'very fast' ash peak or multiple atomize peaks composed of the atomic signal followed by a sharp emission peak (identified by H_2-continuum lamp).

A summary of the instrumental parameters for determining lead in natural waters is given in Section 1, 6.7.

(ii) lead in whole blood

The precision and accuracy of CRA results are affected by the nature of the matrix during the dry, ash and atomizing cycles. Whole blood is a major example. Being a complex matrix which cannot be easily simulated, whole blood contains many volatile substances that can influence the production of the atomic vapour of lead. Therefore it is not enough to say that calibration curves determined using lead standards prepared in aqueous matrices are sufficiently accurate to determine the lead content of whole blood. For this reason the analytical technique used was a form of the method of standard additions. The whole blood which is used for preparing the standards is derived from a low natural lead environment.

In general, natural lead levels of whole blood are below 1.0 µg/ml. Therefore unlike the range of lead concentrations investigated for water analysis (0-5 µg/ml Pb), a desirable lead range for whole blood analysis would be 0.1-1.0 µg/ml.

Variation in the absorbance signal obtained from 1 µl samples (Triton X-100, 'lead-spiked' whole blood standards) atomized from the rod using several different ashing and atomizing voltages are shown in Figure I.2

Atomization of the whole blood sample shows optimum instrumental parameters of 5.0v (ash) and 4.0v (atomize). Long dry and ash time settings were found to give more reproducible results. This appears to be consistent with a steady release of lead atoms from an ashed matrix layer spread evenly along the carbon rod. During the dry cycle, to prevent frothing of the solution, the dry voltage setting must be maintained at a minimum

Figure I.2.

Analytical (absorbance) curves obtained from 1μl samples
of lead (as $Pb(NO_3)_2$-'spiked' whole blood diluted with
Triton X-100), atomized from the rod using several
different <u>ashing</u> (above) and <u>atomizing</u> (below) voltages.
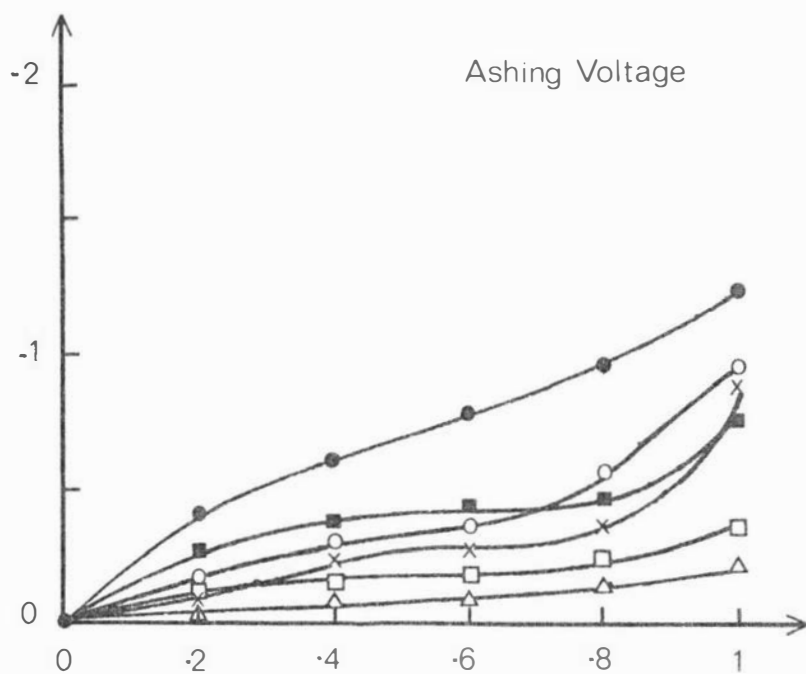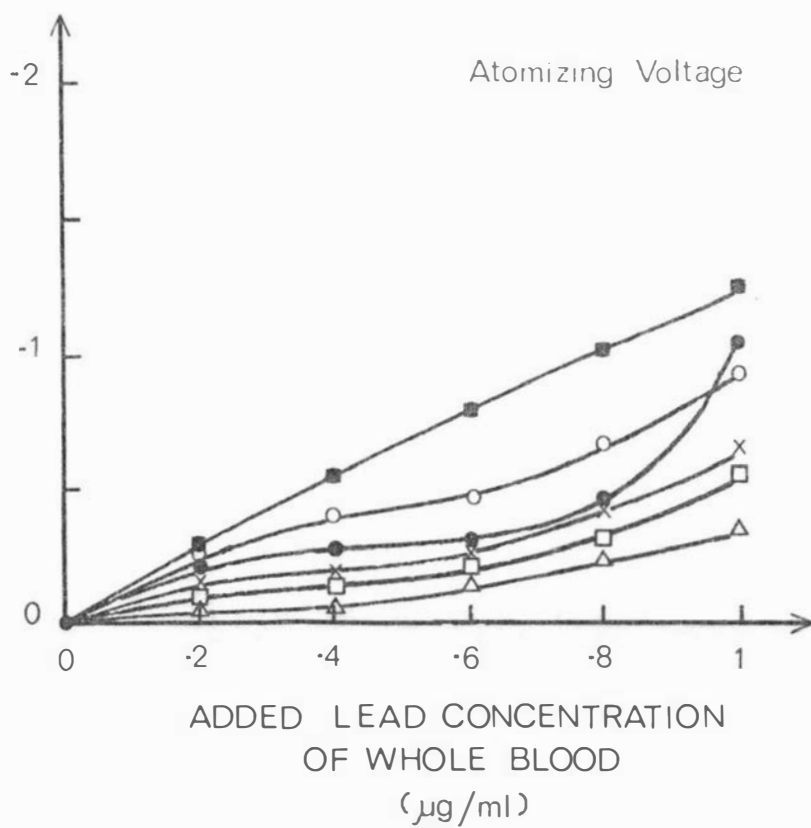
level (4-5v). This enables the solvent to evaporate gently and is demonstrated by a recorder trace that decreases to the baseline before the ash stage. Voltage settings greater than 5.0v during the ashing cycle, decompose and volatilize all the blood matrix components too rapidly causing the production of a peak signal which does not return to the baseline before the atomize stage begins. This non-atomic absorption which is generated during the ashing stage, when checked by the H_2- continuum lamp shows that there has been an initial loss of lead atoms during ashing or preatomization of lead during the ash stage. Similar observations are made for atomize voltage settings >4.0v which generally produce atomize peaks that are not complete so that the recorder trace has not returned to the baseline before the power cycle is finished.

Recorder traces or signal profiles of lead in whole blood diluted with Triton X-100 at a wavelength of 217.0nm are shown in Figure I.3. Variation in absorbance recorded during the dry, ash and atomize stages at the optimum instrumental voltage settings, and at settings above and below the optimum voltage settings are shown compared with the non-atomic peaks (measured using the H_2-continuum lamp).

A summary of the instrumental parameters used for the analysis of lead in whole blood is given in Section 1.0.7. Slight variations in the voltage settings used at each stage may be necessary owing to heating variations caused by changes in the geometry of the rod with aging.

(c) Effect of additives on signal profiles, and analytical (absorbance) curves.

The numerous methods suggested in the literature for the preparation of samples for the determination of lead in whole blood by CRA introduce many difficulties. Although most techniques are based on direct sample analysis avoiding solvents such as in APDC/EDTA-type extractions, a comparison should be made to investigate the effect of additives (used to hemolyze or digest the whole blood matrix) upon the efficiency of lead recovery

Figure I.3.

Signal profiles of lead in whole blood using CRA.
Variation in absorbances for three voltages (optimum;
and above and below optimum) for dry, ash and atomize
stages of the atomic (Pb. lamp) and non-atomic (H_2. lamp)
absorption peaks.

ABSORPTION

OPTIMUM SETTINGS
(atomization, Pb lamp)

dry

ash

atomize

25 ⊥
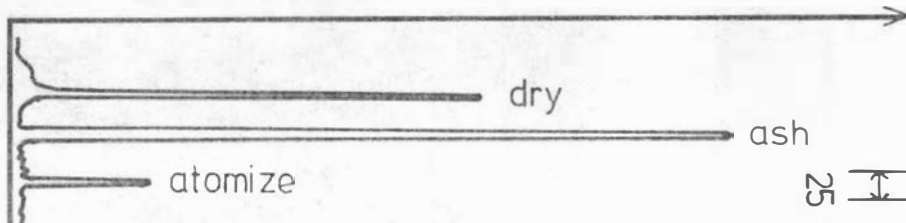
OPTIMUM SETTINGS
(background, H_2-
continuous lamp)

dry

ash
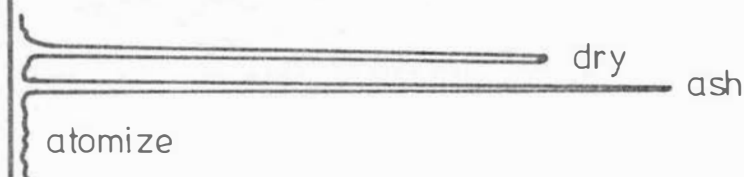
atomize

LOW VOLTAGE SETTINGS
(incomplete atomization,
Pb lamp)

dry

ash

atomize

LOW VOLTAGE SETTINGS
(background, H_2-
continuous lamp)

dry

ash

atomize

HIGH VOLTAGE SETTINGS
(loss of lead during
ashing, Pb lamp)

dry

ash

atomize

HIGH VOLTAGE SETTINGS
(incomplete atomization,
H_2-continuous lamp)

dry

ash

atomize

by CRM.

Four different extraction methods were investigated in comparison to whole blood diluted with Triton X-100 and whole blood analysed directly without any physical or chemical pre-treatment. A series of lead standards was prepared from a 'pooled' whole blood sample over the lead concentration range 0.1-1.0 $\mu g/ml$ added lead. Each standard was then diluted by a 1:1 volume with the following additives :

(i)   whole blood (no physical or chemical pretreatment),

(ii)   whole blood + double-distilled water,

(iii) whole blood + nitric-perchloric acid, (Baily and Kilroe-Smith, 1975),

(iv)   whole blood + conc. ammonia solution,

(v)   whole blood + 1000 $\mu g/ml$ NaCl solution,

(vi)   whole blood + Triton X-100.

The influence of these additive solutions on the corrected analytical (absorbance) curves for lead is shown in Figures I.4. and I.5.

In all cases, compared with the Triton X-100 method used in this study, the added 'interferent' depresses the absorbance. With no physical or chemical pretreatment of the whole blood sample, the lead signal is markedly depressed, probably due to premature loss of lead from the atomizer during the dry and ashing stages. This is shown in Figure I.6. which illustrates the signal profiles obtained from lead atomization in the presence and absence of the various additives. The major effect of no pretreatment is the influence of 'carbonisation' from the blood matrix on the rod causing a change in the rate of vaporization of lead atoms. A dense smoke is produced during the ashing stage with the resulting preatomization of lead atoms. One method of altering the presence of this 'carbon-lining' to the rod is to increase the drying and ashing voltage settings, but this still results in a reduction in the absorbance.

In nearly all cases, the "interferent" causes either the production of a slow broad dry and ashing peak (as a result of incomplete ashing of the matrix components) or a reduction in

Figure I.4

Calibration curves for added lead in whole blood after
addition of various solutions: double-distilled water
(symbol O), conc. ammonia solution (symbol △), Triton-
X-100 (symbol ⬡).

Additives

   O   double-distilled water

   △   conc. ammonia solution

   ●   Triton X-100

ABSORBANCE

ADDED LEAD CONCENTRATION
'SPIKED' WHOLE BLOOD
(μg/ml)
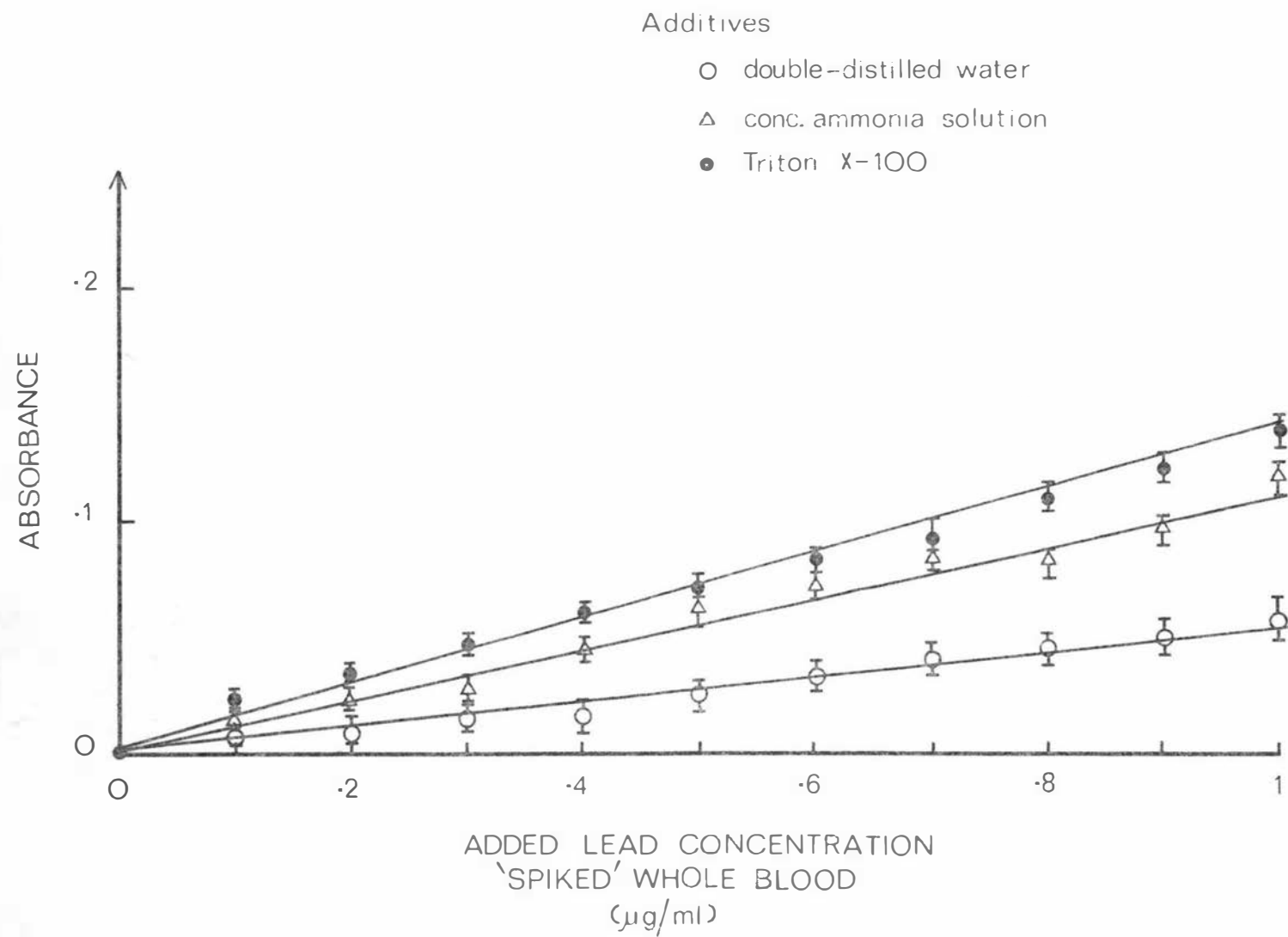
Figure I.5.

Calibration curves for added lead in whole blood after
addition of various solutions: no physical/chemical
pretreatment (symbol △), nitric-perchloric acids (symbol △)
and 1000µg/ml NaCl solution (symbol ▨).

Additives
- □ no pretreatment
- ▲ nitric-perchloric acids
- ■ 1000 μg/ml NaCl solution

ABSORBANCE

·2

·1

O

O   ·2   ·4   ·6   ·8   1

ADDED LEAD CONCENTRATION
'SPIKED' WHOLE BLOOD
(μg/ml)
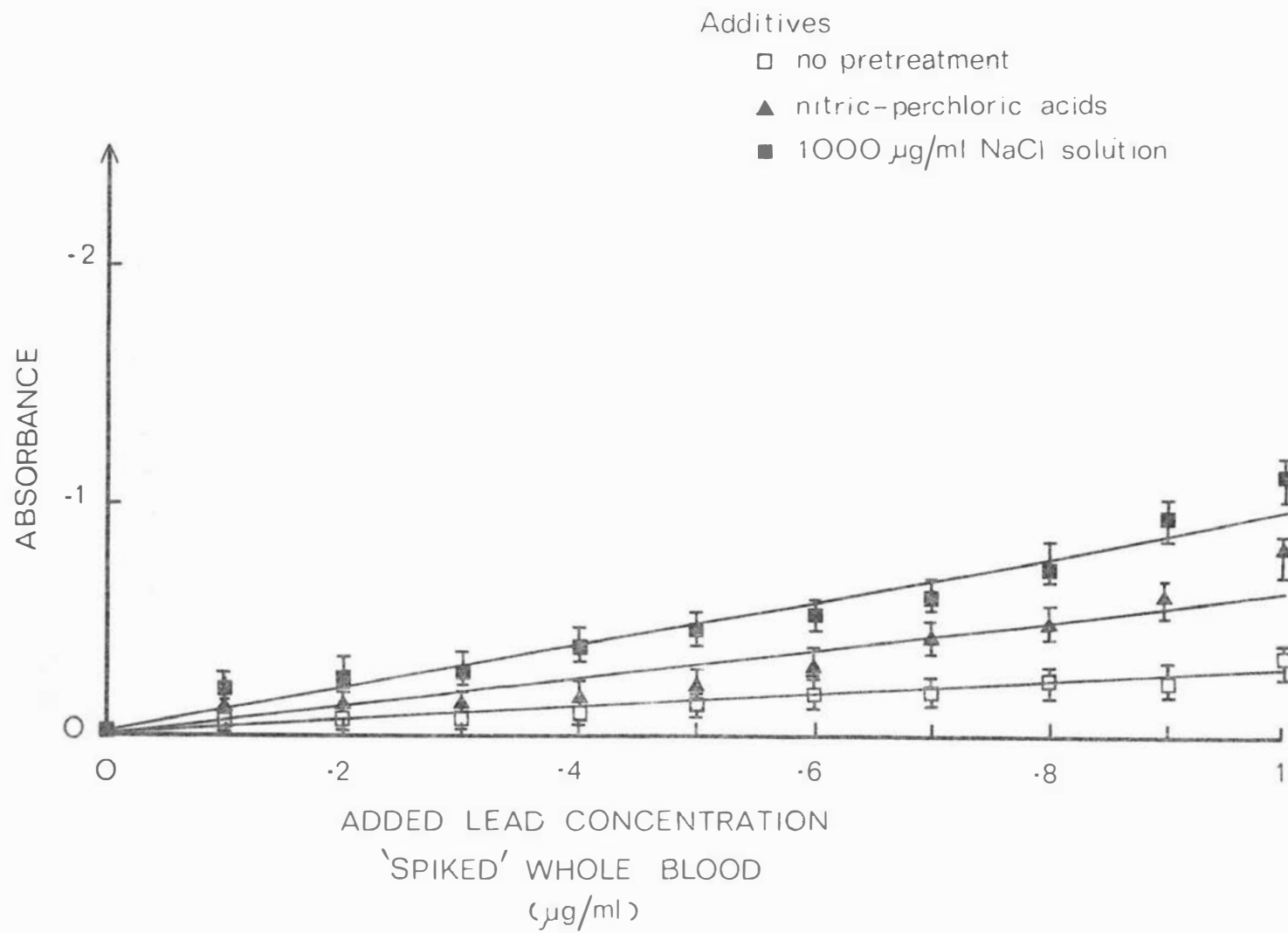
Figure I.6.

Signal profiles (absorption peaks) obtained from lead atomization in the presence and absence of various solutions added to whole blood (lead atomization, Pb lamp; background, H_2 lamp).

(a) No Treatment
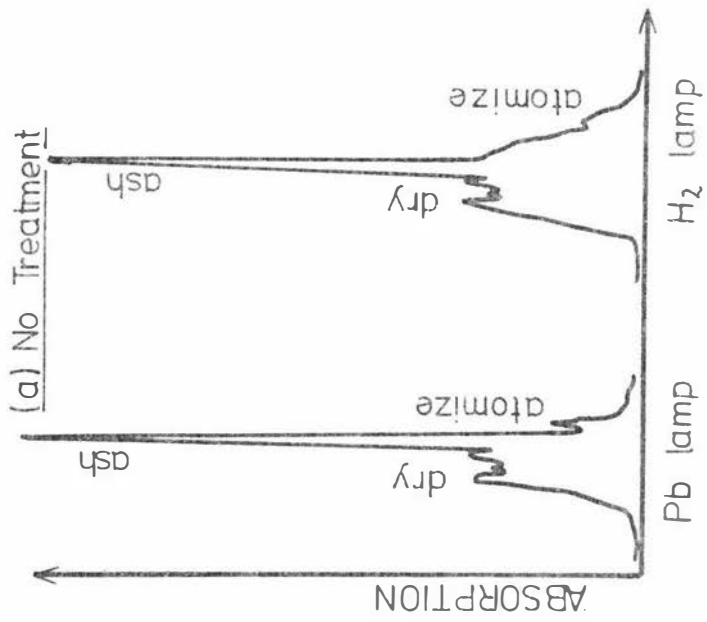
(b) Double-distilled water
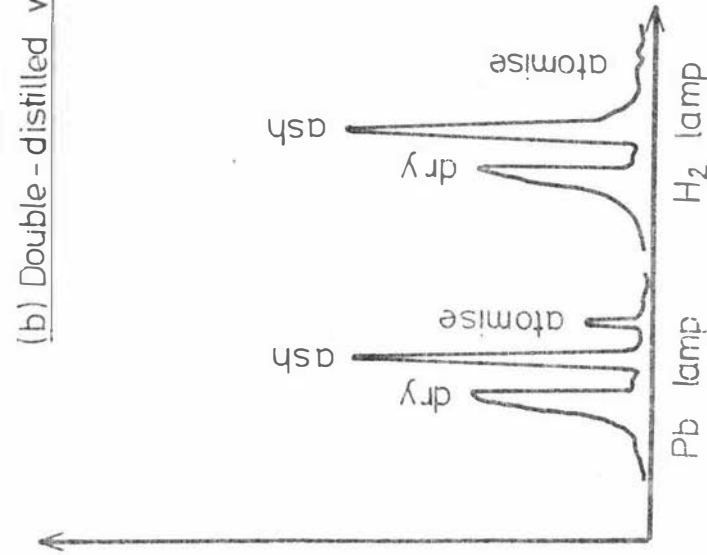
(c) Nitric-perchloric acids
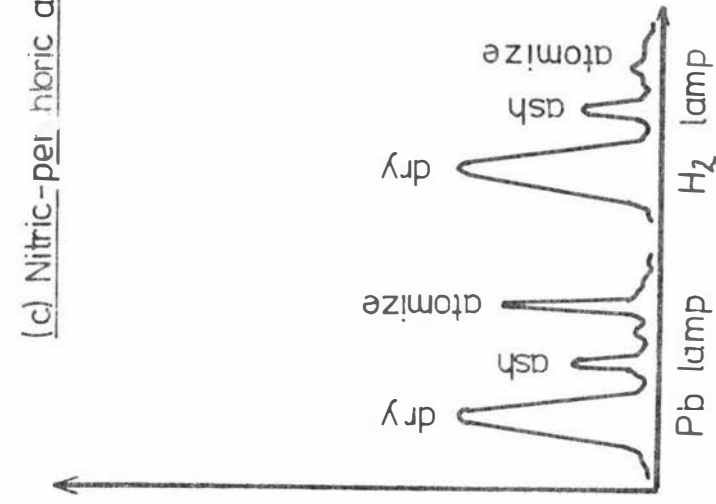
(d) Concentrated Ammonia
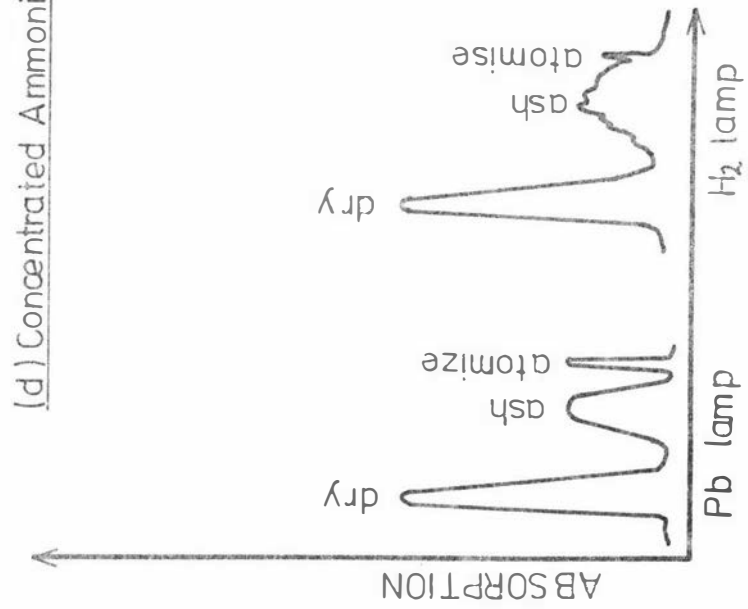
(e) 1000 μg/ml NaCl
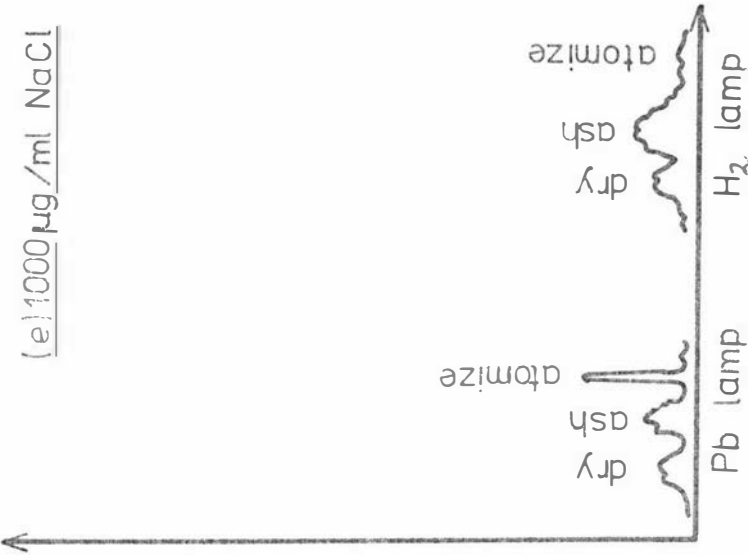
(f) Triton X-100
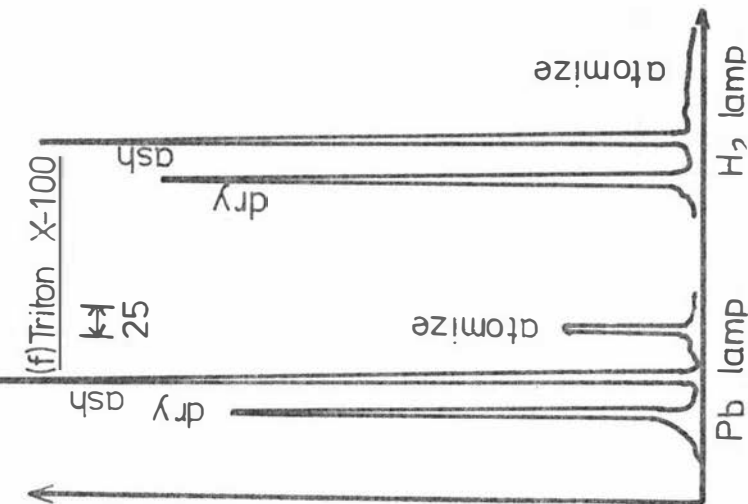
the height of the ash and atomize peaks (through loss of lead by 'sputtering' or preatomization). This results in poor sensitivity and reproducibility.

The method using Triton X-100 over the lead concentration range of 0.1-1.0 µg/ml had a R.S.D. < 5% whereas the other methods exceeded 5% with a maximum R.S.D. of 15%.

Comparison of the absorbance measured at each lead concentration as a result of the presence of an 'interferent' solution resulted in a percentage lead recovery of less than 60% ((i), (ii) and (v)) and up to 94% ((iii) and (iv)) relative to the absorbance for dilution with Triton X-100.

(d) Effect of EDTA and heparin (Whole blood anti coagulants) on analytical (absorbance) curves.

The clinical application of CRA for lead analysis of whole blood is very much dependent upon the effect of EDTA and heparin which are used as anti coagulants or chelating agents and are normally present in clinical Vacutainer bottles. Kahn & Sebestyen (1970) reported that EDTA interferes with most extraction or colorimetric methods and that samples containing it must generally be ashed. EDTA is a better anti coagulant than heparin. The advantage of such anti coagulants is in the prevention of small blood clots forming which interfere with the application of whole blood samples on to the surface of the atomizer. Moller & Bloom (1975) reported a method for removing clots formed in whole blood during storage enabling the sample to be analysed by CRA. This method requires the sample tubes to be dipped into a Dewar flask of liquid nitrogen which freezes the blood. After thawing at room temperature, blood clots are broken and the sample is ready for analysis.

Kubasik & Volosin (1974) reported that although EDTA causes a serious lowering in the analysis of urinary lead utilizing an extraction technique, the CRA methods they investigated showed no interferences from EDTA. Therefore the effect of EDTA and heparin (0.005 to 0.01 molar) added to freshly collected whole blood over the added lead concentration range of 0.1-1.0 µg/ml

was investigated. A series of lead whole blood standards was prepared in the following 1:1 ratios:

(i)   whole blood + EDTA,
(ii) whole blood + EDTA + Triton X-100,
(iii) whole blood + heparin,
(iv) whole blood + heparin + Triton X-100.

The results were compared with the standard CRA method used in this study (dilution with Triton X-100).

The effect of added EDTA and heparin to whole blood is shown in the analytical (absorbance) curves for added lead concentrations of 0.1-1.0 µg/ml in Figure I.7.

The absorbance of lead in the presence of EDTA is variable and reduced, particularly at higher lead concentrations. In contrast, heparin shows very little effect. However, improved absorbance is obtained when 5% Triton X-100 is added to the solution which causes preliminary hemolysis. During the determination with EDTA by CRA the heights of the non-atomic peaks during the dry and ashing stages are somewhat higher than those for lead solutions with EDTA and added Triton X-100. Heparin causes a broadening of the ashing non-atomic peak without any significant change in the atomization peak. The signal profiles for lead solutions in the presence of EDTA and heparin, with and without Triton X-100 added, are shown in Figure I.8.

The major problem with the use of EDTA and heparin in clinical whole blood Vacutainers during sampling is the risk of introducing lead contamination. The precision of the Triton X-100 method is not affected, as any significant interferences caused by EDTA are controlled by the presence of Triton X-100.

(e) Effect of variation of time between sample applications.

The maximum atomic absorption signal is very much dependent upon the time of application of the sample on to the rod surface. The dispersion of lead atoms into the optical path can be influenced by the position of the sample on the rod surface and the degree of sample soaking into the rod (Kubasik et. al.,1972). As such, one possible factor is the time interval between the

Figure I.7.

Calibration curves for added lead in whole blood after addition of EDTA and heparin in the presence and absence of Triton X-100.

ABSORBANCE

Whole blood + Triton X-100

Whole blood / EDTA + Triton X-1C

Whole blood / EDTA

Whole blood + Triton X-100

Whole blood / heparin + Triton X

Whole blood / heparin

ADDED LEAD CONCENTRATION

'SPIKED' WHOLE BLOOD (µg/ml)
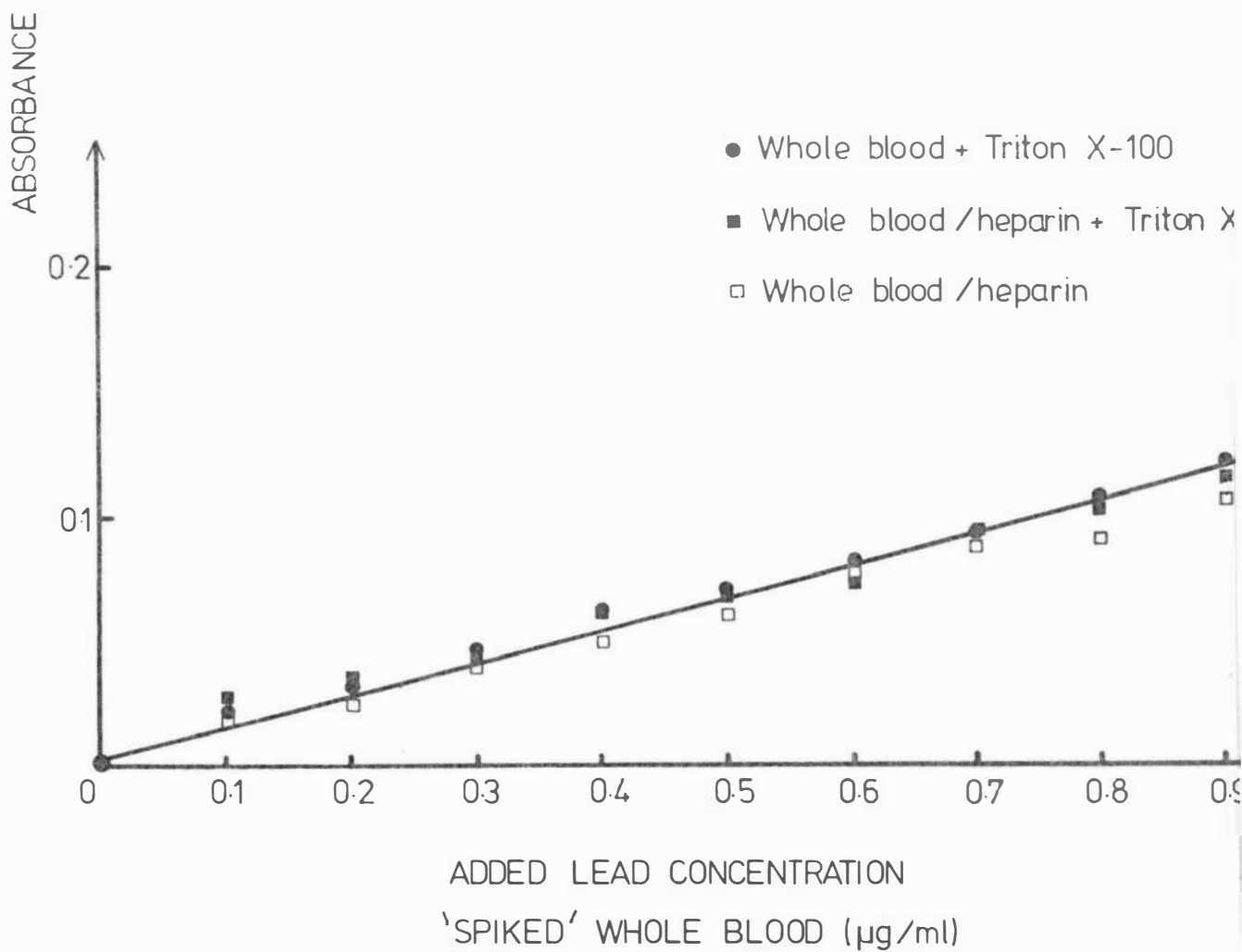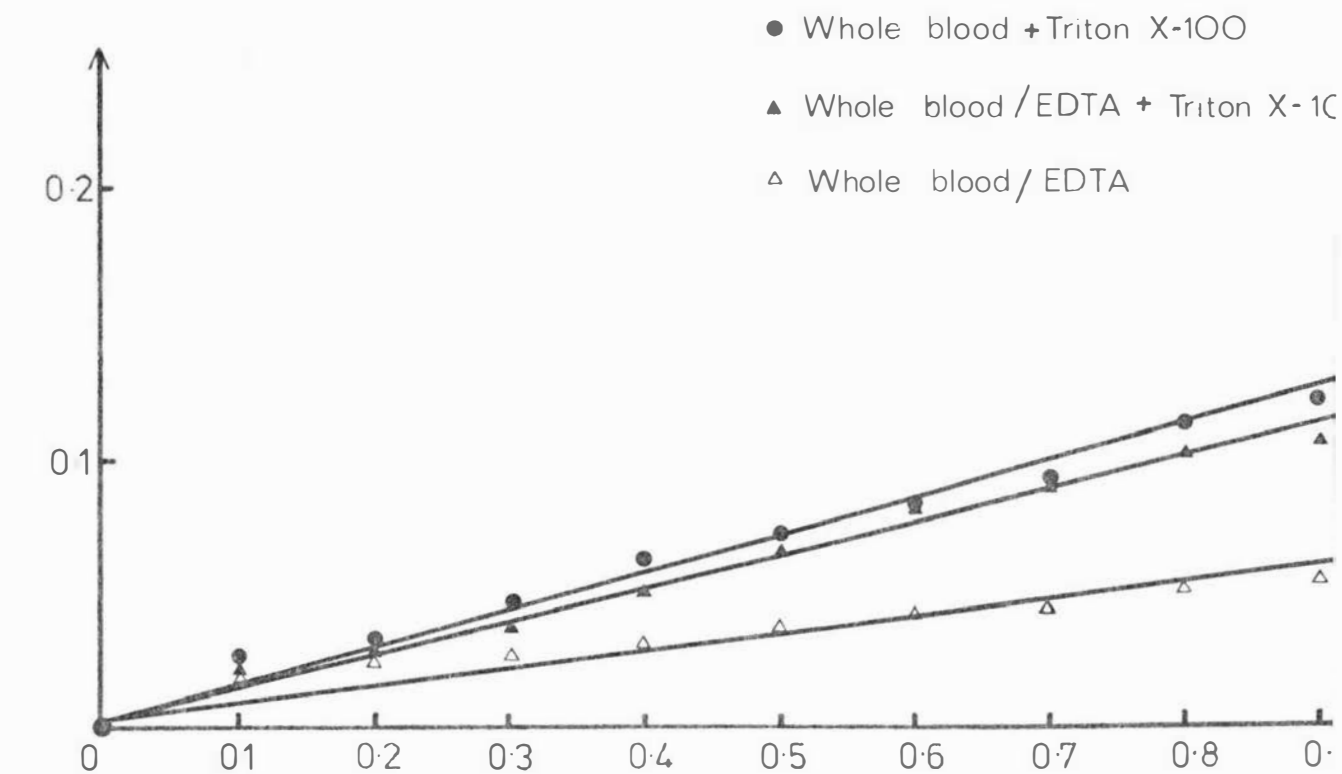
Figure I.8.

Signal profiles (absorption peaks) obtained from lead
atomization in the presence of EDTA and heparin with
or without addition of Triton X-100 (lead atomization,
Pb lamp; background, H_2 lamp).

Whole blood + Triton X-100
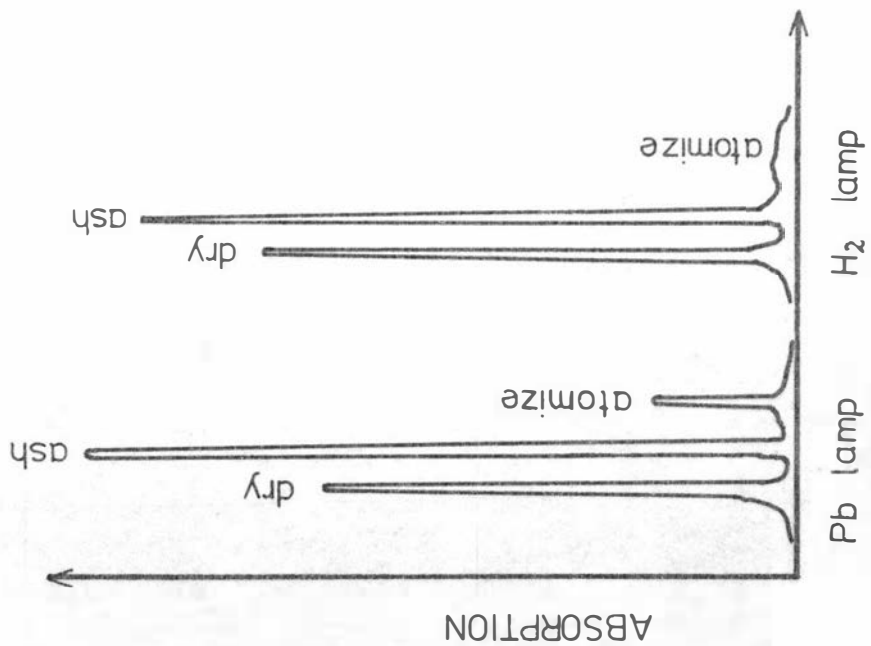
Whole blood + EDTA
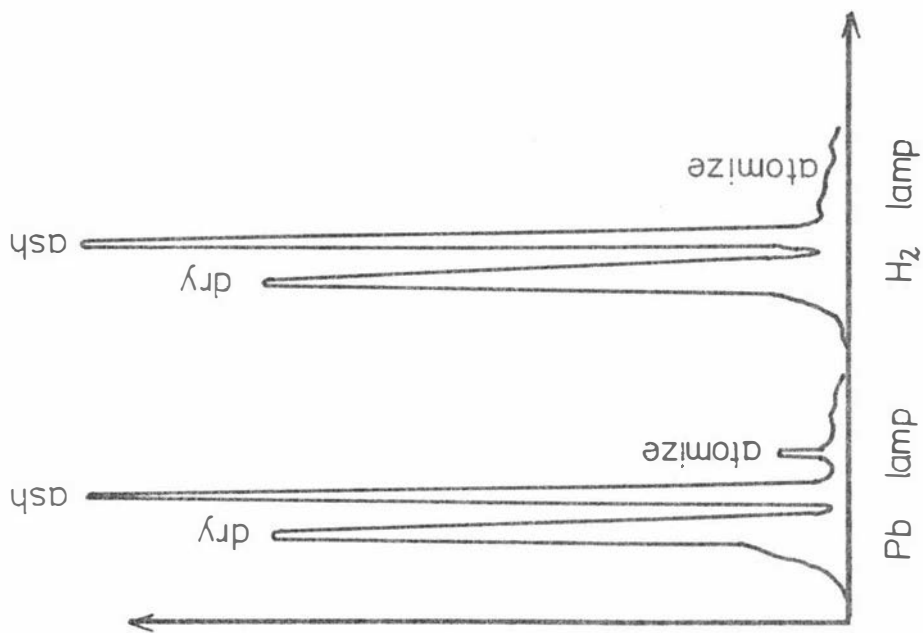
Whole blood + heparin

ABSORPTION
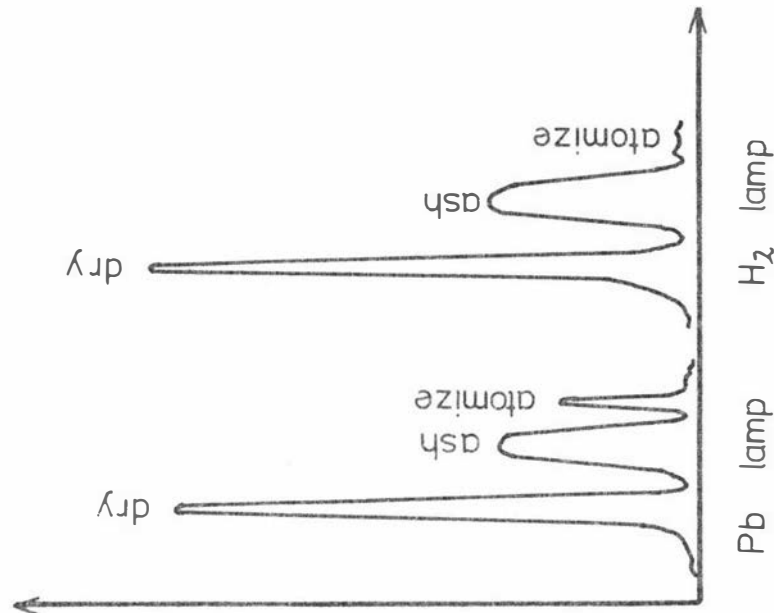
previous atomization and the application of the next sample on to the atomizer surface.

In order to demonstrate this variable 'lead-spiked' whole blood samples with an added lead concentration of 1.0 µg/ml diluted with Triton X-100 were applied to the rod in the normal manner (described in Section I. C3a.) after various time intervals since the completion of the previous atomization cycle.

Figure I.9. shows the variation in absorbance for the atomization of lead as a variable of time (in seconds) between the completion of an atomization cycle and sample application. For efficient reproducible lead absorption signals, a standard time interval of at least 120-150 seconds is required before sample application to the rod is carried out. The major loss of lead atoms is through 'sputtering' of the sample on the rod before complete cooling has occurred from the previous atomization.

The variation in signal profiles is shown in Figure I.10.

The longer time intervals produce sharp atomic signals, with higher peak absorbances. At reduced time intervals, the temperature is too high on the rod surface causing preatomization with a reduction in sensitivity and reproducibility. Therefore during routine analysis of batch samples requiring over 50-100 determinations, the time interval between atomization and sample application is important. Reduction of this time interval to reduce the overall operational time also reduces the efficiency of the CRA method.

6. Interferences and background absorption.
(a) Interferences.

The success of atomic absorption as an analytical method depends on the production of uncombined (free) non-ionised ground-state atoms in an atomic vapour for absorption of radiation at a unique and specific wavelength for a given element. Any substance which hinders or masks the process will be an interferent in atomic absorption. Most interference work has been outlined for non-flame cells using elements in various matrices (L'vov, 1961, Massmann, 1968; Manning and Fernandez, 1970; Anderson et. al.,

Figure I.9.

Variation in the lead atomization absorbance as a function of the time interval (seconds) between sample applications.
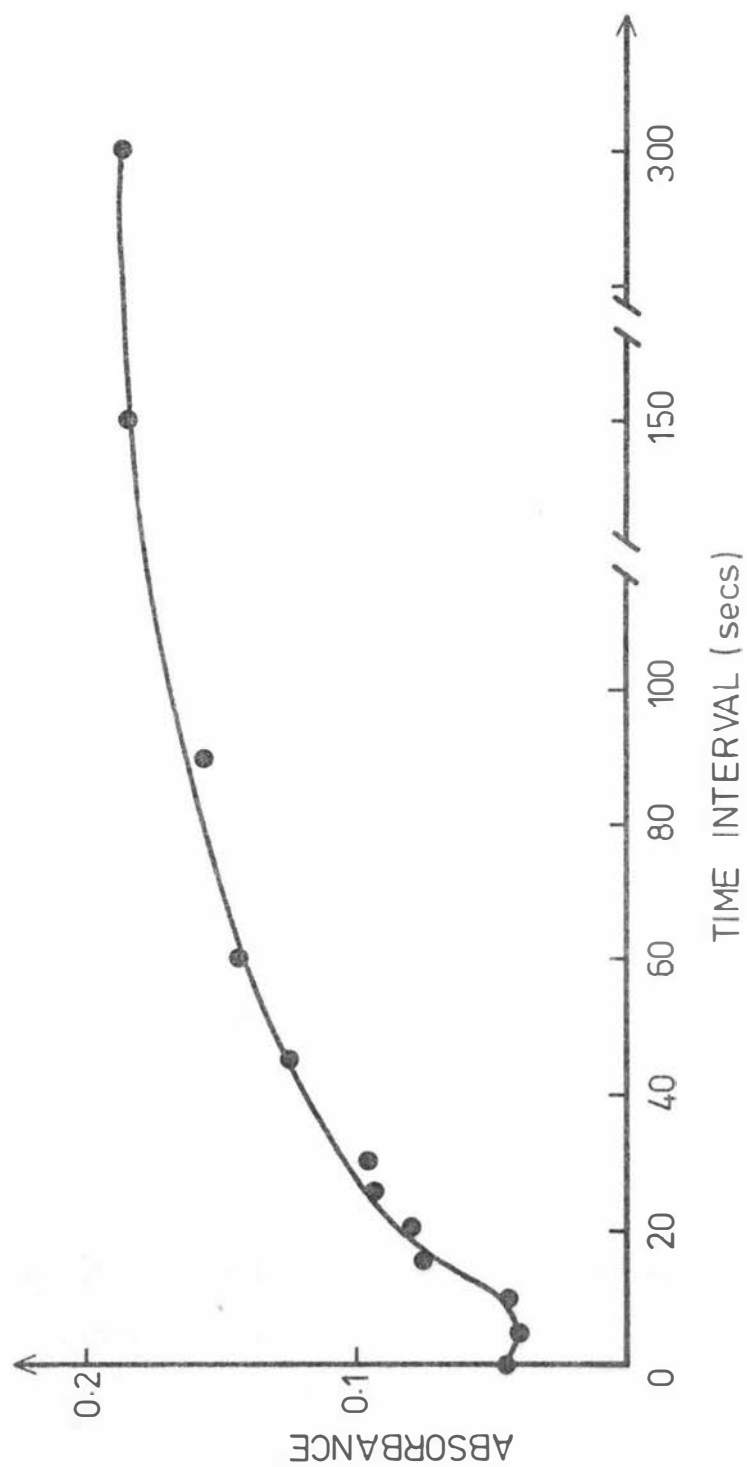
Figure I.10

Signal profiles (absorption peaks) at time intervals of 5,60 and 150 seconds between completion of atomization and application of the next sample (lead atomization, Pb: lamp; background,; H_2 lamp).

TIME INTERVAL
5 sec.

TIME INTERVAL
60 sec.

TIME INTERVAL
150 sec.

ABSORPTION

Pb lamp · dry · ash · atomize · H₂ lamp · dry · ash · atomize

Pb lamp · dry · ash · atomize · H₂ lamp · dry · ash · atomize

Pb lamp · dry · ash · atomize · H₂ lamp · dry · ash · atomize
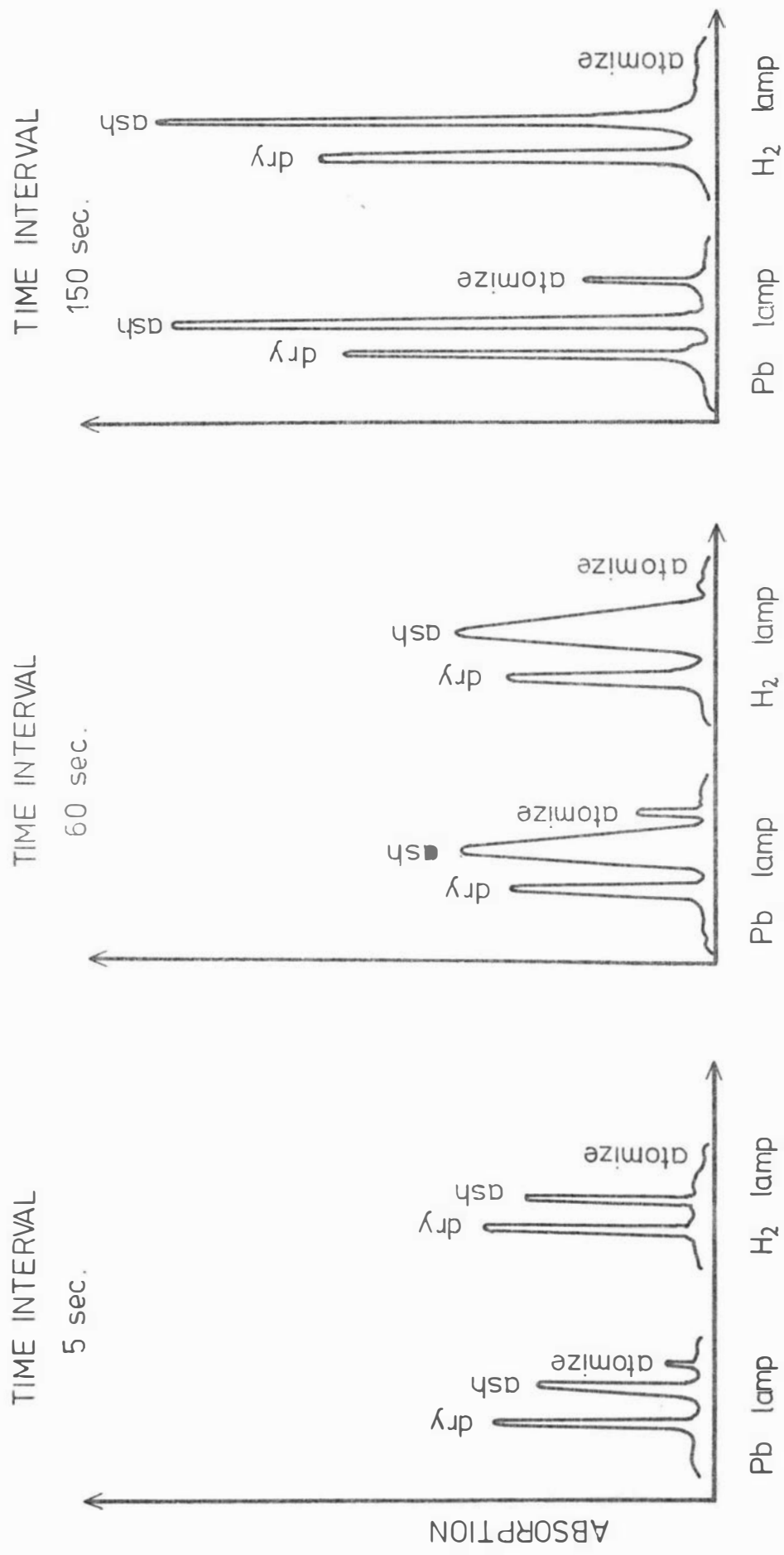
1971; Dipierro and Tessari, 1971; Segar and Gonzalez, 1972;
Takeuchi et. al., 1972).

It is not the purpose of this study to investigate this
subject which is extensively outlined in the literature in part-
icular a review by Winefordner (1970). It should be pointed out
however, that some chemical interferences play a major role when
non-flame cells are used. Baudin et. al. (1971) reported that
there are four possible types of interference:

(i)   physical effects (e.g. variation in the volatility of
        the elements),

(ii)   absorption by molecular compounds or so called
        spectral interference,

(iii)   formation of stable compounds in the solid phase
        (during ashing),

(iv)   formation of compounds in the gaseous phase (during
        atomization.)

Matoušek (1971) showed the effect on the absorption peak
height obtained when analytes were atomized from several solutions
of different matrices and mentioned the effect of some parameters
(e.g. voltage/time settings) on the peak height. He concluded
that the peak height is proportional to the vaporization rate
and that the presence of any extraneous ions in the sample
decreased the peak height only by decreasing the vaporization
rate of the analyte. This was questioned by Amos et. al. (1971)
who suggested that interference was caused by incomplete dis-
sociation of molecules formed either in the solid state or vapour
state in the presence of large numbers of extraneous ions,
rather than by different vaporization rates. They studied the
absorption signals for lead in the presence of several compounds
(H_3PO_4, NaCl, KCl, $MgCl_2$, $CaCl_2$) which were all present in blood.
It was observed that the depressant interference that occurred in
varying degrees with all of the compounds could be reduced by
using an argon/hydrogen atmosphere and a limited field of view
immediately above the rod. Matoušek & Stevens (1971) used a
synthetic blood standard for the analysis of lead and other
elements in blood without any direct interference studies being

reported. Manning & Fernandez (1970) showed that a NaCl concentration of 300 mg/cm^3 reduced a lead signal by 30%., which indicates that NaCl may be a major interferent in natural water matrices. On the other hand Baird et. al. (1972), in an investigation of the effect of eleven cations on cadmium determinations, found no interference with 200 µg/ml KCl; 500 µg/ml NaCl severely depressed the signal whereas 1000 µg/ml KCl and 1000 µg/ml NaCl enhanced the signal. The other reported investigations on non-flame cell interferences have been made for cadmium (Bratzel et. al., 1969), lead (Anderson et. al., 1971; Hwang et. al., 1972); Silver (Alder and West, 1972) and cadmium, lead and silver with other elements (Alger et. al., 1971; Jackson and West, 1972; Reeves et. al., 1973).

Several conflicting theories and results on the effect of interferences using flameless atomization devices can be summarised as:

(i)   a vapour recombination effect, causing occlusion of atoms of the analyte,

(ii)   the formation of compounds volatilised concurrently with the element but not dissociating, preventing the occurrence of atomic absorption,

(iii) a combination of components in the matrix resulting in rate-of-vaporization changes.

On the basis of this literature survey it was assumed that it was necessary to check the chemical interference of 1000 µg/ml ion solutions (as nitrates) on the absorbance for cadmium, lead and silver in natural water analysis. The ions investigated were: Al^{3+}, Ba^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Ce^{3+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Sr^{2+}, and Zn^{2+}. Using an argon/hydrogen atmosphere and a limited field of view immediately above the rod, no ion showed an 'interferent' effect greater than 5% of the normal absorption signal.

(b) Background absorption.

In flameless atomic absorption all peaks other than atomic absorption peaks are termed non-specific absorption which includes

background absorption (light scattering and molecular absorption).

Light scattering from carbon particles released at high temperatures was investigated by L'vov (1961), Dipierro & Tessari, (1971). Molecular absorption has been reported by L'vov (1968); Takeuchi et. al. (1972); Culver & Surles (1975); Pritchard & Reeves (1976). Molecular absorption by organic compounds is predominantly found during the ash stage when the presence of molecular species in the absorption cell causes absorption of light at the same wavelength as the analyte resonance line.

Molecular absorption can arise during the atomize stage when ashing of the matrix components is not completed during the prior ash stage or if the matrix contains large amounts of inorganic salts. There may also be light scattering caused by carbon particles during the atomize and ash stages.

Correction for non-atomic absorption or background absorption is only required in those instances when a composite non-atomic/atomic absorbance peak due to incomplete ashing is obtained during the atomize stage. Correction is achieved by the quantitative measurement of the non-atomic signal by means of the hydrogen continuum source. For routine analysis of samples during this study the BC 6 Background corrector attachment for the atomic absorption spectrophotmeter was used.

7. Instrumental operating conditions.

Although the instrumental operating parameters and methods for the determination of lead in whole blood and natural waters have been reported in detail in this section, the instrumental operating conditions for the analysis of cadmium and silver in natural waters and tree ring-core samples were also investigated using the same procedures as outlined for lead.

In summary, the instrumental operating conditions used for flameless CRA analysis of lead in whole blood and natural waters, and cadmium and silver in natural waters and tree ring-core samples are shown in Table I.3.

The calibration curves (analytical absorbance curves) for cadmium and silver (natural water and tree ring-core samples and

Table I.3.

Instrumental Operating Conditions Used for Flameless (CRA) Analysis of Lead (in whole Blood); Cadmium, Lead and Silver (in natural Waters and Tree Ring-core Samples).

General Parameters		Elements	
	Cadmium	Lead	Silver
Wavelength (nm)	228.8	217.0	328.1
Slit width (µm)	150	150	150
Slit height (mm)	4-5	4-5	4-5
Lamp current (mA)	3	6	3
Gas flow rate (1/min) Ar.	3.8	3.8	3.8
H$_2$.	2.2	2.2	2.2

Lead in Whole Blood		Voltage	Time (s)
	Dry	5	20 to 25
	Ash	5	20 to 30
	Atomize	4 to 4.5	1.5 to 1.8

Elements in Natural Waters and Tree Ring-cores.

Cadmium	Dry	3.5	20 to 25
	Ash	2.5 to 3.5	15
	Atomize	3.5 to 4.0	2.5
Lead	Dry	4.5 to 5.0	20 to 25
	Ash	3.0	10 to 15
	Atomize	3.5 to 4.0	2.5
Silver	Dry	4.5	15 to 20
	Ash	4.0	10
	Atomize	2.8	2.5 to 3.0

Variations in voltage/time setting depending upon geometry and age of rod.

lead (natural water samples) are shown in Figures' I.11 (cadmium)
I.12. (lead) and I.13 (silver) respectively. The calibration
curve for lead added to whole blood diluted with Triton X-100
is shown in Figure I.7.

8. Conclusion.

In this section the development of various analytical
techniques associated mainly with the determination of lead in
whole blood were outlined. Following a review of the main dis-
advantages of flame atomic absorption spectrophotometry, a more
detailed investigation into the application of non-flame AAS
indicated the advantages of using the carbon rod atomizer (CRA)
for the determination of lead levels in whole blood with the
addition of Triton X-100 (an alkyl phenoxy polyethoxy derivative
of ethanol).

The main conclusions of this investigation can be summarized
as follows:

(i) the CRA method required a 1:1 dilution of whole blood
samples with Triton X-100 before sample application
(1 μl) to the atomizer;

(ii) an evaluation of the optimum instrumental parameters
led to attainment of maximum absorbance with a reprod-
ucibility of < ±5%.

(iii) when the absorbance of lead in whole blood without
additives was compared with solutions such as double-
distilled water, nitric - perchloric acid, conc.
ammonia solution, Triton X-100, and 1000 μg/ml NaCl
solution; maximum absorbance in the lead concentration
range of 0.1-1.0 μg/ml was obtained by addition of
Triton X-100;

(iv) the effect of EDTA and heparin (whole blood anti-
coagulants) in reducing the absorbance of lead was
eliminated by the addition of Triton X-100;

(v) a study of time between sample applications, showed
that the longer the time interval, the higher the
peak absorbance so that during routine analysis, the

Figure I.11.

Calibration curve for added cadmium using a CRA method for natural water and tree ring-core analyses. Added cadium concentrations were in the range 0.1-1.0µg/ml.

ABSORBANCE

CADIUM CONCENTRATION (μg/ml)
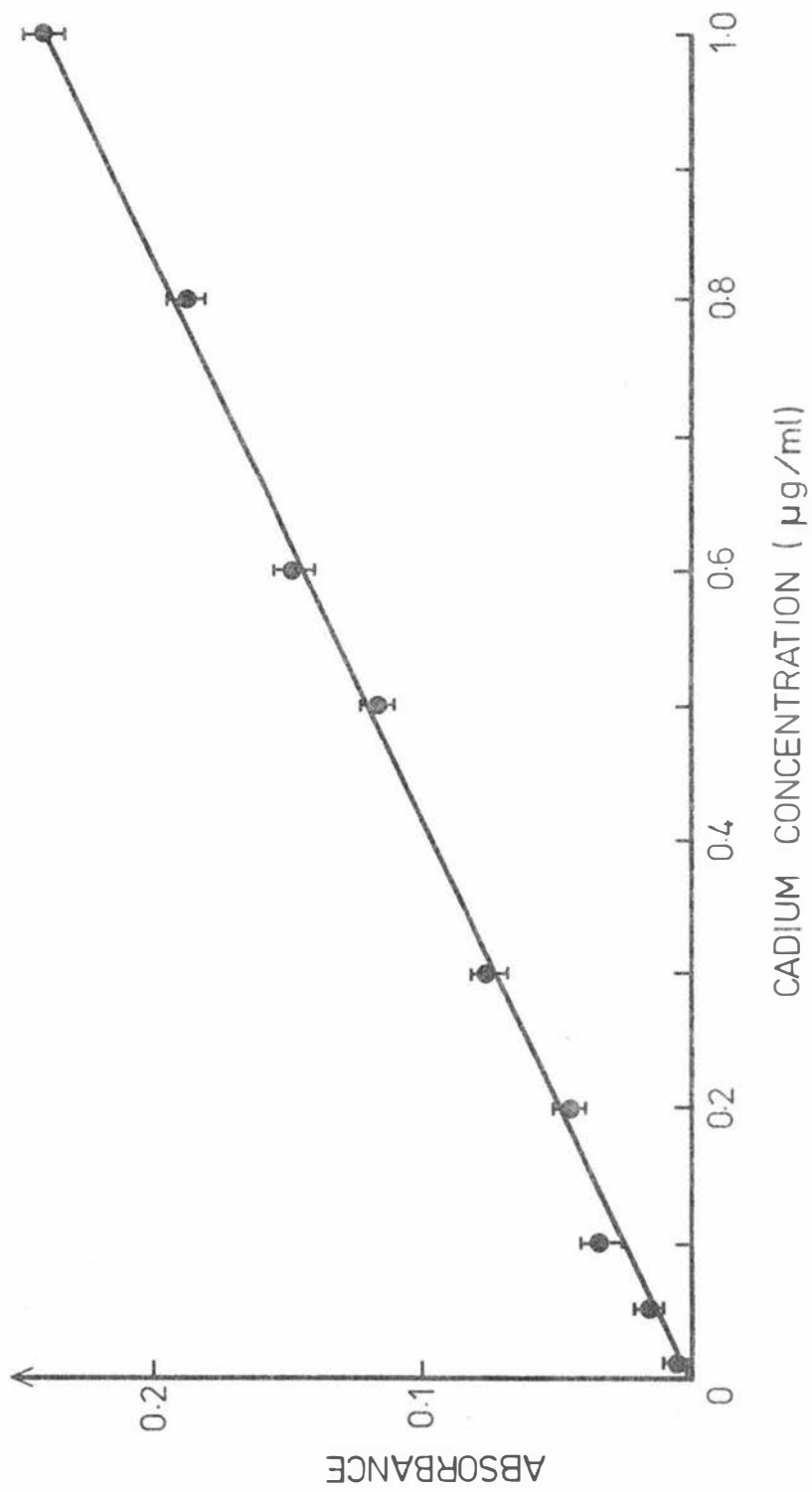
Figure I.12.

Calibration curve for added lead using a CRA method for natural water analysis. Added lead concentrations were in the range 0.1-1.0µg/ml.

ABSORBANCE

LEAD CONCENTRATION (µg/g)
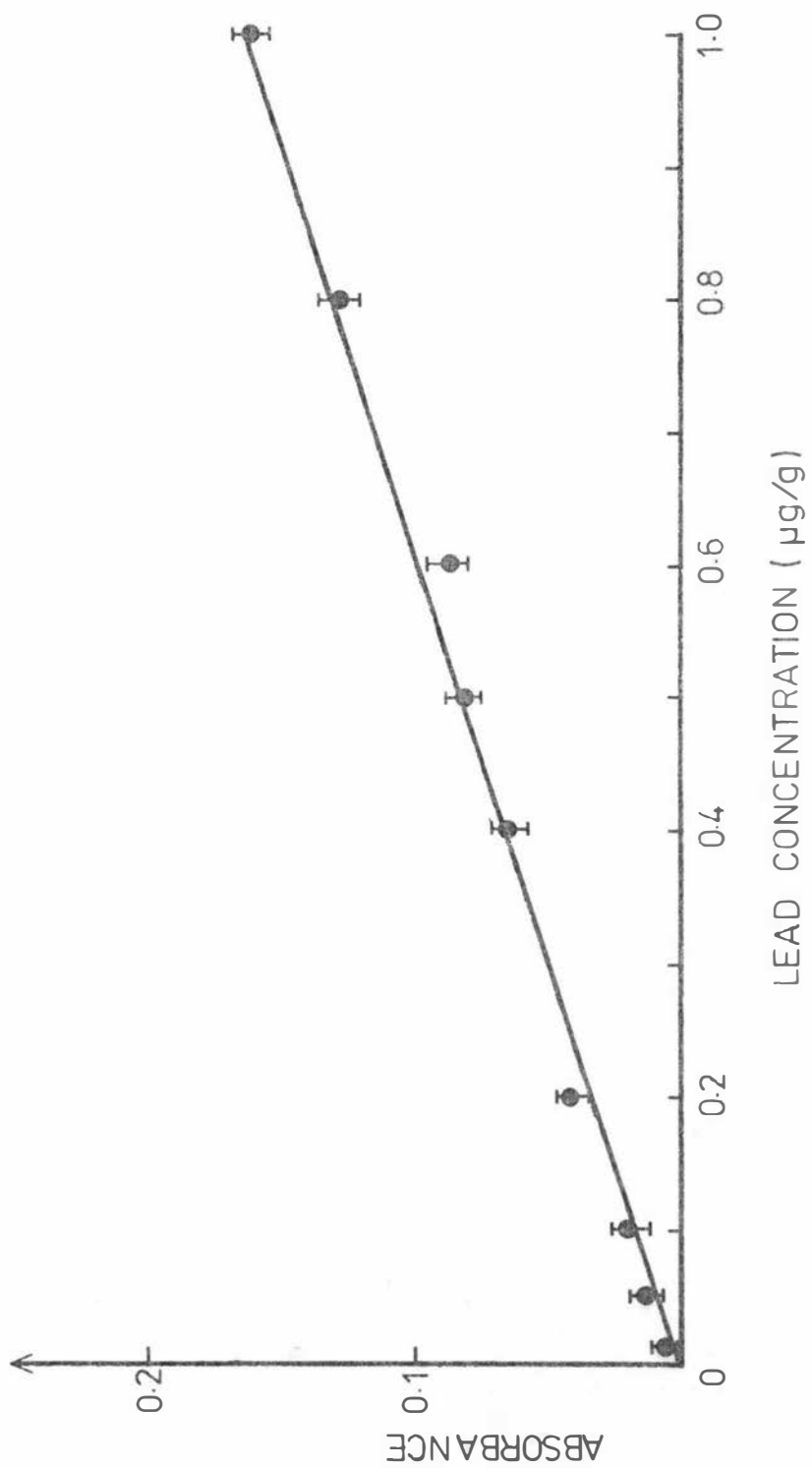
Figure I.13.

Calibration curve for added silver using a CRA method for natural water and tree ring-core analysis. Added silver concentrations were in the range 0.1-1.0μg/ml.

Figure: Standard calibration curve of absorbance versus silver concentration (µg/ml).
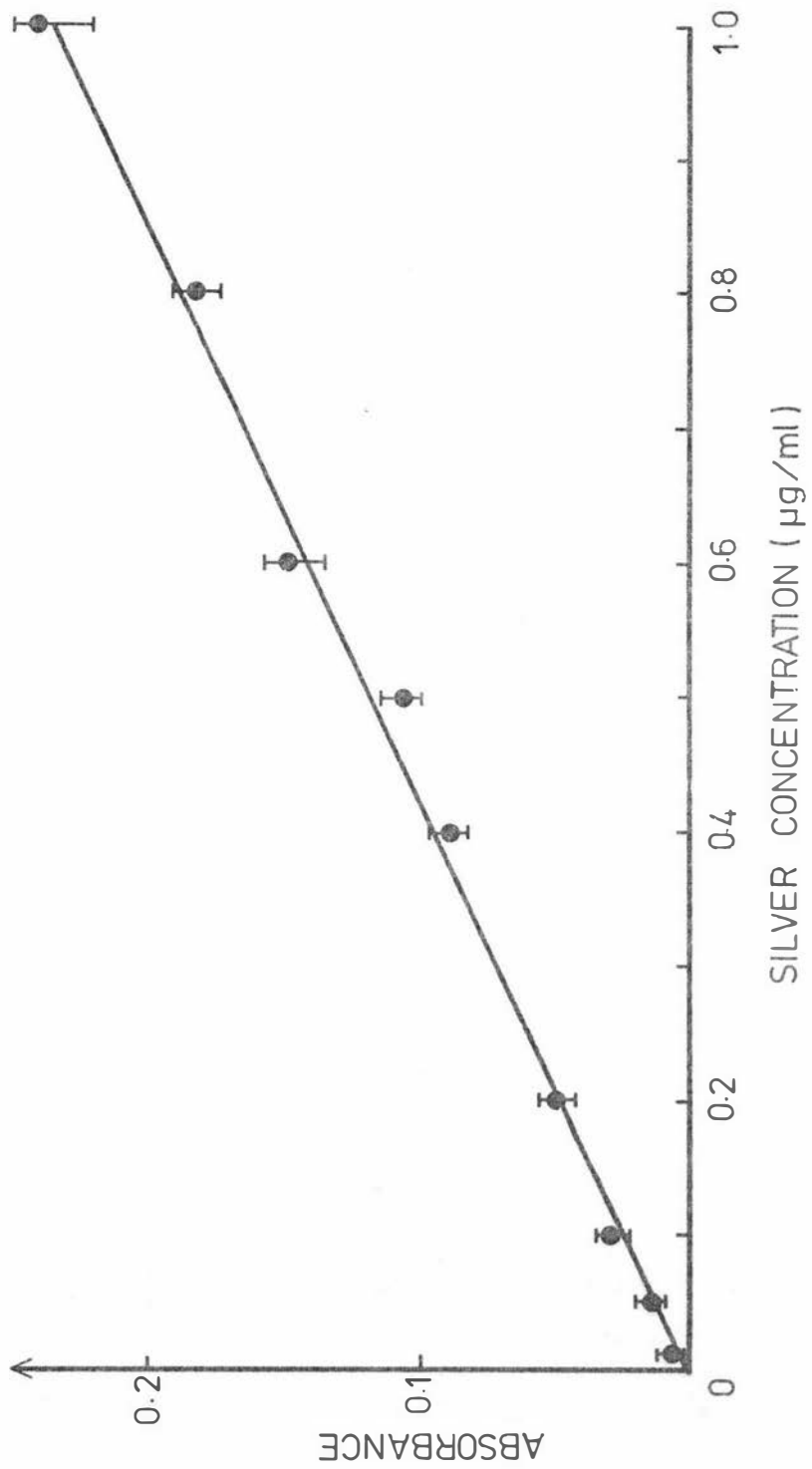
time interval between the last atomization and the
next sample application is important, and there is
a considerable reduction in sensitivity if the time
interval is reduced below 2 minutes:

(vi)   the possibility of interfering ions was examined and
correction for background absorbance was achieved
by the use of a BC6 background corrector as a
supplementary unit to the atomic absorption spectro-
photometer.

The optimum instrumental operating parameters using the
CRA method for cadmium and silver analysis of natural water and tree
ring-core samples and lead analysis of natural water, were also
determined.

SECTION II

LEAD LEVELS IN WHOLE BLOOD OF NEW ZEALAND

DOMESTIC ANIMALS.

1. INTRODUCTION.

Domestic animals may be exposed to substantial amounts of lead in their environment. This occurs frequently in dogs and cattle, and is related to the habit of chewing or licking objects indiscriminately (Waldron and Stöfen, 1974).

Individual susceptibilities in animals vary considerably. Cumulative lead poisoning of the type commonly found in man has also been described in cats and dogs (Garner, 1967; Bloom et al, 1976). The sources of lead available to domestic animals are numerous (Zook and Carpenter, 1971). Dogs often develop symptoms of plumbism as a result of chewing objects covered with lead-based paint or by eating metallic lead. Cats, which are selective eaters are not directly subjected to lead poisoning like dogs although they may ingest lead-containing dusts or other substances that contaminate their coats. Another source of lead poisoning for most domestic animals is the result of licking discarded batteries or drinking water transported by lead piping. Poisoning of horses is normally associated with lead from lead mining and smelting operations. Brazell (1971) reported a case where New York ZOO animals developed lead poisoning after chewing paint on bars or woodwork of cages. Another potential source of lead to domestic pets may be the large quantities of canned food and meat consumed. These meats contain a large proportion of offal such as liver and kidneys which tend to accumulate lead (Hankin et al., 1975 a,b).

A major source of lead poisoning in domestic animals is the increased atmospheric fall-out of lead deposited directly on vegetation alongside roadways as a result of motor vehicle exhaust emissions. Campbell et al (1971) investigated the effects of lead chlorobromide on groups of cynomolgus monkeys and rats. Reports of increased lead levels in rodents invertebrates and earthworms within the vicinity of highways have been made by Smith et al (1970) Jefferies & French (1972); Williamson & Evans (1972); Gish & Christensen (1973); Quarles et al (1974) and Frøslie & Norheim (1975).

Wildgoose (1970) reported on lead toxicity in domestic pets including pathology and symptoms and treatment of absorbed lead. Lead enters the body principally by inhalation or ingestion. On absorption, the bulk of the lead enters the portal circulation, is excreted as bile and passes through the intestines unchanged. Lead that reaches the systemic circulation is deposited in bone and in soft tissue particularly the liver, kidney, pancreas and brain.

From the extensive literature of clinical symptoms of lead poisoning, mention should be made of work by Zook & Carpenter (1971); Zook et al (1972) and Waldron & Stöfen (1974).

Table II.1. summaries the major contributions to the investigation of lead poisoning and toxicity in various domestic animals over the past five years.

The effect of lead as a particularly serious pollutant is reflected in whole blood levels where in some cases concentrations in animals and humans are close to levels considered toxic by many health authorities. Although the lead content of human whole blood seldom falls below 0.20 µg/ml (Tinker, 1971), safety limits ranging from 0.20 µg/ml (Hernberg and Nikkanen, 1970) to 0.80 µg/ml (Hunter and Russell, 1954) have been proposed.

For domestic animals, Zook et al (1972) reported 0.19 ± 0.08 µg/ml lead for whole blood of healthy dogs and 0.94 ± 0.64 µg/ml for animals showing symptoms for lead poisoning. Zook & Carpenter (1971) concluded that values over 0.60 µg/ml were indicative of poisoning, whereas Wilson & Lewis (1963) reported a mean of 0.30 µg/ml for healthy dogs and 0.93 µg/ml for animals showing signs of lead poisoning. Thomas et al. (1975) considered a whole-blood lead concentration $\geqslant 0.60$ µg/ml as the limit for diagnostic lead poisoning. In a recent study, Bloom et al (1976) reported mean values including 0.064 µg/ml for lead in the whole-blood of healthy dogs (considerably lower than those reported by any other workers).

Lead data for other domestic animals are relatively sparse. However, Willoughby & Brown (1971) reported normal values of 0.11 ± 0.09 µg/ml for horses. Data for cats are somewhat lacking,

Table II.1

Summary of the Major Literature (1971-1976) Concerning Lead
Poisoning and Toxicity in Various Domestic Animals.

Domestic animals (general)

Priester & Hayes (1974)	lead poisoning in cattle, horses, cats and dogs.
Neathery & Miller (1975)	metabolism and toxicity (including Cd, Hg).
Neathery & Miller (1976)	metabolism and toxicity of lead.

Cattle

Dinius et al (1973)	subclinical lead intake in calves.
Williams (1973)	lead poisoning in cattle.
Tolleson (1974)	lead toxicity in angus calves.
Lynch et al (1976)	young calf response to low doses of lead.

Cats

| Zook & Carpenter (1971) | neurological and haematological signs in cats. |
| Bloom et al (1976) | age and sex variation for cats and dogs. |

Dogs

Zook (1972)	pathological anatomy of lead poisoning.
Zook et al (1972)	analysis of dog's blood, urine, hair and liver.
Stowe et al (1973)	oral lead toxicity to young dogs.
Zook (1974)	urban dogs.
Schalm & Holliday (1975)	haematology.
Thomas et al (1975)	3 groups of dogs from a suburban community
Dodd (1976)	lead poisoning.

Horse

    Aronson (1972)   long term exposure of lead causing poisoning

    Willoughby et al (1972)   interactions of toxic amounts of lead and zinc.

    Knight & Burau (1973)   chronic lead poisoning.

    Dollahite et al (1975)   poisoning in horses.

Sheep

    Carson et al (1973)   low level lead ingestion.

    Gelder et al (1973)   behavioural toxicological assessment of the neurological effect of lead.

    Fick (1975)   lead toxicity.

    Fick et al (1975)   dietary lead.

    Fick et al (1976)   dietary lead, tissue mineral composition and absorption.

though Bloom et al (1976) reported 0.05 ± 0.04 µg/ml for 26
animals. Allcroft (1950) has reported normal levels of 0.14 ±
0.01 µg/ml for sheep and 0.13 ± 0.01 µg/ml for cattle.

Because data for whole blood of domestic animals are
sometimes contradictory and are unevenly distributed among the
various classes of domestic animals, there is clearly a need for
a large-scale survey involving a single analytical method applied
to specimens from large numbers of several domestic animals from
a single geographical unit. Such a survey would avoid differ-
ences due to climate or interanalyst variability.

2. Study area.

Between January 1975 and December 1976, whole blood samples
for cattle, cats, dogs, horses and sheep were collected at the
Animal Health Research Centres, Massey University (central North
Island) and Lincoln University (northern South Island). These
whole blood samples were part of normal Veterinary Field collect-
ions, and included general information such as breed, sex, age,
and history. In all 1142 domestic animals (252 cattle, 113 cats,
271 dogs, 258 horses and 248 sheep) were tested for lead levels
in whole blood. The results of this survey are reported in this
section.

3. Results and discussion.
 (a) The age distribution of lead concentrations in whole blood.

The age distribution of whole-blood lead concentrations
(µg/ml) in domestic animals is shown in Table II.2. For the sake
of clarity, only means and ranges are given. Standard deviations
are shown in the text whenever necessary.

The data showed no significant differences for cats, dogs
and sheep, but the larger ruminants (cattle and horses) consist-
ently showed lower lead levels (0.12 and 0.13 µg/ml) for animals
in the first age group compared with those over 18 months.
Results of a t-test for differences in mean values for older and
younger groups within each animal classification were : 4.67
(250 d.f.)* for cattle and 5.81 (256 d.f.) for horses, and
*Note. d.f. :degrees of freedom

Table II.2.

The Age Distribution of Whole-blood Lead Concentrations (µg/ml) in New Zealand Domestic Animals.

Animals	Total No.		Lead concentrations by age (Years).			
			1.5	1.6-4.0	4.1-8.0	8.0
Cattle	252	Mean	(64) 0.12	(63) 0.19	(62) 0.18	(63) 0.23
		Range	0.06-0.21	0.05-0.24	0.04-0.28	0.06-0.32
Cats	113	Mean	(38) 0.23	(32) 0.21	(26) 0.22	(17) 0.19
		Range	0.06-0.32	0.07-0.40	0.08-0.32	0.06-0.28
Dogs	271	Mean	(86) 0.21	(82) 0.23	(64) 0.25	(39) 0.23
		Range	0.08-0.36	0.10-0.40	0.06-0.35	0.06-0.42
Horses	258	Mean	(78) 0.13	(70) 0.17	(61) 0.23	(49) 0.23
		Range	0.04-0.22	0.04-0.20	0.03-0.30	0.03-0.40
Sheep	248	Mean	(65) 0.18	(64) 0.21	(66) 0.20	(53) 0.21
		Range	0.07-0.24	0.06-0.26	0.08-0.26	0.05-0.26

Value in brackets indicates the number of animals per age group.

indicated a very-highly significant (P less than 0.001) difference between them.

Mean lead concentrations, µg/ml (for all ages) were : 0.18 ± 0.10 for cattle; 0.21 ± 0.05 for cats; 0.25 ± 0.06 for dogs; 0.19 ± 0.10 for horses and 0.20 ± 0.05 for sheep. These values are similar to those obtained by most other workers although in the case of cats and dogs they are considerably higher than the values obtained by Bloom et al (1976).

(b) The sex distribution of lead concentrations in whole blood.

The sex distribution of lead concentrations in whole blood is shown in Table II.3.

There was some evidence that male cattle have significantly lower lead levels than female or neutered cattle. There was a very-highly significant difference in the mean of male cattle considered as one group and female and neutered animals considered as another. A t-test gave 3.85 (250 d.f.). No other differences according to sex were noted for other domestic animals. Similar findings have been reported for cats and dogs by Zook & Carpenter (1971) and Bloom et al (1976).

(c) Variation of whole-blood lead concentrations among different breeds.

The variation of whole-blood lead concentrations among different breeds of domestic animals is shown in Table II.4. There were no detectable differences among different breeds of sheep, horses or cats. However, sheep dogs from rural areas had only just over half the lead content (0.15 ± 0.08 µg/ml) of pedigree dogs, 87% of which were from city areas and which had a mean lead content of 0.27 ± 0.07 µg/ml. This difference was very-highly significant (t = 3.1 for 80 d.f.). It should be noted that only 82 dogs were included in this survey because it was restricted to sheep dogs and the three commonest breeds among city dogs.

Table II.3.

The Sex Distribution of Whole-Blood Lead Concentrations (µg/ml) in New Zealand Domestic Animals.

Animals		Lead Concentration by Sex.		
		Male	Female	Neutered
Cattle	No.	118	92	42
	Mean	0.14	0.18	0.19
	Range	0.06-0.22	0.06-0.26	0.07-0.31
Cats	No.	44	46	23
	Mean	0.21	0.23	0.22
	Range	0.08-025	0.08-026	0.08-0.24
Dogs	No.	156	90	25
	Mean	0.22	0.22	0.20
	Range	0.05-0.28	0.08-0.30	0.06-0.28
Horses	No.	87	90	43
	Mean	0.24	0.23	0.20
	Range	0.04-0.34	0.04-0.30	0.08-0.26
Sheep	No.	148	100	-
	Mean	0.19	0.21	-
	Range	0.08-0.24	0.08-0.26	-

Table II.4.

Variation of Whole-Blood Lead Concentrations (µg/ml) Among Different Breeds of New Zealand Domestic Animals

Animals	Total No.	Breed	Individual Breed No.	Lead concentrations by breed	
				Mean	Range
Cattle	46	Angus	10	0.28	0.08-0.36
		Friesian	12	0.13	0.06-0.30
		Jersey	14	0.17	0.04-0.24
		Friesian/Jersey X	10	0.29	0.08-0.40
Cats	23	Siamese	11	0.20	0.07-0.25
		Others	12	0.19	0.06-0.24
Dogs	82	Corgi	20	0.26	0.10-0.33
		German Shepherd	25	0.29	0.14-0.38
		Labrador	15	0.25	0.11-0.32
		Sheep dogs	22	0.15	0.06-0.22
Horses	66	Standard breed	40	0.20	0.05-0.26
		Thoroughbred	26	0.21	0.06-0.26
Sheep	60	Perendale	20	0.20	0.06-0.26
		Romney	28	0.20	0.04-0.26
		Southdown	12	0.19	0.06-0.28

The significantly lower lead levels in farm dogs compared with city dogs has already been observed by Bloom et al. (1976) who reported mean values of 0.045 and 0.068 µg/ml respectively. Ratio wise these values are similar to our own, but in absolute terms are considerably lower.

Thomas et al (1975) reported that there was no significant association between whole-blood lead levels and size expected at maturity or breed of dogs, in particular terrier, poodle, collie, and mixed.

Lower lead levels measured in the whole blood of rural dogs must surely be a reflection of reduced access to pollution from motor vehicle exhaust emissions, since other forms of pollution such as lead from piping and paints would presumably not be greatly different in both types of environment.

Among different breeds of cattle, there was a significant (P less than 0.05) difference in the means of Angus and Friesian/Jersey X cattle considered as one group and the remaining breeds considered as another. Mean values were 0.29 ± 0.07 and 0.15 ± 0.08 µg/ml respectively and the value of t was 1.87 for 44 degrees of freedom.

(d) Whole-blood lead concentrations in domestic animals with suspected lead poisoning.

Table II.5. gives data for a number of domestic animals suspected of having died from lead poisoning.

In all cases lead levels in whole blood exceeded 0.50 µg/ml and the highest values were in dogs from service station areas. These high values must surely result from poisoning from leaded petrol either from fumes of idling motors or by contamination of food or water.

There were no recorded cases of poisoning of cats or sheep, probably because they tend to be less highly regarded than dogs or larger ruminants so that post mortems are seldom carried out on them. The significantly higher lead levels found in dogs compared with larger animals may be because dogs will require much less lead to give elevated concentrations in the whole blood than will cattle or horses. Obviously, the high values found in

Table II.5.

Whole-Blood Lead Concentrations (μg/ml) in New Zealand Domestic Animals with Known Histories of Lead Poisoning

Animal	Source of Poisoning	Pb in blood	Normal Pb
Dog			
2 -yr Corgi (m)[*]	Water (Pb piping)	3.67	0.26
2 -yr G.Shep.(m)	Water (Pb piping)	4.82	0.29
5 -yr G.Shep.(m)	Service station area	6.42	0.28
7 -yr Labr. (F)	Service station area	7.40	0.25
Cattle			
1 -yr Friesian (m)	Water (Pb piping)	0.52	0.13
3 -yr Jersey (F)	Water (Pb piping)	0.70	0.17
Horse			
5 yr - Std. (m)	Water (Pb piping)	0.54	0.20

*Sex denoted in brackets (m: male; F: female)

animals near service stations must cause some concern about the
health of humans working in these areas.

4. Conclusion.

The development of a rapid, precise and reproducible method
to determine whole-blood lead levels using the carbon rod atom-
izer enables surveys involving large numbers of samples to be
carried out. In this section the results of a survey to deter-
mine the lead levels of whole-blood of New Zealand domestic
animals was reported.

In summary, cats, dogs and sheep showed no significant
differences in lead levels according to age, whereas larger
ruminants such as cattle (t = 4.67 for 250d.f.) and horses
(t = 5.81 for 256 d.f.) showed a very-highly significant
(P < 0.001) difference between those animals younger than 18
months compared with all other age groups. Generally there is no
significant difference in lead content as a result of sex for all
animal groups investigated (although cattle showed a very-highly
significant difference between male and female - neutered animals).
Detectable differences among different breeds were only measured
for dogs and cattle. Sheep dogs from rural areas showed a very-
highly significant difference (t = 3.1 for 80 d.f.) compared with
pedigree dogs from city areas. It should be emphasized that the
whole-blood lead level of a domestic animal is very much dependent
upon the eating/drinking habits of the animal and the type of
environment in which it lives.

The lower lead levels measured in the whole blood of rural
dogs is obviously (as already pointed out) a reflection of the
reduced contact with lead pollution predominantly from motor
vehicle exhaust emissions, industrial smelter fumes and service
station pollutants. This is supported by results from Bloom et al
(1976), and Thomas et al(1975) who investigated the lead concen-
trations in three groups of dogs from a suburban Illinois
community where normal urban dogs (total no. 89) showed a mean
whole-blood lead concentration of 0.07 ± 0.073 (S.D.) compared
with dogs from the city pound (total no. 50, mean Pb 0.262 ±
0.157) and dogs owned by families from low income areas of the

city (total no. 98, mean Pb 0.172 ± 0.174). This clearly shows the influence of the type of environment where dogs from city pounds are directly subjected to high levels of motor vehicle exhaust emissions and city lead dusts/fumes and those dogs from low income areas were most of the housing consisted of old, deteriorating dwellings in which peeling and chipping lead-based paints are the main lead source.

SECTION III.

LEAD LEVELS IN SHEEP EXPOSED TO MOTOR VEHICLE EMISSIONS.

A. WHOLE BLOOD LEAD LEVELS IN SHEEP EXPOSED TO MOTOR
   VEHICLE EMISSIONS.

1. Introduction.

Elevated lead concentrations in the whole blood of domestic
animals as a result of lead poisoning, have been well documented
following the original work of Blaxter (1950) and Allcroft (1951).
These and later papers (Prigge and Hapke, 1972; Hapke, 1973; Fick
et. al., 1976; Van Gelder et. al., 1973) have been concerned
mainly with lead poisoning from contaminated water and other
similar sources, and have involved numerous artificial experiments
in which lead salts (usually acetates) were fed to domestic
animals. Although recent work (Bloom et. al., 1976; Ward et. al.
1977a – Section II) on whole blood levels in various domestic
animals has by inference, taken into account the possibility of
poisoning from motor vehicle lead emissions, it is surprising
that very little work has been done on whole-blood lead levels in
animals grazing or living adjacent to busy motorways. Where such
investigations have been made, they have mainly involved rodents
and other small animals (Quarles et. al., 1974; Jefferies and
French, 1972; Williamson and Evans, 1972).

Because of the sparsity of data on lead uptake by ruminants
grazed near roadsides, and because of the potential seriousness
of such uptake to a country such as New Zealand, which is heavily
dependent on agricultural exports, the following series of studies
were carried out to investigate the effect of motor vehicle exhaust
emissions upon the lead content of the blood of sheep grazing near
roadsides. The experiments were designed to simulate real
conditions and to avoid feeding artificially with lead salts
which can never resemble the end product of motor vehicle
emissions. The results of these experiments are reported in
this Section.

2. Description of experiments.

Lead levels in whole blood were determined by use of the carbon rod atomizer as outlined in Section I.6.

The following experiments were carried out:

(a) The lead content of the whole blood of a flock of 62 sheep (Romney breed of various sexes and ages) was determined. This flock had been grazed for nearly six months along the verges of a major highway (5000 vehicles/24 hours). Comparative data were obtained for another flock of sheep from the same area but well removed from the effect of motor vehicle exhaust emissions.

(b) Four sheep (Romney ewes of 2, 2, 4 and 5 years of age) were removed from the above contaminated area and transferred to a paddock well away from motor vehicles. The lead content of the whole blood was monitored at regular intervals for 185 days.

(c) Four sheep (Romney ewes of 2, 2, 4 and 5 years of age) from an uncontaminated area were placed in a paddock at Massey University. This pasture was adjacent to a busy road (8000 vehicles/24 hours). The whole-blood lead levels were monitored at regular intervals.

(d) Ten sheep (Romney ewes and wethers of various ages) were kept in a pen well away from motor vehicles and were fed with fresh grass collected from the verge of a busy roadway. The whole-blood lead levels were monitored over a 9 day period.

(e) Four sheep (Romney ewes of 2, 5, 5, and 5 years of age) were placed in a pen near a busy highway (8000 vehicles/24 hours) without access to local forage. The sheep were fed with feed from a non-contaminated area and the whole-blood lead levels were monitored for a period of 5 days.

3. Results and discussion.

(a) The whole blood lead content of sheep grazing near a highway.

The lead content of whole blood of a flock of sheep grazed for 6 months near a highway at Dannevirke was compared with an adjacent flock in Figure III.1. The other flock was from a non-contaminated area. The means and standard deviations of the two populations

Figure III.1.
Histogram of whole-blood lead levels (µg/ml) in sheep
grazing near to, and away from, a major highway.
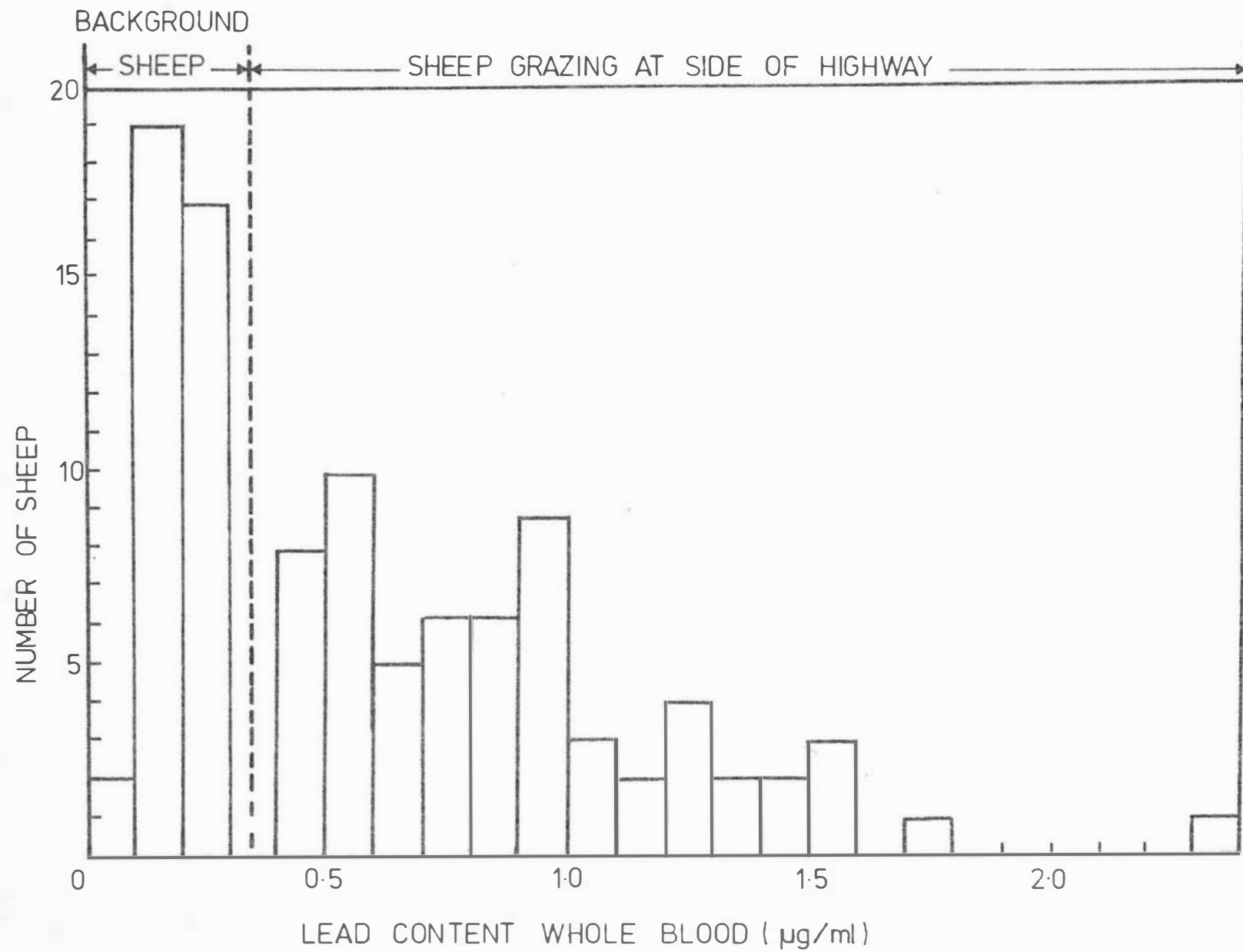
were 0.90 ± 0.05 µg/ml and 0.20 ± 0.01 µg/ml respectively.

The histogram shows that both populations can be separated completely on the basis of the lead content of their whole blood. Eighteen sheep had lead levels exceeding 1.0 µg/ml. These concentrations are extremely high and are comparable with levels found in sheep fed artificially with lead salts as reported by Blaxter (1950). The same author found a maximum of 1.30 µg/ml in the whole blood of a sheep fed with 30g of lead as acetate. This level was reached by one third of the sheep in this study.

The mean lead content of the contaminated pasture was 60 µg/g (dry weight) and corresponds to an ingestion of 7.2g of lead over a period of 150 days if a daily intake of 800g of feed is assumed. The mean lead content of a 'background' pasture was < 5 µg/g (dry weight) and corresponds to <0.6g of lead ingested over the same time period.

(b)   The rate of decrease of whole-blood lead levels after removal of animals from a contaminated area.

When 4 sheep from the Dannevirke experimental area (see above) were removed to a paddock well away from motor vehicle emissions, the whole-blood lead levels decreased during a period of 185 days. The data are shown in Figure III.2.

The concentration decreased from about 2.00 to 0.60 µg/ml during the first 10 days. Background values (0.20 µg/ml), though approached, had still not been reached after 185 days. Unfortunately 1 sheep died after 85 days as a result of inhalation pneumonia and septicaemia following routine sheep "dipping".

Lead is known to be stored in the bones of sheep (Fick et. al., 1976) and these form a convenient reservoir for gradual release of lead into the blood over a long period.

(c)   Uptake of lead by sheep brought from an uncontaminated area to a paddock near a highway.

When 4 sheep from an uncontaminated area (lead content of pasture 5 µg/g, dry weight) were placed in a paddock near a major highway (lead content of forage, 19 µg/g dry weight), the

Figure III.2.

Decrease of whole-blood lead levels (µg/ml) in four
sheep after removal from a contaminated area.
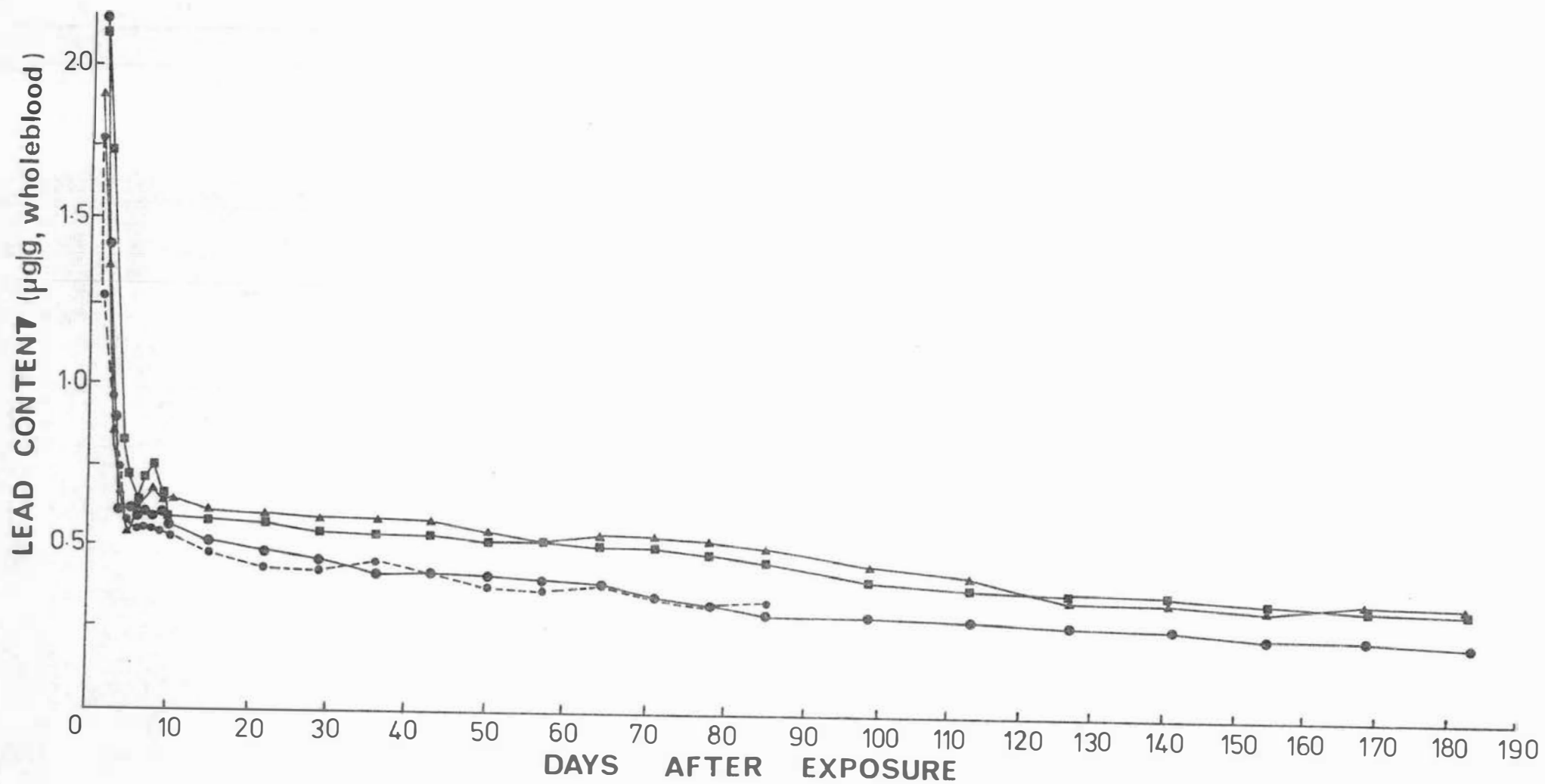
lead content of the whole blood rose from 0.20 to about 3.00 µg/ml during the first 24 hours. Thereafter, there was a gradual decrease over 14 days to a value of about 1.5 µg/ml. This is shown in Figure III.3.

The pasture used in this experiment was lucerne (Medicago sativa L.). During the initial period the sheep were consuming leafy material almost exclusively. This had been exposed to lead contamination during the preceding rest period. As the experiment continued, the diet contained a greater proportion of stem material with a lower lead content. It was also likely that intake was reduced slightly as the palatability of the feed declined. The combination of these two factors is suggested as the cause of the post peak reduction in whole-blood lead. It is also possible that lead was being removed from the blood for storage in other body organs as will be outlined in Section III.B.

(d) Uptake of lead by sheep placed away from motor vehicle emissions but fed with grass from roadside verges.

When 10 sheep were placed in a concrete pen well away from motor vehicle exhaust emissions and were fed with grass freshly cut from the verges of a busy highway, there was an immediate rise in the whole-blood lead levels as shown in Figure III.4.

The mean values increased from 0.17 µg/ml to 1.1 µg/ml over a period of 9 days. The lead content of the feed varied from 40-70 µg/g (dry weight basis) Figure III.4. also shows (broken lines) the total daily intake of lead. Increased intakes towards the end of the test period are due partly to the higher lead content of later feeds and partly to increased consumption of grass as the animals became used to the new environment. There appeared to be some relation between the lead content of the whole blood and the daily intake of lead.

Figure III.3.
Whole-blood lead levels (µg/ml) in sheep transferred
from a background area to a contaminated paddock.
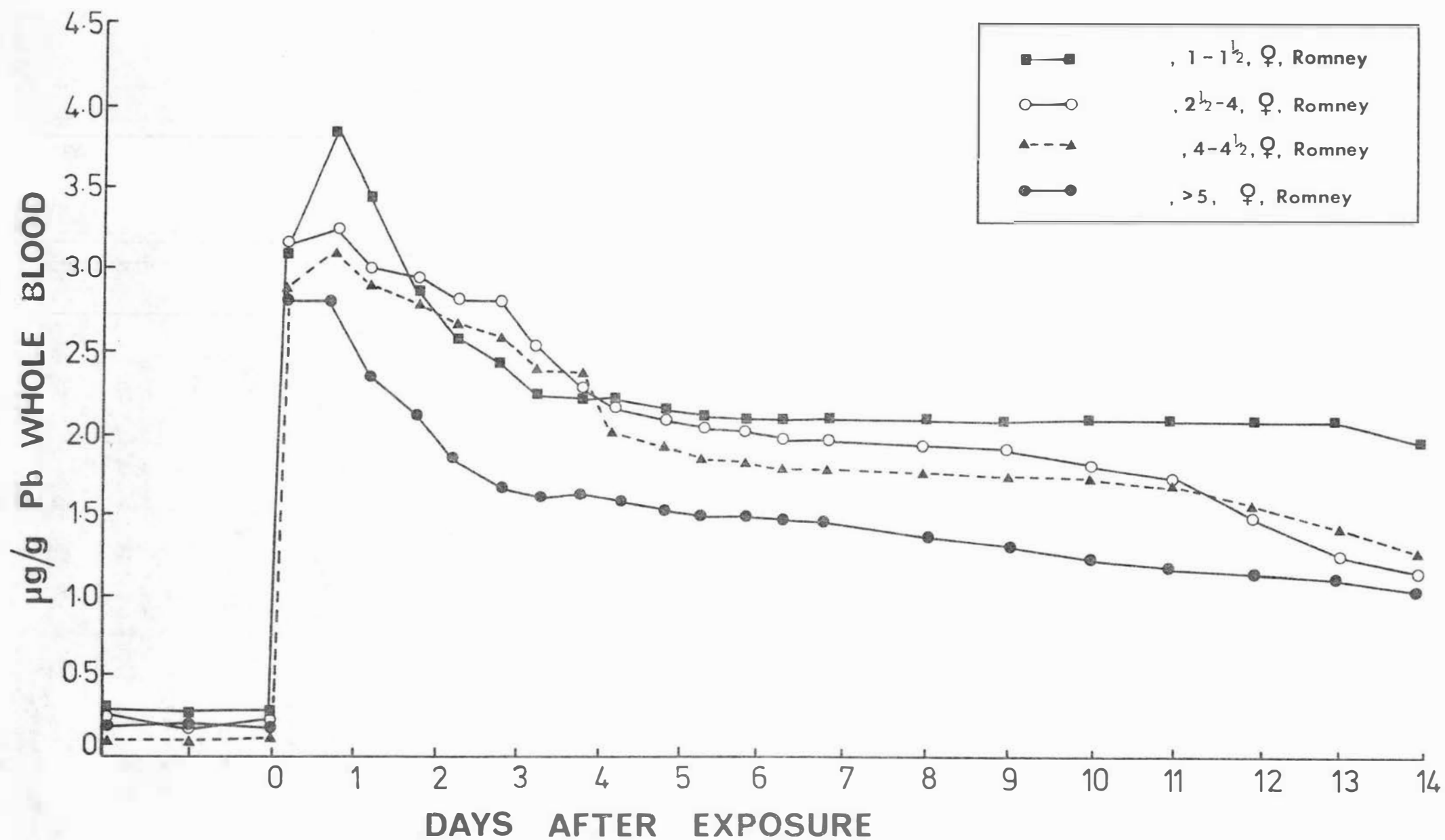
Figure III.4.

Whole-blood lead levels in µg/ml (continuous line) in sheep placed in a background area and fed with grass from roadsides. Daily uptake of lead is shown as a broken line.
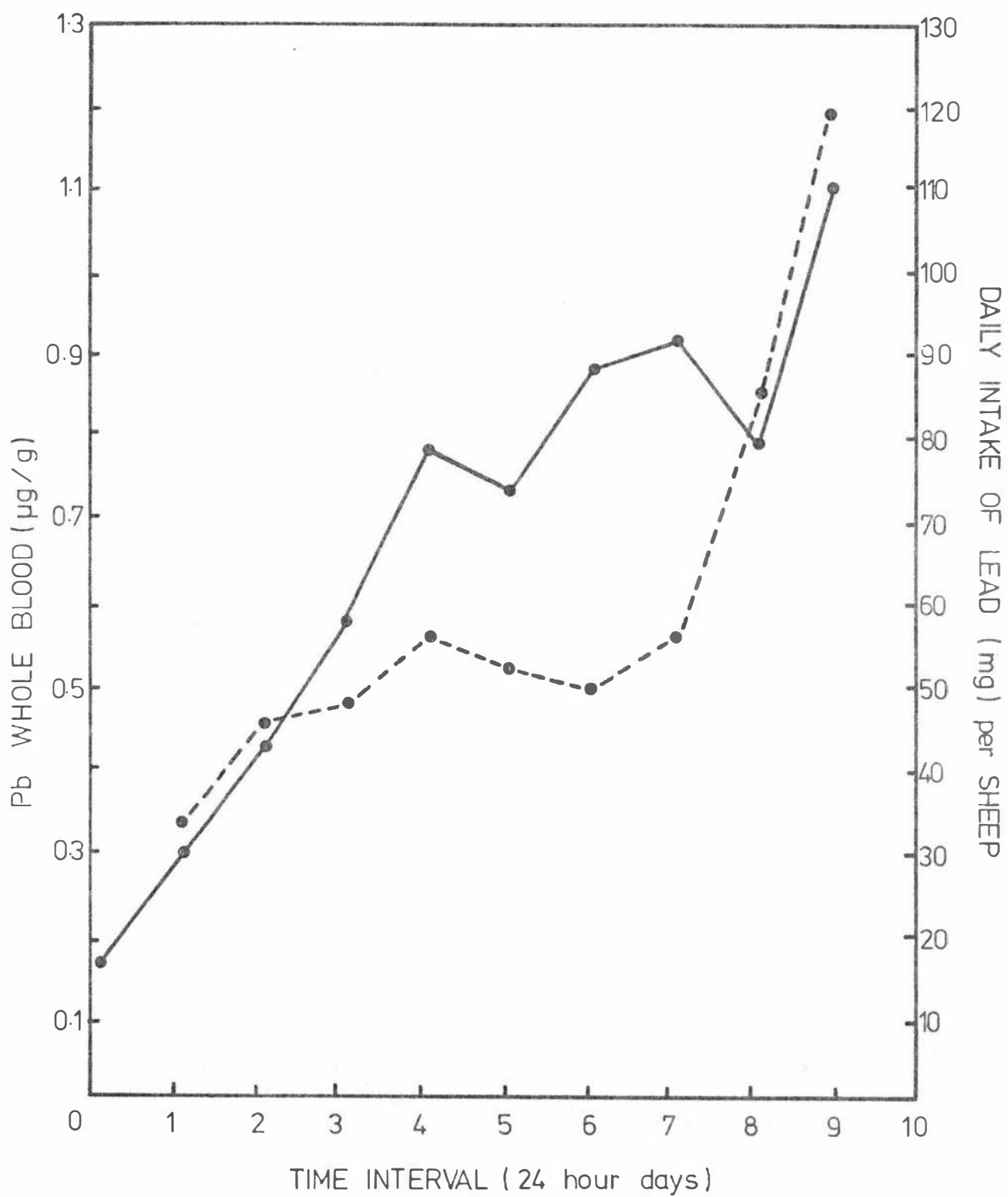
(e) <u>Uptake of lead by sheep placed near a busy highway and given feed from an uncontaminated area.</u>

The experiments so far had shown that the lead content of the feed was an important factor determining the lead content of the whole blood in the experimental animals. In order to establish whether inhalation of lead particulates was a contributing factor, 4 sheep were placed near a busy highway without access to local feed. The sheep were fed with forage (2.5 µg/g lead - dry weight) from an uncontaminated area. As before there was an immediate increase in the whole-blood lead level as shown in Figure III.5.

The rate of uptake was very similar to that of the previous experiment and would seem to indicate that ingestion by forage, and inhalation of particulates in the air were equally important in affecting the lead content of the whole-blood.

4. <u>General discussion and summary.</u>

Enhanced lead levels in the whole blood of sheep are in themselves only symptomatic of elevated concentrations in bones and reservoir organs such as liver and kidneys, all of which have been found by Fick <u>et</u>. <u>al</u>. (1976) to have enhanced lead levels after feeding artificially with lead salts. Whether or not lead will be found in the same reservoirs after experiments under natural conditions of grazing near highways is somewhat uncertain and an investigation into this subject is described in part B. of this section.

In summary, the lead content of whole blood of 62 sheep grazed continuously for 6 months near a major highway was compared with 38 sheep from a nearby uncontaminated area. Mean values of 0.90 and 0.20 µg/ml were obtained. Four sheep from the contaminated area were placed in an uncontaminated paddock and the lead content of the whole blood decreased rapidly during the first 10 days and thereafter more slowly. After 185 days, whole-blood lead levels had still not quite reached normal levels.

Figure III.5.

Whole-blood lead levels in sheep (four individuals shown as different symbols) placed near roadside but fed with uncontaminated forage.
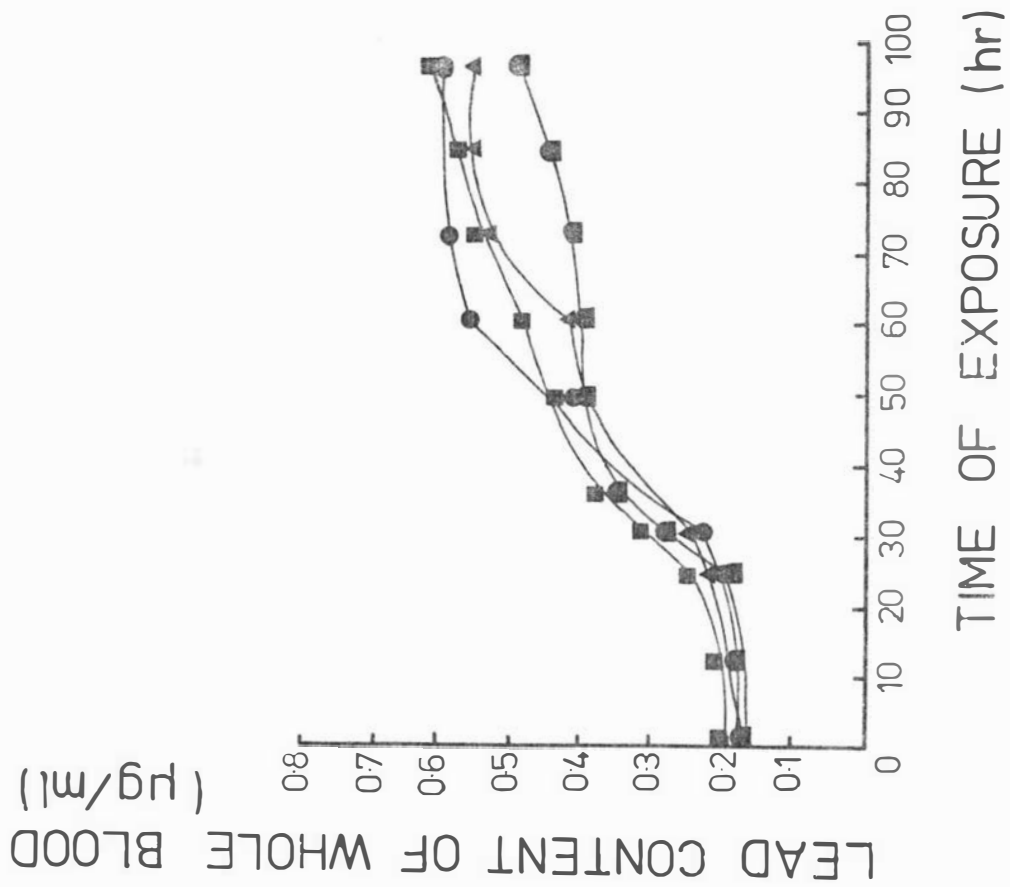
TIME OF EXPOSURE (hr)

LEAD CONTENT OF WHOLE BLOOD ($\mu g/ml$)

Animals from an uncontaminated area showed an immediate rise in the whole-blood lead levels when placed near a major highway. Sheep placed in a concrete pen away from motor vehicle exhaust emissions showed a rise in lead levels when fed with forage cut from the verges of a busy highway. Sheep placed near a highway and fed with forage from an uncontaminated area showed an increase of lead levels in the whole blood, comparable to that of the previous experiment.

It was concluded that lead uptake by ingestion of polluted forage and by inhalation of airborne particulates are both mechanisms responsible for enhanced lead levels in ovine whole blood.

B. LEAD LEVELS IN SHEEP ORGANS, MUSCLE TISSUE, BONES AND
WOOL.

1. Introduction.

As outlined in the previous sub-section, numerous experiments
have been carried out on lead levels in organs of domestic
animals since the early work of Allcroft & Blaxter (1950) and
Blaxter (1950) who found enhanced levels of lead in bones, livers,
kidneys and lungs of sheep after artificial dosage (orally and
intravenously) with lead salts. Similar studies were obtained
in recent studies (Prigge and Hapke, 1972; Fick et. al., 1976)
although again, dosage was carried out artifically with lead
salts.

Since motor vehicle emission is environmentally by far the
greatest source of lead pollution, there is clearly a need for
research orientated specifically to this problem and with
experiments designed to reproduce as closely as possible to the
natural conditions encountered by animals grazing close to road-
sides. There have been few experiments of this nature; although
Quarles et. al. (1974) investigated the lead content of small
mammals living near roadsides. Othere studies (Hapke, 1972;
Gelder et. al., 1973; Fick et al., 1975) based on the effect of
dietary lead on sheep have been related to neurological and
pathological effects with lead levels of whole blood only being
reported instead of a more detailed account of the absorption and
distribution of lead in the body organs, muscle tissue and bones.

Because of the known accumulation of lead in human hair
(Renshaw et. al., 1972; Reeves et. al., 1975), there was the
possibility that elevated lead levels in sheep organs would be
reflected in the wool. If this were to be the case, wool sampling
would offer a much simpler method of assessing the lead burden
in sheep. For this reason, the lead content of sheep wool was
investigated in addition to that of other organs of the animal.

It was considered that the above work was necessary because
of the risk to domestic pets and humans of meat contaminated with
lead (Hankin et. al., 1975) and because of the potential damage
to export markets of countries such as New Zealand which are

heavily dependent upon the export of meat. Section III.A. reported the associated lead levels in the whole blood of these sheep.

2. Materials and methods.

Three experiments were carried out as follows:

(i) A flock of sheep (Romney ewes of various ages) was grazed continuously for 6 months along the grass verge of a highway (average daily traffic density of 5000 vehicles) near Dannevirke, North Island. The flock was contained by a moveable electric fence. The lead content of each of 62 sheep was monitored and ten individuals were selected on the basis of relatively high blood lead levels as reported in Section III.A.3a. Six of these sheep were immediately slaughtered and their organs analysed for lead. The remaining 4 sheep were kept for a further 185 days in a paddock well away from motor vehicle emission and then slaughtered. The lead content of various organs was again determined.

(ii) Ten sheep (Romney ewes and wethers of various ages) were kept in a pen well away from motor vehicle emissions and were fed with contaminated feed from the grass verge of a busy highway (8000 vehicles/24 hours) at Palmerston North. After 9 days, 4 of the sheep (individuals with the highest blood lead levels) were slaughtered and their organs analysed for lead.

(iii) Four sheep (Romney ewes) were placed in a pen near a busy highway (8000 vehicles/24 hours) at Palmerston North and fed with lucerne hay from a non-contaminated area. The sheep were slaughtered after 5 days and the organs analysed as before.

The above experiments were designed to test the effects of:

(i) lead received via the lungs and digestive system;

(ii) lead ingested from the feed alone;

(iii) lead inhaled via the lungs alone.

Background values for lead in sheep organs were obtained by analysing random samples from a freezing works. Sheep organs were prepared for analysis and analysed as outlined in Section I.B. Lead levels in the wool of 12 sheep were also analysed as an alternative method to whole blood analysis for determining the potential

lead burden in sheep. Sampling and the method of analysis for wool is outlined in Section I.B.4(a)(ii).

3. Results and discussion.

(a) Lead in organs of sheep grazed near a highway.

Lead concentrations for organs of 6 sheep grazed near a busy highway are shown in Table III.1. Standard deviations represent real differences among the individuals of a population because of the experimental error (obtained by analysis of 10 replicates and not shown in the table) accounts for only about 10% of the overall standard deviation.

A series of t-tests were used to establish the significance of differences between groups. Because they are self weighting, t-test are valid even for very small populations.

From table III.1. it can be noted that very-highly significant differences ($P \leq 0.001$) existed between means of lead levels in organs of 'contaminated' animals and in organs of 'background' animals. The only exceptions were in the kidney medulla after 6 months (B) and in the short digital extensor (A and B).

In absolute terms easily the highest lead concentrations were in the kidney cortex (154 µg/g wet weight), liver (20 µg/g) and bones ($\sim$30 µg/g). These findings parallel the data of Prigge & Hapke (1972) and Fick et. al. (1976) in experiments involving artificial feeding with lead salts.

With animal production and meat quality in mind, it is fortunate that muscle tissue shows the smallest concentrations of lead in absolute terms (though not relative to background values).

Bones, because of their high proportion of total body weight, represent the greatest reservoir of lead within the animals. Their rate of lead loss is also very slow. After 6 months, lead concentrations in bones had not changed appreciably although the level of this element in kidney cortex had decreased from 154 to 12 µg/g. The high level of lead in bones will clearly ensure that the animals will have above-normal levels of lead in their organs probably for the whole of their natural life-span. It is probably these high levels in bones that accounts for the very

Table III.1.

Mean Lead Concentrations (µg/g wet weight) in Organs of Sheep
Grazed Near a Busy Highway.

A - immediately after removal from roadside (6 sheep)
B - 6 months after removal from roadside (4 sheep)
C - background values (10 sheep)

Organ	A	B	C
Abdominal muscle	* 0.6 ± 0.2	* 0.5 ± 0.05	0.11 ± 0.02
Bone (shoulder)	* 24.4 ± 4.0	* 28.5 ± 4.5	0.12 ± 0.02
Bone (vertebrae)	* 36.5 ± 4.6	* 34.4 ± 5.0	0.13 ± 0.03
Brain (cerebrum)	* 1.5 ± 0.3	* 1.4 ± 0.04	0.44 ± 0.10
Caecum	* 1.9 ± 0.4	* 0.6 ± 0.2	0.30 ± 0.09
Heart muscle	* 1.3 ± 0.4	* 1.0 ± 0.2	0.45 ± 0.14
Intestine (large)	* 3.2 ± 0.8	* 0.9 ± 0.1	0.41 ± 0.09
Intestine (small)	* 4.0 ± 1.8	* 1.5 ± 0.4	0.39 ± 0.10
Kidney (cortex)	* 154.0 ± 34	* 12.0 ± 8.4	0.8 ± 0.1
Kidney (medulla)	* 3.0 ± 1.0	2.0 ± 1.5	0.7 ± 0.1
Liver	* 20.0 ± 6.0	* 5.0 ± 1.0	0.7 ± 0.2
Lung	* 2.0 ± 0.8	* 1.7 ± 0.2	0.6 ± 0.2
Pancreas	* 2.2 ± 0.7	* 1.3 ± 0.4	0.25 ± 0.13
Rumen	* 3.1 ± 1.1	* 1.4 ± 0.5	0.26 ± 0.08
Shoulder muscle	* 0.45 ± 0.14	* 0.45 ± 0.06	0.14 ± 0.01
Short digital extensor	0.29 ± 0.07	0.28 ± 0.06	0.20 ± 0.04
Spleen	* 1.8 ± 0.6	* 1.8 ± 0.4	0.6 ± 0.1

* Very-highly significant differences from background as determined
by t tests (P ≤ 0.001)

slow reduction of whole-blood lead levels to background values
when the source of pollution has been removed (Section III.A.).

Although the lead levels of edible muscle tissue were
probably within existing safety limits for human consumption, the
high lead content of other organs could be reflected in unaccept-
able concentrations in pet foods (Hankin et. al., 1975), since
liver and kidneys form a high proportion of such foods. Livers
and kidneys are also occasionally consumed by humans, imposing a
direct threat on human lead uptake.

(b) Lead in organs of sheep away from motor vehicle emissions
but fed with contaminated grass.

The data for lead levels in sheep kept away from motor
vehicle emissions but fed with contaminated pasture are shown
in Table III.2.

As before, nearly all organs showed a very-highly significant
increase of lead content compared with background. The only
exception was the kidney medulla. Probably because of the
shorter exposure to lead (9 days instead of 6 months), the
absolute concentrations of this element were not as great as
in the previous experiment. This particularly is evident in
bones where values were ten times lower than in the previous
experiment, though still very much higher than background.
Highest absolute values were in the kidney cortex and liver.
It is clear that accumulation in these organs takes place very
rapidly.

(c) Lead in organs of sheep exposed to motor vehicle
emission and fed with uncontaminated grass.

The data for lead in organs of sheep exposed to motor
vehicle emissions and fed with uncontaminated grass are also
shown in Table III.2.

Table III.2.

Mean Lead Concentrations (µg/g wet weight) in Organs
of Sheep

D - not exposed to motor vehicle emissions but fed with grass
from a roadside for 10 days (3 sheep)

E - exposed to motor vehicle emissions but fed with uncontaminated
grass for 5 days (4 sheep)

Organ	D	E
Abdominal muscle	* 0.44 ± 0.22	* 0.44 ± 0.04
Bone (shoulder)	* 1.9 ± 0.2	* 1.6 ± 0.07
Bone (vertebrae)	* 1.4 ± 0.2	* 1.4 ± 0.03
Heart muscle	* 1.1 ± 0.1	* 1.5 ± 0.4
Intestine (small)	* 3.1 ± 0.2	* 1.5 ± 0.2
Kidney (cortex)	*39.7 ± 8.3	* 3.5 ± 0.8
Kidney (medulla)	1.1 ± 0.1	* 1.6 ± 0.3
Liver	* 8.4 ± 1.9	* 4.0 ± 0.7
Lung	* 2.0 ± 0.05	* 8.0 ± 3.6
Pancreas	* 1.4 ± 0.4	* 1.6 ± 0.4
Rumen	* 1.3 ± 0.1	* 1.2 ± 0.3
Shoulder muscle	* 0.37± 0.01	* 0.46± 0.03
Spleen	* 2.3 ± 0.1	* 3.6 ± 0.9

* Very-highly significant differences from background
(see Table III.1.) as determined by t-tests (P ≤ 0.001)

Although the exposure time was only 5 days, * significant concentrations of lead were apparent in the bones and other organs, all of which had levels which were very-highly significantly $(P \leqslant 0.001)$ higher than background. The essential difference between the data for this experiment and for the preceding one lies in the high relative concentration of lead in lungs (8.0 µg/g compared with 2.0 µg/g for experiment B) and the low relative accumulations in the liver (4.0 and 8.4 µg/g) and kidney cortex (3.5 and 39.7 µg/g) respectively. It is clear from this experiment that a relatively high lead burden can be accumulated by sheep by inhalation through the lungs instead of the alternative mechanism of ingestion.

(d)   Lead content of sheep wool as a result of exposure to motor vehicle emissions.

The sheep exposed to motor vehicle emission lead whilst grazing along the grass verge of State Highway 2, near Dannevirke and from background areas (Part B2(i)) were sampled by taking 10cm lengths of their wool (noting which was the inside end). Figure III.6. shows the mean lead content (µg/g dry weight) of 5 replicates for unwashed (continuous lines) and washed (broken lines) wool samples from sheep subjected to motor vehicle emissions (above) and those from a background area (below), expressed as a function of distance (cm) measured from the inside to the outside. The mean whole-blood lead level is also shown. All 4 sheep were Romney ewes ranging in age from 4-5 years.

It is apparent that there is no evidence to suggest that sheep in fact 'excrete' lead from the body organs, muscle tissue and bones into the wool. Those sheep grazing in lead-contaminated areas show a predominant pattern of elevated levels towards the

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* The experiment was of necessity limited to only 5 days because of the risk of leaving sheep unattended over a weekend where there was some risk of interference from, "anti-social" elements of the population.

Figure III.6.

The mean lead content (µg/g dry weight) of washed (broken lines) and unwashed wool samples from sheep subjected to motor vehicle emission lead (above) and low background lead levels (below), expressed as a function of distance (cm) measured from the inside to the outside.

LEAD CONTAMINATED AREA

Whole blood level (0·64 µg/ml)

Whole blood level (0·80 µg/ml)

BACKGROUND AREA

Whole blood level (0·12 µg/ml)

Whole blood level (0·18 µg/ml)

MEAN LEAD CONTENT (µg/g dry weight wool)
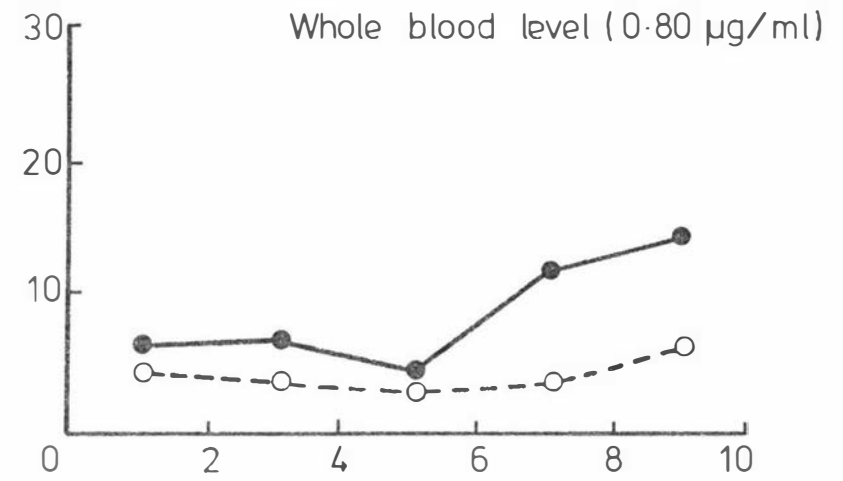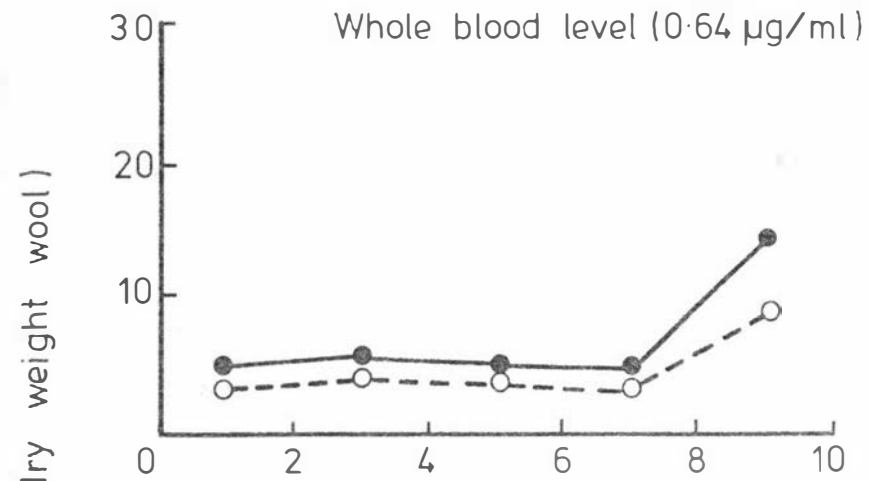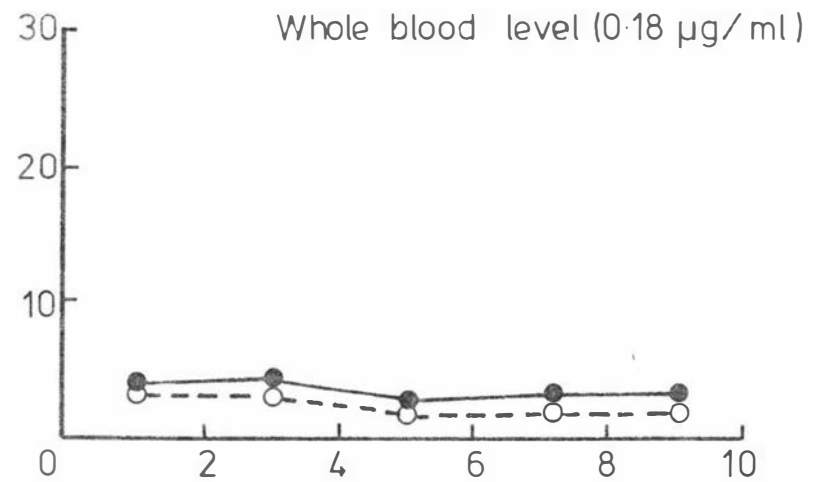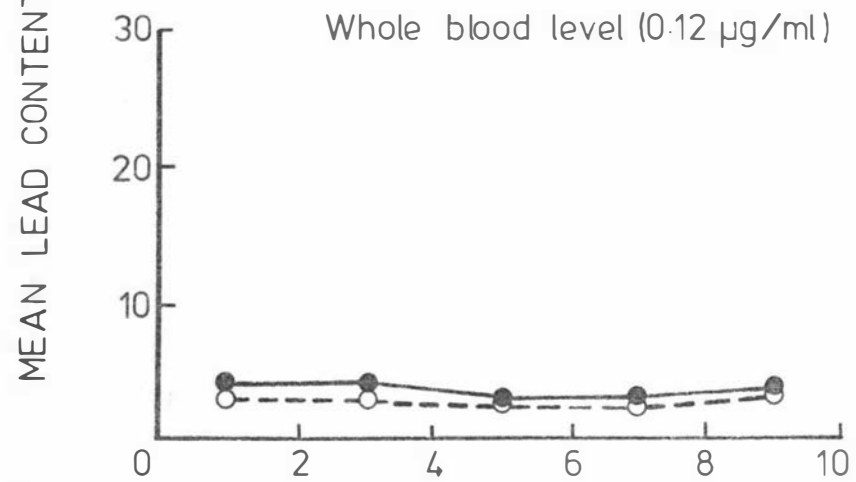
LENGTH OF WOOL FROM INSIDE TO OUTSIDE (cm)

outside with an associated increase in the amount of lead removable by washing which suggests that such lead levels are due to the impact of airborne lead particulates adhering to the wool fibres (which act rather like an air filter). Obviously some percentage of these particulates is chemically or physically bound into the wool fibre whilst the rest can be removed by washing. Those sheep sampled in background areas show no relative pattern of lead absorption towards the skin-contact or outside ends. A normal lead level for sheep wool would be 5 µg/g (dry weight).

There was an extremely good correlation between the lead content of the outer 2 cm of wool and the content of whole blood. This is shown in Figure III.7. A total number of 12 sheep were sampled from contaminated and background areas. The correlation was very-highly significant ($P \leq 0.001$). The correlation was preserved even for washed wool samples. The significance of this finding is that it is apparently possible to use easily sampled wool material in place of whole blood to assess the lead burden of sheep. It may be argued that 12 individuals do not represent a very large sample but the assessment of significance is carried out by a self-weighting statistical technique where progressively higher values of r are necessary to establish a given degree of significance as the number of samples decreases.

4. Conclusion.

The experiments show that significant lead concentrations can be found in organs of sheep grazing adjacent to busy highways. Patterns of lead uptake follow closely those found in experiments involving artificial feeding with lead salts. It is clear also that this lead burden is acquired partially by direct inhalation of airborne lead from motor vehicle exhausts and partially indirectly by consumption of contaminated forage. Although it is difficult to establish which mechanism is the more important, it is apparent that both can result in lead levels in organs which are well above background values. The major differences are in accumulation of lead in the lungs in the former case and in the

Figure III.7.

The lead content of the outer 2cm wool (µg/g dry weight) of twelve sheep from lead contaminated and background areas as a function of the lead content of their whole blood (µg/ml).
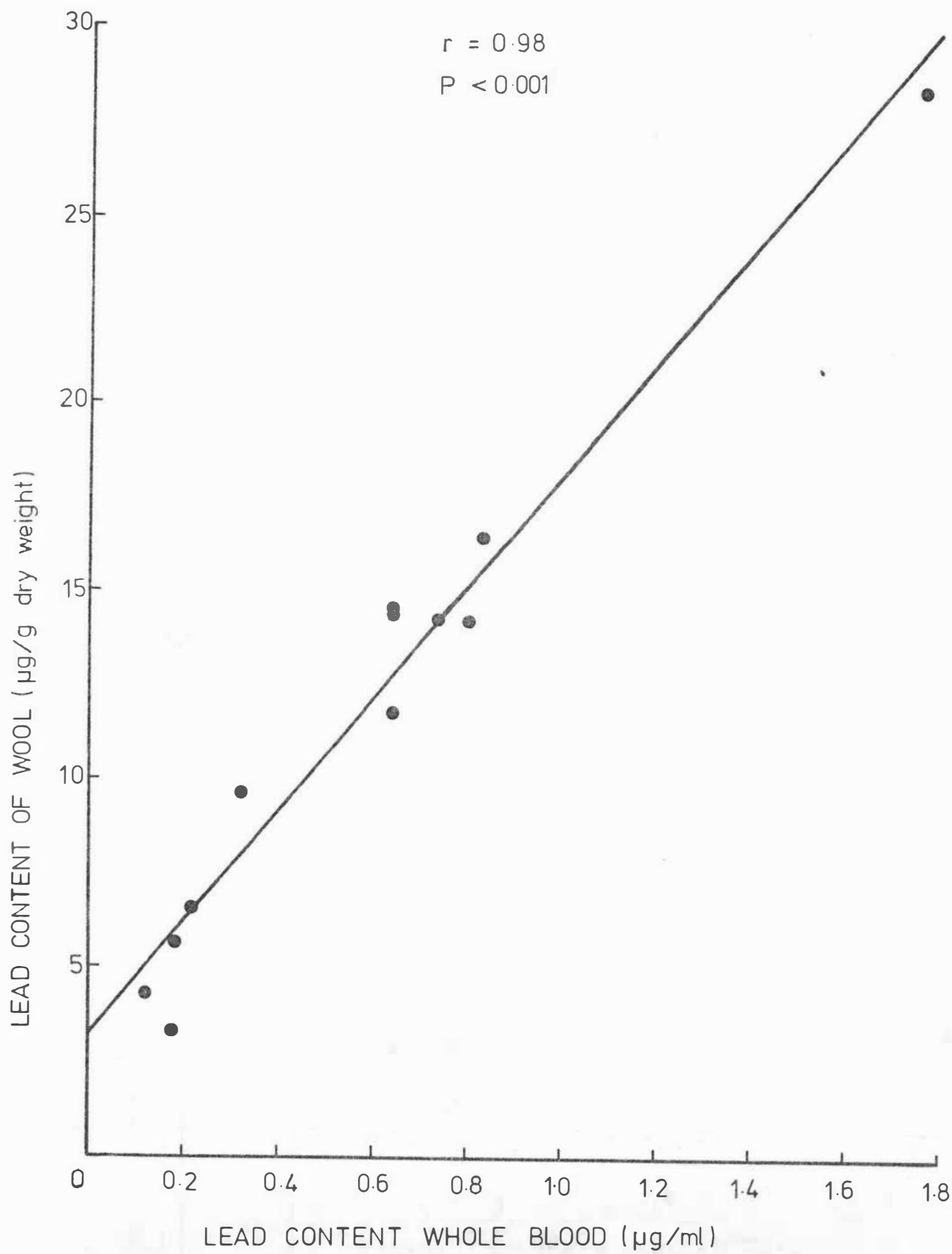
kidney cortex and liver in the latter.

There is no evidence to suggest that sheep 'excrete' lead from the body organs into the wool. Although washing removes a significant percentage of lead from the wool of sheep exposed to motor vehicle emissions, airborne lead particulates adhere and may become incorporated into the wool fibres, especially in the outer 2cm of wool exposed to fallout. A normal lead level for sheep wool would be 5 $\mu g/g$ (dry weight) with elevated levels of >15 ug/g being reached. A very-highly significant correlation ($P < 0.001$) was obtained between the lead content of the outer 2cm of wool and the content of the whole blood.

Because of increasing worldwide concern about meat quality, it would seem to be advisable to avoid grazing stock on the grass verges adjacent to highways. If such grazing has to be done due to economic circumstances, at least the offal should be discarded in an effort to reduce lead levels in pet food which is sometimes consumed by humans (Hankin et. al., 1975). In addition to the perhaps minor hazard presented by pet food, there remains the possibility of direct consumption of contaminated livers or kidneys by humans. Assuming an acceptable daily intake of 0.4mg of lead (W.H.O., 1972) by adult humans (children should have a much lower intake), it is clear that a single serving of 200g of liver containing 20 $\mu g/g$ lead would supply the maximum permissible elemental intake for a period of 10 days.

SECTION IV.

HEAVY METAL (Cd, Cr, Cu, Ni, Pb and Zn) POLLUTION FROM MOTOR
VEHICLE EMISSIONS AND ITS EFFECT ON ROADSIDE SOILS AND PASTURE
SPECIES ALONG THE AUCKLAND MOTORWAY, NEW ZEALAND.

1. Introduction.

The magnitude and distribution of lead particulate
pollution from motor vehicle emissions has been extensively
investigated in recent years. The presence of lead in soils and
pasture species near highways has been related by many authors
to such variables as traffic density (Cannon and Bowles, 1962;
Kloke and Riebartsch, 1964; Daines et. al., 1970; Page and Ganje,
1970) and predominant wind directions (Ward et. al. 1974b). The
possible hazard to health by lead pollution from this source has
been highlighted by work on lead levels in soils (Chow, 1970;
Olson and Skogerboe, 1975) and highway pastures and plants
(Lagerwerff, 1970; Schuck and Locke, 1970; Ter Haar, 1970;
Rabinowitz and Wetherill, 1972; and Ward et. al., 1975b)

Apart from lead, very little attention has been paid to the
possibility of pollution from other heavy metals derived from
motor vehicles. Studies on particulate components in motor
vehicle emissions have been centred on lead, sulphate, nitrate,
halides (their associated gaseous mixtures) and hydrocarbons
(Habibi, 1970, 1973; Lee et. al. 1971; Heichel and Hankin, 1972;
Moyers et. al, 1972; Te Haar et. al., 1972; Lonneman et. al.,
1974). However, Lagerwerff & Specht (1970) reported the presence
of cadmium, nickel and zinc (as well as lead) in soils and
grasses at roadsides. These elements were presumably derived
from motor vehicle emissions and for a site with 48,000 vehicles
per day, had the following range of concentrations ($\mu g/g$ dry
weight) for surface soils in the interval 8-32 meters from the
road : cadmium, 0.94-0.24; lead, 540-140; nickel, 7.40-2.40;
zinc, 162-114. Corresponding values for grasses were : cadmium,
0.75-0.48; lead, 51.3-18.5; nickel, 3.8-1.3; zinc, 40-30.3.
Gish & Christensen (1973) also measured concentrations of these
elements in soils and earthworms and showed a decrease with
increasing distance from the road.

The toxicity of all the above elements towards humans has
been well documented (W.H.O., 1972) and because of the paucity of
data on pollution by these elements (except in the case of lead)
from motor vehicle exhausts, there is clearly a need for further

studies on these and other heavy metals. This need is further
reinforced by the fact that none of the previous studies had
included chromium or copper (both of which are components of
motor vehicles), and none had attempted to correlate elemental
concentrations with traffic densities.

Therefore, in this section, work is reported on concentrations
of cadmium, chromium, copper, lead, nickel and zinc in soils and
pasture species along a busy motorway in Auckland City, New
Zealand. Elemental concentrations **were** also correlated·with
the traffic densities at each collection locality.

2. Study area.

The Auckland Motorway is situated to the south of New
Zealand's largest city, Auckland (population approximately
700,000). The sampling sites were selected on a 1meter wide,
grassed median strip located in the centre of the motorway,
which at some locations has three lanes on either side, (Market
Road to Ellerslie). Seventeen sites, corresponding to the
various motorway interchanges are listed in Table IV.1.

Surface soils (0-1 cm.) were collected at all seventeen
sites and soil profiles were sampled at sites 1, 3, 5-9, and 12.
Background soil samples were taken from the same soil type at
distances well away from the effect of motor vehicle emissions.

The pasture species sampled from the median strip of the
Auckland Motorway were :

Lolium perenne L. (perennial ryegrass), Trifolium repens L.
(White clover), Poa annua L., Dactylis glomerata L. (Cocksfoot),
Holcus lanatus L. (Yorkshire fog), Bellis perennis L. (daisy),
Paspalum dilatatum L., and "flatweeds" of the genera : Plantago,
Bellis and Crepis.

Sample preparation and analysis of these samples were
carried out as explained in Section I.B.

Table IV.1.

Mean Concentrations (μg/g dry weight) of Heavy Metals in Surface Soils from Various Interchanges
of the Auckland Motorway,
New Zealand.

No.	Interchange		Opening Date	Distance (km) from Central P.O.	Traffic Density Vehicles/24 hr.	Concentrations (mean of 5 replicates)					
						Cd	Cr	Cu	Ni	Pb	Zn
1				1.4	28,000	<0.6	60	40	40	800	144
2	Symonds St.	– Khyber Pass	12/66	2.0	47,500	2.5	75	70	90	2330	338
3	Khyber Pass	– Gillies Ave.	9/66	3.1	63,500	1.9	75	50	115	2798	550
4	Gillies Ave.	– Market Road	6/65	4.5	50,000	1.3	80	250	70	2264	663
5	Market Road	– Greenlane	4/65	5.8	57,000	3.8	110	130	150	3064	450
6	Greenlane	– Racecourse	12/63	6.8	54,000	2.6	70	480	110	1265	400
7	Racecourse	– Ellerslie	12/63	8.0	51,750	1.2	65	120	70	1665	350
8	Ellerslie	– Mt. Wellington	7/53	11.2	43,000	<0.6	55	110	70	1332	275
9	Mt. Wellington	– Otahuhu	12/55	13.8	45,000	0.7	60	40	95	2000	263
10	Otahuhu	– Otara	12/55	16.7	43,000	<0.6	65	35	120	1400	175
11	Otara	– Papatoetoe	12/55	17.2	43,000	<0.6	75	30	60	1200	200
12	Papatoetoe	– Wiri	12/55	20.6	28,600	0.7	65	25	70	1398	250
13	Wiri	– Manurewa	5/63	23.4	28,500	<0.6	50	25	65	1232	156
14	Manurewa	– Takanini	5/63	25.7	21,500	0.7	50	20	85	1465	175
15	Takanini	– Papakura	12/65	29.8	19,000	<0.6	60	25	85	800	175
16	Papakura	– Drury	12/65	31.9	14,000	<0.6	45	20	25	533	113
17	Drury	– End of Motorway	12/65	32.5	12,000	0.7	45	20	70	1000	135
	background					<0.3	9	12	8	14	64

3. Results and discussion.

(a) Soils.

The mean concentrations of cadmium, chromium, copper, lead, nickel and zinc in surface soils sampled from the various interchanges of the Auckland Motorway are presented in Table IV.1. All six elements show significantly higher levels along the motorway compared with background areas. Measurements of pH gave values of 6.10 to 7.40 which were sufficiently high to ensure minimum movement of trace elements through the soil profiles (Chow, 1970).

Although elemental levels are considerably higher than background for all elements, there was a possibility that in some cases, the soil had been transported from elsewhere in the city during the construction of the motorway and that the high levels were due to naturally high concentrations of some elements in the basaltic soils of the Auckland area. This could apply to chromium and nickel, though not to the other elements which are not usually enriched in basaltic substrates. In order to confirm the true origin of heavy metals in the soils, a number of soil profiles were analysed. Decrease of elemental concentrations with depth would indicate surface contamination from motor vehicles, whereas unchanging concentrations would show that anomalous heavy metal levels were a function of the substrate itself.

Figures IV.1 and IV.2 show concentrations of six elements in soil profiles from nine interchanges divided into three groups according to traffic densities.

It is clear from these figures that elemental concentrations invariably decrease with depth of all sampling sites and that this is most apparent at the interchanges with the heaviest traffic densities. At the busiest sites, elemental concentrations decrease by an order of magnitude in a depth of only 10cm. Concentration patterns of elements in all soil profiles, indicate that these elevated levels in surface soils are due to extraneous sources (presumably motor vehicle emissions) and are not a function of soil type.

Figure   IV.1.

Concentrations (µg/g dry weight) of lead, copper and
zinc in soil profiles from nine interchanges of the
Auckland Motorway, New Zealand.

AVERAGE DAILY TRAFFIC VOLUME

0-45000 | 45000-52000 | >52000

Pb

Mt. Wellington
Orahuhu
Wiri

Symonds St.
Market Rd.
Ellerslie

Khyber Pass
Greenlane
Racecourse

Cu

Zn
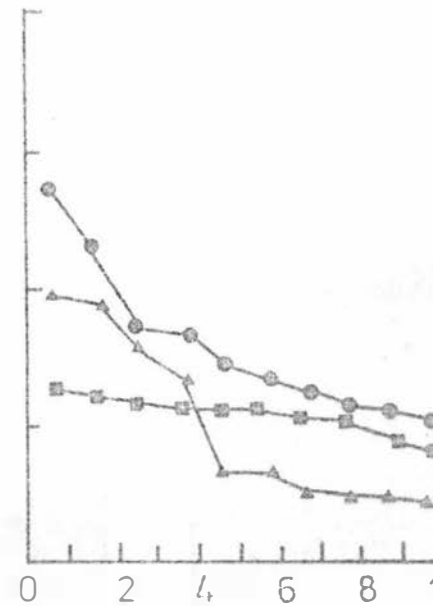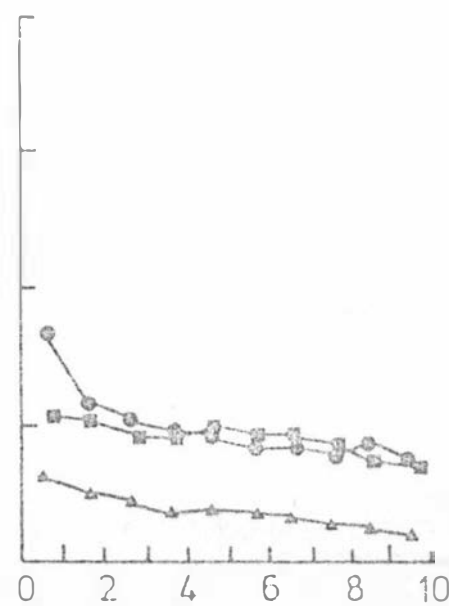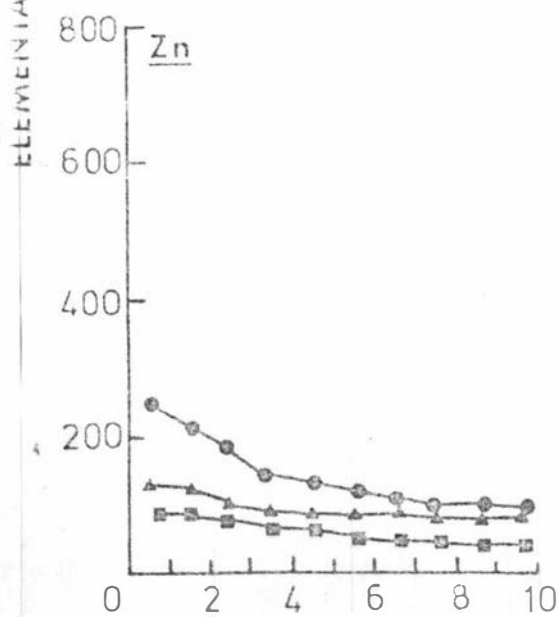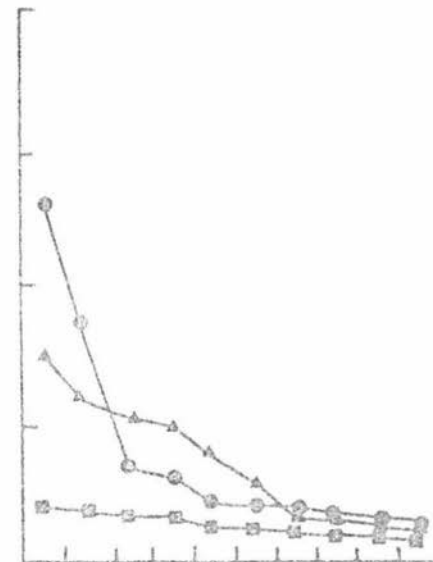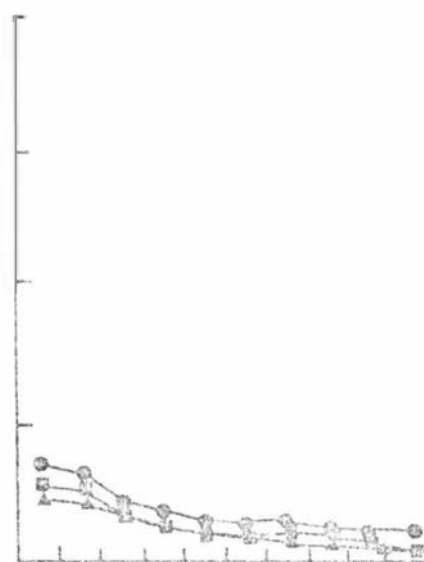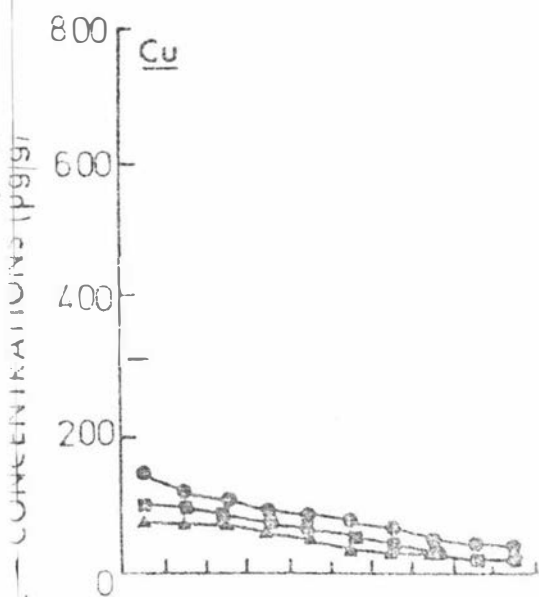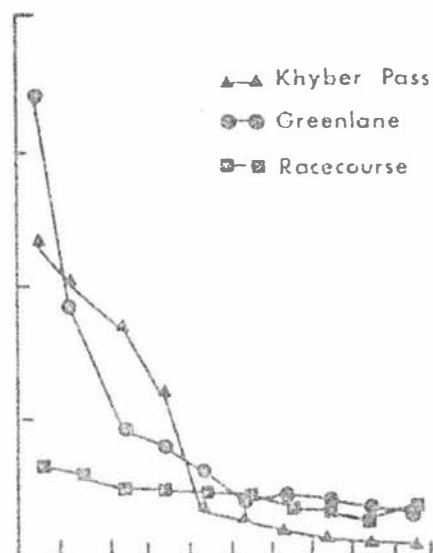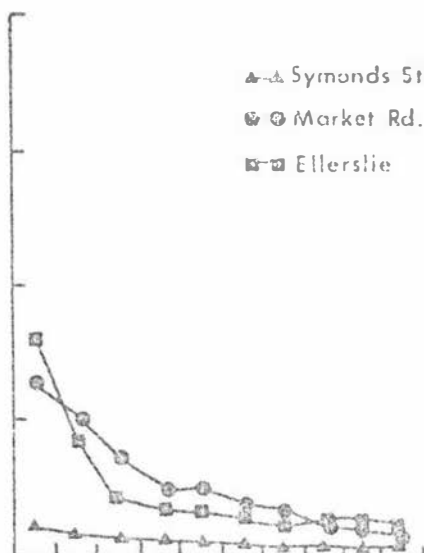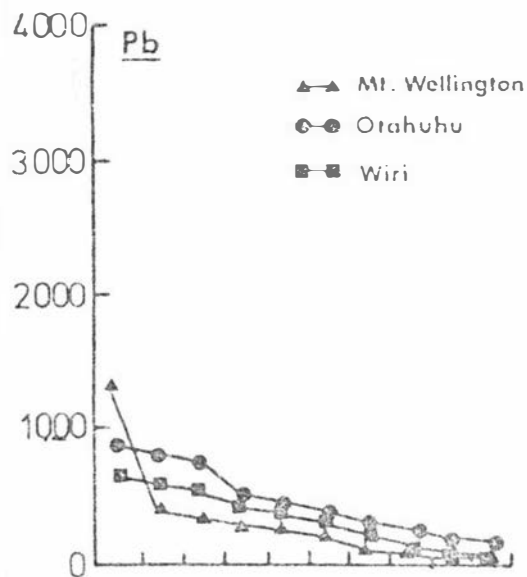
ELEMENTAL CONCENTRATIONS (pg/g)

DEPTH (cm)

Figure IV.2.

Concentrations (μg/g dry weight) of nickel, chromium and cadmium in soil profiles from nine interchanges of the Auckland Motorway, New Zealand.

AVERAGE DAILY TRAFFIC VOLUME

Figure showing elemental concentrations (μg/g) versus depth (cm) for Ni, Cr, and Cd across three traffic volume categories (0–45000, 45000–52000, >52000).

Sites for 0–45000: Mt. Wellington, Otahuhu, Wiri.
Sites for 45000–52000: Symonds St., Market Rd., Ellerslie.
Sites for >52000: Khyber Pa, Greenlane, Racecourse.
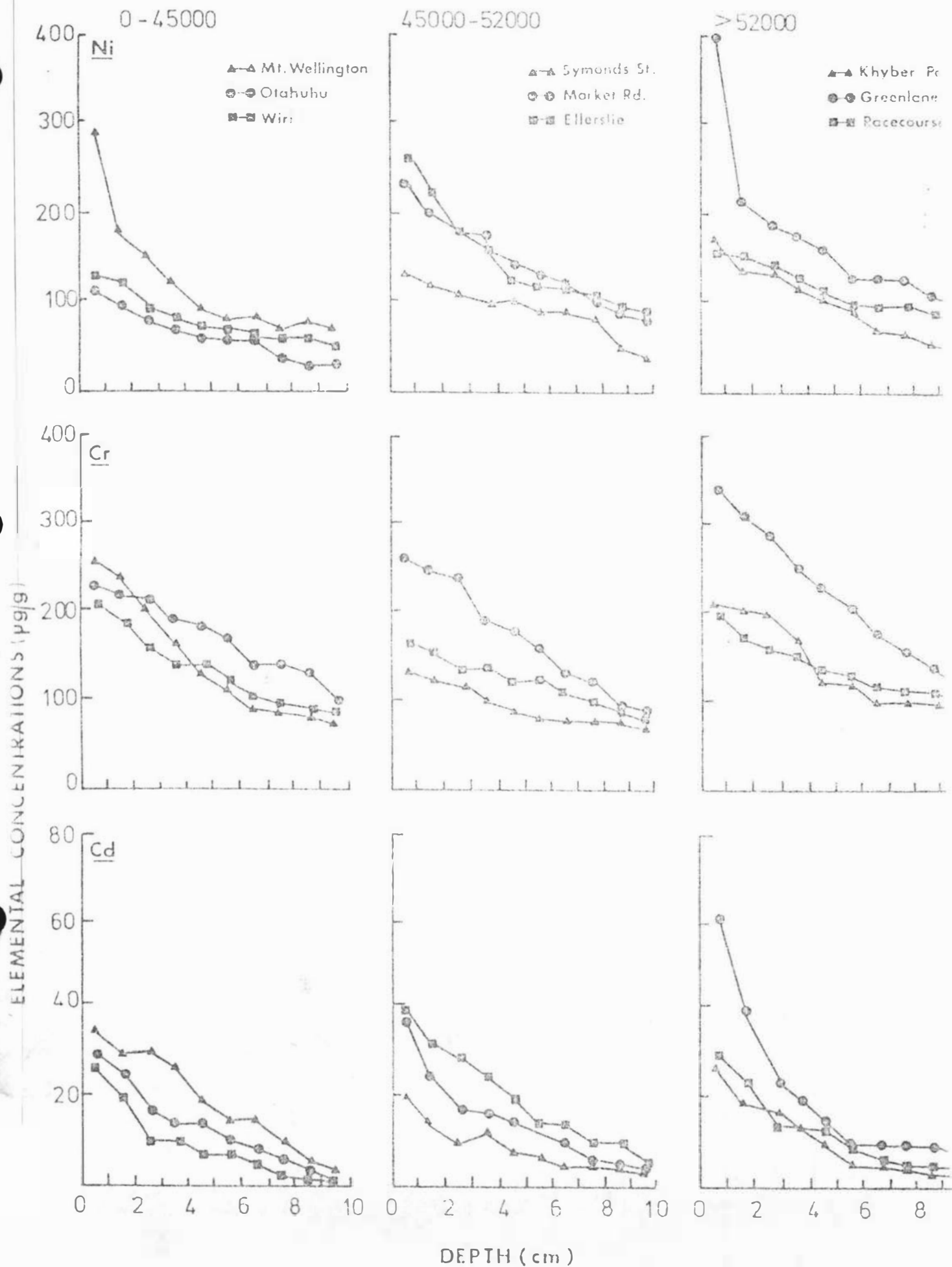
(b) Pasture species.

Elemental concentrations in pasture plants (without regard
to species) are shown in Table IV.2. The data does not include
figures for cadmium because concentrations were at or below the
limit of detection (0.2 μg/g) and were scarcely distinguishable
from background. Zinc values have also been excluded because
the natural concentration of zinc in vegetation is relatively
high (50 μg/g dry weight) and it was not possible to different-
iate values from background.

It is clear from Table IV.2., that washing removes about
one third of the heavy metal burden of the vegetation and
indicates its superficial deposition upon the pasture species.
For unwashed material, concentrations on the busiest intersections
are about eight times higher for chromium, three times as high
for copper, six times higher for nickel and one hundred times
as high for lead. As may be expected, lead is quantitively the
greatest pollutant among the four elements studied.

These values for heavy metals in soils and vegetation when
compared with those obtained by Lagerwerff & Specht (1970) for
a site with similar traffic density (400,000 vehicles per 24
hours) are higher for lead and nickel in soils and higher for
lead in vegetation. This difference can be explained by the
greater proximity of these sites to the line of traffic.

Although elemental concentrations were obtained for all
pasture species at each sampling site, for the sake of brevity,
values for only one site (No. 5) are shown in Table IV.3. The
data show obvious interspecific differences in uptake of
pollutants. All parts of white clover (roots, leaves and stolons)
usually show considerably greater uptake of chromium, copper,
lead and nickel. This enhanced uptake does not appear to be
a function of the shape of the leaf, because other broad-leafed
species such as daisy and flatweeds have considerably lower
accumulations of most elements. Washing usually removes about
one third of the aerial burden from leaves of all species.
Paspalum grass tends to have the lowest aerial burden of any of

(95)

Table IV.2.

Mean Concentration (µg/g dry weight) of Heavy Metals in Washed and Unwashed Pasture Leaves (without regard to species) Sampled from the Various Interchanges of the Auckland Motorway, New Zealand.

Site No.	Cr Washed	Cr Unwashed	Cu Washed	Cu Unwashed	Ni Washed	Ni Unwashed	Pb Washed	Pb Unwashed
1	1.0	1.6	8.6	13.6	1.5	2.3	153	236
2	1.9	3.8	14.2	22.6	2.2	4.8	236	363
3	2.2	3.0	22.4	32.1	2.0	3.2	267	371
4	2.0	2.8	23.6	32.2	1.8	2.5	221	305
5	1.5	2.3	19.4	25.6	1.7	2.6	341	510
6	3.7	5.1	15.6	22.0	3.0	4.7	132	250
7	3.4	7.1	18.6	28.1	3.0	5.4	203	297
8	2.4	3.2	18.3	26.5	3.4	4.8	237	399
9	1.8	2.5	14.6	24.1	2.3	4.0	254	318
10	2.5	3.7	17.7	25.6	2.5	4.9	199	277
11	1.7	2.6	13.0	17.0	2.2	2.9	175	248
12	1.4	3.0	12.1	18.9	2.1	3.1	171	218
13	1.7	2.3	8.9	14.6	2.3	3.9	160	303
14	2.0	3.3	12.6	20.9	2.2	3.0	245	329
15	1.7	2.9	9.1	13.6	1.9	3.8	99	155
16	1.0	2.0	6.7	11.8	0.9	1.6	63	99
17	1.3	2.2	6.5	12.6	1.6	2.3	86	165
Background	0.4	0.6	9.0	9.5	0.7	0.9	3	5

Table IV.3.

Mean concentrations (µg/g dry weight) of Heavy Metals in Pasture
Species (roots, leaves and white clover stolons) Sampled at Site No. 5
(Greenland Interchange) of the Auckland Motorway, New Zealand.

Vegetation Sampled	Concentrations (mean of 5 replicates)							
	Cr		Cu		Ni		Pb	
	Washed	Un-washed	Washed	Un-washed	Washed	Un-washed	Washed	Un-washed
White Clover (Wc)								
roots	3.1	3.9	29.7	60.6	1.9	5.2	155	645
leaves	2.3	3.8	37.8	50.4	3.8	4.7	365	638
stolons	1.9	3.4	27.3	43.9	1.3	3.3	481	707
P.Ryegrass (PR)								
roots	1.9	5.8	15.2	28.8	1.4	4.0	360	480
leaves	1.6	2.3	14.3	20.8	1.9	2.6	306	345
Poa Annua (PA)								
roots	1.0	1.1	16.0	22.0	2.3	2.5	315	460
leaves	3.1	3.9	23.4	31.2	2.6	3.3	501	546
Yorkshire Fog (YF)								
roots	1.0	2.9	12.0	25.6	0.8	2.8	228	408
leaves	1.6	2.3	16.9	27.3	1.3	3.3	390	553
Flatweeds (FW)								
roots	1.1	2.2	15.0	27.0	0.6	1.8	186	225
leaves	0.5	1.7	20.9	22.6	1.3	3.1	352	1044
Daisy (D)								
roots	0.6	0.9	7.5	9.2	0.7	0.7	122	165
leaves	1.0	1.6	15.7	18.3	1.1	1.5	248	313
Paspalum (P)								
roots	1.1	1.7	9.7	18.0	0.2	0.7	84	213
leaves	0.8	1.0	14.8	18.3	1.3	1.3	278	305
Cocksfoot (C)								
roots	1.0	2.2	9.6	28.8	1.0	2.0	152	376
leaves	1.2	1.9	11.7	15.6	0.6	0.7	286	332

the pollutants studied. The experiments indicate expected
elemental levels in pasture species adjacent to major highways
and it is clear that if grazing close to such sources of pollution
must be undertaken, then white clover should be avoided and grasses
such as paspalum encouraged.

(c) Statistical analysis.

In order to assess the relationship between traffic densities
and the two further variables of pollutant concentrations in soils
and vegetation, Spearman rank correlation coefficients were
computed for all possible pairs of variables involving each of
the six heavy metals studied. These relationships are shown in
Table IV.4.

In all cases there is at least a significant ($P \leqslant 0.05$)
relationship between traffic density and elemental concentration
in surface soils. These relationships are very-highly significant
for the elements chromium, copper, lead and zinc. The less
definite correlations for cadmium is probably because there were
relatively few sites at which this element could be measured
accurately.

The relationships between traffic density and concentration
in vegetation, show that the grass, yorkshire fog, is usually the
best overall indicator of traffic density from its content of
four heavy metals. By contrast, only the copper content of
cocksfoot reflects traffic density.

As may be expected, the vegetation/soil relationships which
do not involve a direct correlation with traffic density, are in
general weaker and fewer in number. Most species show a mutual
relationship for copper, lead and nickel, but only white clover and
paspalum give a plant/soil relationship for chromium.

4. Conclusion.

From the data presented in Table IV.4., there can be no doubt
that motor vehicle traffic is responsible for the build-up of all
six heavy metals in soils and vegetation along the motorway. The
source of the lead is obviously leaded gasoline as has been so well
established in the literature. Lagerwerff & Specht (1970) have

Table IV.4.

Significances[a] of Relationships between the Three Variables of Traffic Densities, Concentration of Pollutants in Vegetation, (unwashed leaves) and in Surface Soils from the Auckland Motorway, New Zealand.

Pollutant	First Variable	Concentrations in vegetation[b] (second variable)							
		WC	PR	PA	YF	F?	D	P	C
Cr	Concentrations	S	-	S	-	-	-	-	-
Cu	in	S	S	S	S	S*	S*	S**	S
Ni	surface	S**	S	S	S*	-	-	-	-
Pb	soils	S**	S*	S**	S**	S	S**	S	-

Pollutant	First Variable	Concentrations in vegetation[b] (second variable)							
		WC	PR	PA	YF	F?	D	P	C
Cr	Traffic	S	-	S*	S*	S*	-	-	-
Cu	densities	S*	S	S*	S**	-	S*	S**	S
Ni	at	S	-	S	S*	S	-	-	-
Pb	interchanges	S*	S*	S**	S*	S	S*	-	-

Pollutant	First Variable	Concentrations in soils (second variable)
Cd	Traffic	S
Cr	densities	S**
Cu	at	S**
Ni		S
Pb	interchanges	S**
Zn		S**

[a] Significances calculated from Spearman rank correlation coefficients

S**	very-highly significant	$P \leqslant 0.001$
S*	highly significant	$0.001 \leqslant P \leqslant 0.01$
S	significant	$0.01 \leqslant P \leqslant 0.05$

[b] See Table IV.3. for meaning of symbols.

suggested that cadmium and zinc are found together in lubricating oils as part of many additives such as zinc-dithiophosphates . where cadmium may be an impurity in the original zinc used to prepare the additive. The same authors reported 20-90 µg/g cadmium in car tyres as a probable result of the use of zinc-diethyl-carbonate (and associated cadmium contamination) in the process of vulcanization.

Nickel and chromium are frequently used in chrome-plating, and copper is a common constituent of piping and other components of engines and chassis. The presence of these elements in soils and vegetation along motorways is probably due to mechanical wear and tear which deposits these metals in the fine dust of the roadway and from there to soils and vegetation.

The extent to which the above heavy metals (apart from lead) constitute a hazard to public health is a question somewhat outside the scope of the present work, but because of their known toxicity to humans, this question should be studied further. It is not likely that zinc will present much of a problem because normal background levels in soils, animals and vegetation are so high that further contributions from motor vehicle emissions would need to be extremely high to cause significant effects. Levels in soils, of chromium and nickel, though much higher than background, are nevertheless about the same as in some special soil types such as those derived from basic and ultrabasic rocks and presumably could be tolerated by most organisms. The exceedingly high copper levels (480 µg/g) are some cause for concern as are also the cadmium concentrations of up to 3.8 µg/g in soils. The latter concentration may seem low in absolute terms, but when it is remembered that a level of 1.0 µg/g cadmium for foodstuffs is a limit advocated by many health authorities throughout the world, even a concentration of 3.8 µg/g in soils should not be ignored.

In summary the following conclusions should be pointed out from this investigation:

(i) Cadmium, chromium, copper, lead, nickel and zinc were measured in soils and pasture species along the Auckland Motorway at enhanced levels and correlated well with traffic densities,

(ii)   concentrations in soil profiles decreased with depth and showed that the source of pollution was aerial deposition from motor vehicles,

(iii)   about one third of the aerial burden of each element was removable by washing of vegetation species,

(iv)   highest accumulation of heavy metals was usually found in white clover and the lowest in paspalum grass,

(v)   elemental concentrations in pasture species were usually well correlated with traffic densities, particularly in the case of the grass, yorkshire fog,

(vi)   plant/soil correlations for individual heavy metals were in general poorer than for relationships involving traffic densities and concentrations in plants or soils,

(vii)   apart from lead, build-up of chromium, and copper should give the most concern because of their toxicity and high concentrations compared with background.

SECTION V.

PARTICULATE LEAD DEPOSITION FROM MOTOR VEHICLE EXHAUST EMISSIONS
ON SOIL AND PASTURE SPECIES ADJACENT TO A BUSY NEW ZEALAND STATE
HIGHWAY.

1. Introduction.

The analysis of vegetation and soils to show the distribution and accumulation of lead as a result of petrol combustion and discharge from motor vehicle exhaust emissions along major highways has been investigated extensively in recent years. Early observations by Warren & Delavault (1960), Cannon & Bowles (1962), and Rühling & Tyler (1968) showed that lead levels in vegetation and soils near major highways were inordinately high depending upon the distance from the highway, traffic volume and direction of the prevailing wind.

Approximately 75% of the metallic lead in gasoline combusted by a motor vehicle is exhausted in the form of lead particulates into the atmosphere (U.S.D.H.E.W., 1970). Eighty-five % of the airborne particles are less than 4µ in diameter (Daines et. al., 1970). Most of these are removed from the atmosphere within approximately 35 meters of the highway due to gravitational settling and impaction on various obstacles. Ward et. al. (1974b) indicated that the magnitude and distribution of lead in trees situated within 5 meters of the side of a busy Palmerston North thoroughfare was a function of the side of the tree facing the highway, the height above ground level and the bark layer sampled. The distribution of lead in the tree ring-cores indicated the released contribution of lead from motor vehicle exhausts. It was also observed that significant elevated lead levels do not occur below a depth of 5cm in the soil at distances of 7-30 meters from the highway.

Work on lead levels in vegetation growing within 100 meters of a New Zealand State Highway with a relatively low traffic volume showed that accumulation gave a close fit to curves showing an exponential decay with distance, for about 50 meters on either side of the highway (Ward et. al., 1975a). Similar patterns of lead distribution in the sweet-corn plant were also measured, (Ward et. al., 1975b).

The results of Section IV indicated that the surface-soil lead content in the median strip of the Auckland Motorway, subjected to maximum traffic volumes of > 60,000 vehicles per day,

reached levels as high as 3000 µg/g (dry weight basis).
Associated pasture species at the same site contained 480 and 345
µg/g (dry weight basis) in the roots and leaves respectively of
ryegrass (Lolium perenne L.). Of the leaf-lead content, some
30% is removable by washing. This fraction in a field situation
could be washed off by rainfall. However, all the lead, whether
as surface deposit or bound to the leaf, is ingested by the
grazing animal.

The work reported in this section was carried out to determine
the distribution of lead within pastures adjacent to a reasonably
busy New Zealand State Highway (average daily traffic density of
5000 vehicles/day) and to observe any seasonal patterns which
may occur in the different pasture species and soil.

2. Study area.

The site selected was on State Highway 1, between Bulls and
Marton in the central region of the North Island. It offered a
reasonably flat contour with pasture on either side of the high-
way which at this point runs more or less north/south, at right
angles to the predominant wind direction (westerly). There were
no hedgerows, trees or other obstructions to air movement.
Between the edge of the carriageway and the fence on either side
was a 6 meters strip of crushed stone and rough grass. This area
was ignored in this study as the prime objective was to study the
pastures grazed by stock.

To the east of the highway, the pasture was on old-established
browntop (Agrostis tenuis) - dominant sheep pasture which has been
subjected to a set stocked regime with little or no fertiliser
applied for many years. To the west, was a more recent perennial
ryegrass (Lolium perenne L), white clover (Trifolium repens L.)
pasture which has been regularly topdressed and was rotationally
grazed during the course of these observations.

The soil type of the area is an Ohakea silt loam, a weakly
leached, moderate to strong gleyed yellow-grey earth.

3. Methods.

A permanent transect was established perpendicular to the highway and extending 50 meters into the pasture on either side. At intervals along this, samples were collected during the four seasons. The pasture was grazed for only 2 months during the summer on the eastern side.

Soil samples from the top two centimeters were taken on all occasions, while soil cores were extracted using a 2.5cm stainless steel corer during the autumn and winter sampling periods for profile distribution studies. Profiles were taken to a depth of 4cm at distances of 1, 3, 5, 25 and 48 meters from the roadside fence during the autumn sampling and to a depth of 10cm at distances of 0, 5, 15, and 35 meters on either side of the highway during the winter period.

Pasture samples collected during the initial sampling (autumn) comprised leaf material only, which was separated into washed and unwashed subsamples prior to analysis. Thereafter, complete plant samples were collected and these were spearated into roots and leaves. Leaf parts were not washed but roots were washed to remove adhering soil particles.

Sample preparation and analysis was carried out as described in Section I.B. and results are expressed as the mean of 5 determinations.

(4) Results and discussion.
(a) Soil lead levels

The mean lead content of surface soil (0-2cm) for the four seasons is shown in Figure V.1.

The data show a decline in lead content with distance from the fence, and seasonal differences are apparent near the fence, inparticular, the high autumn values.

Soil profile analysis for the autumn sample is shown in Figure V.2. The most noticeable feature of these data is the rapid reduction in lead content with depth, particularly near to and on the eastern side of the highway. This indicates the poor mobility of lead within the soil system as has been already

Figure V.1.

The mean lead content of surface soils (0-2cm) sampled at various distances (meters) on both sides of a busy New Zealand state highway for the seasons: autumn (symbol △), winter (symbol ⊛), spring (symbol ⊠), and summer (symbol O).

LEAD CONTENT (µg/g)

PREVAILING WIND DIRECTION

DISTANCE (meters)

WEST

EAST

Autumn ▲
Winter ●
Spring ■
Summer ○
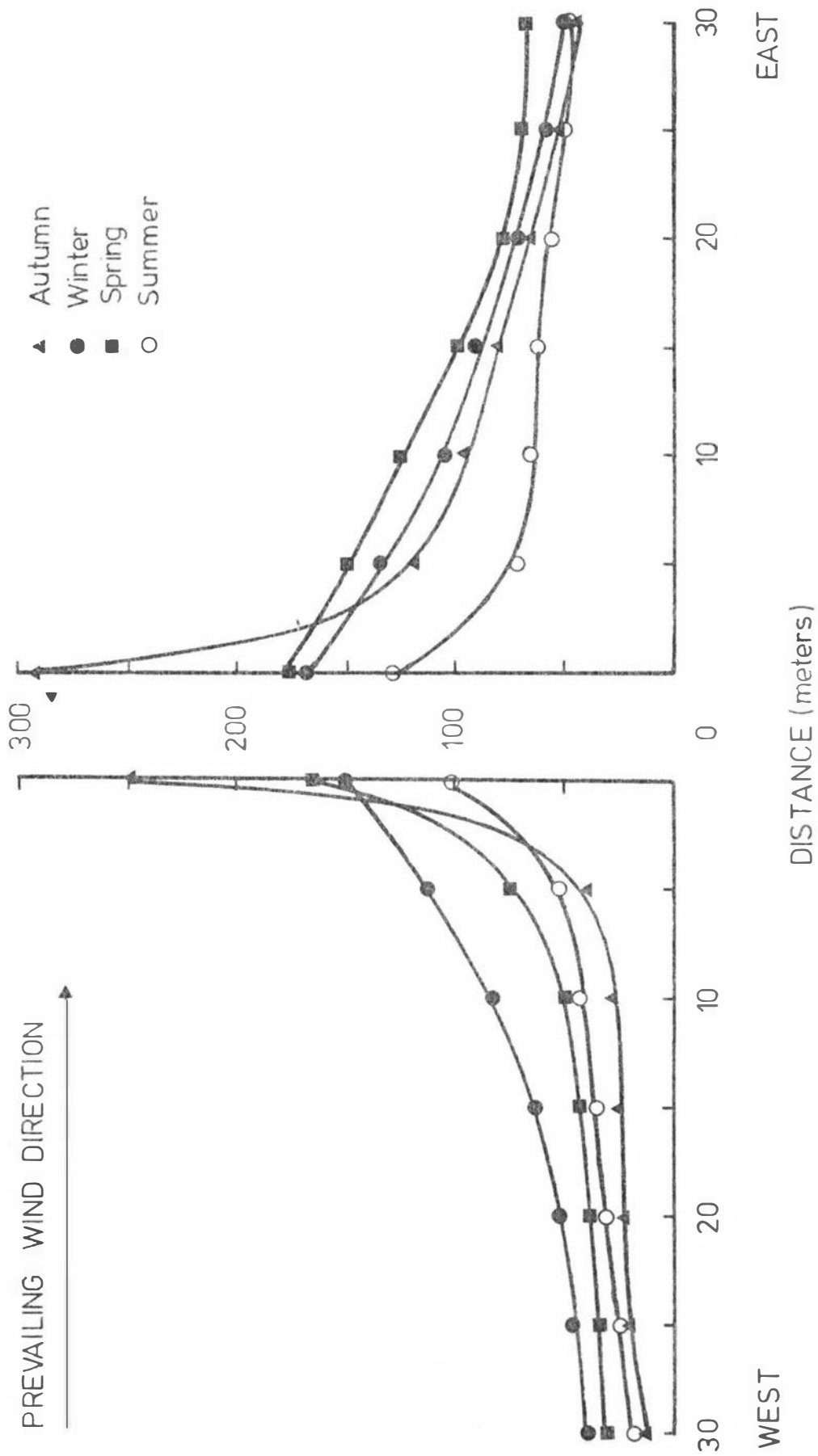
Figure V.2.

Lead levels (μg/g dry weight) in soil profiles : depth (cm) sampled during the autumn, at various distances along a transect across a busy New Zealand state highway. Symbols represent 1 meter O, 3 meters △, 5 meters ●, 25 meters ▢, and 48 meters ▨.

LEAD CONTENT (μg/g)

PREVAILING WIND DIRECTION

○ 1 meter
△ 3 meters
● 5 meters
□ 25 meters
■ 48 meters

300

200

100

4 3 2 1 0 1 2 3 4

WEST

EAST

DEPTH (centimeters)
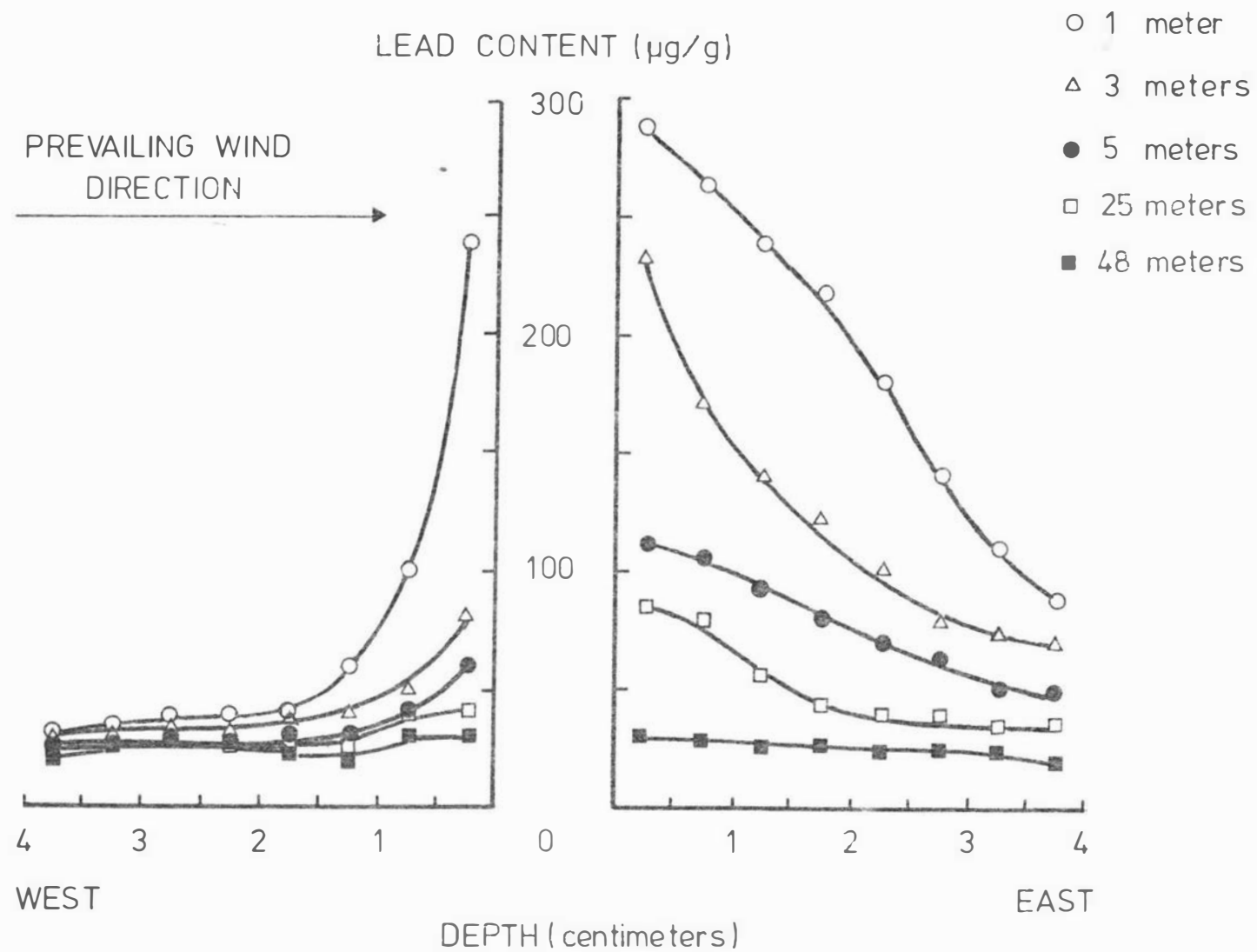
reported by Chow (1970), Page & Ganje (1970) and Ward et. al.,
(1975a,b). This significant accumulation of lead on the eastern
side of the highway also reflects the influence of the annual
prevailing wind direction (westerly).

On the western side of the highway, although the profile at
1 meter from the fence follows the expected pattern, there is then
little difference between the other points on the transect and
there is little evidence of a build up in the surface soil. On
inquiring, it was established that the paddock had been ploughed
some five years previously and inspection of the paddock revealed
an unploughed headland some 2 meters wide along the roadside fence.
Thus, the profile at 1 meter fell on this headland and was similar
to those from the old pasture across the highway, whereas those
profiles more distant from the highway on the western side had
not yet re-established a significant lead build up in the upper
horizons. Therefore agricultural activities such as ploughing may
prevent the accumulation of high lead levels in the upper most
5cm of soil, thereby reducing the availability of lead to the
supported pasture.

In order to establish a more absolute depth to which lead
may be distributed in these pastures, soil cores were taken to a
depth of 10cm during the winter period. The results are shown
in Figure V.3.

Elevated lead levels occur to a depth of 10cm on both sides
of the highway at a distance of 0-1 meters from the fence. How-
ever, the depth distribution of lead is significantly reduced
especially at distances approaching 30 meters from the roadside
fence. Seasonal variation between autumn and winter sampling is
particularly noticeable at distances of 0-3 meters on the eastern
side of the highway. Although the predominant wind direction
during both these seasonal periods is westerly, a significant
southerly wind component occurs during the winter which may
reduce the distribution of lead during this period towards the
eastern side of the highway.

Figure V.3.

Lead levels (µg/g dry weight) in soil profiles: depth (cm) sampled during the winter at various distances along a transect across a busy New Zealand state highway. Symbols represent 0 meter ▪, 5 meters ◆, 15 meters ●, 30 meters ◯.

PREVAILING WIND DIRECTION

LEAD CONTENT (μg/g)

DEPTH (centimeters)

- 0 meter
- 5 meters
- 15 meters
- 30 meters
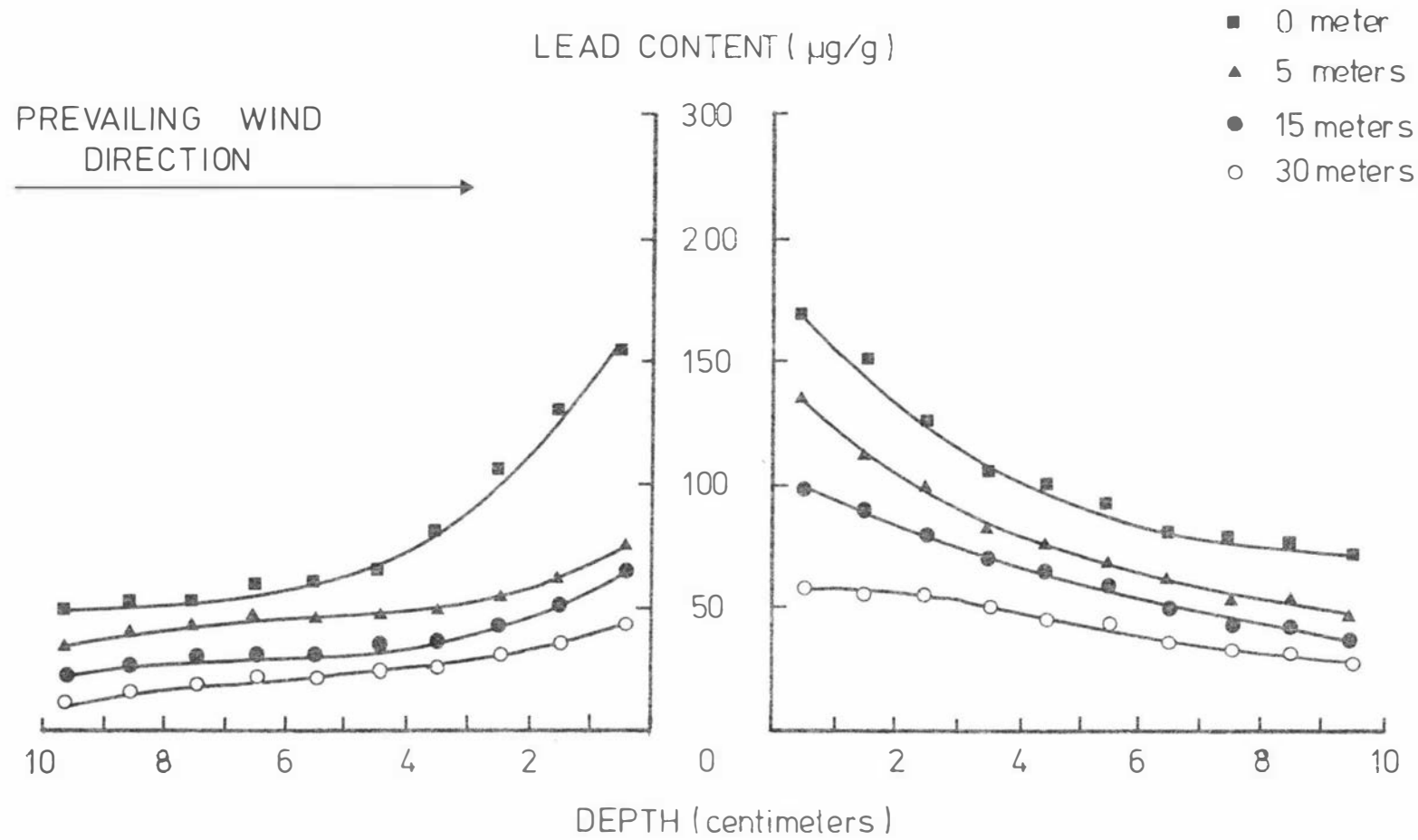
(b) <u>Lead content of pasture species.</u>

(i) ryegrass (<u>Lolium perenne</u> L.)

Figure V.4. shows the lead content of ryegrass along the
transect during the seasons autumn and winter; Figure V.5. for
spring and summer. Again the prevailing wind effect is discernable
particularly during the winter period when the leaf content shows
a marked difference between the east and west side of the road
within the first few meters of the fenceline. There were no root
samples collected during the autumn period so that for the other
seasonal periods and at all distances studied the lead content of
the leaves exceeds that of the roots and is indicative of the air-
borne nature of the source of lead.

(ii) white clover (<u>Trifolium repens</u> L.)

Figure V.6. shows the lead content of white clover along
the transect during the seasons autumn and winter. Figure V.7.
for spring and summer. Again there are no root data for the
autumn sampling. In white clover there is little or no difference
in lead content between plant parts. The winter peak in leaf-lead
observed in ryegrass is again present in white clover close to, and
east, of the highway fence, and is suggested that it is caused in
the same way as outlined for ryegrass. Seasonal differences
occur and the data for the summer sampling show higher levels to
the west of the highway than to the east. This is the only species
which demonstrates this reversal. As indicated by the frequency
wind direction diagrams representing the total seasonal wind run
(Garnier, 1958) shown in Figures V.4-7. it is suggested that the
predominant wind direction during the autumn and winter seasons
is westerly whereas in the spring there is a considerable easterly
component and the summer a relative reduction in total wind run
with light and variable winds with no predominant wind direction.
Therefore the significant balancing out of lead measured in the
leaves of ryegrass during the summer and the elevation of lead on
the western side of the highway for white clover during the summer
may be a direct result of the change in the dominance of the
prevailing wind direction during this season compared with the

Figure V.4.

Lead levels (μg/g dry weight) of leaves (symbol O) and roots (symbol O) of perennial ryegrass (Lolium perenne L) at different distances along a transect across a busy New Zealand state highway sampled during the autumn (above) and winter (below).

PERENNIAL RYEGRASS (Lolium perenne L.)

LEAD CONTENT (μg/g)

PREVAILING WIND DIRECTION →

• Leaves
○ Roots

Autumn
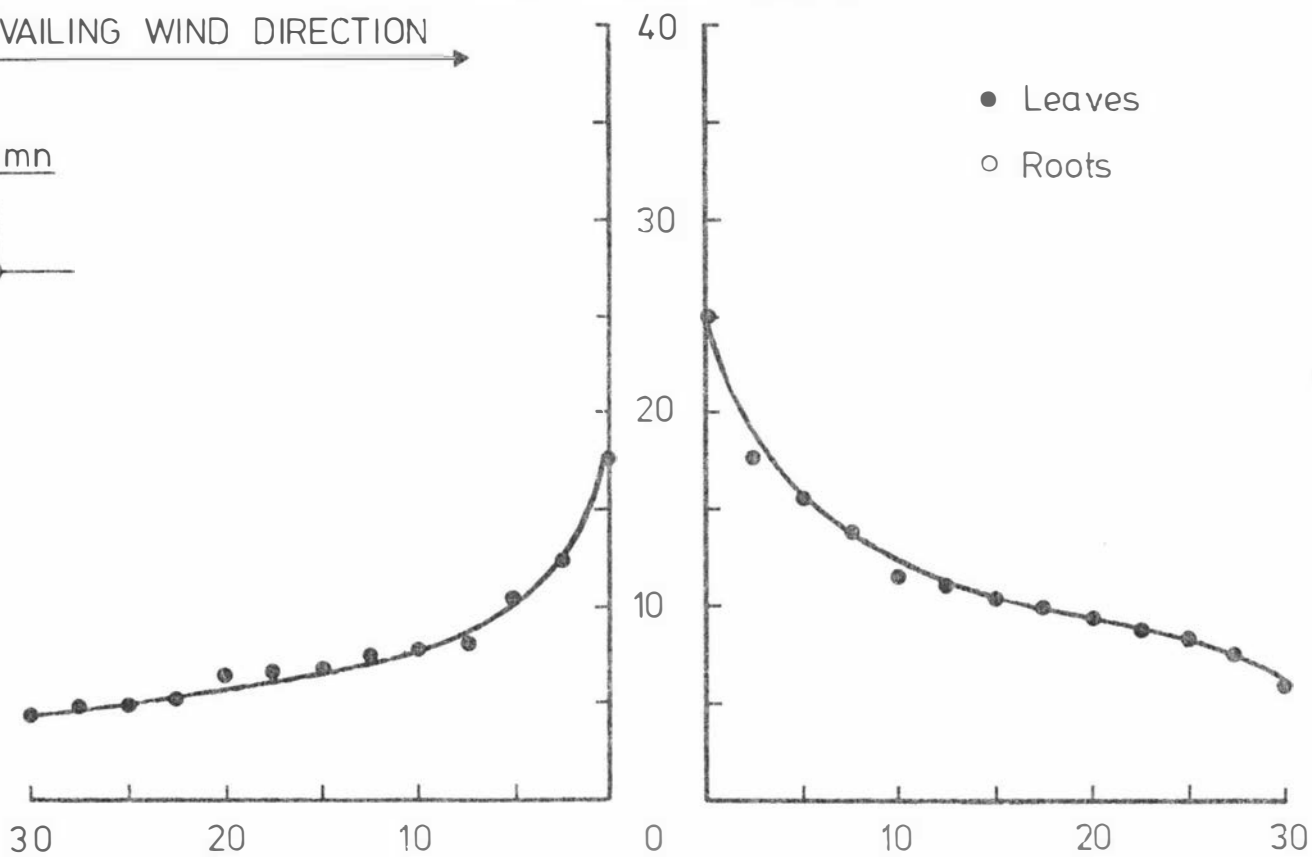
Winter
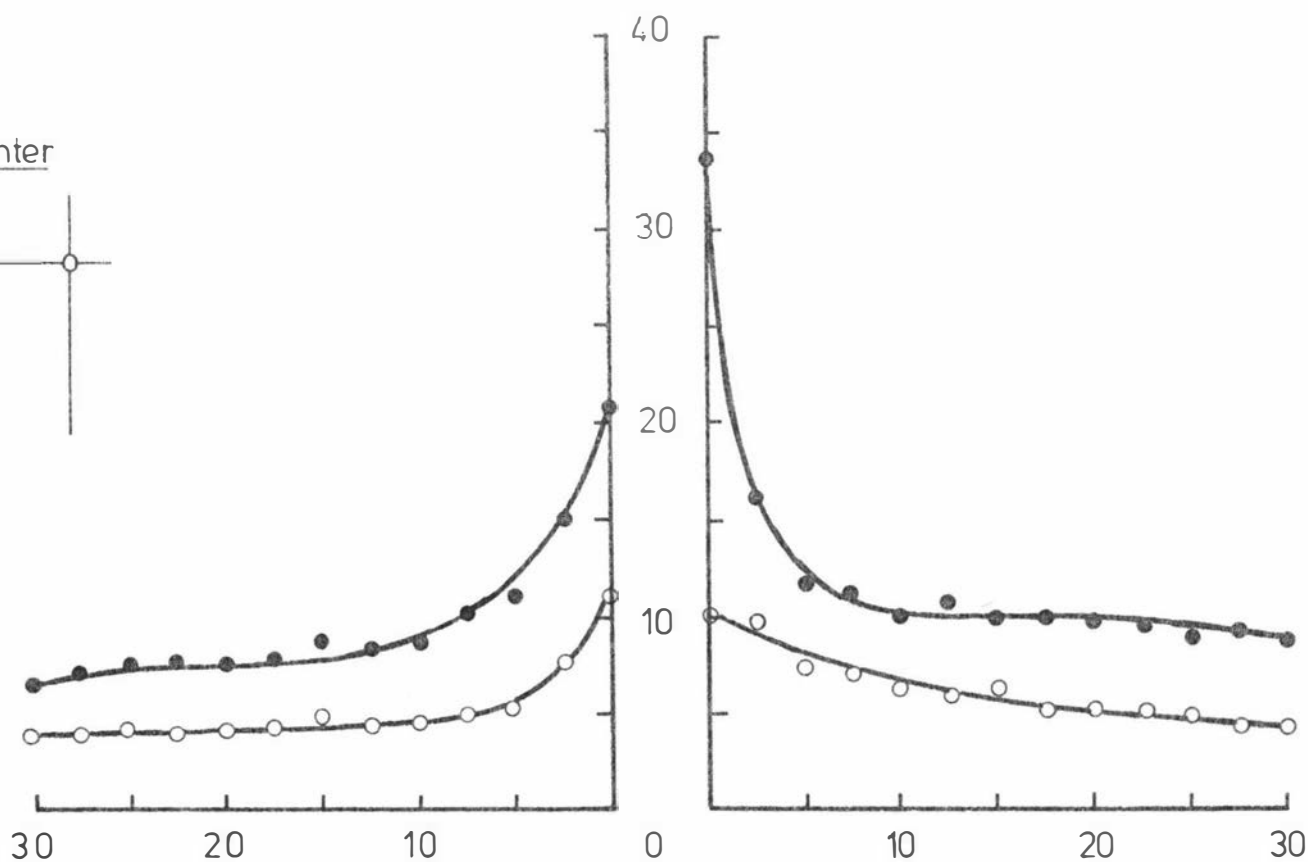
DISTANCE (meters)

+ : — 2000 miles /season (3months)

Figure V.5.

Lead levels (μg/g dry weight) of leaves (symbol $\ominus$), roots
(symbol O) of perennial ryegrass (<u>Lolium</u> <u>perenne</u> L) at
different distances along a transect across a busy New
Zealand state highway sampled during the spring (above)
and summer (below).

PERENNIAL RYEGRASS (Lolium perenne L.)

LEAD CONTENT (µg/g)

PREVAILING WIND DIRECTION

• Leaves
○ Roots

Spring.
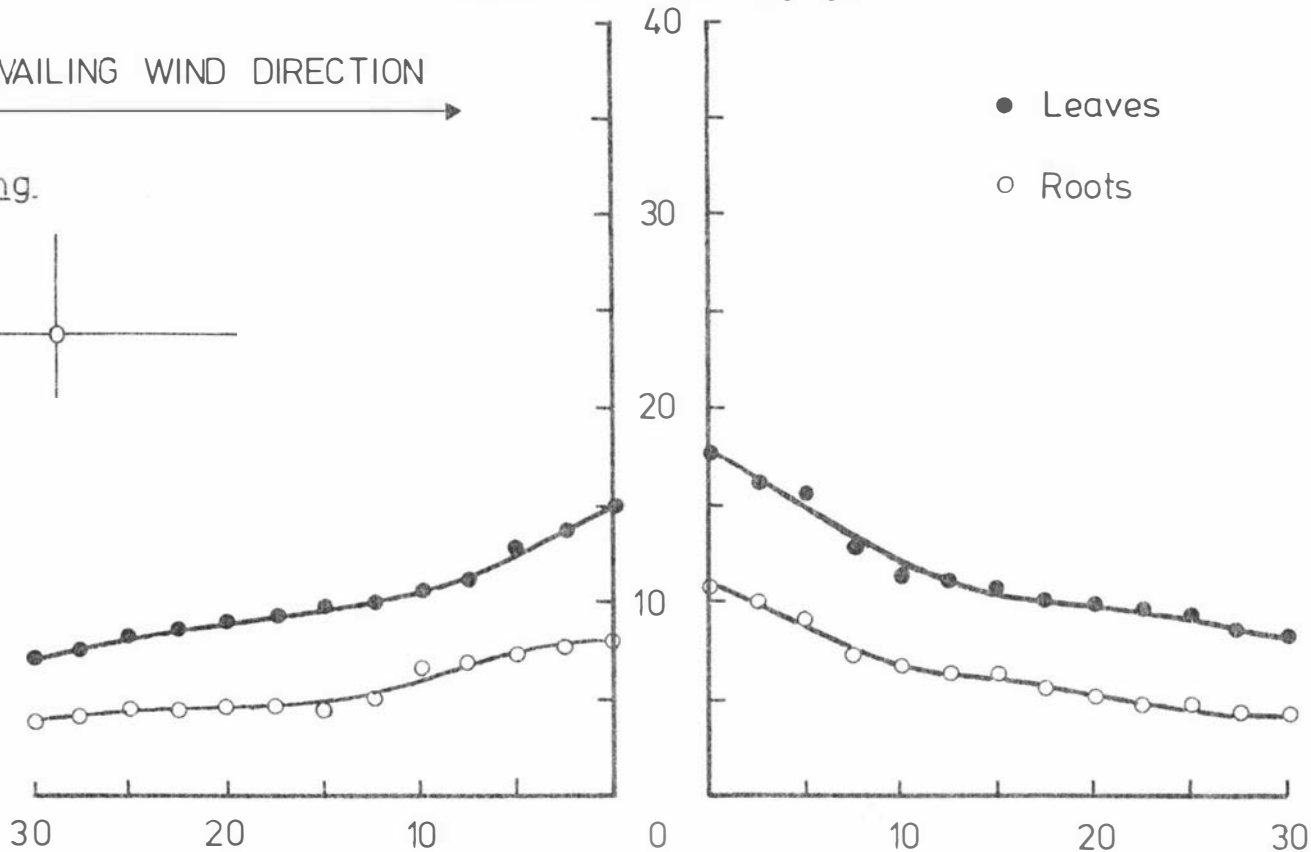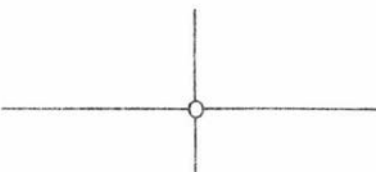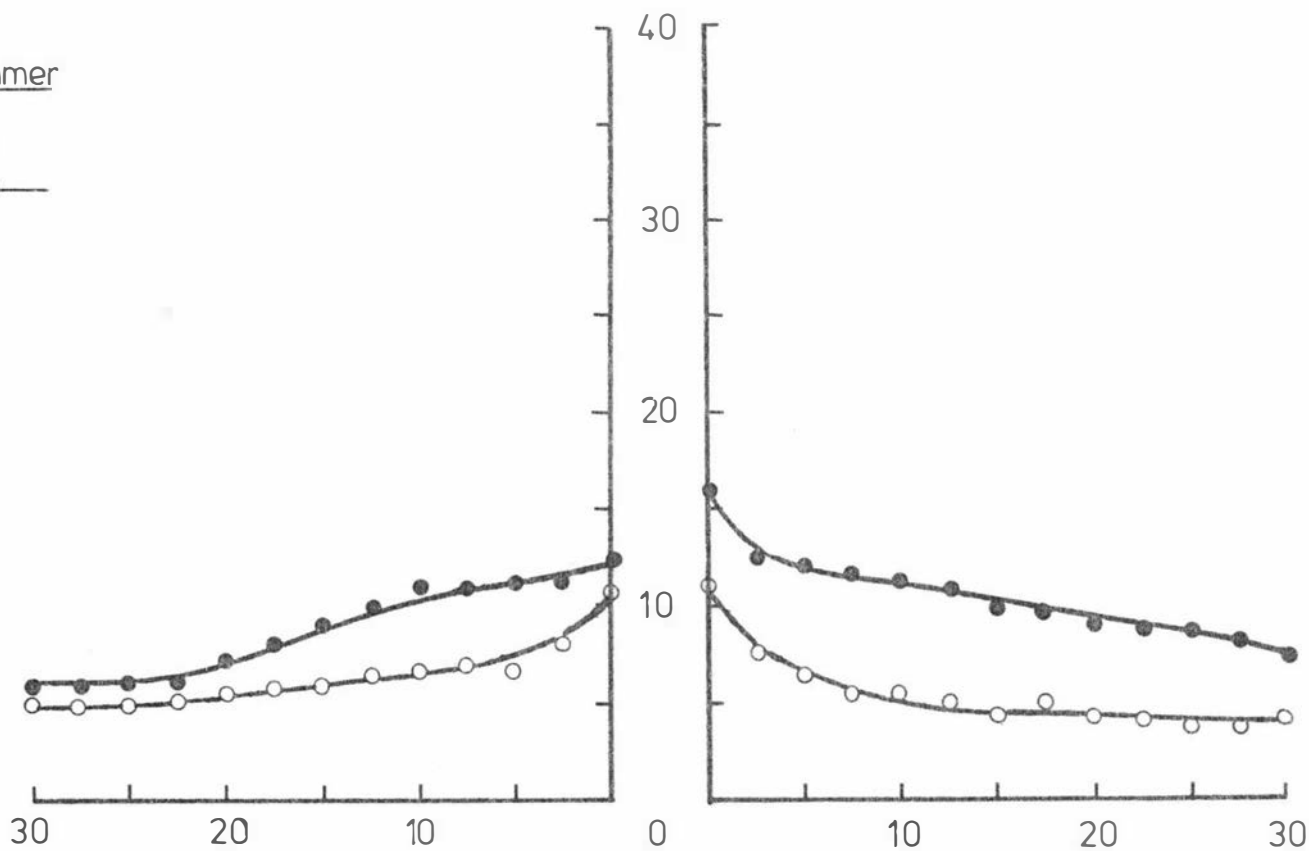
Summer

DISTANCE (meters)

◇ : — , 2000 miles / season
(3 months)

autumn and winter. It was also observed that the white clover leaf canopy on the western side of the highway during the summer was dominated by large leaves compared with the rather smaller leaved white clover (with a density of less than 50% of the canopy) on the eastern side of the highway. Therefore increased lead levels in the leaves of white clover on the western side during the summer may be a result of this increased leaf area index.

Washing procedures removed about one-third of the lead burden of those leaves sampled for both species. Elevated lead levels (particularly in surface soils during the autumn; white clover leaves in the autumn and ryegrass leaves in the autumn and winter) close to the roadside fence on the downwind (eastern) side could be caused by a "road-splash" from passing motor vehicles during the wet weather periods. The seasonal rainfall for this study area is > 10mm during the autumn and winter; and < 1mm for the spring and summer. (per week).

(iii) other pasture species

Browntop (*Agrostis tenius*) provided a pattern very similar to ryegrass, as did *Poa annua* L. except in this species there was significantly greater (25%) lead in the roots than the leaves up to 5 meters from the fence on the eastern side. Flatweeds (largely *Bellis perennis* L.) again showed a similar pattern to ryegrass except during the summer when within 5 meters of the fence line on the eastern side, the leaf content was more than twice as large as the root content.

(5) Conclusion.

There is extensive evidence to show that significant amounts of lead from motor vehicle exhaust emissions are found in soils and pasture species within 30 meters of the roadside fence. Soil profiles showed a rapid reduction in lead content with depth, particularly near to, and on, the eastern (windward) side of the highway during both the autumn and winter. Significant lead accumulation occurred to a depth of 10cm. It is suggested that seasonal variations in the lead content of this soil are directly

Figure V.6.

Lead levels (μg/g dry weight) of leaves (symbol●), roots
(symbol O) of white clover (Trifolium repens L) at
different distances along a transect across a busy
New Zealand state highway sampled during the autumn
(above) and winter (below).

WHITE CLOVER (Trifolium repens L.)

Figure V.7.
Lead levels (ug/g dry weight) of leaves (symbol♣), roots (symbol O) of white clover (Trifolium repens L) at different distances along a transect across a busy New Zealand state highway sampled during the spring (above) and summer (below).

WHITE CLOVER (Trifolium repens L.)

LEAD CONTENT (µg/g)

PREVAILING WIND
DIRECTION

⬤ Leaves

○ Roots

Spring
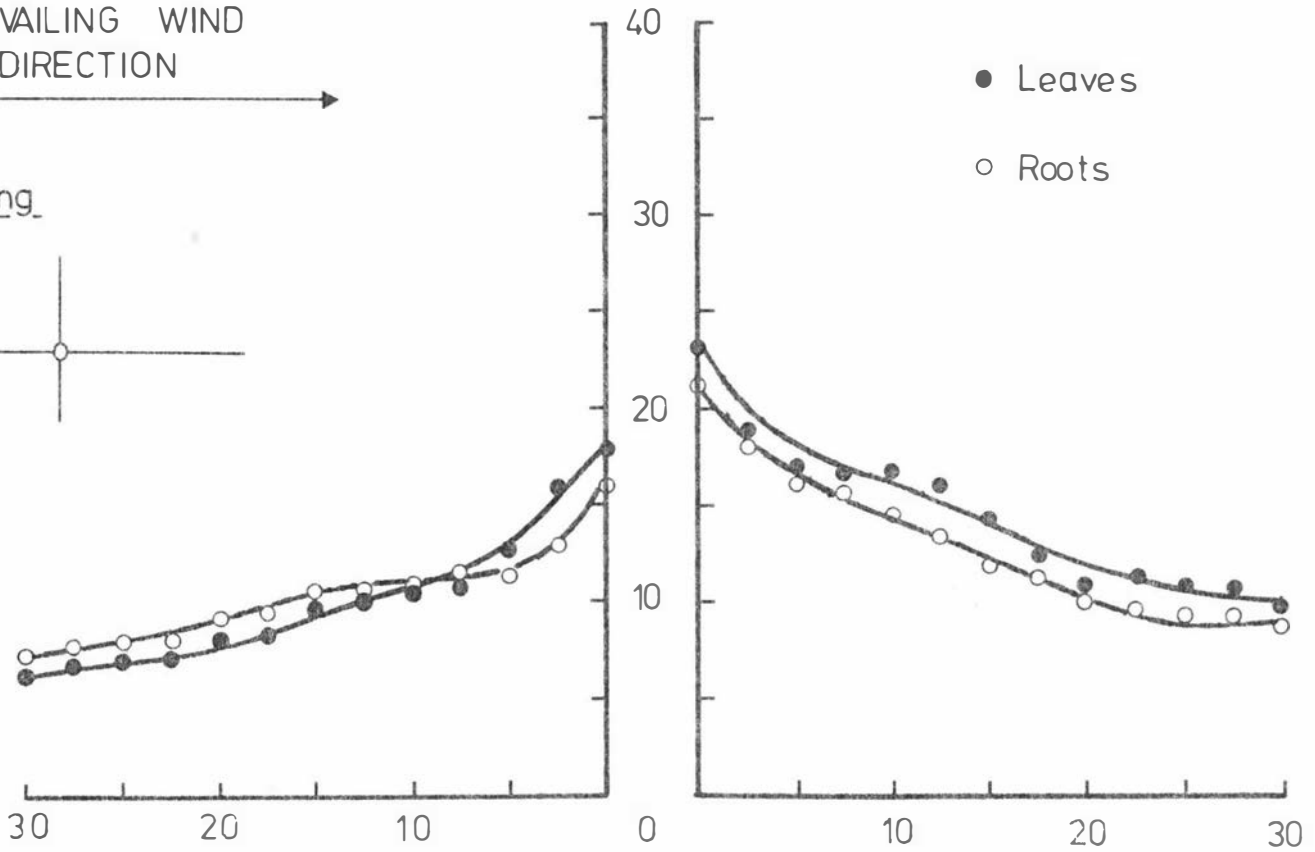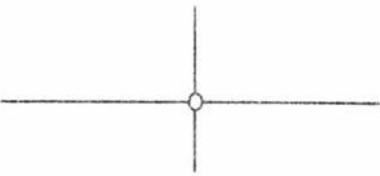
Summer
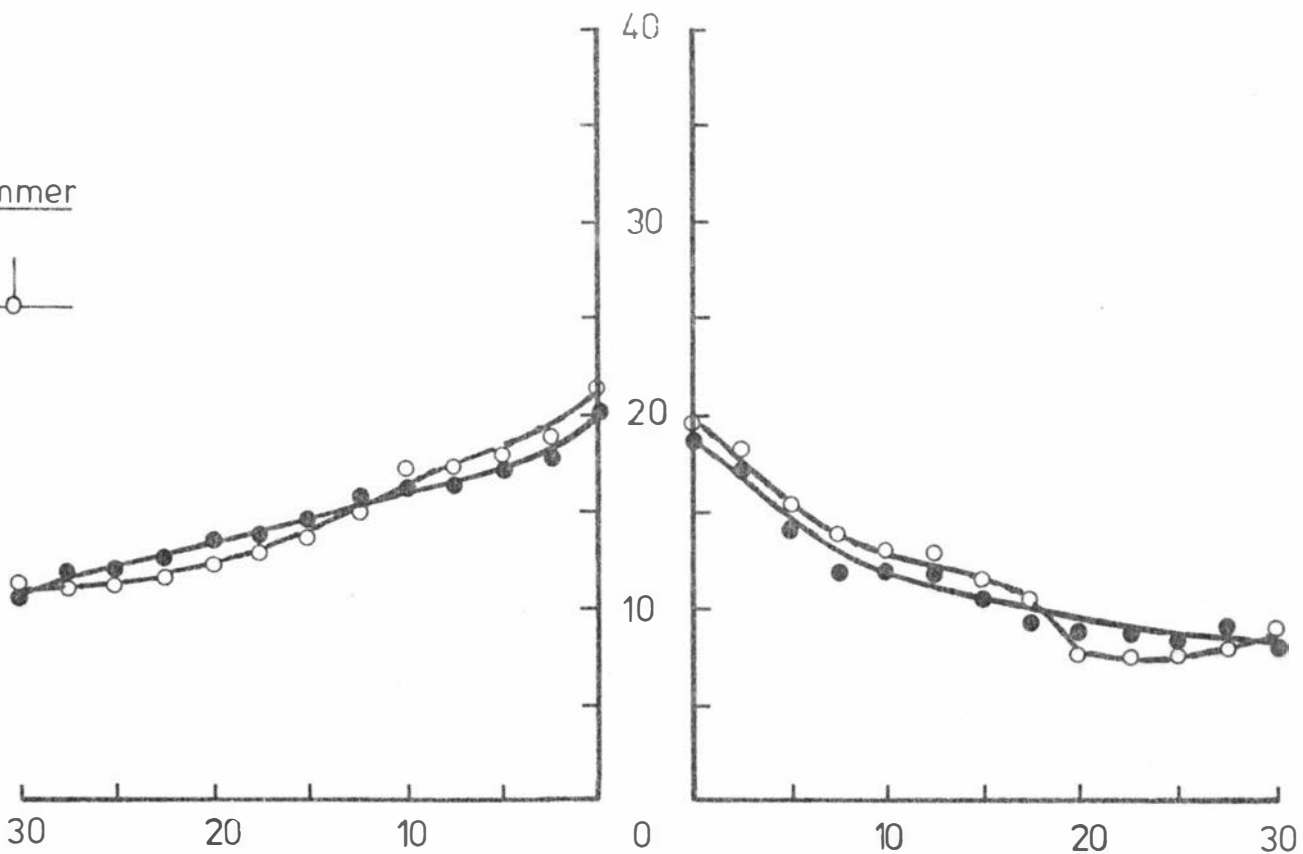
DISTANCE (meters)

○ : — : 2000 miles / season
(3 months)

related to the particular prevailing wind-direction during that season and the influence of "road-splash" from passing motor vehicles especially during the autumn and winter.

All the pasture species studied, in particular ryegrass (_Lolium perenne_ L.) and white clover (_Trifolium repens_ L.), indicated elevated lead levels within 30 meters of the roadside fence with the atmospheric nature of the lead source being reflected in that one-third of the lead burden of aerial plant components being removed by washing. Generally the lead content of the leaves exceeded that of the roots. Seasonal differences occurred but it is suggested that as shown with soils, the predominant seasonal wind direction greatly influenced the degree of lead accumulation on both sides of the highway.

It was observed that agricultural activities such as ploughing may prevent the accumulation of high lead levels in the upper most 5cm of soil and thereby reducing the availability of lead to the supported pasture. Similarly the individual species density within the pasture may influence a particular species accumulation of lead as shown by white clover where during the summer, the increased density and leaf area index of one pasture compared with that on other side of the highway, produced a significant reversal in the degree of lead distribution on the westward side of the highway.

Overall it can be clearly seen that these elevated lead levels in the pastures adjacent to a relatively busy New Zealand State Highway will increase the degree of lead availability to grazing animals.

SECTION.VI.

HEAVY METAL POLLUTION FROM A BASE METAL MINE,

TE AROHA, NEW ZEALAND.

A. GENERAL INTRODUCTION.

The distribution and accumulation of airborne heavy metals from industrial sources has been widely reported. Most interest has been concentrated on soil and vegetation contaminations by zinc, lead, copper and recently cadmium. (Marten and Hammond, 1966; Ender, 1969; Costescu and Hutchinson, 1971; Little and Martin, 1972; Buchauer, 1973). Other environmental components studied were : mosses (Goodman and Roberts, 1971), leaf surfaces (Roberts, 1972; Little, 1973), stream and marine sediments (Goldberg, 1965; Preston et. al., 1972; Hallsworth and Adams, 1973), and waters (Butterworth et. al., 1972; Burkett et. al., 1972).

Elevated levels of heavy metals have been connected predominantly with emissions from smelting complexes (Abdullah et. al., 1972; Burkett et. al., 1972: Butterworth et. al., 1972) and to a lesser degree from mining activities (Chisnall and Markland, 1971; Markland and Vallance, 1971). Pollution from the localised area near mines and its effect on agriculture have been studied by Crudgington et. al. (1973).

The principal object of this study was a comparison of base metal accumulations in plants growing directly over ore deposits with those in plants growing on deposits associated with the mine and its ore processing. Heavy metal concentrations were also measured in sediments and water samples in a stream originating from the vicinity of the ore body. The results of this study for cadmium, copper and zinc are reported in part B. (lead levels were previously reported, Ward, 1974a).

In contrast, part C. reports the accumulations of cadmium, copper, lead and zinc in the local environment, caused largely by airborne particulates from an ore-crushing treatment plant producing a finely-divided concentrate. The effect of this plant on vegetation and soils in a nearby pasture has also been investigated.

B. CADMIUM, COPPER AND ZINC IN SOILS, STREAM SEDIMENTS, WATERS AND NATURAL VEGETATION AROUND THE TUI MINE, TE AROHA.

1. Study area.

The Tui mine commenced operations about 10 years ago. It is about 3 km north/east of the township of Te Aroha and is at an altitude of about 600m on the west side of the southern extension of the Coromandel Peninsula Range of the flank of Te Aroha Peak (952m). The Coromandel Peninsula is in the north/east of the North Island of New Zealand.

The region is steep (slopes of up to 45°) with bush-clad hillsides. The country rock consists of a relatively hard propylitised andesite of the miocene period. There are two mineralised reefs known as the Champion and Raukaka. The Ruakaka Lode has been traced for a strike length of about 600m and has a dip of 60° south/east. The Champion Lode has been traced by surface outcrops for a strike length of over 450m and has a dip to the north/east.

The mineralisation consists principally of galena, sphalerite pyrite, and chalcopyrite (Williams, 1965). Quartz is the main gangue material.

The climate is warm-humid with an annual rainfall of 150-200cm. The predominant wind direction is westerly.

The flora consists of a typical New Zealand broadleaf, evergreen forest with tall species such as Beilschmiedia tawa (Benth. & Hook.f.), 'tawa' being dominant. Smaller trees and bushes such as Brachyglottis repanda ('rangiora') and Schefflera digitata ('five finger') are common beneath the forest canopy.

The soils are classified as yellow-brown earths, and vary in depth from over 200cm on the gentler slopes to almost nothing on the steeper hillsides. A soil survey of the area has been carried out by Weissberg & Wodzicki (1970).

2. Materials and methods.

Samples were collected in four major regions as shown in Figure VI.1. : samples 1-12 Raukaka Lode area; 13-23 Valley Road area (background); 24-39 treatment plant; and 40-130 Champion Lode area. Samples 1-12 and 40-130 were collected in 1967 before extensive disturbance of the areas adjacent to the outcrops of the two lodes.

At each sampling point, leaves ($\underline{B}$ $\underline{tawa}$ and $\underline{S}$. $\underline{digitata}$) were taken from heights of 1-3m, and soils were taken within 5cm of the surface. Tree trunk-core samples (6mm diameter) of $\underline{B}$ $\underline{tawa}$ were taken at sampling sites 3, 5, 12, 13, 17, 22, 26, 33 and 36.

Stream sediments and water samples were obtained at sites S_1 to S_{10} along a stream and S_{11} in the settling pond adjacent to the east side of the treatment plant.

Sample preparation and analysis were carried out as outlined in Section I.3. In particular the use of the carbon rod atomizer to determine cadmium levels in tree ring-core and water samples is explained in Section I.6.4. Copper and zinc levels were determined by conventional flame AAS methods.

3. Results and discussion.

(a) Soils.

The base metal content of soils across the Raukaka Lode is shown in Figure VI.2. Because the data were log-normally distributed, they are shown with logarithmic co-ordinates.

The highest elemental levels occurred at the base of the Raukaka Lode outcrop, situated at sampling site 3'. In this area the metal content of the soil sampled to the south (3') was twice that to the north (3) of the outcrop. Samples along the direction of the lode showed variable metal concentrations, with the highest levels at sites 6 and 10. The metal contents for the Raukaka Lode were : 15-280 µg/g for cadmium, 15-2800 µg/g for copper, and 70-2435 µg/g for zinc (dry weight soil).

Figure VI.1.
Map of the Tui Mine area, Te Aroha, showing sampling
sites. The Champion (C) and Raukaka (R) lodes are
shown as broken lines. Ridges are shown as dotted lines.
(T.P.) represents the ore-crushing treatment plant.
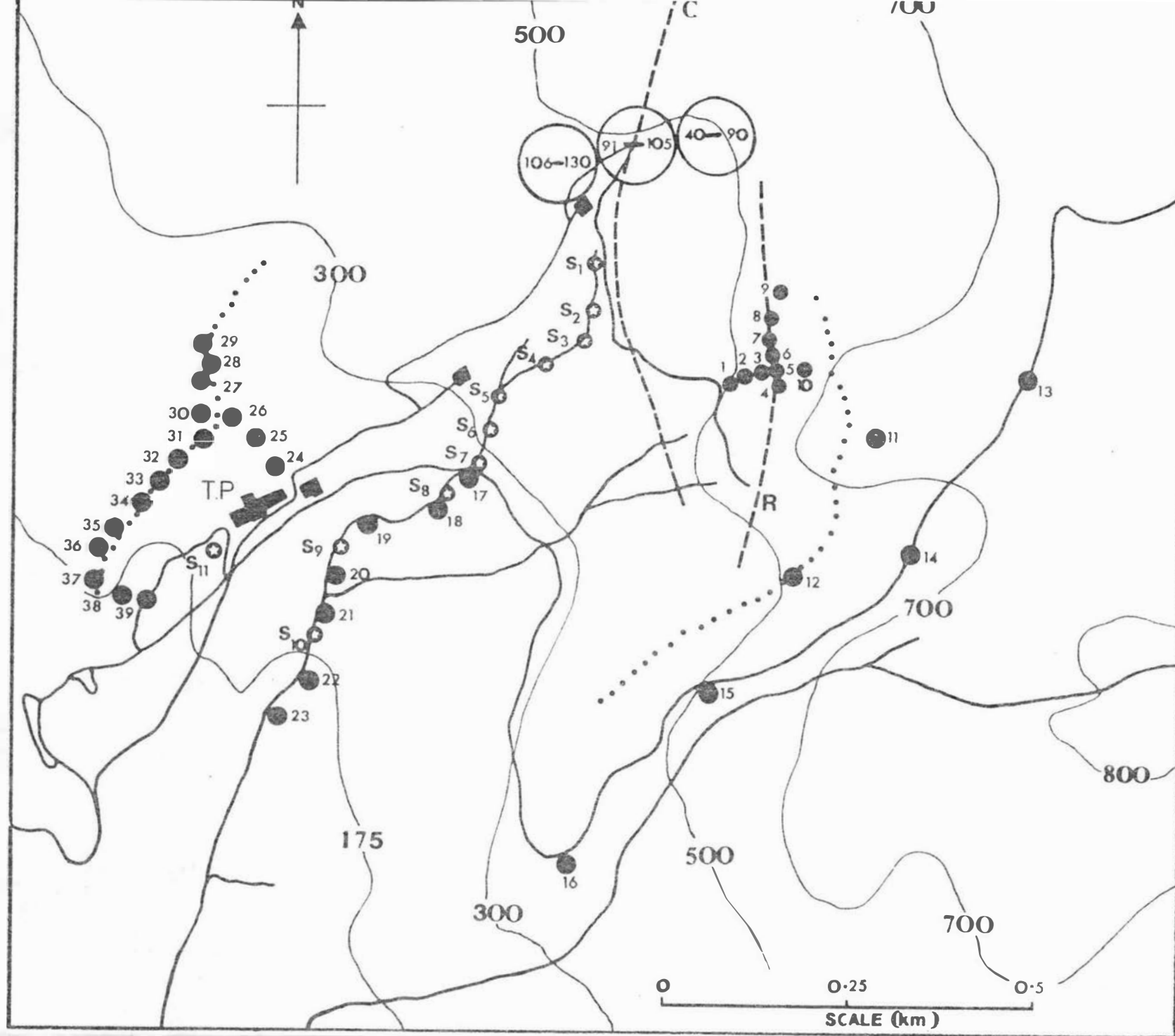
Figure VI.2.

Cadmium, copper and zinc concentrations (µg/g) in soils
from a transect across the Raukaka lodes, Tui Mine,
Te Aroha.

CADMIUM   COPPER   ZINC
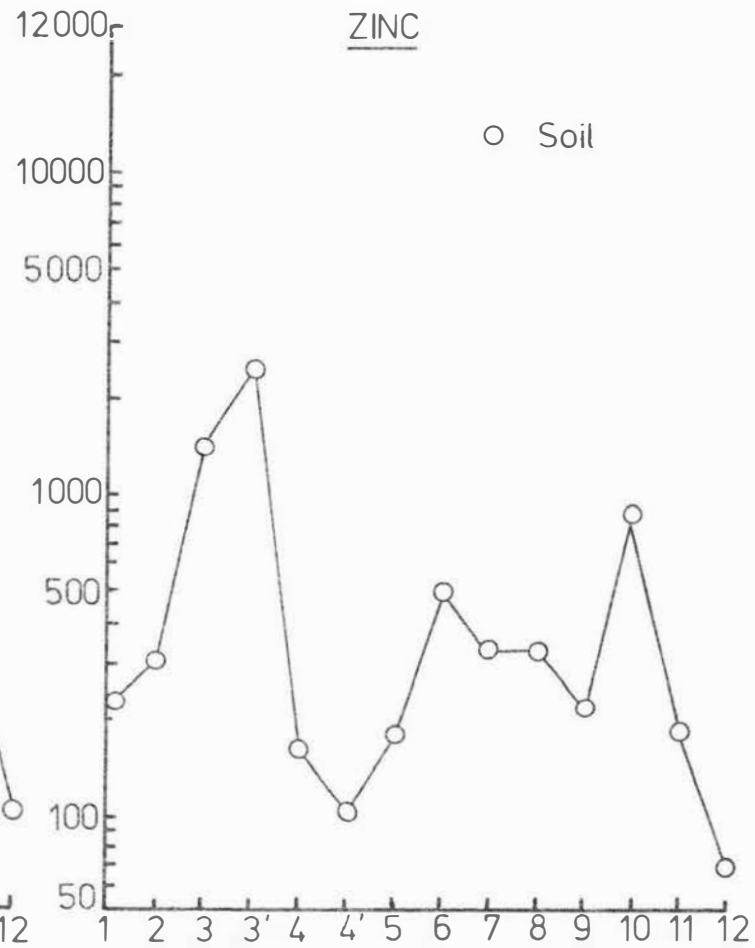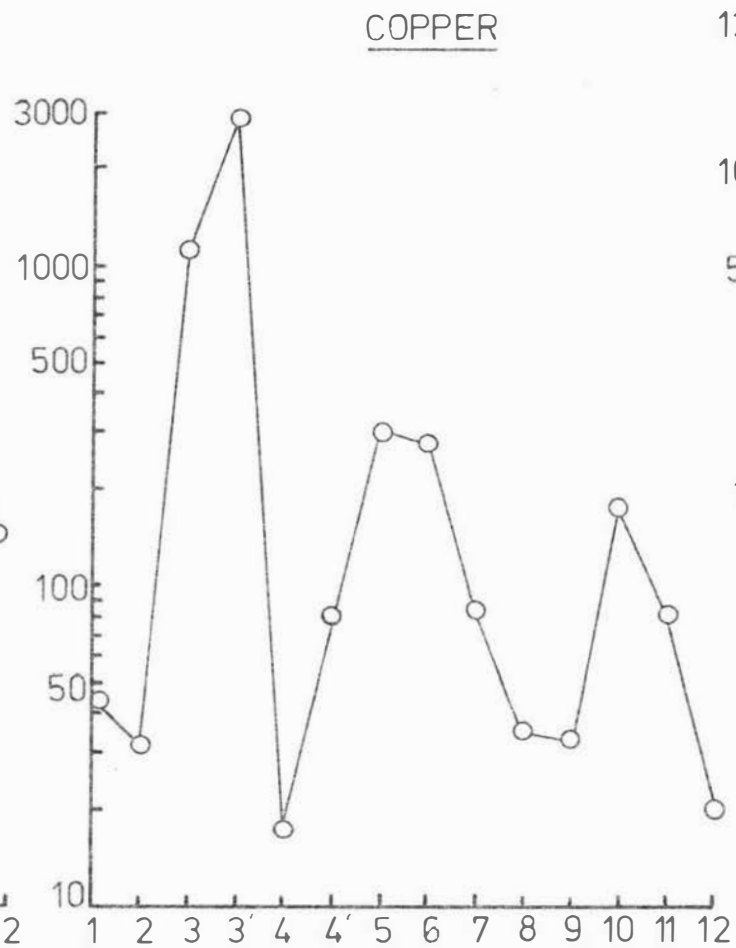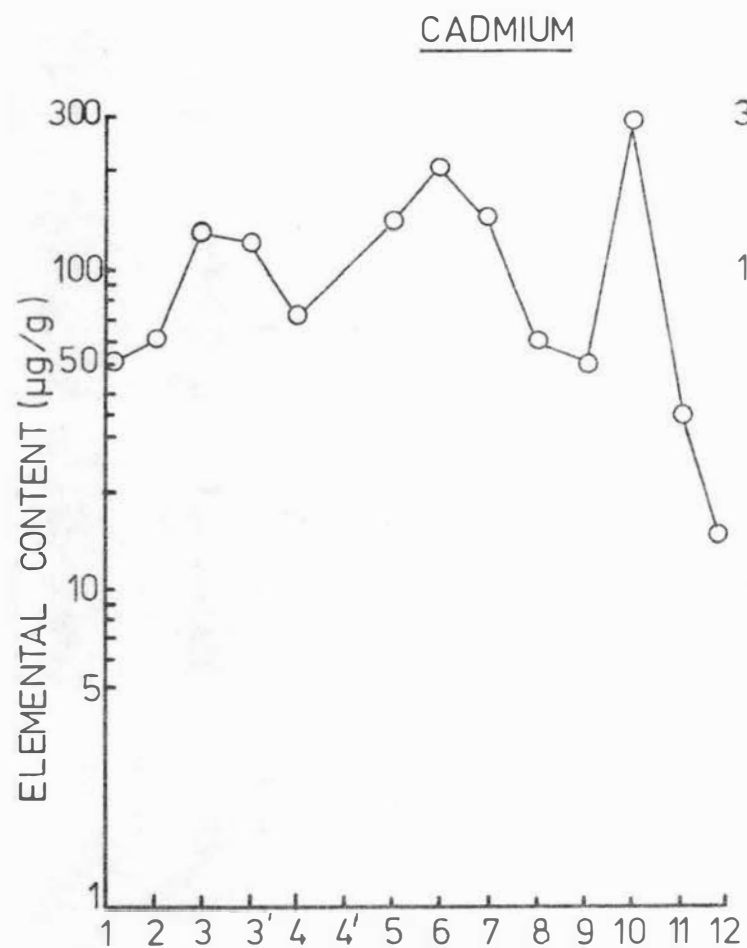
Bacground values for this area were about 0.5 µg/g cadmium, 40 µg/g copper and 50 µg/g zinc.

The elemental concentrations in soils from the Champion Lode area were 12-175 µg/g cadmium, 5-800 µg/g copper, and 30-5300 µg/g zinc.

Samples from the vicinity of the Valley Road area (sites 11-16 which are not shown in Figure VI.3.) showed metal contents of 0.5-2.5 µg/g cadmium, 41-190 µg.g copper and 61-336 µg/g zinc. Values within this area should have presumably been nearer to background levels, but sites 15 and 16 showed high elemental concentrations; these were probably due to road construction with contaminated rocks, and windborne dust deposition from mining activities adjacent to the treatment plant.

The distribution of cadmium, copper and zinc in soils around the treatment plant is shown in Figure VI.3. These soils are derived from non-mineralised country rock and elevated concentrations of base metals must have been due to deposition of airborne material from the treatment plant.

The elemental contents of soils decreased markedly with distance from the treatment plant along sampling sites 24 to 29 (which also increase in elevation). Levels along the ridge decreased towards background values at a distance of greater than 150m. Highly contaminated soils occurred, as a result of direct deposition of windborne dust from the treatment plant, within 30m of the source. The range of metal concentrations in soils adjacent to the plant was 5-50 µg/g cadmium, 48-145 µg/g copper and 77-326 µg/g zinc.

(b) Vegetation.

Elemental levels in the leaves of Beilschmiedia tawa and Schefflera digitata are shown in Figure VI.4. Accumulation of all three metals shows a pattern similar to that of the corresponding soils (Figure VI.2.)

Background values in B. tawa leaves from the Valley Road area were 0.05 µg/g cadmium, 2.0 µg/g copper, 6.0 µg/g zinc, (dry weight basis). The conversion factor for expressing data on

Figure VI.3.

Cadmium, copper and zinc concentrations in soils ($\mu g/g$) in the vicinity of the treatment plant, Tui Mine, Te Aroha. For scale and sample site identification see Figure VI.1.
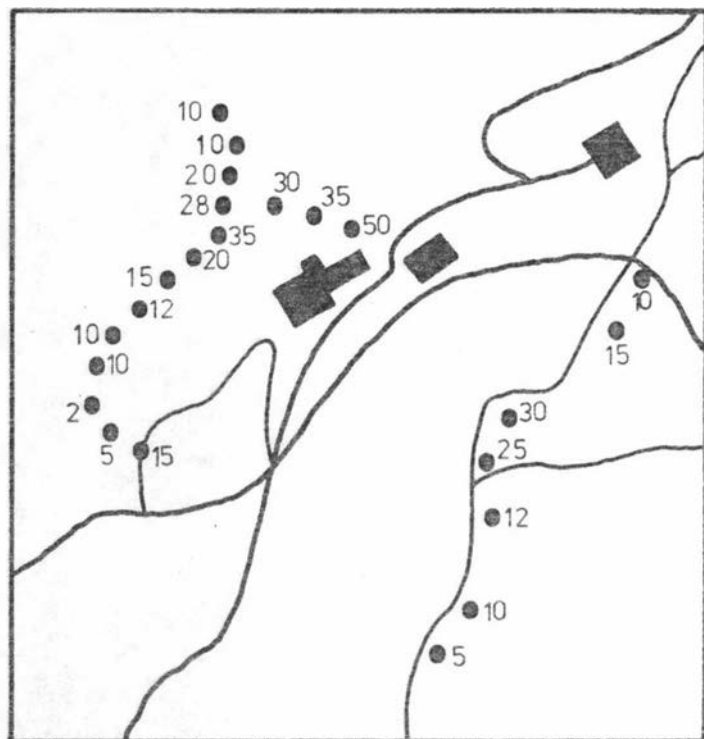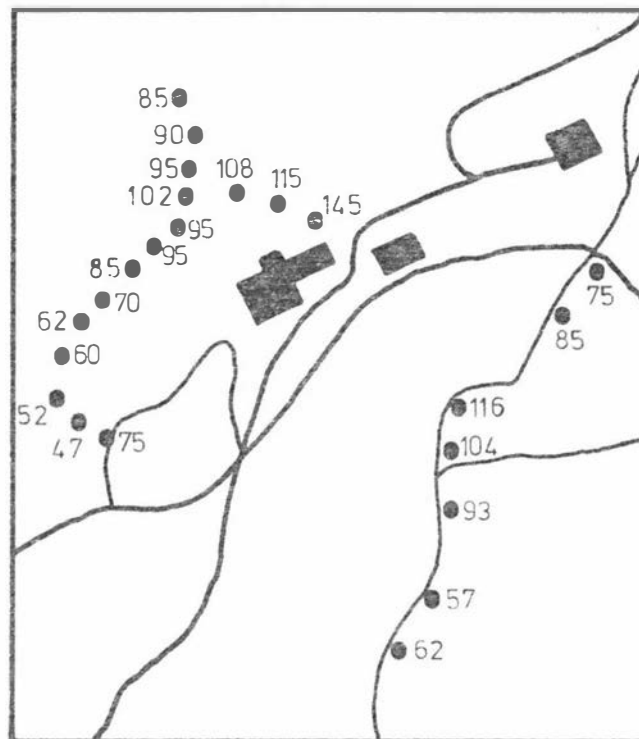
CADMIUM   COPPER   ZINC
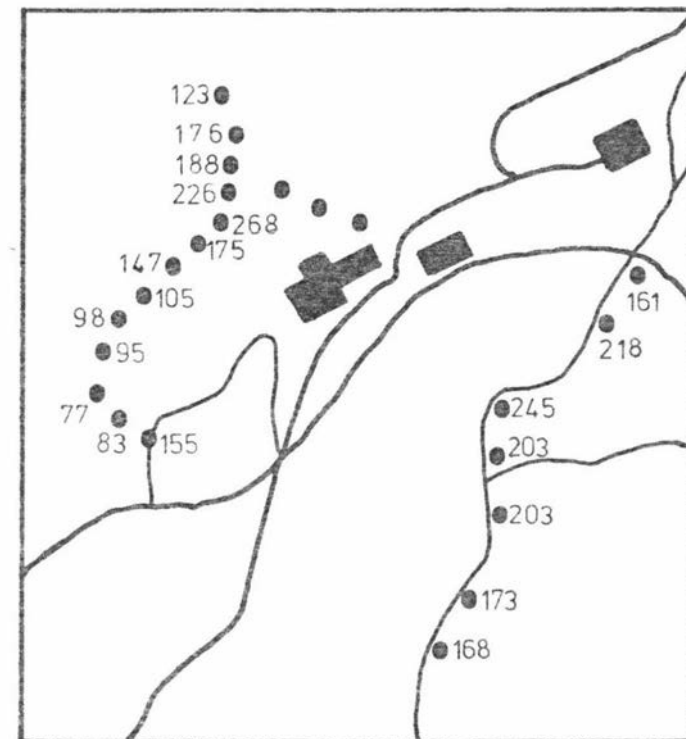
ELEMENTAL CONCENTRATIONS IN THE SOIL (µg/g)

Figure VI.4.

Cadmium, copper and zinc concentrations (µg/g dry weight) in leaves of Beilschmiedia tawa (symbol ▲) and Schefflera digitata (symbol ◉) from a transect across the Raukaka lode, Tui Mine, Te Aroha.

CADMIUM   COPPER   ZINC

△ B. tawa
□ S. digitata

ELEMENTAL CONTENT (μg/g)
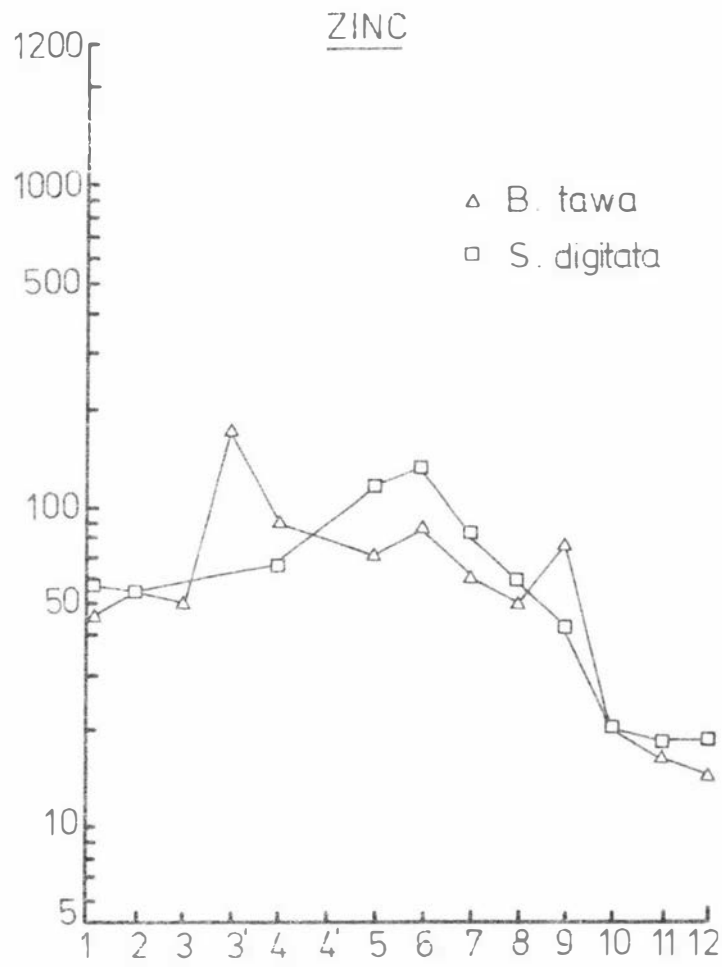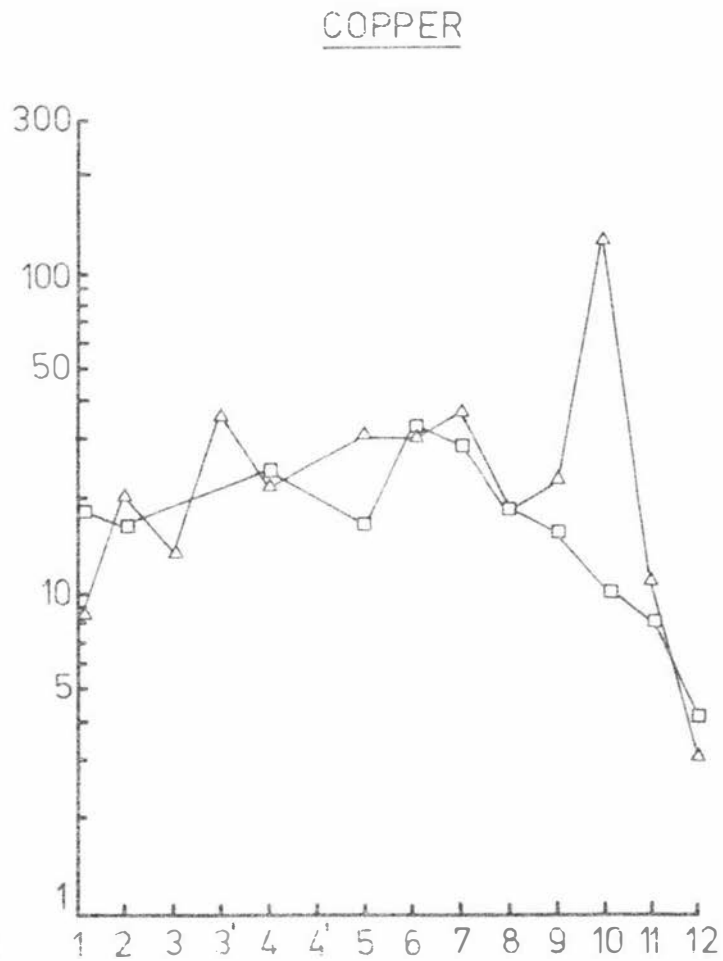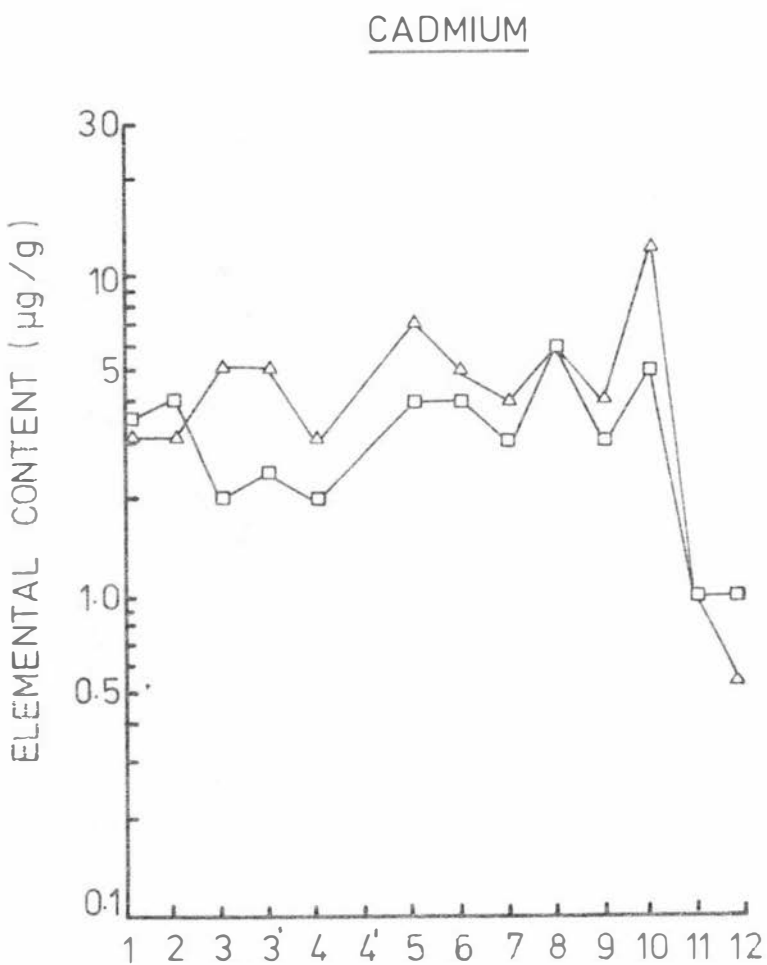
SAMPLING SITES

an ash weight basis is 10.2

In the vicinity of the treatment plant (Figure VI.5.) there was a pattern of zinc concentrations in B. tawa leaves which was similar to that already noted in soils.

The highest metal accumulations were within a 100m radius of the source, although even at greater distances, values above background were obtained, especially for zinc. Distributions seemed to depend mainly on the direction of the prevailing wind. Elemental levels at sites 38 and particularly 39 were higher than expected because these specimens grew within 10m of the settling pond. It is suggested that absorption from the root system may occur at these sites, as only 8-15% of the metal burden could be removed by washing the leaf surfaces.

The degree of absorption or fixation of the metal into B. tawa leaves is shown in Table VI.1. as the percentage (mean of 5 determinations) removed by washing with water.

Inspection of the table shows 3 dissimilar patterns. Near the treatment plant, 55-71% of all 3 metals was removed by washing. This suggests the accumulation is deposits of inert material upon the leaves, which has been previously reported by Little & Martin (1972) for fallout from a smelter. The lower proportion of cadmium and zinc removable by washing suggests that these elements are more firmly bound into the leaf structure than copper. Ready incorporation of cadmium and zinc into the guard cells and cuticles of leaves has been reported by Bukovac & Wittwer (1957) and Francke, (1967).

The samples from the Raukaka Lode, which involve accumulation predominantly via the root systems, show a predictably low elemental component removable by washing with water. Although absolute concentrations of all elements in leaves were appreciably higher than in samples taken from near the treatment plant, the percentage removable by washing was 4 or 5 times lower.

The samples from the background area showed that a very high percentage of the metal burden was removable by washing, particularly (as before) in the case of copper. It is suggested that even these 'background' samples contain an appreciable

Figure VI.5.

Cadmium, copper and zinc concentrations (μg/g dry weight) in <u>Beilschmiedia</u> <u>tawa</u> leaves in the vicinity of the treatment plant, Tui Mine, Te Aroha. For scale and sample site identification see Figure VI.1.
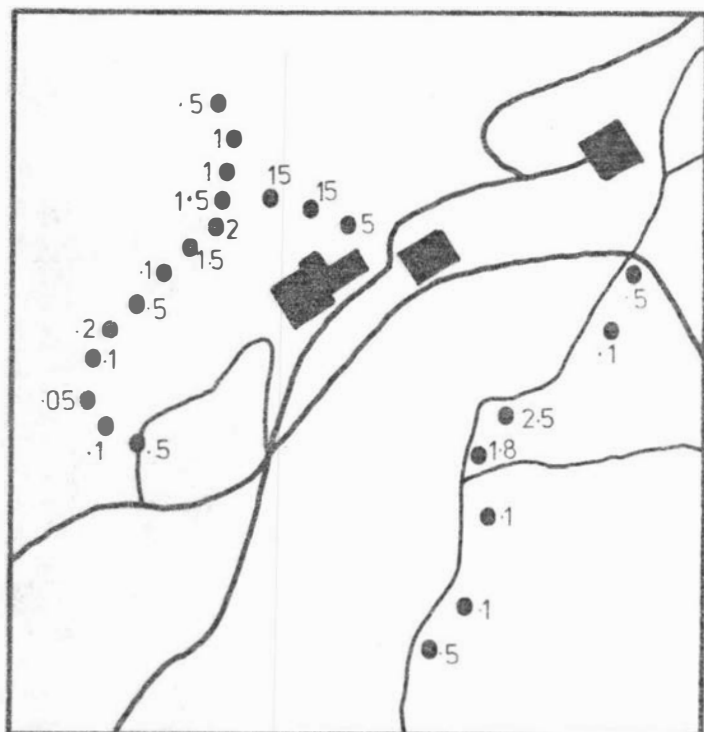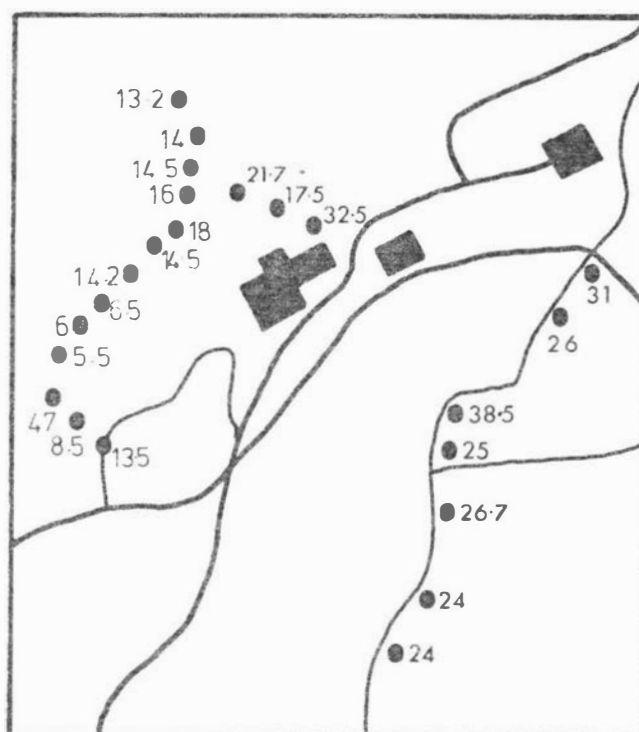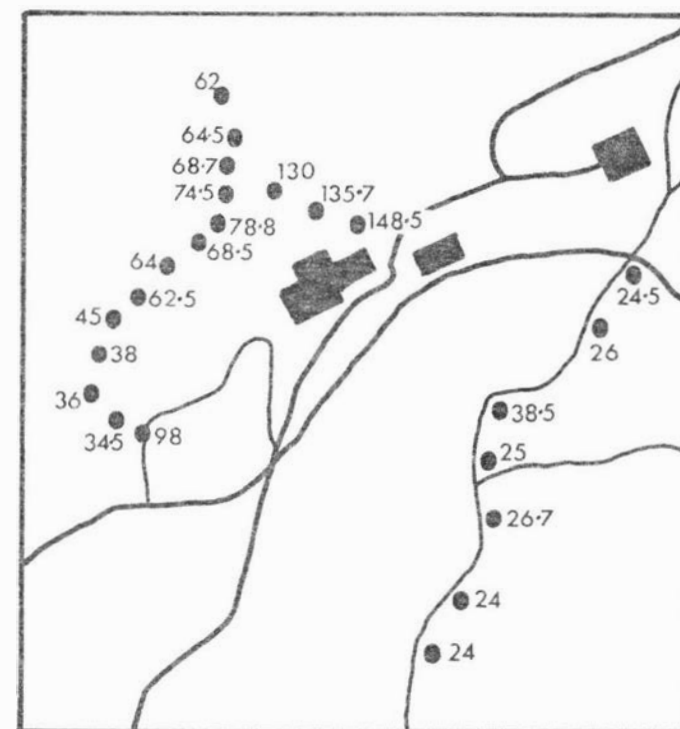
ELEMENTAL CONCENTRATIONS IN THE LEAVES OF
Beilschmiedia tawa (μg/g dry weight)

Table VI.1.

Mean Percentage Elemental Content Removed by Washing Beilschmiedia tawa Leaves

	Location		
	Treatment Plant	Raukaka Lode	Background
Cadmium			
Removed by washing	56%	15%	75%
Copper			
Removed by washing	71%	12%	90%
Zinc			
Removed by washing	55%	14%	75%

Table VI.2.

Cadmium Concentrations ($\mu g/g$ dry weight) in 2cm Lengths of Tree Trunk Ring-Cores of Beilschmiedia tawa

Site	Distance from centre of tree trunk (cm).				
	0-2	2-4	4-6	6-8	8-10
Treatment plant					
26	0.11	0.19	0.17	0.31	.-.
34	0.15	0.11	0.14	0.20	.-
36	0.04	0.08	0.12	0.08	-
Raukaka lode					
3	1.72	1.92	1.32	1.41	-
6	1.68	0.91	1.35	1.29	-
11	0.03	0.07	-	0.08	0.07
Valley road					
22	0.14	0.18	0.18	0.22	-
17	0.18	0.10	0.15	0.19	0.22
13	-	0.05	0.10	0.10	0.10

component of aerial fallout, and that true background samples will probably be found at considerably greater distances away from the mine and treatment plant.

(c) Tree ring-core samples.

The concentrations of copper and zinc (μg/g dry weight) in 2cm lengths of 6mm diameter cores of $\underline{B}$. $\underline{tawa}$ are shown in Figure VI.6., expressed as a function of distance from the centre of the tree trunk. Corresponding data for cadmium are shown in Table VI.2. The conversion factor for expressing data on an ash weight basis is 7.9.

Figure VI.6. shows 2 main patterns of uptake. Samples from near the treatment plant show elevated contents of base metals towards the outside of the tree, whereas specimens growing in the Raukaka Lode show no significant trend to increase or decrease towards the exterior. The 'background' samples also show a tendency to increase towards the outside.

It will also be noted that the trend to have increasing concentration of base metals towards the outside of the tree trunk decreases progressively with increasing distance from the treatment plant.

Uptake patterns of base metals in tree ring-cores seem to reflect the mechanism of uptake. Where accumulation is via the root system, distributions are relatively uniform whereas aerial fallout results in higher levels towards the exterior of the trunk. This accumulation is probably due to absorption via the bark, which in the case of $\underline{Beilschmiedia}$ $\underline{tawa}$ is comparatively thin.

(d) Stream sediments and waters.

The concentrations of cadmium, copper and zinc in stream sediments are shown in Figure VI.7. Samples at site S_{11} are from the settling pond at the treatment plant. The general pattern is for a decrease of values with increasing distances from the source. However, even at the furthest site shown (S_{10})

Figure VI.6.

Copper and zinc concentrations (µg/g dry weight) in tree trunk ring-cores of <u>Beilschmiedia</u> <u>tawa</u> expressed as distance from centre of the tree trunk. Numbers refer to sampling sites shown in Figure VI.1.

Treatment Plant Area

Raukaka Lode Area

Valley Road Area

DISTANCE (centimeters)

ELEMENTAL CONTENT (µg/g)
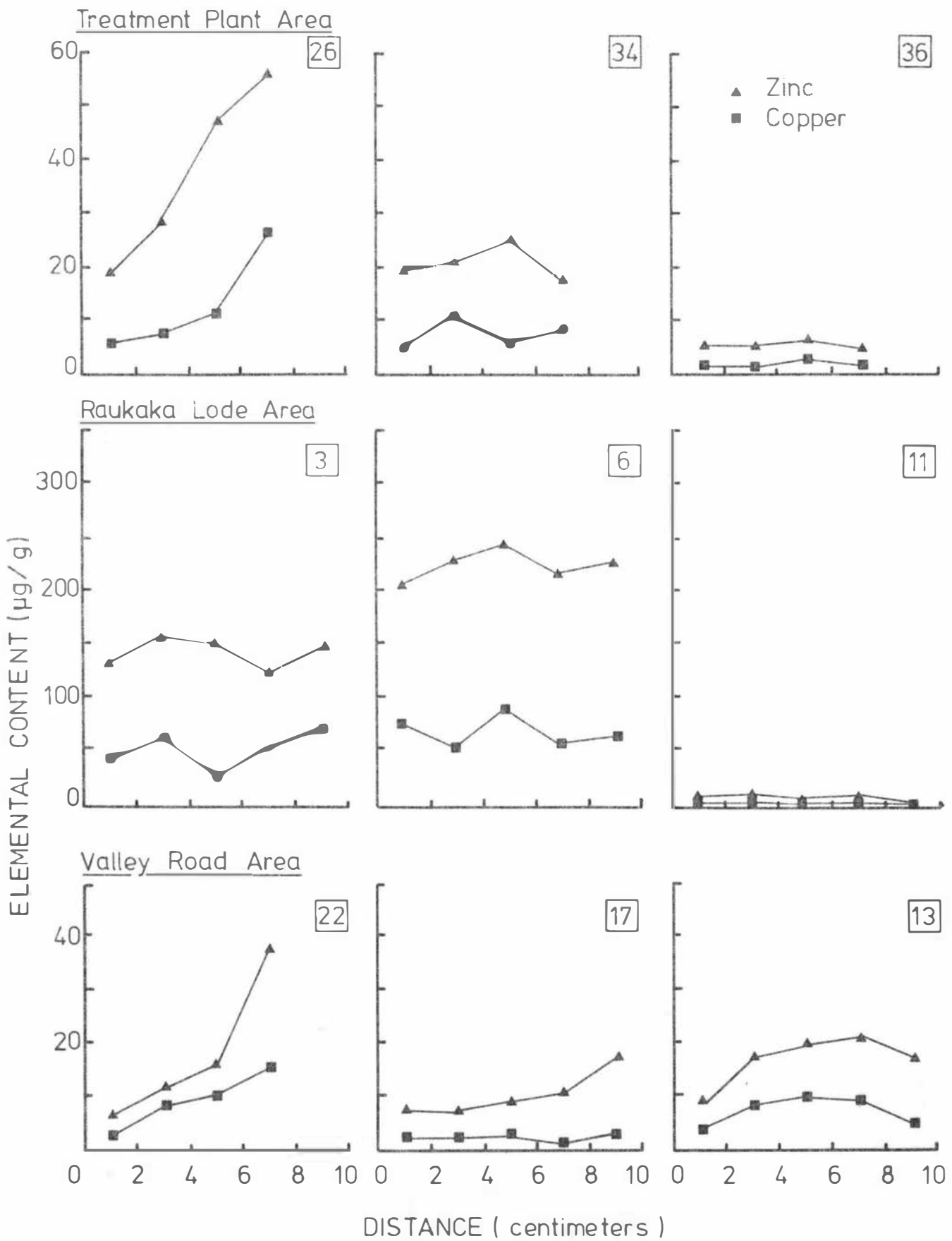
Zinc
Copper

Figure VI.7.

Cadmium, copper and zinc concentrations ($\mu g/g$) in sediments of a stream originating from the vicinity of the base metal deposits, Raukaka lode, Tui Mine, Te Aroha.
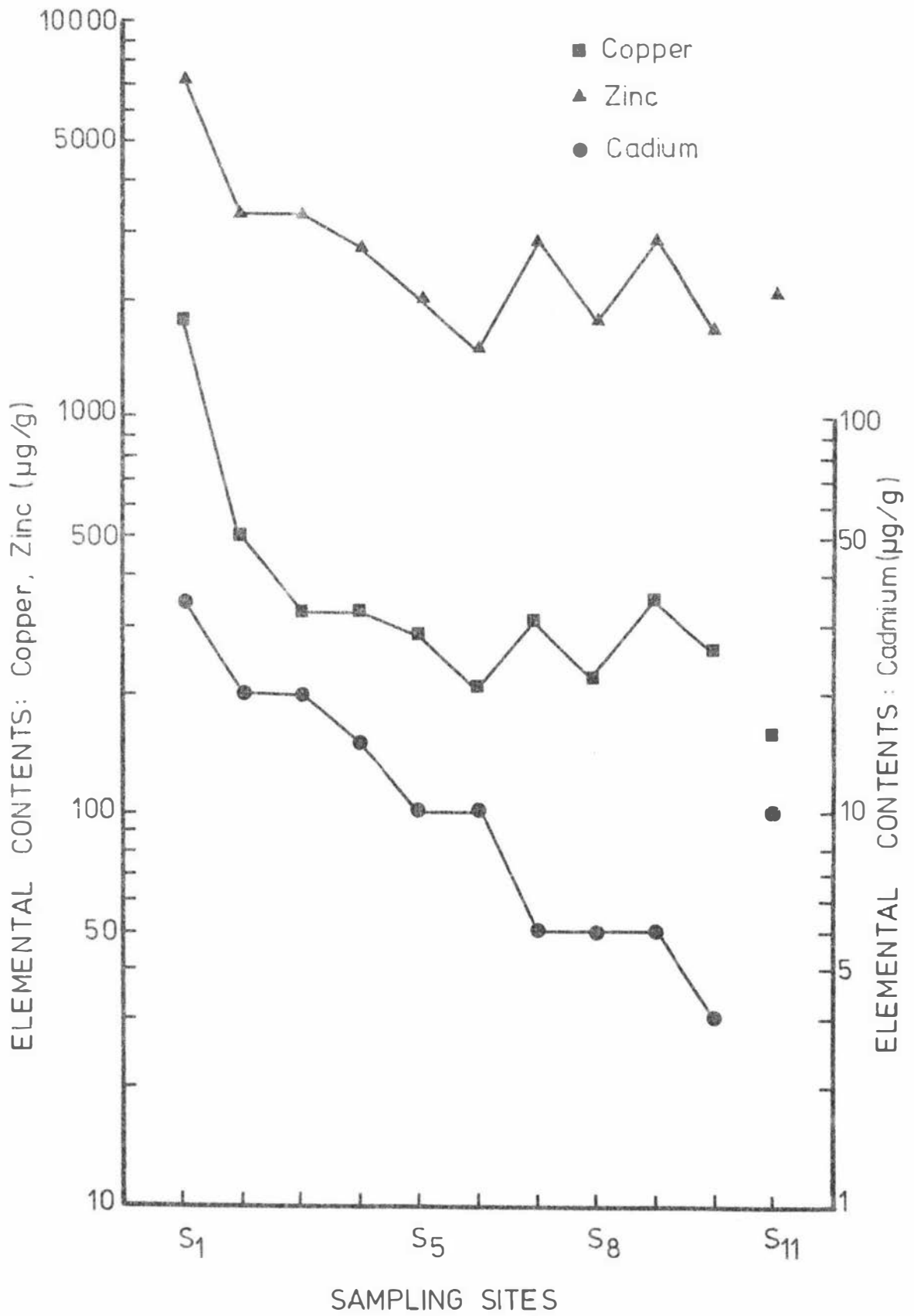
the concentrations are still extremely high.

The corresponding cadmium, copper and zinc levels for water samples are shown in Figure VI.8. Again there is evidence of a decrease of values with increasing distance from the source, although the decrease is much less apparent than for sediments. The values are extremely high and even at site S_{10} are at least an order of magnitude above normal background levels. Analysis of water samples after filtration via a millipore filter ($0.80\mu m$) showed that 35.7% of the copper and 9.6% of the zinc was retained by the filter.

4. Conclusion.

It is clear that there is a widespread distribution of airborne cadmium, copper and zinc from dust particles emanating from the ore treatment plant at the Tui Mine. Stream sediments and waters are also heavily polluted in the immediate area of the mine and treatment plant. It is also evident that trees growing over the ore bodies contain natural levels of these base metals in amounts even greater than those derived from windborne sources.

Analysis of tree ring-core sections showed a dissimilar pattern between airborne deposition and accumulation of metals via the root system. With airborne accumulation, tree ring-cores showed a significant increase of levels towards the outside of the trunk. When elements were accumulated via the root system, concentrations were appreciably uniform through the entire trunk.

At this stage it is important to assess the overall environmental impact of operations at Te Aroha. In part C. an investigation is reported that reveals the accumulations of cadmium, copper, lead and zinc in the local environment, caused largely by airborne pollutants (as finely-divided concentrate particulates) from the ore-crushing treatment plant. The effect of this plant on vegetation and soils in a nearby pasture is assessed and an evaluation is made of the total heavy metal burden before and after 12 months from the completion of mining activities in the area.

Figure VI.8.

Cadmium, copper and zinc concentrations (µg/l) in waters of a stream originating from the vicinity of the base metal deposits, Raukaka lode, Tui Mine, Te Aroha.
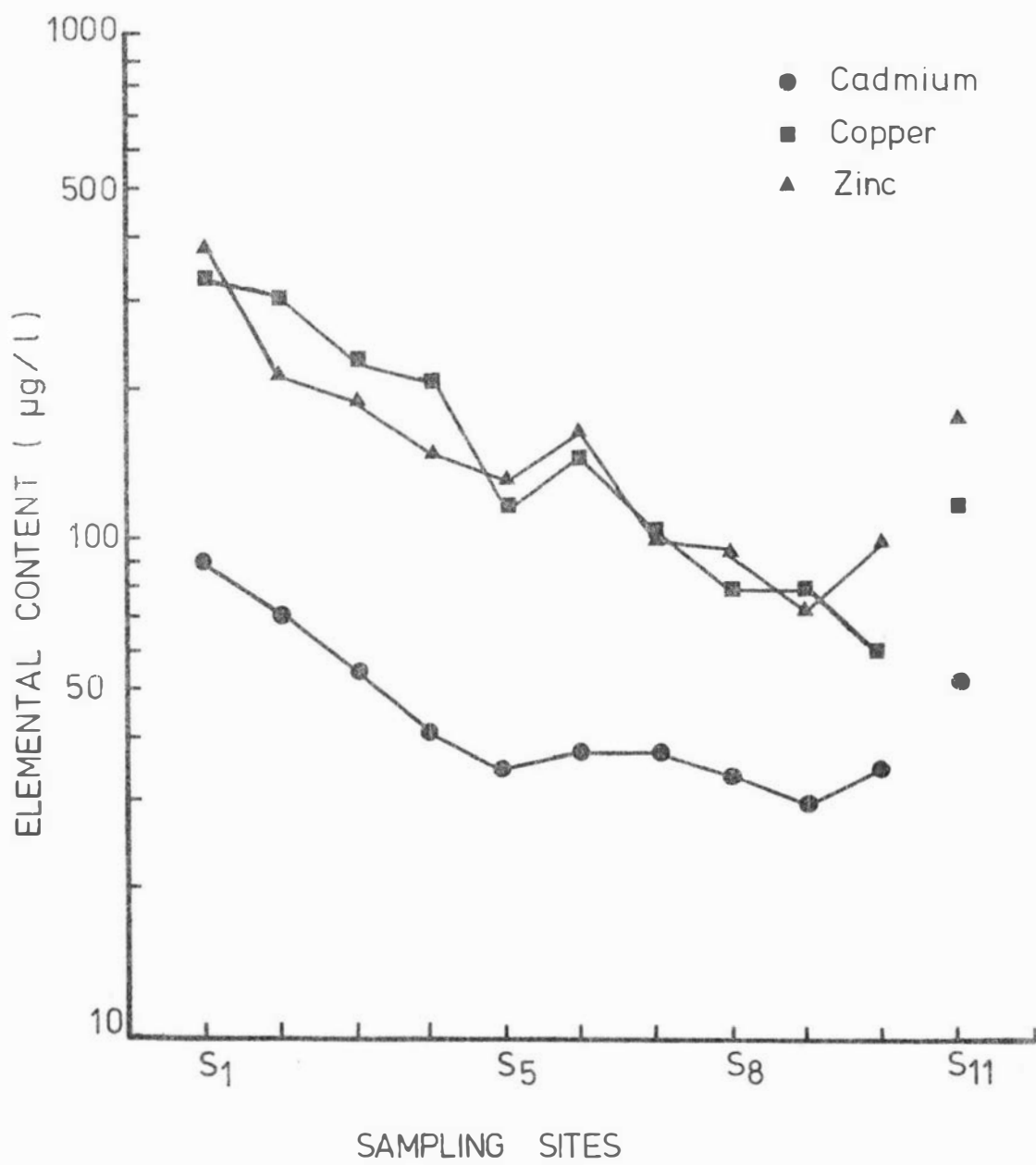
C. CADMIUM, COPPER, LEAD AND ZINC CONTAMINATION OF A
    PASTURE BY THE TUI BASE METAL MINING OPERATIONS,
    TE AROHA.

1. Study area.

The Tui Mine began operations about 10 years ago and closed
in August 1975 because of economic problems. As a result of the
work reported in the previous subsection (for cadmium, copper and
zinc) along with that for lead (Ward, 1974a), the effect of air-
borne particulate deposition from the ore-crushing treatment
plant on a nearby pasture and soil was investigated. The
paddock used for the experiments runs in an east-west direction
down a very steep slope (c. 30°) and is about 500m long and 100m
wide. The upslope end of the paddock is about 700m north-west of
the treatment plant.

2. Materials and methods.

Pasture species and soil samples were taken at intervals of
50m downslope from the end of the paddock closest to the treat-
ment plant. Species studied were : Dactylis glomerata L.
(cocksfoot), Holcus lanatus L. (yorkshire fog), Lolium perenne
L. (perennial ryegrass), Poa annua L., Trifolium repens L.
(white clover), and flatweeds of the genera Bellis, Crepis, and
Plantago.

Soil cores were taken at distances of 0 and 450m from the
upslope end of the paddock. Samples were taken at two different
periods. The first coinciding with the closure of the Tui Mine
(August, 1975) and the second period 12 months later. In this
way it was hoped to determine whether there was any lessening or
change of the heavy metal burden in plants and soils 12 months
after mining operations had ceased.

All plants and soils were analysed for cadmium, copper, lead
and zinc as outlined in Section I.B. All concentrations were
expressed as µg/g dry weight.

3. Results and discussion.

(a) Soil.

The elemental concentrations (µg/g) in surface soils sampled along an east-west transect of the paddock for the time periods of the mining operations ceasing and 12 months later (broken line), are shown in Figure VI.9. Clearly, high concentrations (over 10 times background in some cases) had accumulated in the surface soils (top 1-2 cm) by August 1975. Except for lead, these levels are similar to heavy metal concentrations found in soils adjacent to busy motorways (Ward et. al. 1977b-Section IV. which were 3.8 µg/g cadmium, 130 µg/g copper, 3064 µg/g lead, and 450 µg/g zinc in soils at the Market Road - Greenlane interchange of the Auckland Motorway). However, one year later there had been about a 40% reduction of copper and lead, and 25% of cadmium and zinc. Elsewhere along the transect, levels were consistently lower after 12 months except for copper concentrations which remained virtually unchanged after the first 50m in the downslope direction.

Figure VI.10. shows elemental concentrations in soils as a function of depth for the two time periods at two sites, one nearest the source of pollution (distance 0m from the upmost end of the paddock) and another as far as possible downslope (distance 450m). There is less differentiation after 12 months between elemental concentrations at the surface and at a depth of 5cm, indicating a steady loss of pollutants from the surface soil after the completion of mining activities. Movement down the soil profile is indicated by increased concentrations of copper and lead at depth associated with the more heavily contaminated site. After 12 months, however, even the least polluted part of the paddock contained concentrations of heavy metals well above normal. Normal or 'background' levels for elements in this type of soil in the Te Aroha area were established as being : 0.5 µg/g cadmium, 40 µg/g copper, 20 µg/g lead, and 50 µg/g zinc.

Figure VI.9.

Cadmium, copper, lead and zinc concentrations (µg/g) in surface soils sampled at various distances (m) along an east-west transect of a paddock in the vicinity of the ore-crushing treatment plant, Tui Mine, Te Aroha. Unbroken line represents sampling at time of the mining operations ceasing and broken line 12 months later. Zero distance corresponds to points nearest the source of pollution.

μg/g Zn

μg/g Cd

μg/g Pb

μg/g Cu
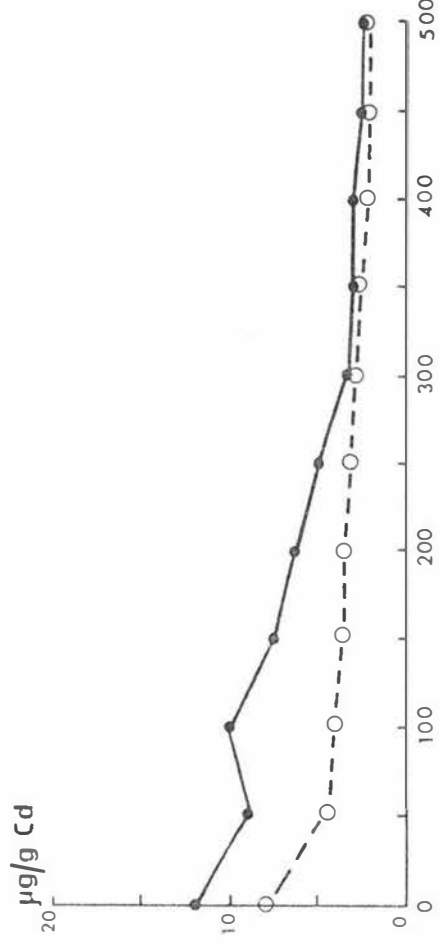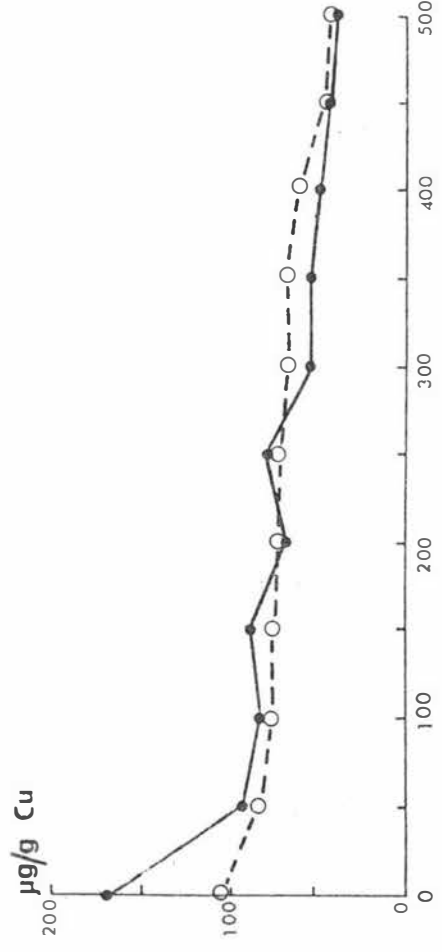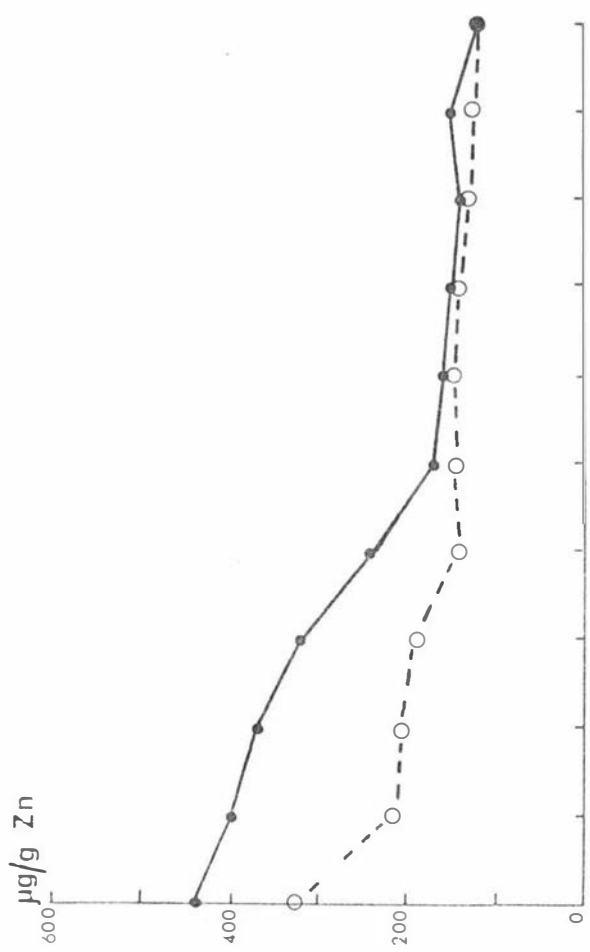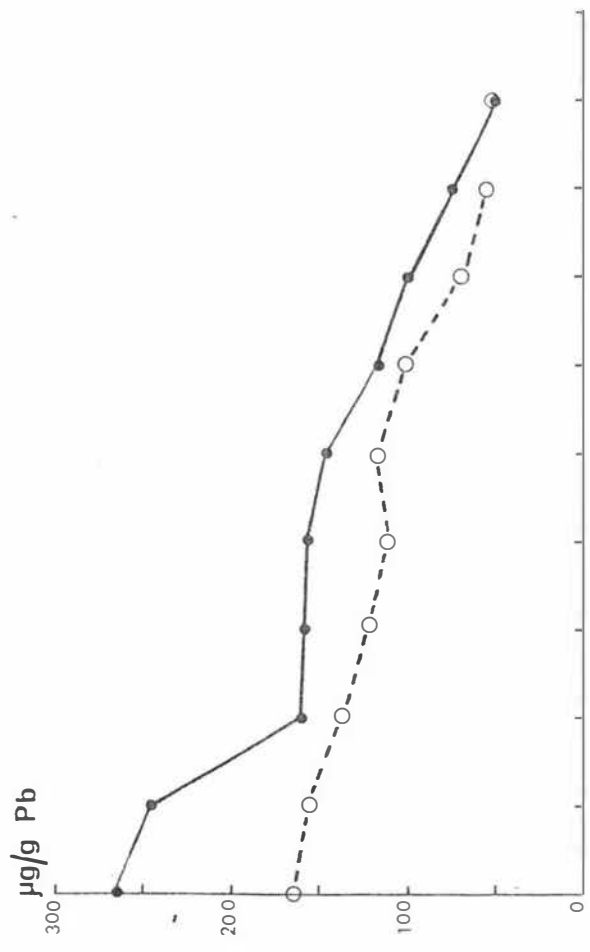
DISTANCE (METERS)

Figure VI.10.

Cadmium, copper, lead and zinc concentrations ($\mu g/g$)
of soils as a function of depth (cm) sampled at the
distances 0 and 450 m along an east-west transect
of a paddock in the vicinity of the ore-crushing
treatment plant, Tui Mine, Te Aroha. Unbroken line
represents sampling at time of the mining operations
ceasing and broken line, 12 months later. Zero distance
 corresponds to points nearest the source of pollution .
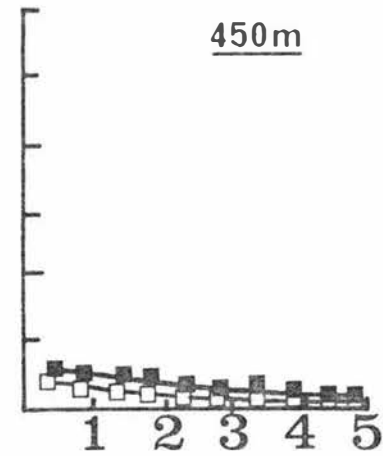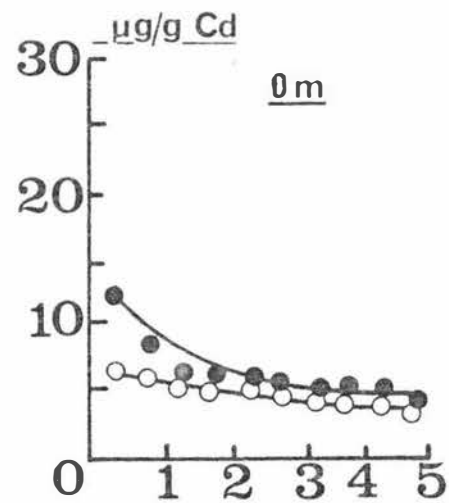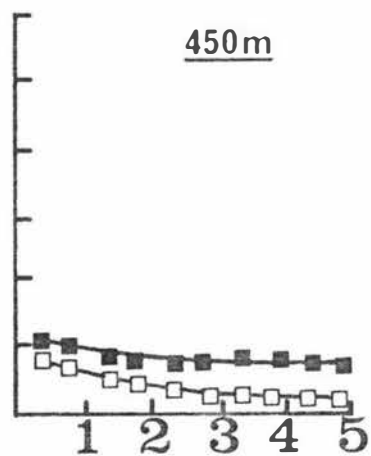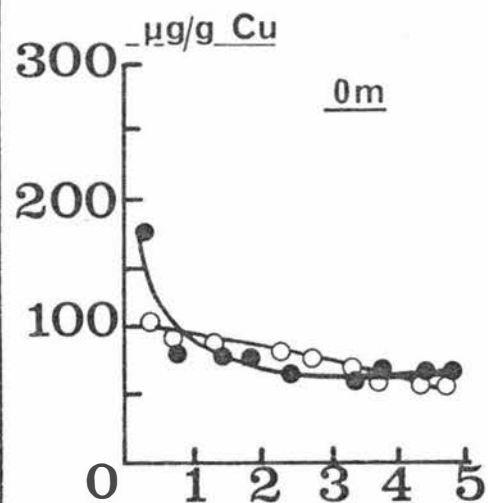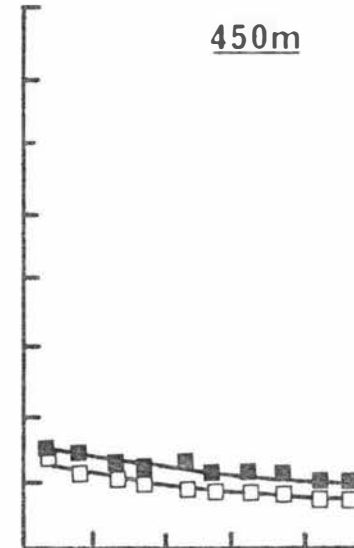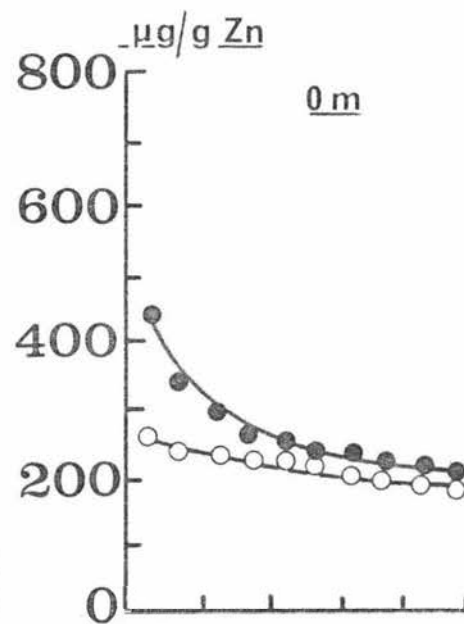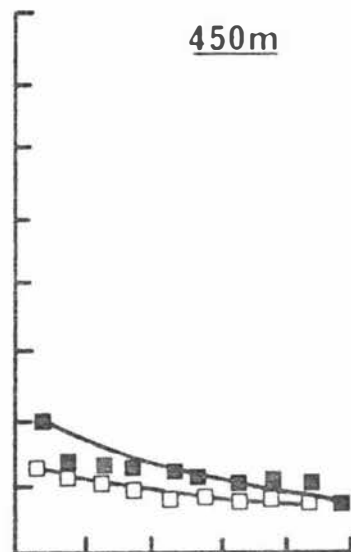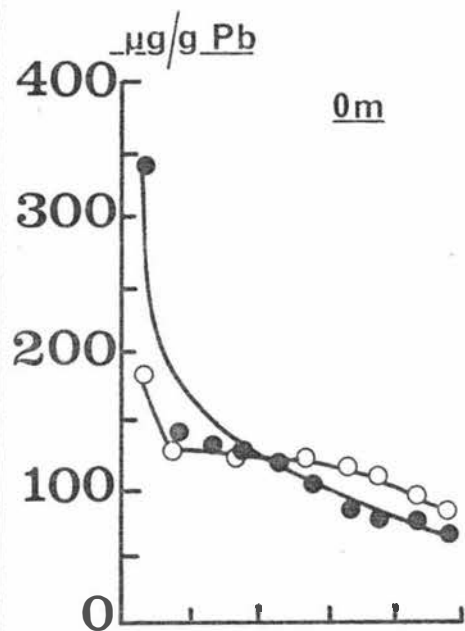
(b) Pasture species.

The distribution of heavy metals in the six pasture species
is shown in Figures VI.11. (cadmium), VI.12 (copper), VI.13 (lead)
and VI.14 (Zinc).

The initial heavy metal burden of pasture species at the
more heavily contaminated parts of the pasture is well above
background, but concentrations show a significant decrease after
12 months, which is greatest for sites closest to the source of
pollution. Decreases of cadmium are usually more pronounced for
leaves than for roots and represent an expected pattern where
the source of pollution from airborne particulates has been
removed.

Copper concentrations in all species decreased with time
(Figure VI.12), particularly in ryegrass and Poa annua, at sites
closest to the treatment plant. This is clearly a species
difference.

As with other elements, lead levels show an overall decrease
in all species at upslope sites (Figure VI.13). Slightly higher
lead levels in cocksfoot and yorkshire fog at downslope sites
may be caused by leaching of lead from the upper parts of the
pasture near the treatment plant.

Figure VI.14 shows zinc concentrations in pasture species
and there is evidence (as before) of reduced levels at sites of
maximum contamination, and slightly enhanced levels downslope in
roots of cocksfoot, leaves of yorkshire fog, stolons of white
clover, and leaves and roots of flatweeds. Since only soluble
forms of these heavy metals would be expected to leach downslope,
it is to be expected that this leaching would be reflected in
higher accumulations by vegetation in the lower-lying parts of
the pasture.

The evidence of movement of heavy metals through the soil
profile (Figure VI.10), and of leaching downslope across the
surface (Figure's VI.13 and 14), indicates that both mechanisms
may reduce the effects of pollution from the treatment plant.

Figure VI.11.

Cadmium concentrations (μg/g dry weight) in pasture species sampled at various distances (m) along an east-west transect of a paddock in the vicinity of the ore-crushing treatment plant, Tui Mine, Te Aroha. Unbroken line represents sampling at time of the mining operations ceasing and broken line, 12 months later. Zero distance corresponds to points nearest the source of pollution. Leaf samples are shown as circles and roots as triangles, (white clover stolons as squares).

POA ANNUA

YORKSHIRE FOG

FLATWEEDS

RYEGRASS

COCKSFOOT

WHITE CLOVER

CADMIUM CONCENTRATIONS (μg/g)
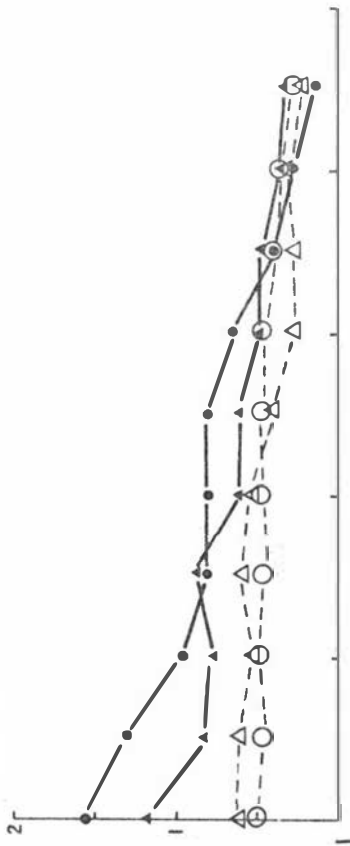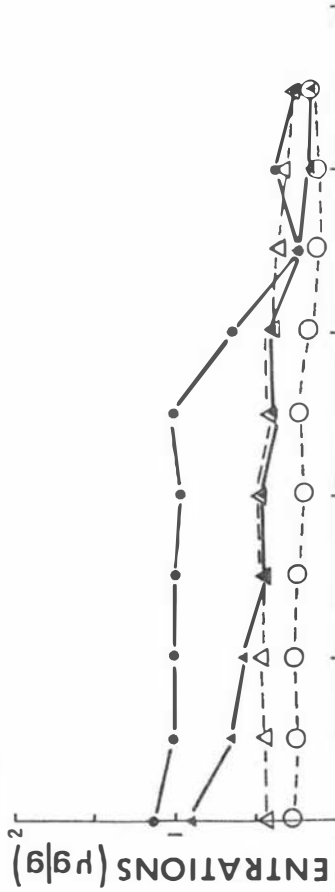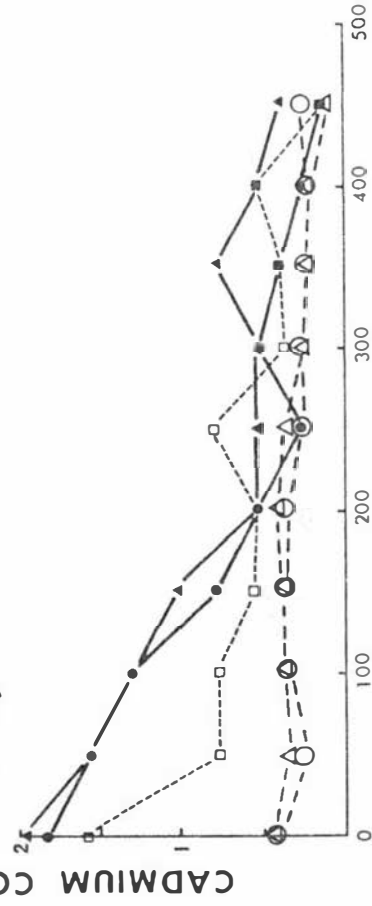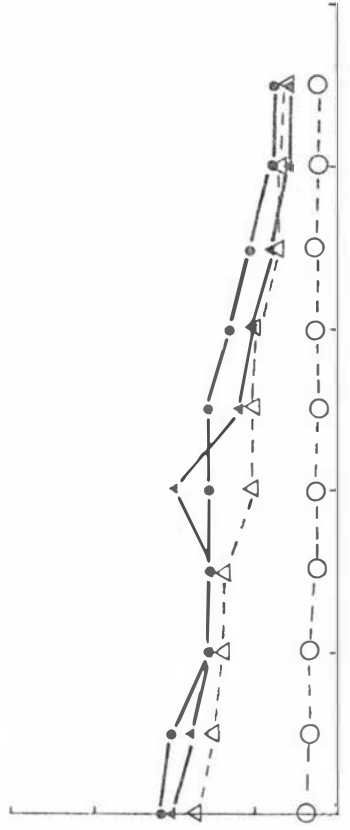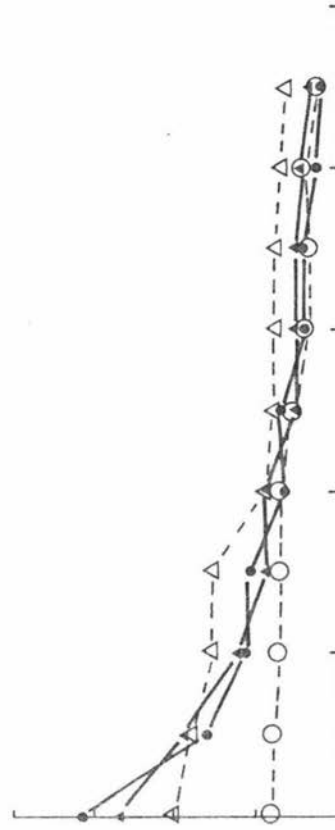
DISTANCE (METERS)
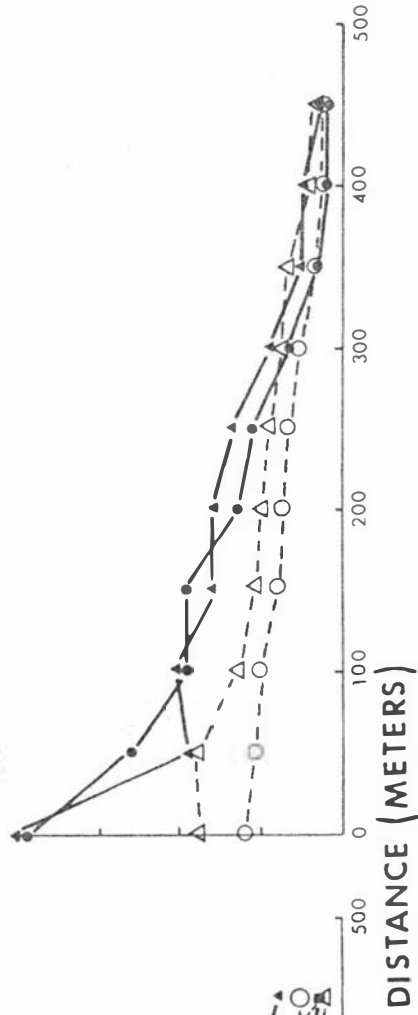
Figure VI.12.

Copper concentrations (µg/g dry weight) in pasture species
sampled at various distances (m) along an east-west
transect of a paddock in the vicinity of the ore-
crushing treatment plant, Tui Mine, Te Aroha. Unbroken
line represents sampling at time of the mining operations
ceasing and broken line, 12 months later. Zero distance
corresponds to points nearest the source of pollution.
Leaf samples are shown as circles and roots as triangles,
(white clover stolons as squares).

COPPER CONCENTRATIONS (μg/g)

DISTANCE (METERS)

YORKSHIRE FOG

FLATWEEDS

COCKSFOOT

WHITE CLOVER
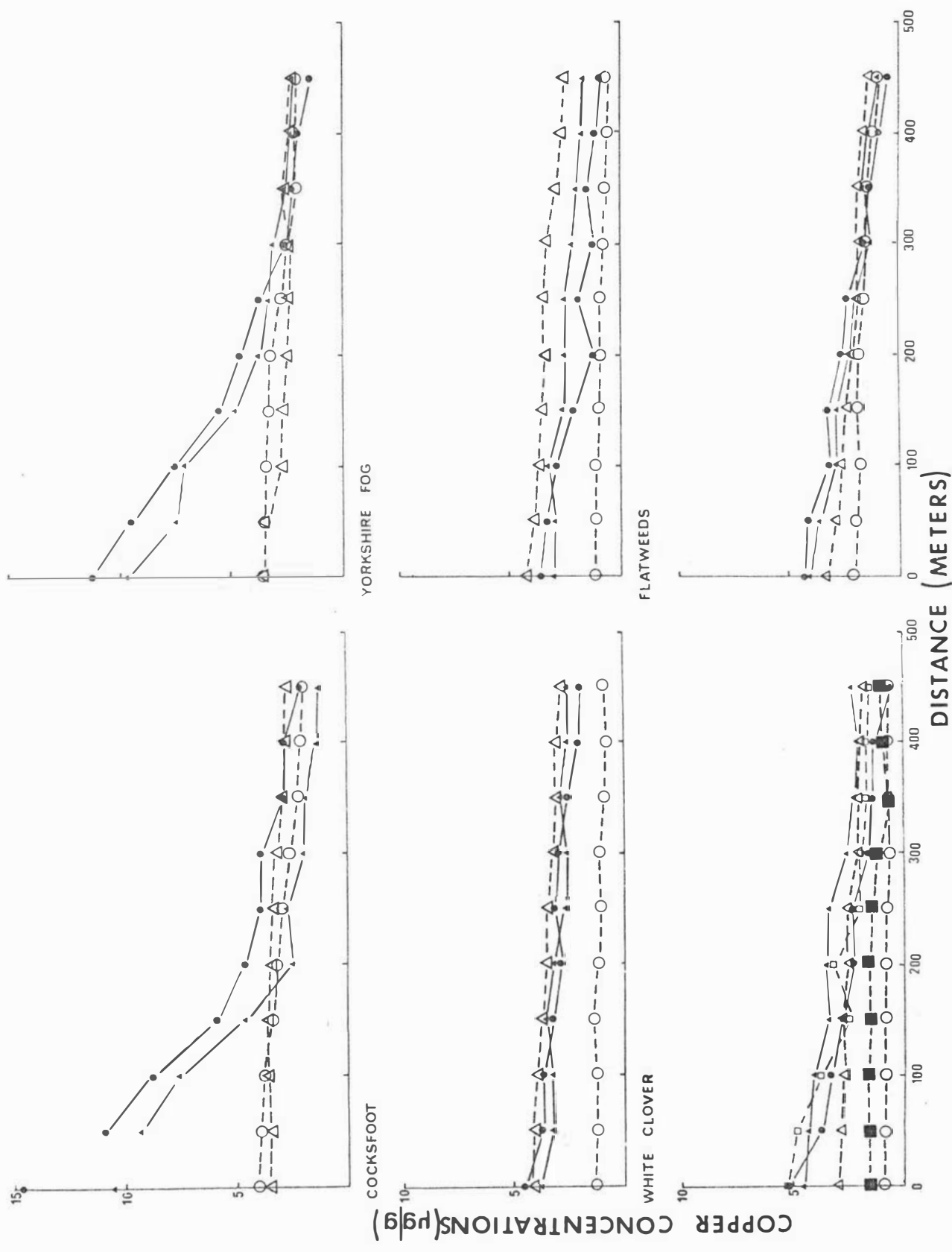
Figure VI.13.

Lead concentrations (μg/g dry weight) in pasture species sampled at various distances (m) along an east-west transect of a paddock in the vicinity of the ore-crushing treatment plant, Tui Mine, Te Aroha. Unbroken line represents sampling at time of the mining operations ceasing and broken line, 12 months later. Zero distance corresponds to points nearest the source of pollution. Leaf samples are shown as circles and roots as triangles, (white clover stolons as squares).

RYEGRASS
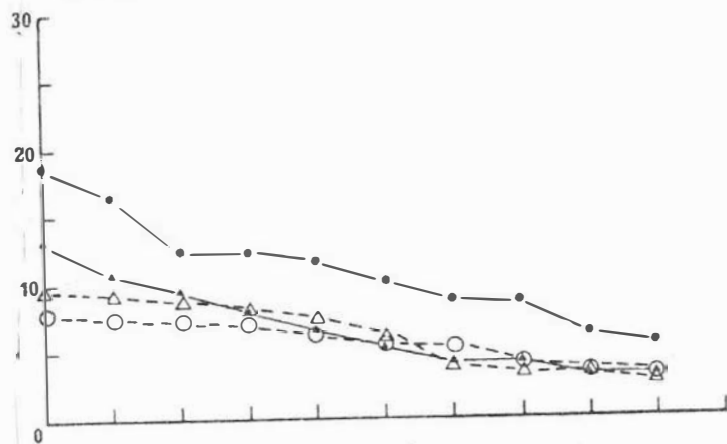
POA ANNUA
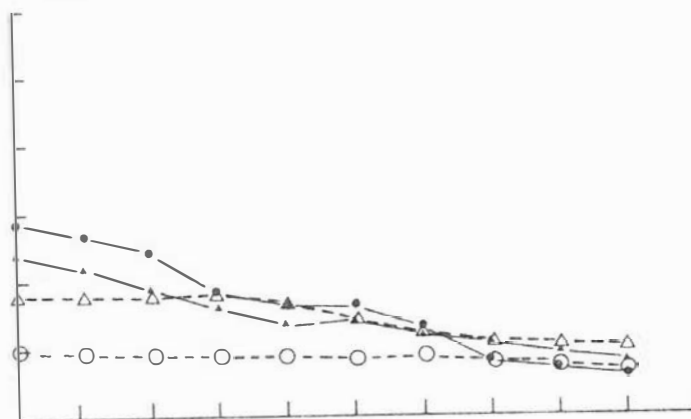
COCKSFOOT
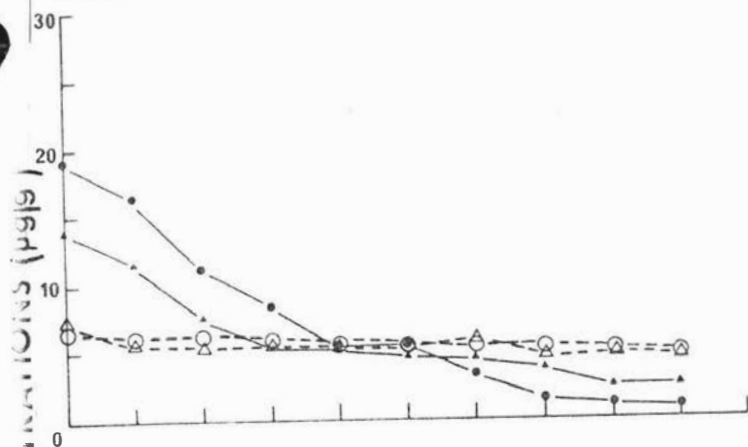
YORKSHIRE FOG

WHITE CLOVER

FLATWEEDS
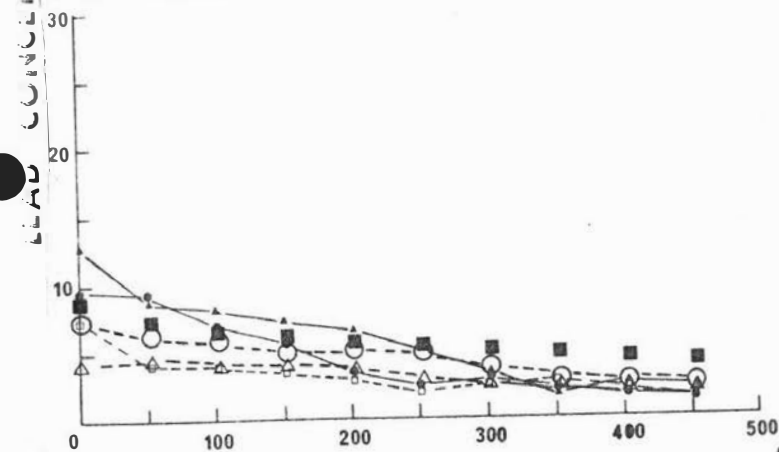
LEAD CONCENTRATIONS (μg/g)
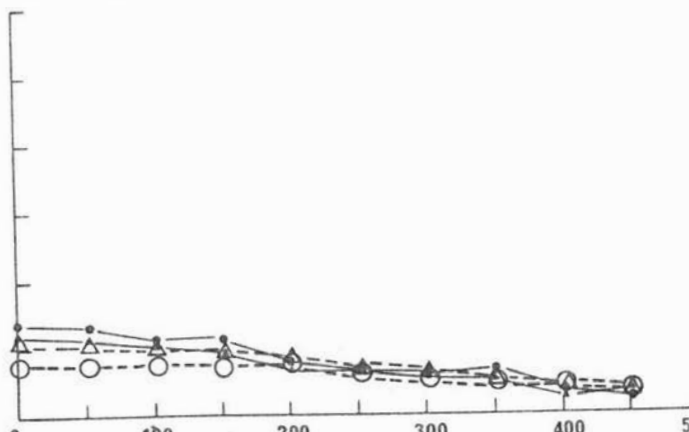
DISTANCE (METERS)

Figure VI.14.

Zinc concentrations (μg/g dry weight) in pasture species sampled at various distances (m) along an east-west transect of a paddock in the vicinity of the ore-crushing treatment plant, Tui Mine, Te Aroha. Unbroken line represents sampling at time of the mining operations ceasing and broken line, 12 months later. Zero distance corresponds to points nearest the source of pollution. Leaf samples are shown as circles and roots as triangles, (white clover stolons as squares).

RYEGRASS

POA ANNUA

COCKSFOOT

YORKSHIRE FOG

ZINC CONCENTRATIONS (μg|g)

WHITE CLOVER

FLATWEEDS

DISTANCE (METRES)
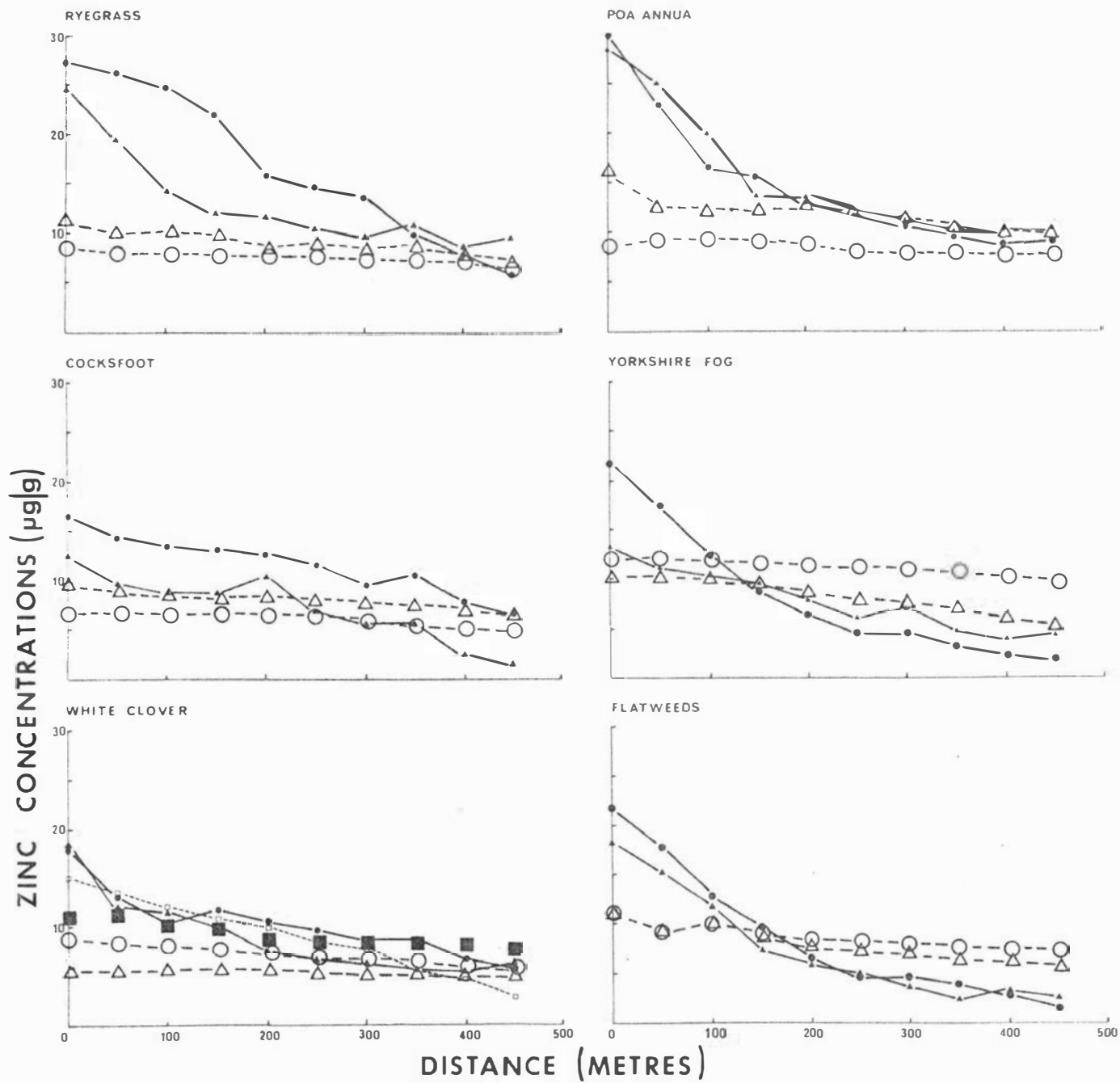
4. Conclusion.

It is concluded that there has been much reduction of heavy metal contamination of surface soils in the paddock at Te Aroha during a period of 12 months after the end of mining. Loss of pollutants appears to have resulted by downward leaching through the soil profile and by downslope movement. Continuation of this process should ultimately result in elemental concentrations in plants and soils approaching background values. This is likely to be achieved more rapidly by the more-mobile, elements cadmium, copper, and zinc. If the experience of lead mining in Great Britain is any indication (e.g. Crudgington et. al., 1973; who found considerable residual lead pollution of soils from 2000-year-old Roman lead mines), lead levels will never approach background within the foreseeable future.

The experimental paddock has proved to be a useful subject of study, not so much because it represents an isolated and localised example of contamination from heavy metals, but rather because it has afforded a means of studying the rate at which such effects are reduced.

SECTION VII

LEAD POLLUTION FROM A NEW ZEALAND BATTERY FACTORY
AND SMELTER COMPARED WITH THAT FROM MOTOR VEHICLE
EXHAUST EMISSIONS.

1. Introduction.

The distribution of airborne lead from battery and smelting works into the surrounding area has been given considerable attention in recent years. The extensive study of the Avonmouth (U.K) industrial complex by such authors as Abdullah et al.(1972), Burkitt etal. (1972), Butterworth et al.(1972) and Little & Martin (1972), illustrates the potential pollution problems in such environments. Similar studies have also been undertaken in such countries as the German Federal Republic (Garber, 1970), South West Africa (Marchand, 1974), and Australia (Beavington, 1975).

Following investigations into environmental lead levels from motor vehicle exhaust emissions in New Zealand (Ward et al., 1974b, 1975a,b), the following survey of a New Zealand battery factory and smelter situated in the industrial region of Auckland City was undertaken to assess lead levels in soils and vegetation from this industrial source, and to compare them with lead concentrations derived from motor vehicle emissions from a nearby major suburban thoroughfare. The purpose of this comparison was to study the relative atmospheric and soil mobilities of lead and to assess which was the more significant source of pollution in that immediate environment.

2. Study Area.

The battery factory and smelter are situated in an industrial region of Auckland City, at the intersection of two major suburban thoroughfares (mean daily traffic density of about 5200 motor vehicles). The surrounding area consists of many grassed areas and gardens from which samples were collected. There are no other major sources of lead in the area other than from the battery factory and smelter or from motor vehicle emissions in the thoroughfares.

The smelter associated with the battery factory is a secondary smelter (i.e. processing scrap from old batteries). The main chimney is approximately 30m high, giving a direct source for lead fallout and distribution to considerable distances from the battery factory area.

3. Materials and methods.

Samples were collected from 5 main areas as shown in Figure VII.1: samples 1-3 (battery factory and adjacent thoroughfare area); 4-7 (battery factory area); 8-13 (smelter area); 14-16 (varying distances from the smelter) and 17-22 (thoroughfare transect not associated with the battery factory or smelter areas).

At each sampling point, suface soils (0-5cm) and the following pasture species were collected : Lolium perenne L. (perennial ryegrass), Trifolium repens L. (white clover), Poa annua L., Holcus lanatus L. (yorkshire fog), and flatweeds (of the genera : Plantago, Bellis and Crepis. Soil cores were taken to a depth of 20cm at sites 5, 8, 16, and 17 using a 2.5cm diameter core extractor.

Sample preparation and analysis were carried out as described in Section I.3. The appropriate dilutions were carried out when necessary, especially for soils when the lead concentrations were very high.

4. Results and discussion

(a) Soils.

The mean lead content of surface soils at the various sampling sites is shown in Table VII.1. Each value is the mean of 5 determinations expressed as % on a dry weight basis.

The extensive accumulation of lead about the smelter and battery factory areas is shown clearly at several sites. The levels at sites 8 and 11 are even higher than those for soils collected from lead mineralization at Te Aroha (Ward et.al, 1976) but in these two sites, additional pollution is derived from the presence of numerous stored batteries and their shedding of oxidized lead compounds. Apart from these two sites, there is a trend for decrease of lead levels in the soils at increasing distance from the smelter. Sites 17-22 had a mean lead content of about 0.1% which is typical of soils adjacent to roads of similar traffic density (e.g. Ward et.al., 1977). It is probable therefore that most of the lead burden at these sites is derived from motor vehicle emissions rather than fallout from the industrial plant.

Figure VII.1.

Sketch of the Te Papapa battery factory and smelter,
with a nearby major thoroughfare (inset), Auckland.
Sampling sites are shown by numbers 1-3 (battery
factory and adjacent thoroughfare area); 4-7 (battery
factory area); 8-13 (smelter area); 14-16 (varying
distances from the smelter) and 17-22 (thoroughfare
transect not associated with the battery factory or
smelter areas).

N

19
18
17

>200m from battery factory and smelter

20
21
22

Thoroughfare Inset

1

2

Office Building

Driveways

4

Private Sections

3

New Battery Storage Area

Battery Factory

5

Private Sections

6

10

9

7

8

Driveways

Smelter

Chimney

Boundary Fence

Old Battery Storage Area

11

12

14

13

Open Ground

15

0   100m

16
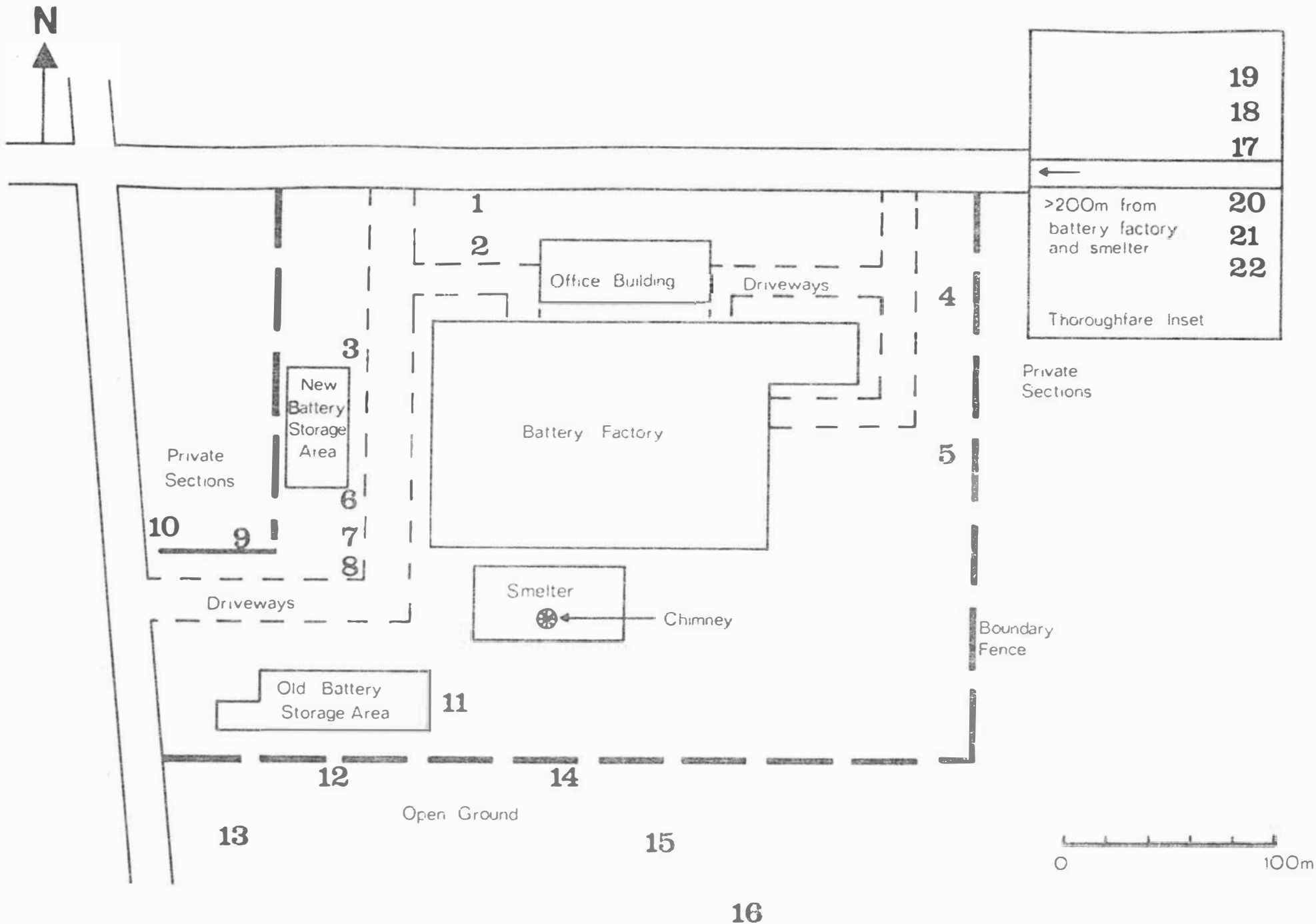
Table VII.1.

The Mean Lead Content of Surface Soils at Various
Sampling Sites Around a Battery Factory, Smelter
and Thoroughfare.

Sampling site	Mean lead content soil (% dry weight)
Battery factory and adjacent thoroughfare area	
1	0.16
2	0.51
3	0.97
Battery factory area	
4	1.5
5	3.1
6	2.2
7	4.1
Smelter area	
8	12.4
9	8.15
10	0.11
11	10.50
12	0.31
13	0.46
Distance from the smelter	
14	0.23
15	0.13
16	0.02
Thoroughfare transect	
17	0.10
18	0.08
19	0.05
20	0.11
21	0.08
22	0.07

High lead levels in surface soils as a result of probable contamination by airborne particulates, raise the question as to the mobility of this lead burden in the soil, and whether this lead can be taken up via the root systems of plants growing in these soils. The logarithm of the mean lead content of soil (µg/g dry weight) expressed as a function of depth (cm) at sites 5 (battery factory area), 8 (smelter area with additional pollution from stored batteries), 16 (some distance away from the smelter), and 17 (thoroughfare), is shown in Figure VII.2.

Soils contaminated only from motor vehicle exhaust emissions show a characteristic exponential decrease in lead content as a function of depth. Significant accumulation exists only in the first few centimeters. This is supported by similar findings of Chow (1970) and Ward et.al (1975b). Soils contaminated with very high lead levels from the battery factory, smelter, and stored batteries, show extensive concentrations even at a depth of 12cm. However, these high levels are probably due to the magnitude of the lead burden on the surface of the soil rather than to any difference of mobility within the soil profile. At sites greater than 90m. from the industrial complex, distribution patterns for lead were similar to those for motor vehicle exhausts.

(b) Vegetation.

The mean lead content of various organs of unwashed pasture species at the various sampling sites is shown in Table VII.2. The general pattern is for the highest lead levels to occur in the pasture species located within the vicinity of the industrial complex. The mean lead contents (expressed as µg/g dry weight and without regard to species) at the various sites are invariably lower in roots than in aerial parts of the plants and indicate deposition principally from airborne particulates. The background lead levels for these pasture species would be less than 5 µg/g dry weight (Ward et.al., 1976).

Since lead is transported primarily in particulate form (Daines et.al., 1970; Schuch and Loche, 1970; Sealey et.al., 1972; Habibi et.al., 1970) in the course of airborne distribution, the higher lead content of the leaves compared with roots reflects

Figure VII.2.

The logarithm of the mean lead content of soil (μg/g dry weight) expressed as a function of depth (cm) at sites 5 (battery factory area), 8 (smelter area with additional pollution from stored batteries), 16 (some distance away from the smelter), and 17 (thoroughfare).
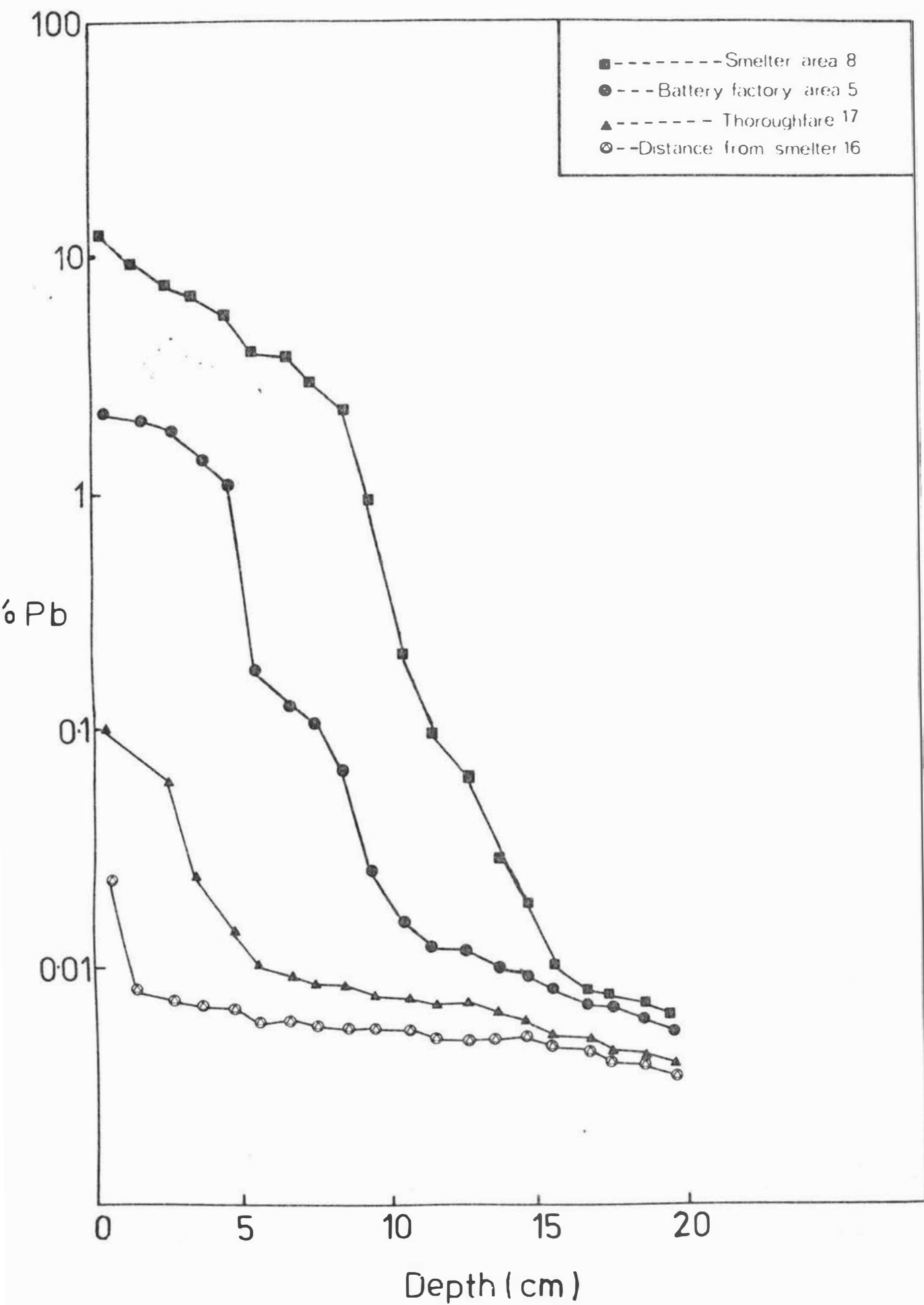
Table VII.2.

The Mean Lead Content of Unwashed Roots, Leaves and Stolons
(white clover) of Pasture Species at Various Sampling Areas
Around a Battery Factory, Smelter and Thoroughfare. Values at
Each Site are for Roots (R) and Leaves (L). Concentrations in
Parentheses Refer to Stolons.

| Sampling site | Mean lead content µg/g dry weight | | | | |
	Perennial ryegrass	White clover	Poa annua	Yorkshire fog	Flat-weeds
Battery factory and adjacent thoroughfare area					
1 R	595	465	350	361	307
L	1048	1078(713)	428	530	943
2 R	566	948	985	515	258
L	1088	1138(660)	1216	1840	678
3 R	1407	1041	1039	1144	786
L	.2329	2007(1115)	1162	1617	1418
Battery factory area					
4 R	586	980	864	680	775
L	1456	1864(1432)	1675	1345	1205
5 R	560	2156	2059	761	956
L	1784	2364(1543)	2923	1227	1058
6 R	1721	1635	572	561	1220
L	1948	2023(1512)	2509	2882	1995
7 R	1412	1528	1586	1309	1429
L	2484	2297(1223)	2427	2391	2514
Smelter area					
8 R	2830	2379	1659	2533	2881
L	4305	3012(2714)	2232	3896	4667
9 R	958	1487	1402	1121	1429
L	1747	2156(1952)	1617	1562	1528
10 R	1098	1246	1290	572	1125
L	1710	1763(1321)	1974	1896	1645
11 R	7322	2923	3904	3573	3526
L	8923	4295(2394)	6864	5143	8397

12	R	172	130	887	761	440
	L	642	372(205)	874	1189	846
13	R	258	246	157	206	208
	L	524	465(264)	223	372	425

Distances from the smelter

14	R	561	744	551	389	482
	L	706	808(743)	585	734	856
15	R	68	75	94	112	84
	L	186	211(139)	129	148	126
16	R	28	191	29	34	46
	L	149	195(145)	59	75	88

Thoroughfare transect

17	R	186	165	192	165	140
	L	345	405(260)	398	325	385
18	R	120	105	119	121	145
	L	248	265(210)	260	265	240
19	R	65	48	56	60	54
	L	205	185(65)	202	165	145
20	R	205	185	195	256	245
	L	465	470(345)	480	548	546
21	R	145	125	120	135	160
	L	260	280(205)	275	290	275
22	R	60	52	55	75	60
	L	195	145(80)	186	192	160

the overall efficiency of atmospheric deposition of lead compared with the alternative pathway via the soil.

Table VII.3. expresses the mean percentage of the original lead content (without species differentiation) which was removeable by washing.

The data show that an increase in the lead burden of the vegetation usually results in a concomitant increase in the proportion removable by washing. This is particularly noticeable at sites 8 and 11 (near the smelter). The proportion removable by washing is always higher for samples from the complex than in those obtained from near the thoroughfare. This may reflect the different physical and/or chemical forms of lead at the two types of location. It has been suggested by Ter Haar & Bayard (1971) that the lead particulates derived from motor vehicles initially exist as lead bromochloride followed by conversion into oxides, carbonates, oxycarbonates, sulphates and oxysulphates after fallout processes have occurred. More recently, Olson & Skogerboe (1975) have suggested that following dissolution processes, especially in soil systems, there is a high probability that the resulting lead compound is insoluble lead sulphate. Because lead sulphate is just as likely to be the end product of fallout from the smelter and is even more likely to be so at sites 8 and 11 where batteries are stored in the open, the question must arise as to why a greater percentage of the lead burden of vegetation is removable by washing, for sites of maximum accumulation of lead. There is clearly a limit to the degree of physical adsorption of lead particulates upon vegetation. The threshold of such 'supersaturation' can only be determined by pot trials on selected species, but it is significant that the values reported here for lead in leaf material, greatly exceed the highest values reported for vegetation near motorways (1044 µg/g at the Auckland Motorway - Section IV.), and ore treatment plants (2855 µg/g -see Ward et al, 1976). It is likely therefore that conditions of supersaturation exist in the vicinity of the battery factory and smelter.

Table VII.3.

Mean Percentage Lead Content Removeable by Washing
regard to species) at Various Sites Near a Battery
Factory, Smelter and a Thoroughfare

Sampling site	Mean % lead content removed by washing	
	roots	leaves
Battery factory and adjacent thoroughfare area		
1	26	33
2	25	38
3	27	42
Battery factory area		
4	32	56
5	30	58
6	37	58
7	27	50
Smelter area		
8	45	65
9	30	52
10	27	47
11	46	72
12	31	55
13	30	53
Distances from the smelter		
14	26	36
15	25	43
16	22	42
Thoroughfare transect		
17	20	32
18	18	30
19	18	30
20	24	36
21	20	32
22	20	28

The pattern of lead concentrations in soils and pasture species, reflects the dilution and fallout rates and provides information about the atmospheric mobility of lead (Lee, 1972). In Figure VII.2. it can be seen that high lead concentrations derived from the industrial complex are found at depths of up to 12cm, whereas near the thoroughfare (motor vehicle emission) the metal is confined mainly to the top 5cm. From Table VII.3. it will be noted that up to 45% of the 'industrial' lead could be removed from roots by washing, compared with only up to 24% at sites near the thoroughfare. This behaviour can be explained either by higher lead levels in the industrial complex area producing an initially higher surface burden which washes down to the root systems, or it can be explained on the basis of lead being in a different physical and/or chemical form which is more mobile in the soil. Since the slope of all the curves in Figure VII.2. is approximately the same, the mobility of lead in the soil profiles appears to be similar and the higher percentage of 'soluble' lead at the root system for plants at sites near the industrial complex is presumably a reflection of the initially higher deposition of lead at the surface of the soil, a deposition which is also reflected by higher levels at depth.

5. Conclusion

It is clear that there is a widespread distribution of airborne lead from motor vehicle emissions, the battery factory, and smelter within the study area. A further component is derived from weathered compounds of lead from the battery storage areas near sites 8 and 11. The significant contamination of soil and pasture species reflects the extensive lead deposition as airborne particulates, and the products of weathered batteries from all the above sources. It is also evident that pollution from the industrial plant is by far the greater source within the study area, compared with emissions from motor vehicles.

It is difficult to determine the area affected by lead contamination from this industrial complex because of other adjacent sources from motor vehicle emissions and other

industrial complexes. The pattern is further complicated by the influence of topography and building densities. These two factors mitigate against any consideration of the effect of prevailing wind direction and velocities.

Although this industrial complex will have a local effect considerably in excess of that from motor vehicle emissions, it cannot be of such overall concern, because exhaust depositions are so much more universal in their distribution.

SECTION VIII

LEAD UPTAKE BY SEEDLINGS OF LOLIUM perenne L. AND

TRIFOLIUM repens L.

1. Introduction.

Elevated lead concentrations in vegetation bordering road-sides was first detected in Canada by Warren & Delavault (1960). The lead was derived from motor vehicle emissions and this source of pollution has been investigated very extensively. The earlier work (e.g. Cannon and Bowles, 1962) on lead uptake by vegetation did not differentiate among different species, but later workers (Ter Haar, 1970; Ward et. al., 1975a; Goldsmith et. al., 1976) studied lead uptake by individual species and in all cases found that a sizeable proportion of the lead burden removable by washing, was presumably derived from airborne particulates as a result of combustion of tetraethyl - and tetramethyl lead from gasoline.

Accumulation of lead by pasture species and food crops is clearly a significant health hazard and in a recent survey of pasture plants growing along a motorway in Auckland City, New Zealand, Ward et. al. (1977b) - Section IV., found a mean value of 638 µg/g lead (dry weight basis) in unwashed leaves of Trifolium repens L., (white clover) and 345 µg/g in Lolium perenne L. (perennial ryegrass). In the case of the clover, washing reduced the lead concentration to 365 µg/g, and reduced the value in ryegrass to 306 µg/g.

Although it has been widely assumed by many workers that lead accumulation from motor vehicle exhausts is largely by air-borne particulates, there is ample evidence for accumulation of lead in surface soils (Chow, 1970; Page and Ganje, 1970; Singer and Hanson, 1969; Ward et. al., 1975a), and there remains the question as to what extent uptake by root systems from the soil is responsible for the high concentration of lead in roadside vegetation. In order to investigate this problem, the following pot trials were carried out to determine the uptake of lead by seedlings of L. perenne and T. repens and the results of these investigations are presented in this section.

2. Literature review.

Studies centred on lead uptake from soil sources have been numerous but inconclusive. Martin & Hammond (1966) studied lead uptake by bromegrass (Bromus inermis, Leyss.) from sandy loam soils with a range of lead content between 12 and 680 $\mu g/g$. Results indicated that only plants grown in the soil with the 680 $\mu g/g$ level accumulated a significant amount of lead. This accumulation was enhanced by the addition of a chelate, but the maximum accumulation was only 34 $\mu g/g$.

Previous to this study significant contributions were made by Ishizuka & Tanaka (1962) and Rasmussen & Henry (1963). The former authors showed that 50 $\mu g/g$ lead added to culture solutions supporting rice plants, did no harm as the lead was precipitated as $PbSO_4$. When no SO_4^{2-} was present, 10 $\mu g/g$ lead was the critical level before yield and chemical composition of the plant was affected. Rasmussen & Henry (1963) reported the effects of lead on the growth of sweet orange seedlings in nutrient solution cultures. Levels of 0-31.25 $\mu g/g$ lead at pH 4.5-6.5 in the nutrient solution were investigated. Root growth was stimulated by intermediate levels of lead and inhibited by the highest level at pH 4.5-5.5; root and shoot growth were inhibited by all but the lowest lead levels at pH 6.5.

Ter Haar et. al.(1969) studied the uptake from air, water and soil of lead by perennial ryegrass and radishes. They concluded that uptake of lead from water applied to the leaves and from the soil was not significant. Half of the lead content of the grass was obtained from the soil with little absorption from simulated rainfall.

Motto et. al. (1970) grew several crop species in contaminated soil and in acid-washed sand to which soluble lead was added in low concentrations. Their results established that lead can be absorbed through the root system and that some translocation to other plant parts does occur. However, most lead taken up by plants remains in the root system.

In an experiment designed to assess the relative importance of air, water, and soil as sources of lead for ryegrass (Lolium

perenne L.) and radish (Raphanus sativus L.), Dedolph et. al.
(1970) showed that only air and soil were significant sources
and that both grass and radish leaves derived 2 to 3 µg/g of
lead from soil sources.

Typical results of adding lead to soil are summarized by
the work of Baumhardt & Welch (1972). Lead was added to soil
in field plots in amounts varying from about 20 to 1000 µg/g.
Then corn, (Zea mays L.) was grown for 2 years. Significant
concentrations of lead were found in the corn kernel. The
results indicate that the length of time following the addition
of lead has an influence on its biological availability. Thus,
in the second year, lead content of the plant was significantly
less than in the first year. Similar solution culture and soil
pot trials to determine the absorption of lead by plant roots
have been reported by Miller & Koeppe (1970), Broyer et. al.
(1972); Zuber & Bovay (1972) and Bazzaz et. al. (1974).

In controlled - environment experiments, Jones & Clement
(1972) grew perennial ryegrass plants in 16 soils with contents
of extractable lead in the range 5.3-59 µg/g. Lead contents in
whole plants increased with increasing levels of soil lead,
mainly as a result of accumulation in the roots. In solution-
culture experiments it was shown that lead was readily taken up
by perennial ryegrass roots, but that only a small proportion
was passed to the shoots.

Finally, Rolfe (1973) reported on the lead uptake by
selected tree seedlings and concluded that uptake was significan-
tly affected by the soil lead concentration with higher uptakes
associated with higher soil lead levels. Lead uptake by plants
was reduced by approximately half when high levels of soil
phosphorus were present.

Although considerable research has been done on contamin-
ation of vegetation by lead, the overall picture is incomplete,
especially concerning the extent to which uptake of lead by root
systems of L. perenne and T. repens is responsible for the high
concentration of lead in leaves and stolons. In such controlled-
environment experiments a more significant interpretation of the

mechanism by which lead is distributed throughout these particular pasture species can be obtained to enable comparison with the observations made from pollution studies of the natural environment. (Section IV to VII).

3. Materials and methods.

Seedlings were grown in 250 ml plastic pots containing a chemically-inert silica sand. This substrate was chosen because previous tests showed only a 5% absorption of a 1% solution of lead nitrate, in contrast to local soils and pumice which absorbed 80%. Lead nitrate was mixed thoroughly with the sand to provide a large number of pots containing various concentrations (0-10,000 μg/g) of lead in the substrate (all in triplicate). Seeds (20 in each pot) of Trifolium repens L. or Lolium perenne L. were placed in selected pots at a depth of 1cm below the surface of the substrate. Each pot was saturated with a modified Hoagland solution in which the sulphate and phosphate concentrations were reduced to avoid precipitating lead. All pots were placed in separate dishes, and were watered from below during the experiments. Experiments were carried out in a glasshouse with random placement of pots and constant rearrangement of them to avoid variations due to exposure to sunlight. The experiments were allowed to run for up to 14 weeks.

At predetermined periods, plants were harvested and divided into, roots, stolons (for white clover only), and leaves. Leaves and stolons were not washed, but roots were washed for 30 minutes in deionized water and rinsed three times.

Plant material were prepared and analysed as outlined in Section IB.

4. Results and discussion.

(a) Uptake of lead as a function of the lead content of the substrate.

Figures VIII.1 and 2 show the lead content of perennial ryegrass (Figure VIII.1) and white clover (Figure VIII.2) expressed as a function of lead concentrations in the substrate

Figure VIII.1.

The lead content (µg/g dry weight) of leaves and roots of perennial ryegrass (<u>Lolium</u> <u>perenne</u> L.) expressed as a function of the lead content of the substrate (µg/g) for various periods of growth: 6 weeks (symbol◐), 8 weeks (symbol■), 12 weeks (symbol◆), and 14 weeks (symbol▲).

P. RYEGRASS, Leaves

P. RYEGRASS, Roots

●—● 6 weeks
■—■ 8 weeks
◆—◆ 12 weeks
▲—▲ 14 weeks

LEAD IN PLANT (µg/g dry wt.)

LEAD IN SUBSTRATE (µg/g)

Fig
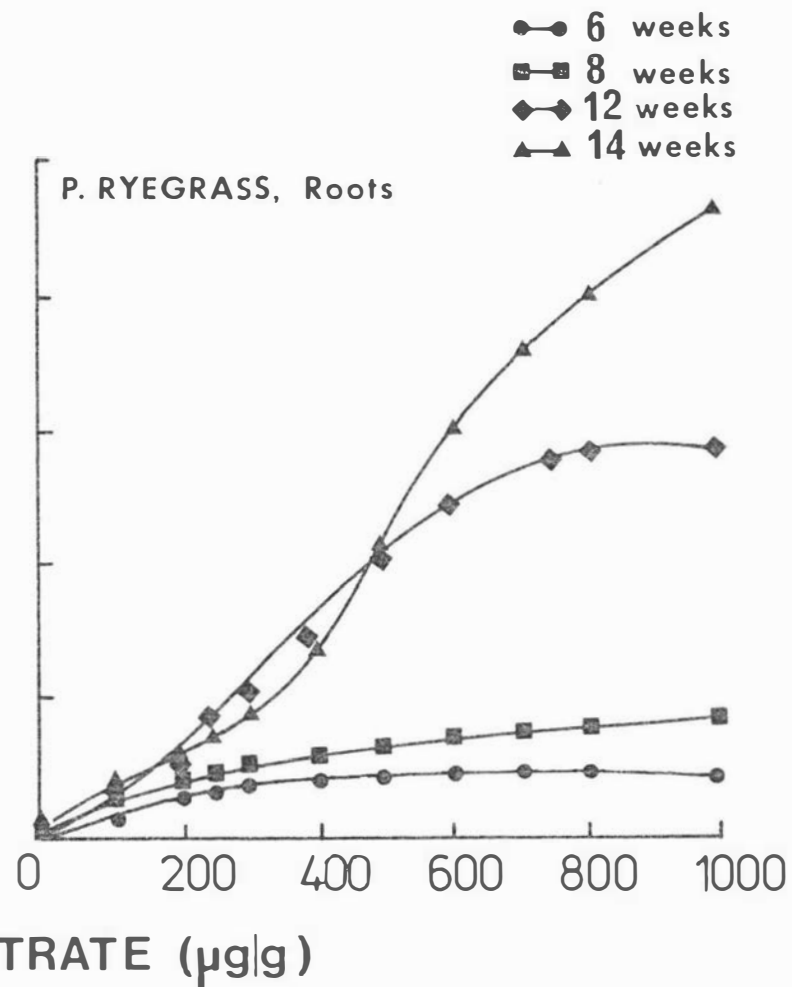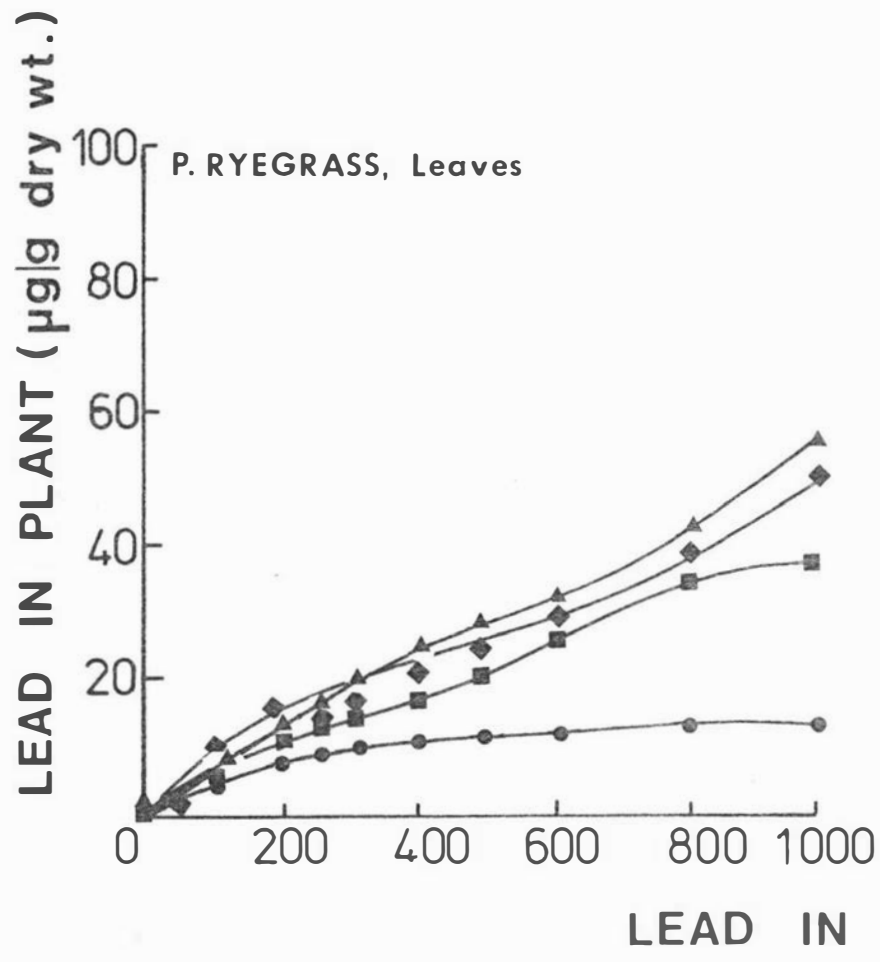
Figure VIII.2.

The lead content (μg/g dry weight) of leaves, roots and
stolons of white clover (Trifolium repens L) expressed
as a function of the lead content of the substrate
(μg/g) for various periods of growth: 6 weeks (symbol ⬣),
8 weeks (symbol ▨), 12 weeks (symbol ◀), and 14 weeks
(symbol ▲).

WHITE CLOVER, leaves

● 6 weeks
■ 8 weeks
◆ 12 weeks
▲ 14 weeks

WHITE CLOVER, stolons

WHITE CLOVER, roots
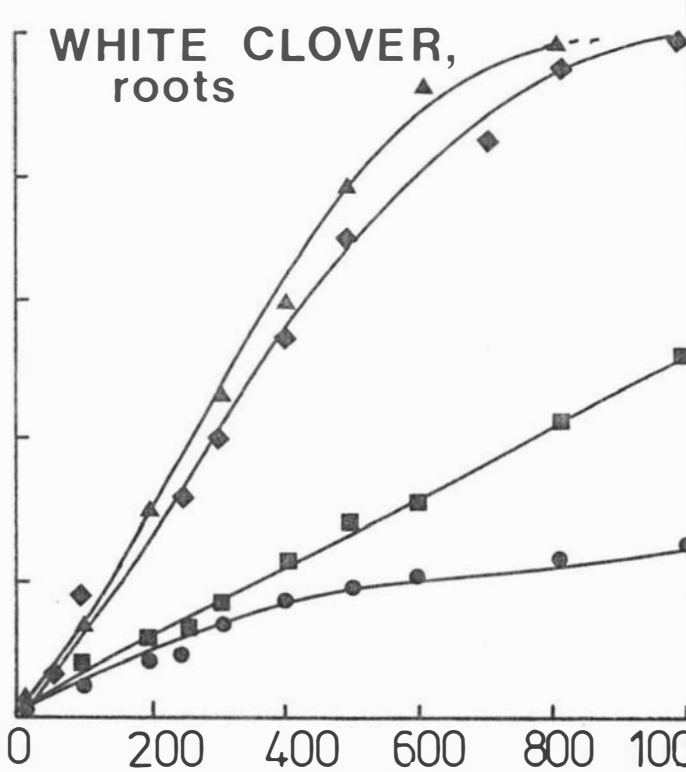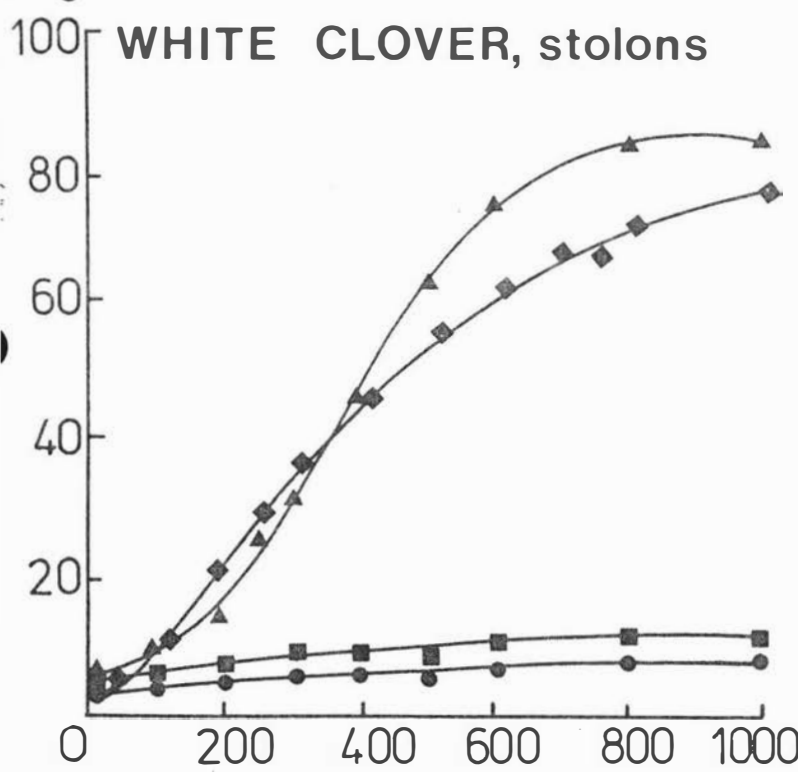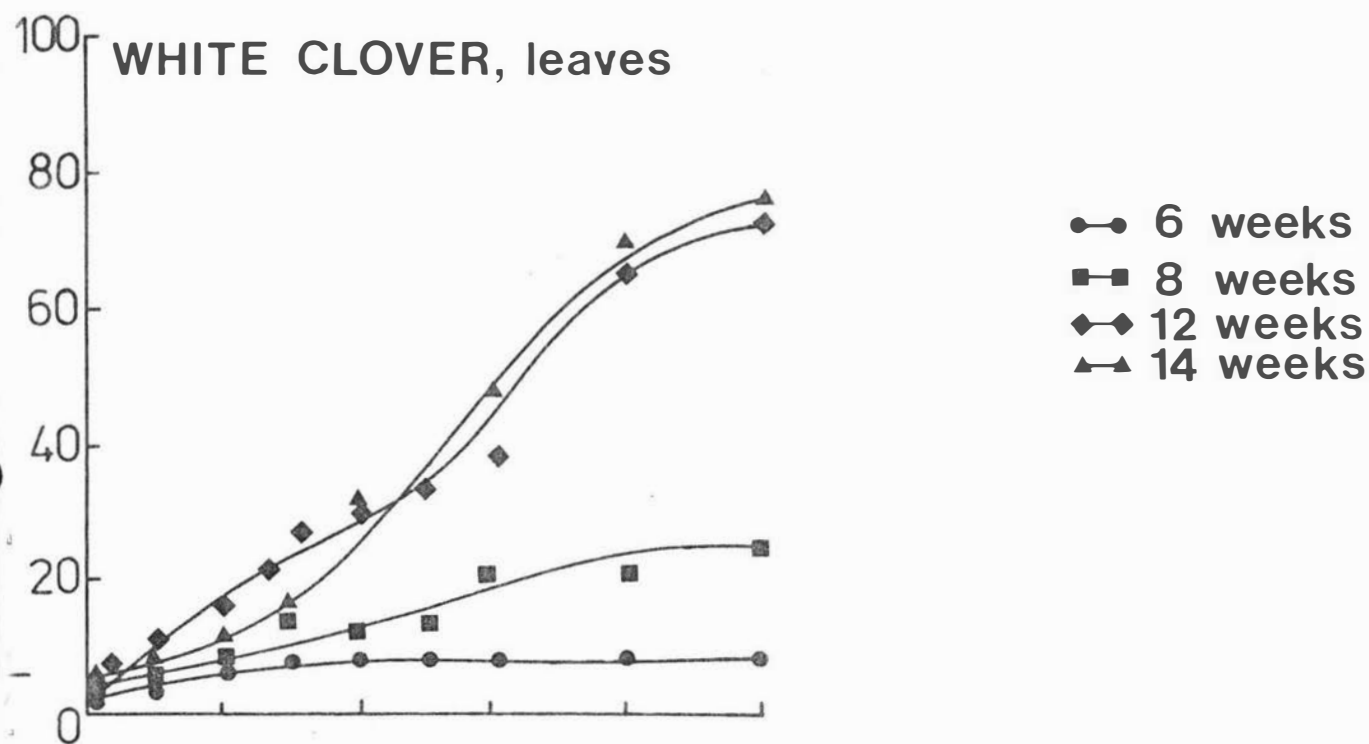
LEAD IN SUBSTRATE (µg|g)

and at periods of 6, 8, 12 and 14 weeks after germination of
the seeds.

Leaves and roots of clover ultimately accumulated more
lead than the corresponding organs of ryegrass. The roots of
both species contained somewhat more lead than the corresponding
leaves (or stolons). For white clover, an approximate limiting
value for uptake seemed to be reached after 12-14 weeks for lead
concentrations exceeding 800 µg/g. This limiting value was also
in evidence for ryegrass. It is also evident that there was
some delay in maximum lead uptake by both species. After 8 weeks,
comparatively little lead had been accumulated by leaves and
stolons of white clover but there was a considerable increase
during the interval 8-12 weeks. A reason for this increase may
be a breakdown in the mechanism whereby plants are able to
precipitate lead at root systems (as phosphate or sulphate) as
has been known for nearly 50 years (Hammett, 1928). The same
pattern of enhanced uptake is shown in clover roots. In the
case of ryegrass, uptake of lead by leaves and accumulation at
roots, increased considerably after 6 weeks and reflected a
similar uptake pattern as for clover.

For plants growing in substrates containing 5000 and 10,000
µg/g (0.5% and 1.0%) lead, values in all organs of both species
were the same (or even a little lower) as for the 1000 µg/g
substrates and indicated that a limiting value for lead in plant
organs does in fact exist. The data are not shown in Figures
VIII 1 and 2 because of problems of scale.

In general, concentrations of lead in plant material were
only about one tenth of those in the substrate but represent
nevertheless an appreciable uptake in absolute terms. As out-
lined in Section IV it was found that 345 µg/g lead was measured
in unwashed leaves of ryegrass and 638 µg/g in clover leaves.
These plants were growing adjacent to a busy motorway where the
soil contained 3064 µg/g lead. If the results of these pot
trials are applied to the real situation, and if 80 µg/g and
60 µg/g are approximately limiting values for lead in leaves of
clover and ryegrass respectively for plants accumulating this

element via root systems only, then clearly most of the lead
burden of roadside plants must be derived from airborne partic-
ulates. These particulates must account for about 85% of the
lead burden of white clover and about 80% of that of ryegrass.

(b) Morphological effects of lead.

The effect on plant height of various lead concentrations
in the substrate is shown in Figure VIII.3 and illustrated in
Plate. VIII.1 (4 months after germination).

After 35 days, the mean height of ryegrass seedlings was
nearly 8cm for substrates free of lead but was less than half
this height for a substrate containing 560 µg/g lead. At the
1000 µg/g lead level, plant height was less than a quarter of
that of normal plants. In the case of white clover, a very
similar pattern was obvious, though overall plant heights were
always less than for ryegrass in all substrates.

It is clear from the above experiments, that high lead
levels in the substrates have a marked stunting effect on both
white clover and ryegrass and when these results are applied to
the real situation, it is obvious that high lead levels in soils
near major highways must have a serious effect on the growth of
economically important pasture species. In such situations,
retarded growth will be also aggravated by the very large air-
borne component of the lead burden of roadside pastures.

(c) The effect of lead upon germination of seeds.

Figure VIII.4 shows the effect on seed germination of
different lead concentrations in the substrate. Each pot
contained 20 seeds of either species and germination was 100%
complete after 35 days in cases where a lead-free substrate was
used. Percentage germination decreased in a linear manner for
increasing contents of lead in the substrate. For substrates
containing 1000 µg/g lead (levels commonly found in soils near
busy thoroughfares), germinations were reduced to 20% for rye-
grass and 10% for white clover.

Plate VIII.1.

The effect on plant height of perennial ryegrass
(<u>Lolium</u> <u>perenne</u> L) and white clover (<u>Trifolium</u> <u>repens</u> L)
as a function of various lead concentrations in the
substrate four months after germination.

P RYEGRASS

μg / g Pb   0   10   50   100   500   1000

(4 months after
germination)
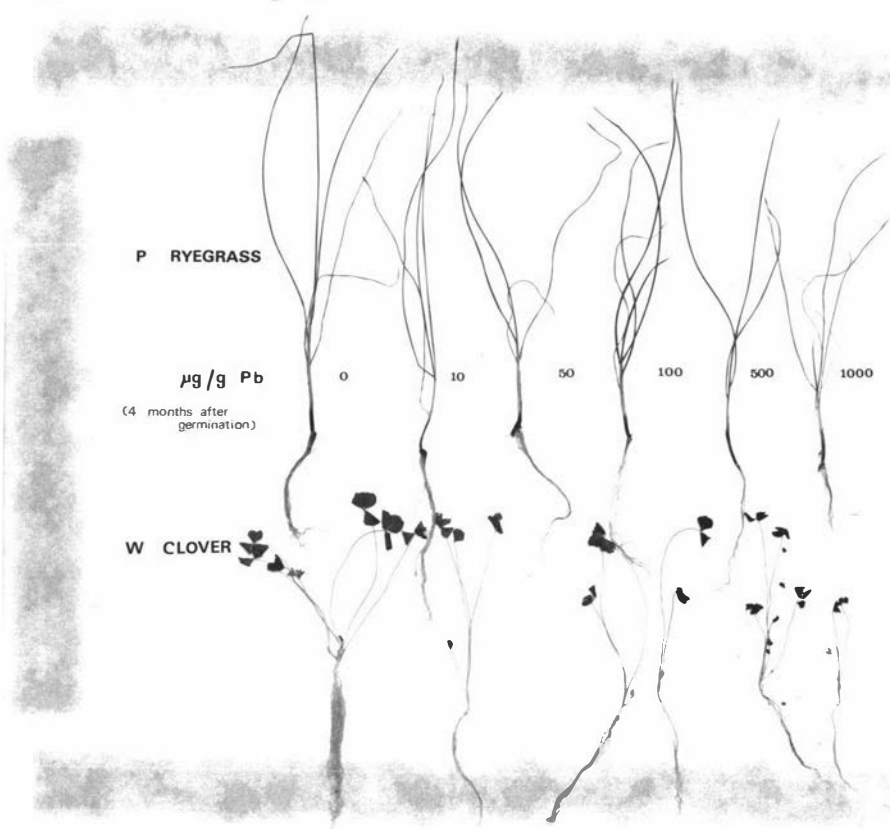
W CLOVER

Figure VIII.3.

The effect on height (cm) of perennial ryegrass (<u>Lolium</u> <u>perenne</u> L) and white clover (<u>Trifolium</u> <u>repens</u> L) of varying concentrations of lead in the substrate: 0μg/g (symbol ●), 100μg/g (symbol ▲), 500μg/g (symbol ○) and 1000μg/g (symbol ▩).

Lead Concentration of Substrate: ●—● 0 — µg|g
▲—▲ 100
○—○ 500
■—■ 1000

P. RYEGRASS

WHITE CLOVER

MEAN HEIGHT (cm)

NUMBER of DAYS AFTER GERMINATION
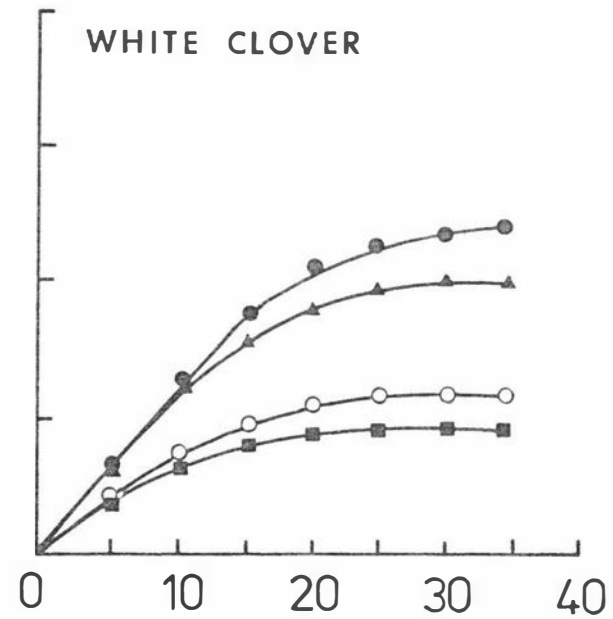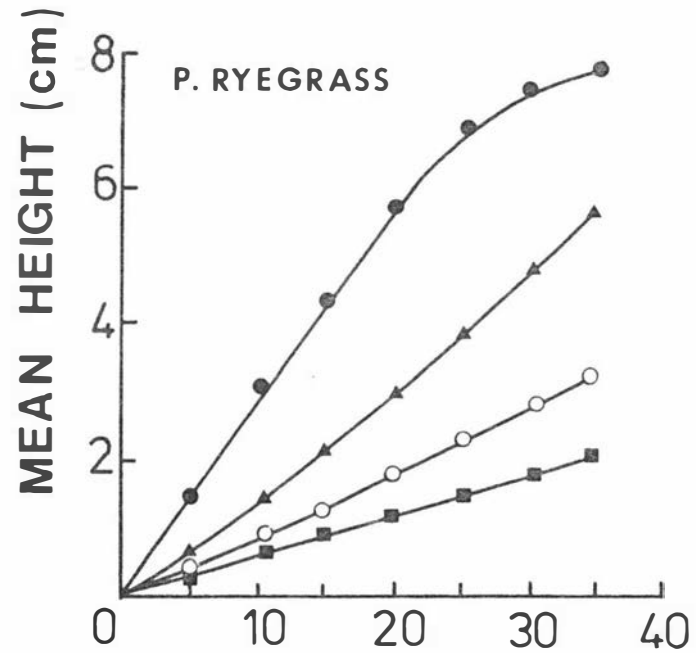
Figure VIII.4.

The effect on germination of seeds of perennial ryegrass
(Lolium perenne L) and white clover (Trifolium repens L)
of various concentrations of lead in the substrate:
$0\mu g/g$ (symbol ●), $100\mu g/g$ (symbol ▲), $500\mu g/g$ (symbol ○)
and $1000\mu g/g$ (symbol ▣).
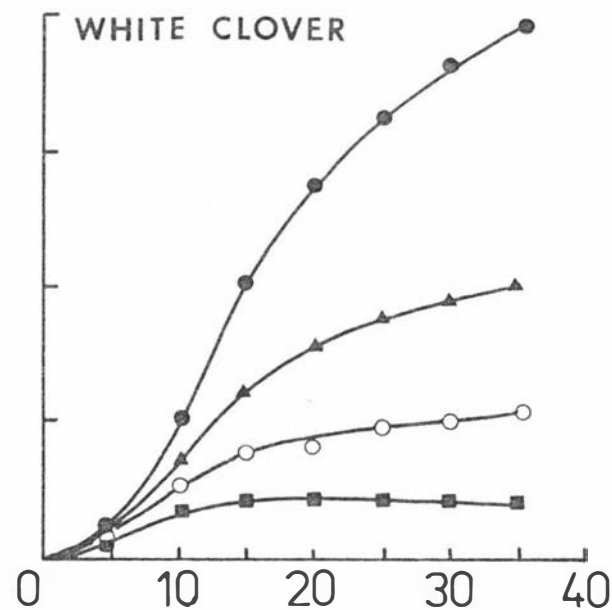
5. Conclusion.

The experiments have highlighted the serious effect on pasture species, of elevated lead levels in the substrate. If the data are applied to the real situation of pasture species growing adjacent to major thoroughfares, the following conclusions can be made:

(i) Lead accumulation by aerial parts of clover and ryegrass can total about 10% of the lead content of the soil and is somewhat greater for white clover than for ryegrass. This accumulation is however very small compared with the lead burden from airborne particulates, and by itself probably does not present a serious hazard for grazing animals;

(ii) elevated lead concentrations in soils affect the plant height of both species to an equal degree. Concentrations of lead exceeding 500 $\mu g/g$ in the substrate (values typical of most roadsides of major thoroughfares) are sufficient to reduce plant heights by one half. The actual situation must be considerably worse than this because of the much higher lead burden derived from airborne particulates;

(iii) the germination of seed of perennial ryegrass is less affected by high lead levels in the substrate than is germination of white clover. This indicates the necessity for altering the balance of seed mixtures in favour of white clover where a balanced ryegrass/white clover pasture is desired in a contaminated site adjacent to busy highways.

SECTION IX.

SILVER IN SOILS, STREAM SEDIMENTS, WATERS AND VEGETATION NEAR
A SILVER MINE AND TREATMENT PLANT AT MARATOTO, NEW ZEALAND.

1. Introduction.

Environmental contamination from various heavy metals such as cadmium, copper, lead and zinc has been often reported from the vicinity of smelting complexes and mines. (Little & Martin, 1972; Ward et. al., 1976). However, very few studies have been carried out on silver pollution from industrial and mining activities. Although Klein & Russell (1973), as part of a wider project involving several heavy metals, measured silver concentrations in soils around a coal- burning plant, soil levels of this element increased only very slightly (0.24 to 0.272 $\mu g/g$), and scarcely represented significant pollution.

The background silver concentration in igneous and sedimentary rocks is about 0.3 $\mu g/g$ (Hawkes and Webb, 1972). Several workers (Warren and Delavault, 1950; Hornbrook, 1971; Quin et. al., 1973) have reported silver levels in soils and vegetation in connection with biogeochemical exploration studies.

Because of the known toxicity of silver towards animal and plant life (Sax, 1975) and because of the virtual absence of studies on pollution from this element in the vicinity of industrial establishments and mines, a study was made of the total aerial silver burden in soils and vegetation derived from a mine and treatment plant at Maratoto, New Zealand. It was also hoped to compare the data with silver accumulated naturally by plants growing in the vicinity of an ore deposit in the Silver Queen Reef; the main source of ores for the treatment plant.

Silver concentrations were also measured in sediments and water samples in a stream originating from the vicinity of the ore body, and in pasture species and soil from a paddock adjacent to the access road to the ore treatment plant.

2. Study area and methods.

The Maratoto Valley is situated some 15km east of Paeroa, in the Coromandel Region, New Zealand. The rocks of the area are largely Tertiary calc-alkaline volcanics that range in composition from andesite to rhyolite (Weissberg and Wodzicki, 1970).

The Silver Queen Reef consists mainly of cavernous quartzose replacements after calcite, with minor ribs of massive quartz, the whole being stained rusty brown and black with iron and manganese oxides. Certain lenses of the veinstones carry argentite (Ag_2S) and hessite (Ag_2Te) with a small quantity of gold (Bell and Fraser, 1912; Main, 1972).

The vegetation cover over the Silver Queen Reef appears to be principally secondary growth. The main canopy species of the Maratoto Valley is Beilschmiedia tawa (Benth & Hook, f.) 'tawa.'

The climate of the area is mild, equable and humid. Annual rainfall averages about 2000mm.

In a treatment plant situated in the lower Maratoto Valley, the ore is crushed and converted to a concentrate by a floatation process. Figure IX.1 represents the sampling area : the Silver Queen Reef transect (sites 14-22), treatment plant area (sites 1-13, 23-4) and the pasture transect across a paddock adjacent to the treatment plant access road (sites 28-39). Some other samples were taken from background areas.

Leaves, twigs and tree ring-cores were collected from Beilschmiedia tawa trees located across the Silver Queen Reef at sites 14-17, and at sites adjacent to the treatment plant (1-13). Similarly, pasture samples were collected at sites 14-23, and along the paddock transect at sites 28-39.

Sample preparation and analysis of silver was carried out as outlined in Section I.B. In particular the determination of silver using a carbon rod atomizer for water and tree ring-core samples is covered in Section I.C. Bratzel et. al. (1972) and Rattonetti (1974) have also reported on determining silver levels in biological samples using the carbon rod atomizer.

3. Results and discussion.

(a) Silver in soils

The silver content of surface soils (μg/g dry weight) collected at sites from the Silver Queen Reef, treatment plant and background areas is shown in Table IX.1.

Figure   IX.1.

Map   showing   study   area   and   sampling   sites: S.Q.R.,   Silver
Queen   Reef;   T.P.,   treatment   plant;   and   P.T.,   pasture   transect
(inset)   associated   with   the   silver   mining   operations,
Maratoto.

CAMOOLA REEF

CAMOOLA CREEK

MARATOTO VALLEY

SILVER QUEEN REEF

MAIN CREEK BED

17 16

15 S.Q.R.

18 14

19 20

21

22

SILVER QUEEN BED

13

12

11

10

5 4 3 2 1

6

7

24 8 9

23

T.P

P.T. 28-33

34-39

MARATOTO STREAM

MARATOTO ROAD

N

WHAKAMOEHAU CREEK

MARATOTO STREAM

McBRINN CREEK

25

0   .25   .5
Km
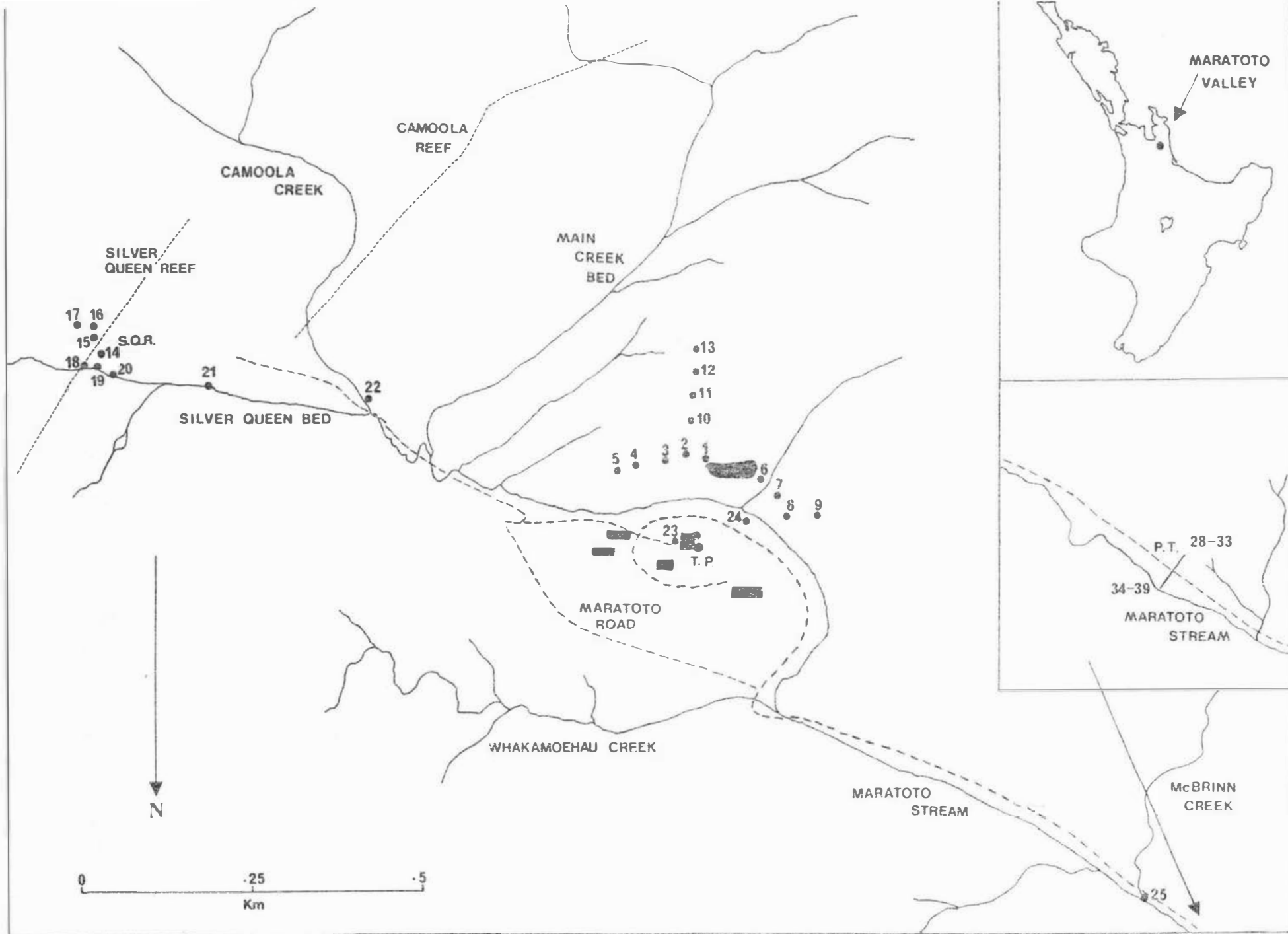
Table IX.1.

Silver Concentrations (mean of five determinations at each site) of Surface Soils, Washed/Unwashed leaves, and Washed Twigs of Beilschmiedia tawa Sampled from the Maratoto Valley.

| Sampling sites[*] | Silver Concentrations μg/g dry weight | | | |
	Soil	Washed leaves	Unwashed leaves	Washed twigs
Treatment plant				
1	3.30	1.70	2.40	1.30
2	2.25	0.77	1.90	1.44
3	2.00	1.09	1.74	1.73
4	1.50	1.05	1.80	1.33
5	1.00	0.92	1.85	1.63
6	1.00	1.38	2.00	2.37
7	1.75	1.77	2.08	1.83
8	1.00	1.64	2.24	1.56
9	0.75	1.72	2.05	1.52
10	2.25	1.48	1.70	1.17
11	2.00	1.04	1.26	0.99
12	1.75	1.22	1.35	1.09
13	1.50	1.01	1.31	0.99
Silver Queen Reef				
14	6.00	1.42	1.68	1.35
15	4.50	1.17	1.31	1.24
16	2.75	0.92	0.96	0.90
17	1.25	0.51	0.66	0.55
Background				
Bdg 1	0.25	0.23	0.25	0.20
2	0.16	0.20	0.22	0.20

* Sampling sites as shown in Figure IX.1.

The highest silver level occurred on the Silver Queen Reef at site 14. In this area the silver content of the soil was more than 10-fold higher than in background areas.

The silver concentrations in soils from the treatment plant area were significantly higher than background values, and as these soils are derived from non-mineralised country rock, the elevated silver concentrations must have been due to deposition of airborne material from the treatment plant.

The silver content of soils decreased with distances from the treatment plant along sampling sites 1-5 and 6-9 (at the same height above the treatment plant) and along 10-13 (which also corresponded to an increase in elevation).

The distribution of silver in surface soils sampled along a transect across a paddock adjacent to the access road to the treatment plant is shown in Figure IX.2. The silver content of these soils shows a considerable accumulation especially within 4 meters from the roadside, as a result of deposition from wind-borne dust from passing ore-trucks. Elevated levels at sites 38 and 39 were probably due to contamination from mineralized sediment derived from the Maratoto stream, which is located within 10 meters of these sites. Similar elevated levels occurred at sites 32 and 33 and were probably derived from a small creek running through the paddock.

The highest silver concentrations in soils from the paddock appear to be associated with sediment/water deposition rather than airborne contamination from vehicles using the road (although the latter is still a significant source of contamination).

Figure IX.2. also shows silver levels (μg/g dry weight) in soils, expressed as a function of depths for each sampling site. Although there is an accumulation of silver to a depth of 1cm, considerable levels of silver are measurable at lower depths. Samples taken at depths of 5 and 10 cm for sites 28, 34 and 39 had mean silver levels of 0.45 μg/g and 0.30 μg/g respectively which are still higher than for background values of about 0.20 μg/g. Therefore, unlike lead (Ward et. al., 1975a), which approaches background values at depths of only a few cm in areas subjected to airborne contamination, silver has some degree of mobility in

Figure   IX.2.

Silver   concentrations   (µg/g   dry   weight)   in   surface   soils
(upper   part   of   figure)   along   a   pasture   transect,   in
the   Maratoto   Valley.   Concentrations   in   soils   are   shown
as   a   function   of   depth   (cm)   in   the   lower   part   of   this
figure.

μg/g
SILVER

DISTANCE FROM ROAD (m)

SAMPLING SITE

28 ●——●
29 ■——■
30 △---△
31 ○——○
32 □——□
33 ●·····●

SAMPLING SITE

34 ●——●
35 ■——■
36 △---△
37 ○——○
38 □——□
39 ●·····●

DEPTH (cm)
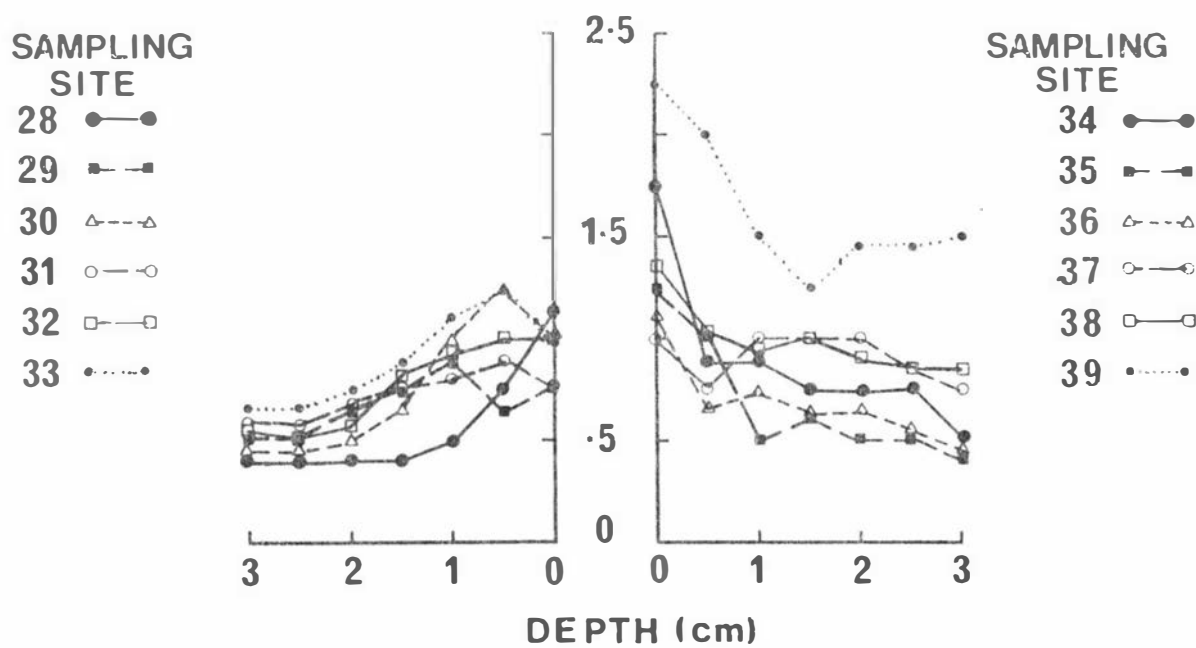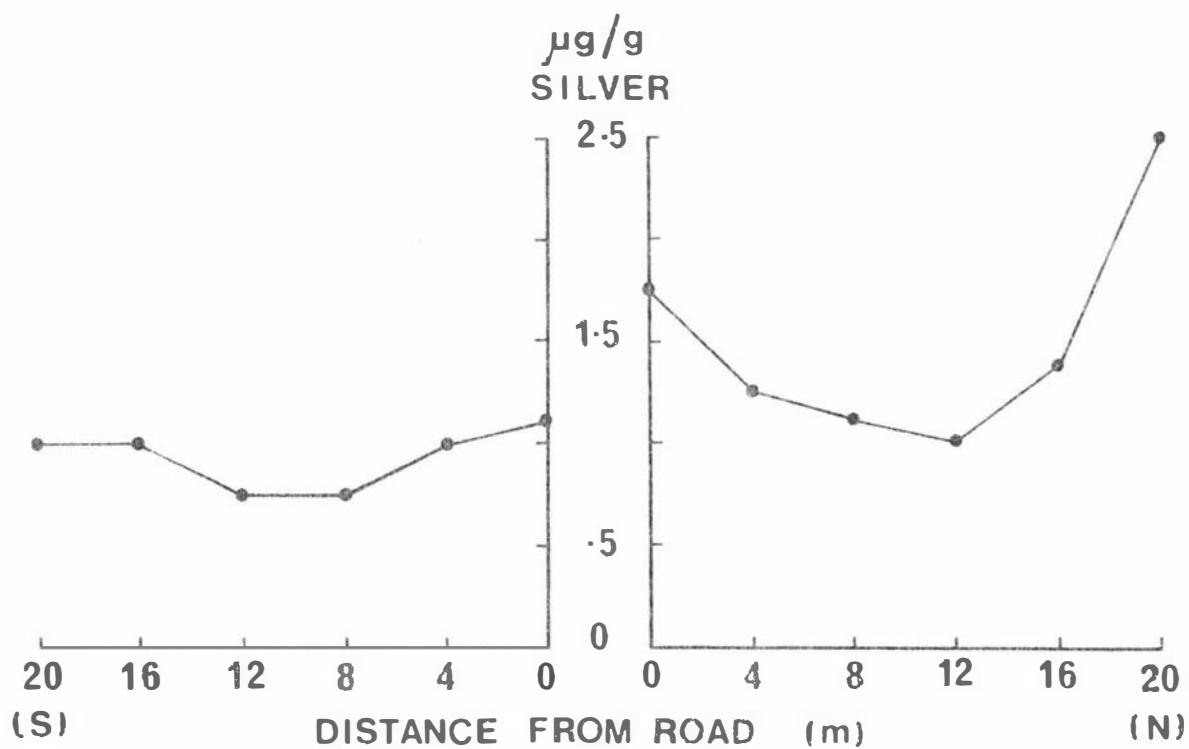
the soil.

(b) Silver in vegetation.

The silver levels (expressed as μg/g dry weight) in
Beilschmiedia tawa leaves (washed and unwashed)and washed twigs
are also shown in Table IX.1.

Accumulation of silver shows a pattern similar to that of
the corresponding soils although levels measured from the Silver
queen Reef are not as high for plant material in comparison with
those values for the treatment plant area. Near the treatment
plant (sites 1-9), a mean value of 36.4% of the silver content
of the leaves was removed by washing, compared with 15.8% at
distances further away from the plant (sites 10-13). Other values
were 12.7% on the Silver Queen Reef, and 8.5% in background areas.

The low proportions of silver removable by washing, reflect
the degree of airborne contamination of each area and suggest that
silver is more firmly bound into the leaf structure than elements
like copper or lead (Little and Martin, 1974; Ward et al., 1975a).

The influence of wind-direction (predominantly N-W) is shown
in the elevated values at sites 3 and 4 compared with the pattern
for soils. The samples from the Silver Queen Reef, which involve
accumulation predominantly via the root systems, show a predictably
low silver component removable by washing with water.

The mean plant/soil ratios of silver for each area are:
treatment plant, 1.29; Silver Queen Reef, 0.36; background, 1.18.
This shows the extensive effect of fallout around the treatment
plant and suggests that even background samples contain an
appreciable component of aerial fallout.

The degree of silver contamination as a result of airborne
particulates emitted from the treatment plant area was measured
using Pinus radiata samples from site 24. The mean silver content
(μg/g dry weight for 10 samples) was: bark, 1.16 with 15.6%
removabl by washing; sporophylls, 0.26 and 38.6%; needles 3.87
and 20.2%. Since the source of silver contamination of these
specimens of P. radiata was presumably aerial, it is suggested
that large particulates accumulate near the fascicle sheath at

needle bases and on bark surfaces, and are subsequently washed
downwards by rainfall. The high silver content of P radiata
needles is directly related to the efficient surface provided for
accumulation due to their high surface-to-volume ratio. Similar
findings have been noted for lead levels on Pinus strobus needles
near major highways. (Smith, 1971).

The mean silver content of pasture samples ($\mu g/g$ dry weight)
taken from the vicinity of the treatment plant (site 23), Silver
Queen Reef (site 14) and background areas is shown in Table IX.2.

The distribution of silver in the roots and leaves of pasture
species appears to be directly influenced by the area in which
they were sampled. The silver concentration in leaves is always
higher than for roots near the treatment plant and reflects the
influence of airborne silver deposition. Silver levels are
always higher in the roots than leaves near the Silver Queen Reef,
where it is suggested that the mechanism of uptake is via the root
systems.

The accumulation of silver in the pasture species (0.07 $\mu g/g$
in roots and 0.09 $\mu g/g$ in leaves) is significantly higher than in
background areas.

The variation in silver content in pasture species sampled
at various distances along a transect across the access road to
the treatment plant is shown in Figure IX.3.

The species sampled were:

Lolium perenne L. (perennial ryegrass), Trifolium repens L.
(white clover), Agrostis tenuis Sibth (browntop), Holcus lanatus L.
(yorkshire fog), Poa annua L., and flatweeds of the genera,
Plantago, Bellis and Crepis.

The pattern of silver contamination in all six species is
similar to that for soils. The highest silver concentrations
appear to be associated with sediment/water deposition from the
Maratoto stream (site 39) and from a creek (sites 32 and 33). It
is suggested that although there is a significant source of air-
borne silver from vehicles using the adjacent road, pasture
species appear to have a predominant fraction of the silver in the
root section of the plant which may be due to washing of silver

Figure IX.3.

Silver concentrations (μg/g dry weight) in some pasture species sampled along a transect in the Maratoto Valley. Symbols: $\triangle$ washed roots, ⊛ washed leaves, ☐ washed stolons (white clover only).

RYEGRASS
µg/g
SILVER

YORKSHIRE FOG
µg/g
SILVER

WHITE CLOVER

POA ANNUA

BROWNTOP

FLATWEEDS

20   16   12   8   4   0   20   16   12   8   4   0
(S)   DISTANCE (m)   (N)   (S)   DISTANCE (m)   (N)
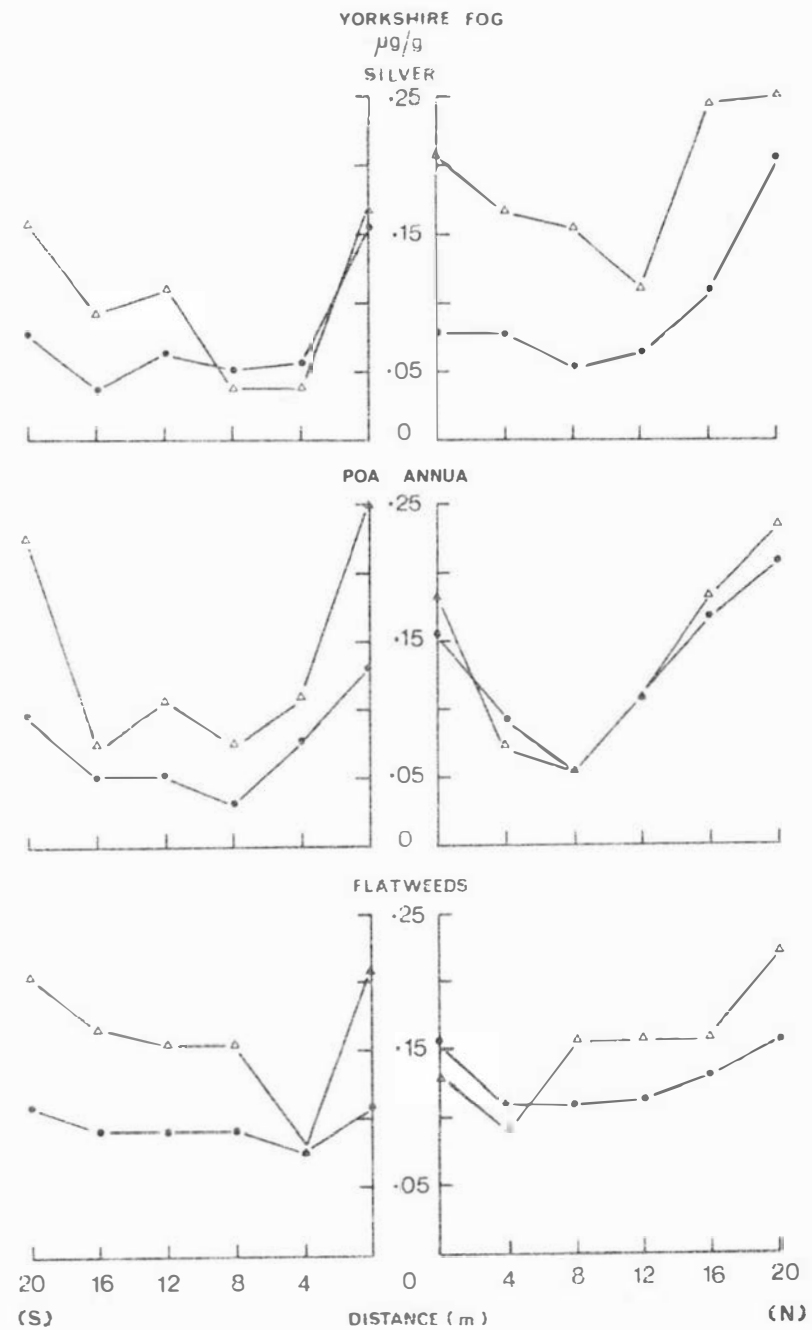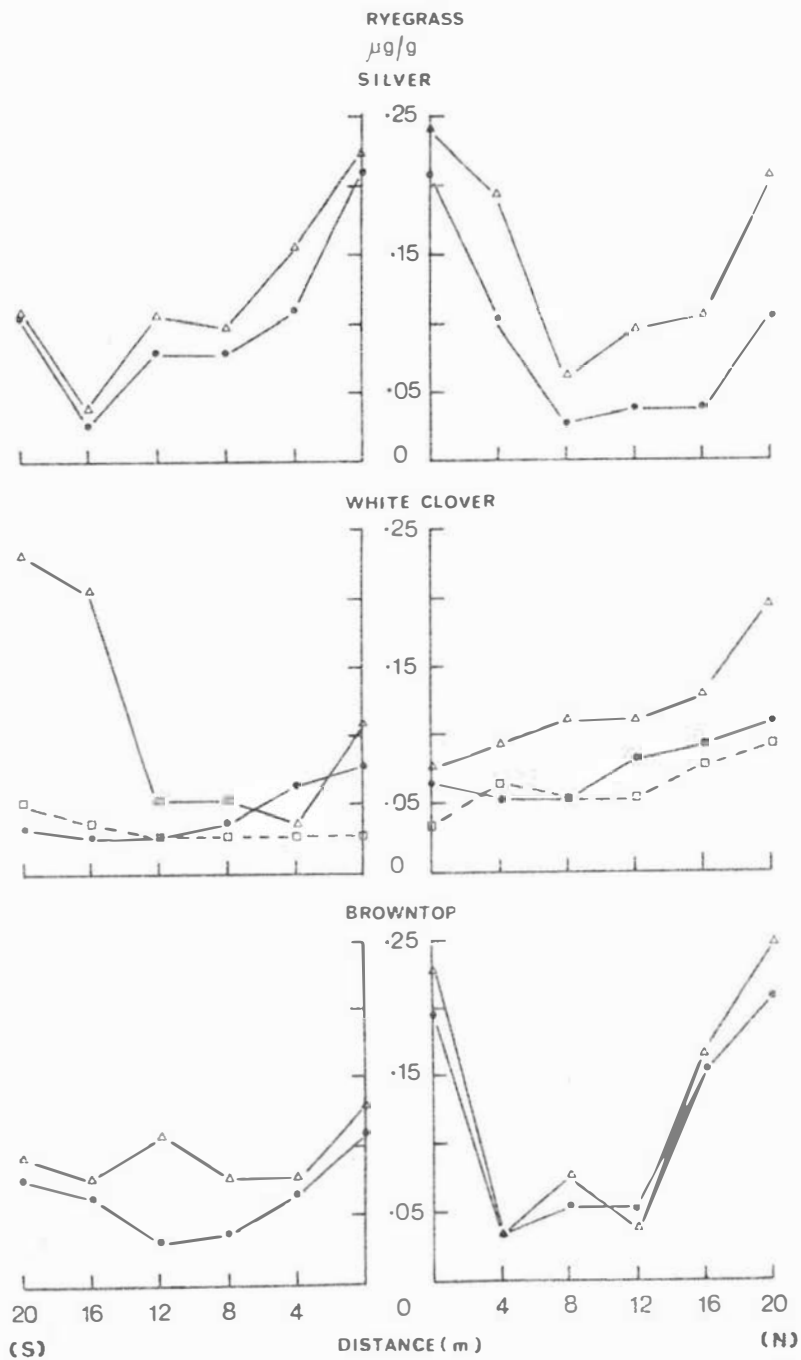
Table IX.2.

Silver Concentrations (mean of five determinations at each site) of Washed Pasture Species (roots and leaves) Sampled From the Maratoto Valley.

| Pasture species | Silver concentrations µg/g dry weight | | | | | |
| | Treatment plant | | Silver Queen Reef | | Background | |
	roots	leaves	roots	leaves	roots	leaves
Lolium perenne L. (Perennial ryegrass)	1.35	1.95	1.26	0.75	0.06	0.08
Trifolium repens L. (White clover)	1.35	1.64	2.31	0.65	0.08	0.10
Poa annua L.	1.07	2.33	1.36	0.78	0.06	0.07
Dactylis glomerata L. (cocksfoot)	0.99	1.63	1.07	0.85	0.10	0.10
Holcus lanatus L. (yorkshire fog)	0.61	1.85	1.64	0.92	0.06	0.08
flatweeds - of the genera Plantago Bellis and Crepis	0.89	1.31	2.74	1.43	0.12	0.14
Lotus corniculatus (lotus)	1.05	1.17	1.56	0.90	0.08	0.08
Anthoxanthum odoratum L. (sweet vernal)	2.09	2.49	0.52	0.31	0.07	0.09

from the leaf surfaces, accumulation in the soil and entry via
the root system.

(c) Silver in tree ring-cores.

The concentration of silver (µg/g dry weight) in 2cm lengths
of 6mm diameter cores of B. tawa is shown in Figure IX.4. and is
expressed as a function of the distance from the outside of the
tree trunk.

Figure IX.4. shows that two main patterns of uptake may
occur. Samples from near the treatment plant (sites 1 and 4) show
elevated silver levels towards the outside of the tree trunk,
whereas specimens growing on the Silver Queen Reef show no
significant trend to increase or decrease levels of silver.
These levels are in general higher than for samples from the
treatment plant area.

It is suggested that accumulation of silver may probably be
due to absorption via the bark (thin in the case of B. tawa) for
specimens sampled near the treatment plant and that there is a
mechanism of accumulation via the root systems for samples from
the Silver Queen Reef area.

It is noted that background values tend to average slightly
below 0.1 µg/g.

(d) Silver in stream sediments and waters.

The mean concentrations of silver in stream sediments
(expressed as µg/g dry weight) and water (mg/l) sampled at various
sites are shown in Table IX.3.

The general pattern is for a steady decrease with increasing
distances from the source. The highest silver levels are found
near the Silver Queen Reef. The influence of airborne particulates
from the treatment plant is less pronounced in the case of plants
and soils.

Silver concentrations in stream sediments and waters from
background areas are about 0.02 µg/g and 0.00013 mg/l respectively.

Figure IX.4.

Silver concentrations (μg/g dry weight) as a function of distance (cm) from the outside of _Beilschmiedia tawa_ tree trunk ring-cores sampled from the Maratoto Valley.

Figure IX.4.

Silver concentrations (μg/g dry weight) as a function
of distance (cm) from the outside of <u>Beilschmiedia</u> <u>tawa</u>
tree trunk ring-cores sampled from the Maratoto Valley.
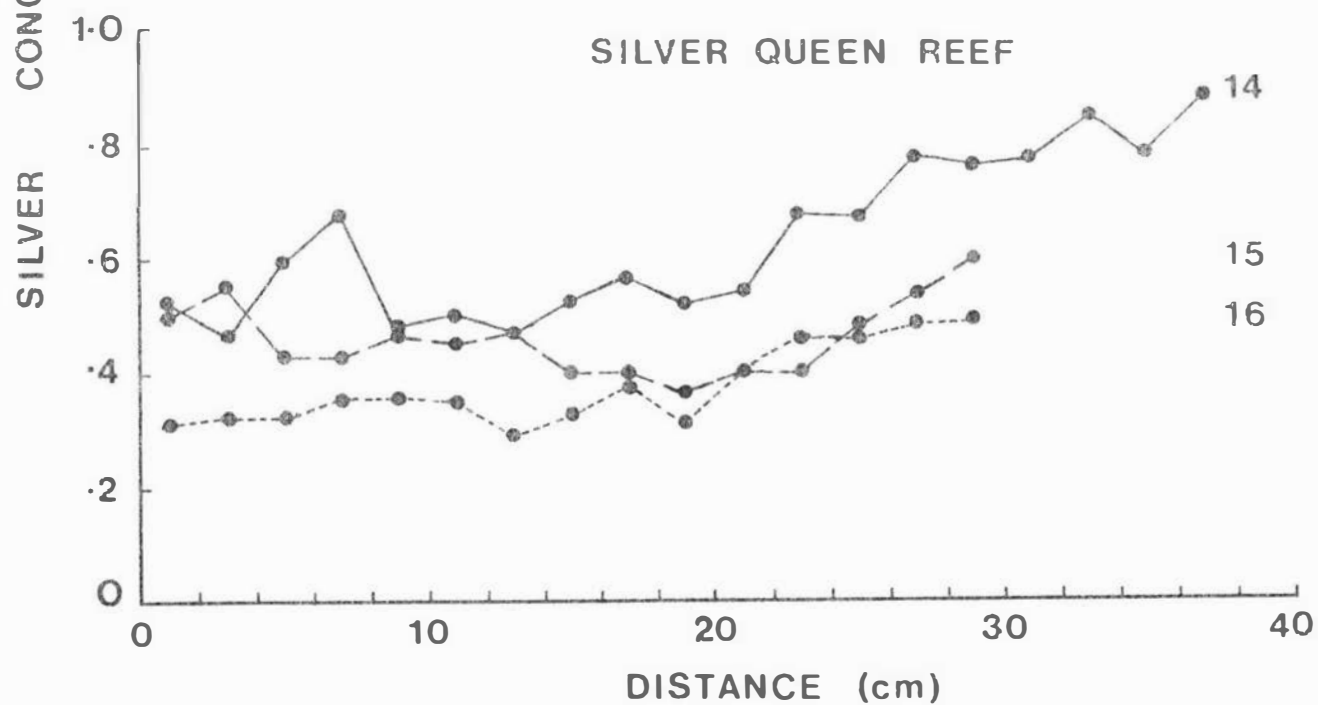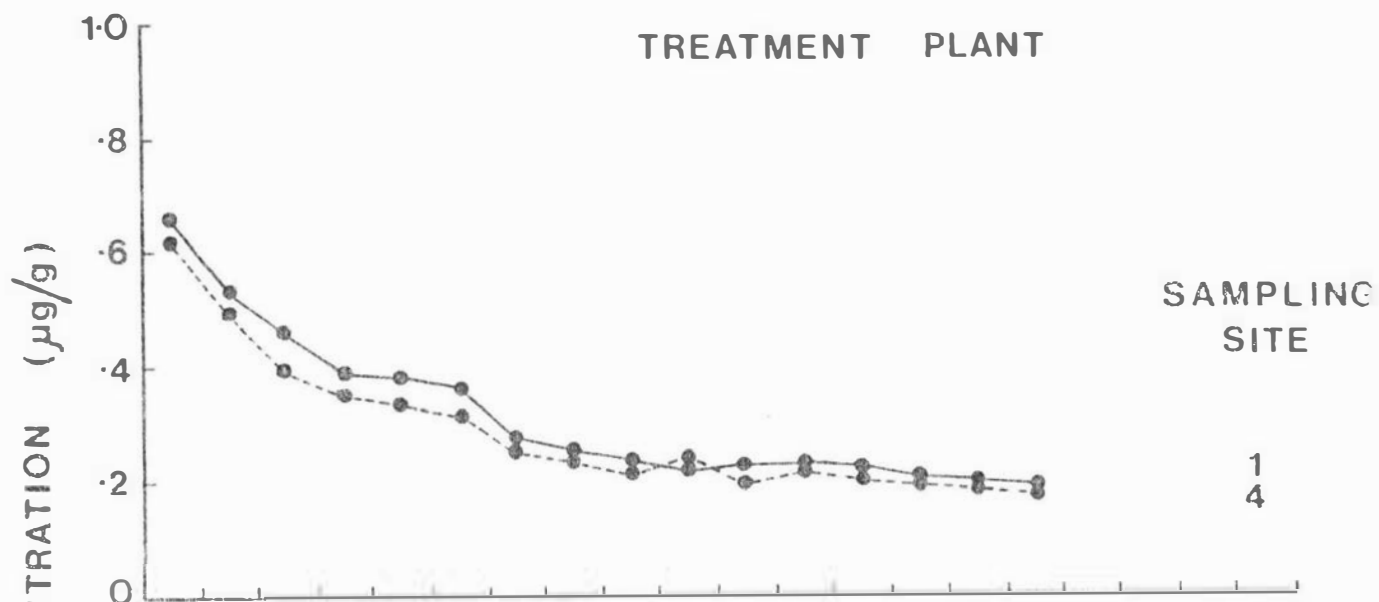
Table IX.3.

Silver Concentrations (mean of five determinations at each site)
of Stream Sediments and Waters Sampled From the Maratoto Valley.

Sampling site	Silver Concentrations	
	Stream sediment (µg/g dry weight)	Water (mg/1)
Silver Queen Reef.		
18	7.00	0.080
19	6.50	0.050
20	6.00	0.030
21	3.70	0.025
22	2.75	0.020
Treatment Plant		
23	3.50	0.025
Background.		
25	2.00	0.020
26	1.25	0.015
27	0.75	0.002

4. Conclusion.

In conclusion to this investigation, the following points can be made:

(i)   Silver in soils showed elevated levels near the treatment plant (due to aerial fallout), and also in natural vegetation growing over the ore deposits;

(ii)   pasture soils showed silver contamination derived partly from deposition from ore trucks and partly from flooding by mineralized stream sediments. Silver in pasture species reflected the same pattern;

(iii) silver levels in leaves and trunks of Beilschmiedia tawa showed distinctly different mechanisms of uptake from the two process of aerial fallout and natural uptake by root systems;

(iv)   the silver content of stream sediments and waters though anomalous near the deposits and treatment plant, showed a progressive decrease with increasing distance from the source.

In assessing the degree of environmental contamination of the Maratoto Valley from the presence of silver deposits and mining activities, it appears that there is a significant increase in silver levels (in some cases more than 10 fold higher than background) which may represent to some degree a pollution problem in the immediate area. Because of the limited dispersion of silver and because of the sparsity of population in this region, it is likely that any pollution problem is occupational rather than environmental.

SECTION X.

HEAVY METALS IN SOME NEW ZEALAND

BRYOPHYTES.

1. Introduction.

The ability of bryophytes and other plants to accumulate trace elements from their substrates is well known and forms the basis of the biogeochemical method of prospecting (Brooks, 1972). Studies in this field have been reported from Finland (Lounamaa, 1956; Erametsa and Yliruokanen, 1971), New Zealand (Whitehead and Brooks, 1969; Brooks, 1971; Brooks et. al., 1973) and the United States (Shacklette, 1967; 1972).

Uptake of heavy metals by bryophytes and other plants (e.g. "Spanish moss" - Martinez et. al., 1971) can also serve as an indication of pollution from industrial sources and has been studied extensively in Finland (Lounamma, 1956), Sweden (Ruhling and Tyler, 1968; 1969; 1970a; 1970b; 1971), the United Kingdom (Goodman and Roberts, 1971) and United States (Martinez et. al., 1971). Sources of pollution were mainly from mining activities (Lounamaa, 1956) and smelters (Goodman and Roberts, 1971). In many cases it was impossible to determine "background" concentrations because of generally high levels of industrial activity in the countries concerned. Goodman & Roberts (1971) and Ruhling & Tyler (1969; 1970a; 1971) working with the ubiquitous moss Hypnum cupressiforme Hedw., listed as "background" concentrations: (µg/g on a dry weight basis) of about 1.0 (cadmium), 7.0 (copper), 40.0 (lead), and 80.0 (zinc). In the vicinity of a South Wales smelter, Goodman & Roberts (1971) reported maximum values of 9.5, 68.0, 348.0, and 345.0 µg/g respectively for these same elements in this species.

Because of the difficulty of obtaining true background values for heavy metals in bryophytes from industrial Europe, it would be of interest to obtain comparative values from a relatively unpolluted country such as New Zealand and furthermore, the assessment of concentration levels determined near sources of mining activity would be of interest. In earlier papers, Ward et. al. (1976; 1977c) surveyed heavy metal concentrations in soils and plants in two mining areas of New Zealand. Hypnum cupressiforme and other bryophytes were present at both locations, and have now been sampled and analysed in order to

assess their value as indicators of heavy metal contamination in
the New Zealand environment. It was also desired to compare
concentration levels in h. cupressiforme with those obtained in
other countries.

2.   Description of sites.

The two areas investigated were the Tui Base Mine of Te Aroha
and the Consolidated Silver Mining Co. mine at Maratoto. The
Tui mine (now closed), a source of base metals (cadmium, copper,
lead and zinc), is situated about 3km N.E. of Te Aroha township
in the foothills of the southern extension of the Coromandel
Peninsula Range. The Consolidated Silver Mining Co. silver mine
is situated some 15km E. of Paeroa in the Maratoto Valley. This
site is about 36km N. of the Tui Base Mine. A comprehensive
description of these two areas are given in Section VI.2. (Te
Aroha) and Section VII.2. (Maratoto).

At Te Aroha, the vegetation of Beilschmiedia tawa (Benth.
& Hook f.) as the main canopy component of the mixed broadleaf
evergreen forest, supports bryophytes which grow in abundance on
the forest floor, on fallen logs, and as epiphytes.

At Maratoto, the vegetation on the Silver Queen Reef is less
mature and consists of scrubby secondary growth with few tall
trees remaining following extensive clearance at the turn of the
century. The reef is traversed by several streams, the banks of
which are well covered with bryophytes.

At both sites underground mining was employed with a surface
crusher and ore treatment plant producing a concentrate. Dust
produced by the crushers and containing heavy metals may be
expected to produce increased metal concentrations near the treat-
ment plant.

3. Materials and methods.

The following bryophytes were studied : all except the liver-
wort D. elegantula are mosses. Ten specimens of each species were
collected.

Group I. Epiphytic, mainly occurring on trees or fallen
        logs:
        Cyrtopus setosus (Hedw.) Hook.f. (C S);
        Hypnum cupressiforme (Hedw.) . (H C);
        Camptochaete ramulosa (Mitt. Jaeg. (C R);
        Weymouthia cochlearifolia (Schwaegr.) Dix.(W C).

Group II.
        Terrestrial, mainly occurring on soil:
        Acanthocladium extenuatum (Brid.) Mitl. (AE);
        Porella elegantula (Mont.)'Hodgs. (PE).
        Leucobryum candidum (Brid.) Hook. f. et Wils. (LC);
Group III. Aquatic, mainly occurring in water or on wet stream
        banks:
        Fissidens rigidulus Hook .f.et. Wils. (FR)

At both Te Aroha and Marototo, collections were made in
three different zones : A - across the mineralized reef; B - in
the vicinity of the treatment plant; C - in a 'background' area
judged to be sufficiently far from the treatment plant and mining
area to preclude serious contamination.

Depending upon which group of bryophytes was sampled,
associated substrate samples of water, soil, sediment or bark were
also collected.

The various sampling methods (in particular the washing
technique for bryophytes) are outlined in Section I, B.4.
Cadmium, lead and silver levels in natural waters were determined
using CRA as outlined in Section I.C.4.

4. Results and discussion.

The means (triangles) and ranges (solid lines) for concen-
trations of cadmium, copper, lead and zinc in bryophytes and their
associated substrates (broken lines) are shown in Figures X1-4.
All values represent samples from the base metal mine at Te Aroha.

Silver values from the Maratoto mine only are shown in
Figure X5. It should be noted that silver was not determined at
Te Aroha, and base metals were not analyzed at Maratoto because

Figure X.1-4.

Heavy metal concentrations (µg/g dry weight) in
bryophytes (solid line) and their substrates (broken lines)
in samples collected near a base metal mine at Te Aroha,
New Zealand. Mean values are shown as triangles. Locations
were: Mineralized area (M), Treatment plant (T.P.) and
Background (B). The bryophyte species:

<div align="center">

CS= Cyrtopus setosus

HC= Hypnum cupressiforme

CR= Camptochaete ramulosa

WC= Weymouthia cochlearifolia

AE= Acanthocladium extenuatum

LC= Leucobryum candidum

PE= Porella elegantula

FR= Fissidens rigidulus

</div>

associated with each element:

<div align="center">

Figure X.1. Concentrations of cadmium.

Figure X.2. Concentrations of copper.

Figure X.3. Concentrations of lead.

Figure X.4. Concentrations of zinc.

</div>

Cd Concentration

Cu Concentration
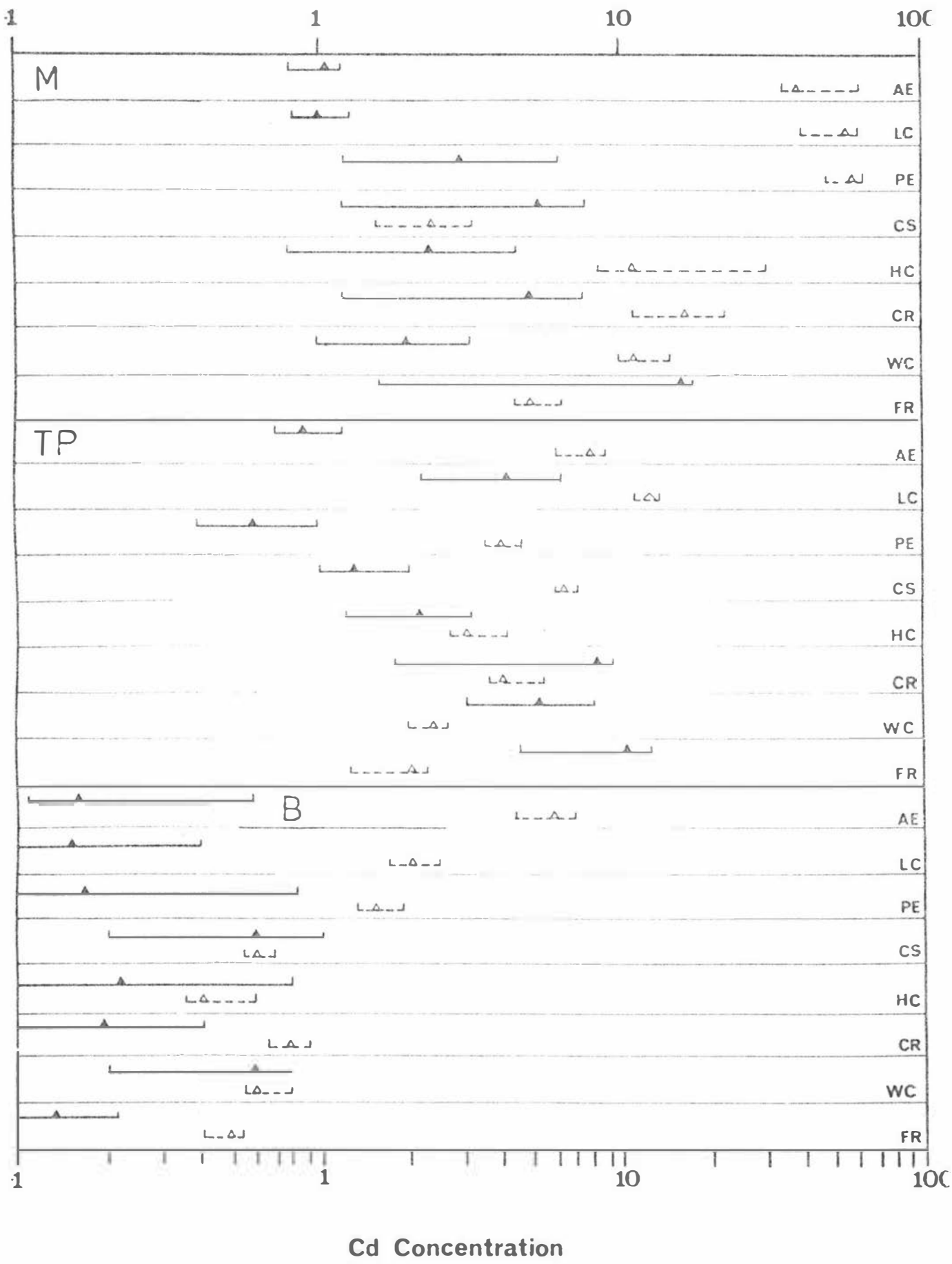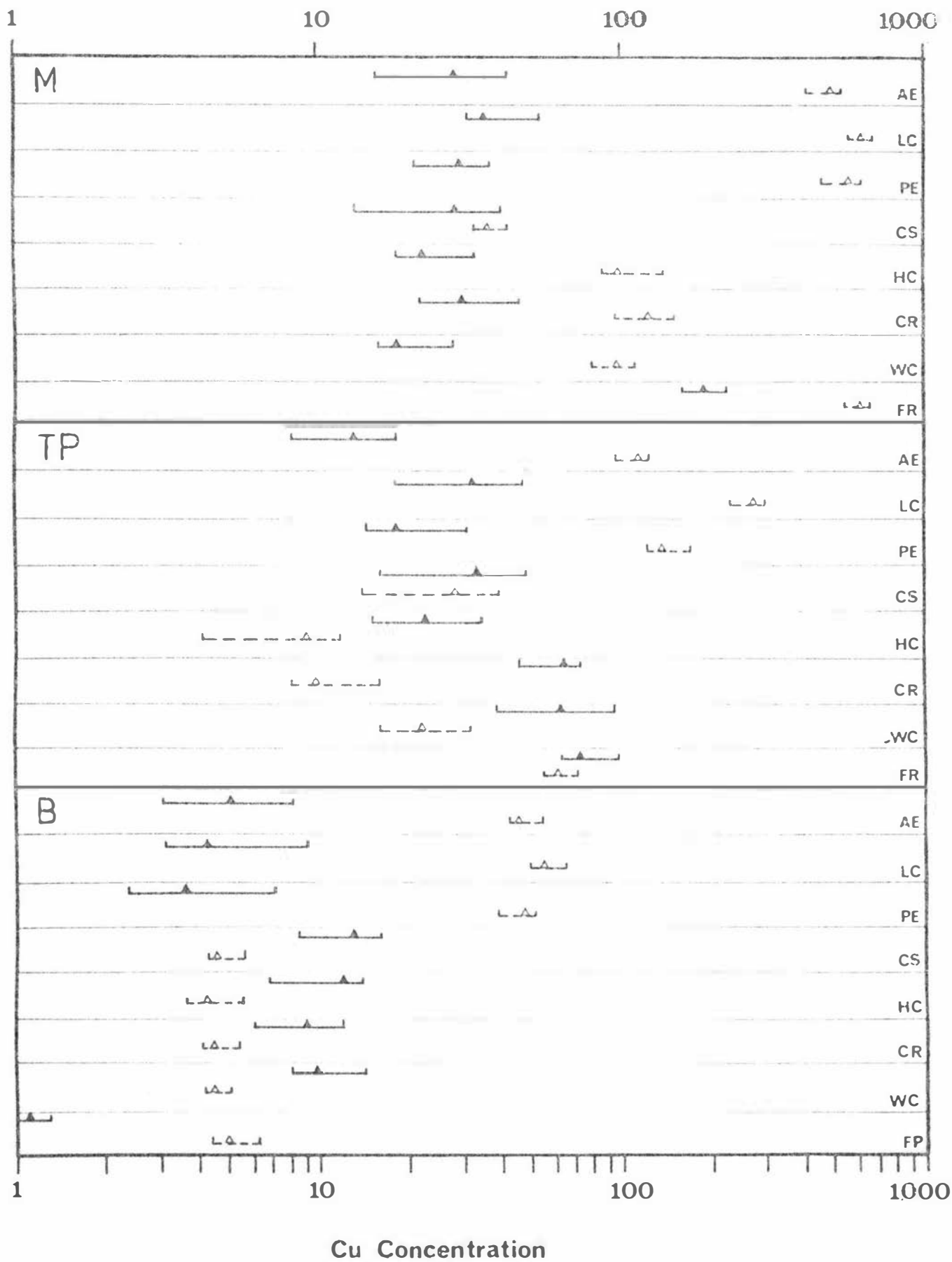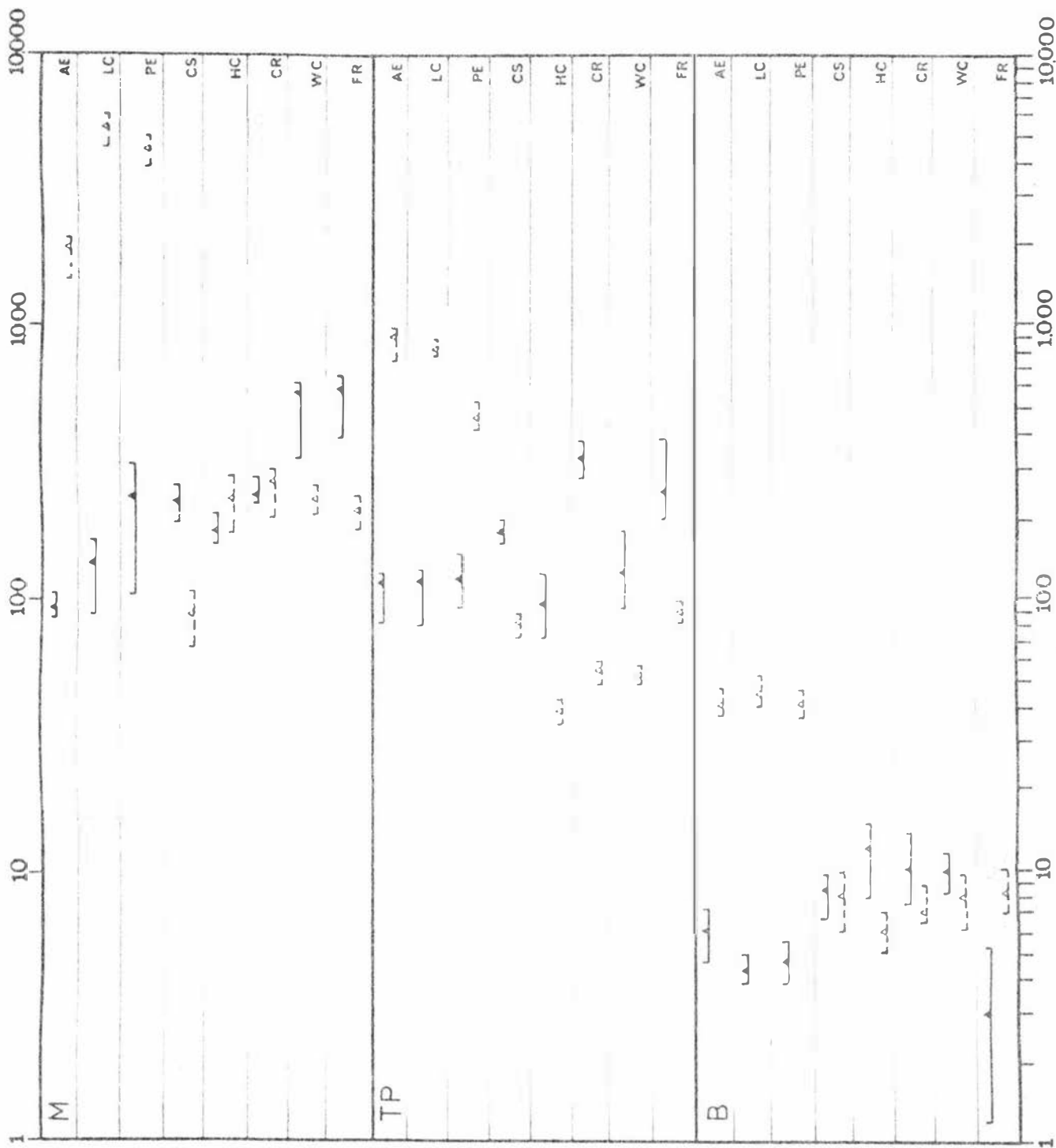
Pb Concentration
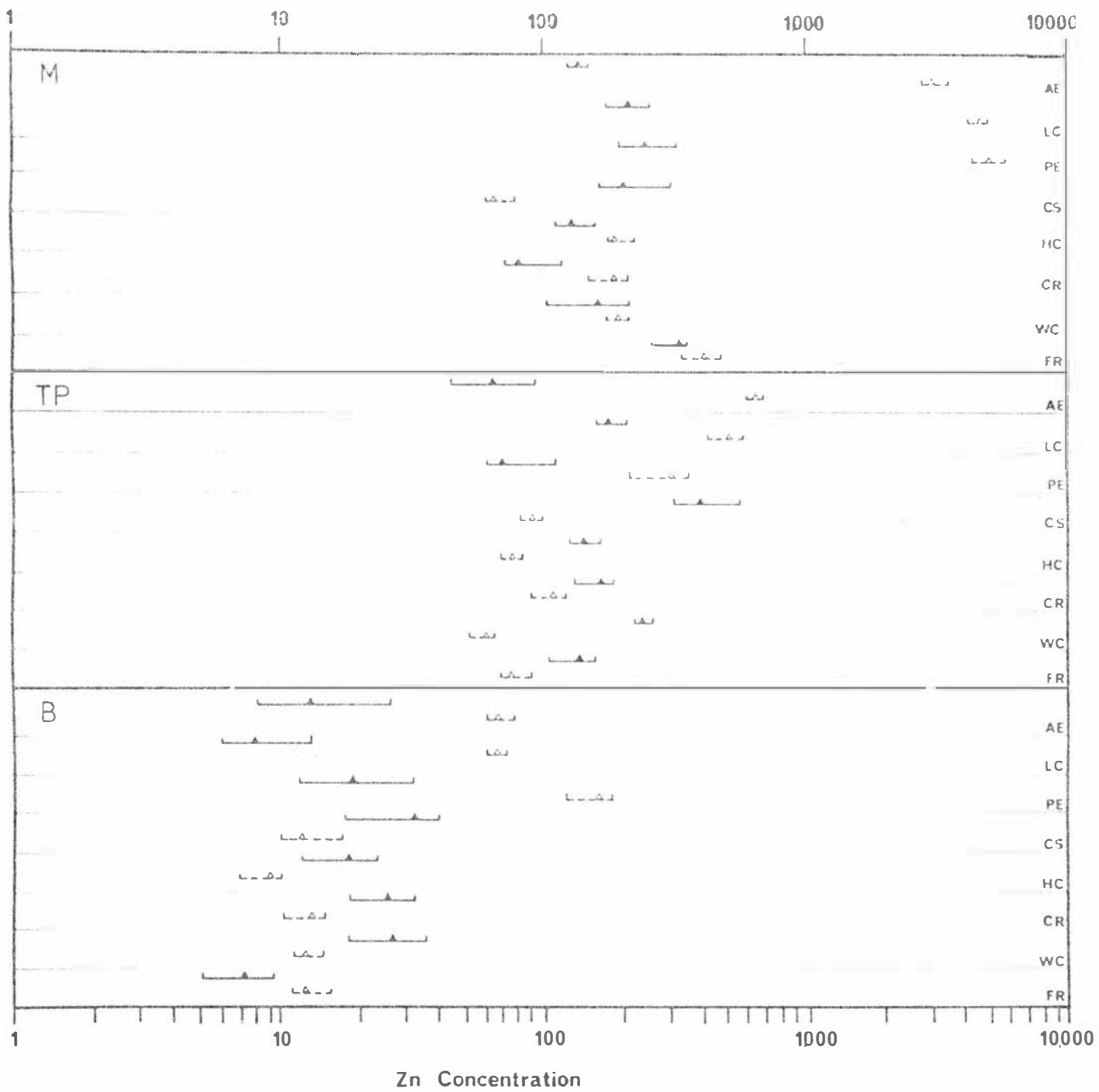
Zn Concentration

Figure X.5.

Silver concentrations (µg/g dry weight) in bryophytes
(solid lines) and their substrates (broken lines) for
plants collected near a silver mine at Maratoto, New
Zealand. Mean values are shown in triangles. Locations
were: Mineralized area (M), Treatment plant (T.P.), and
Background (B). The bryophyte species:

CS= Cyrtopus setosus
HC= Hypnum cupressiforme
CR= Camptochaete ramulosa
WC= Weymouthia cochlearifolia
AE= Acanthocladium extenuatum
LC= Leucobryum candidum
PE= Porella elegantula
FR= Fissidens rigidulus
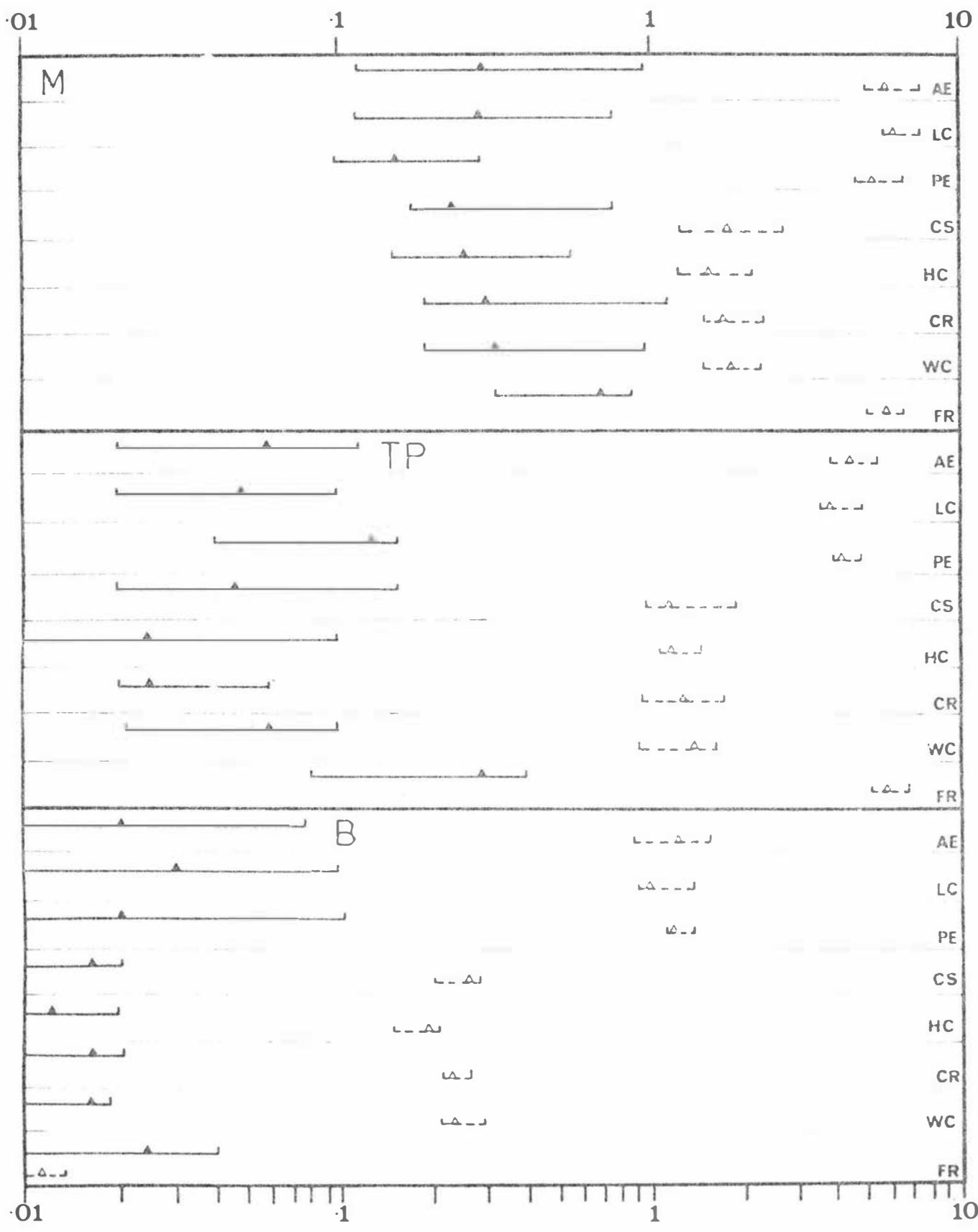
Ag Concentration

entirely different mineralization was present at both locations.

All concentrations were expressed as μg/g dry weight, the only exception being the concentrations in water which were reported as μg/ml. To convert dry-weight concentrations (Table X.1) to ash-weight equivalents, the appropriate factors are 14, 6 and 8 for terrestrial, epiphytic and aquatic bryophytes respectively. These factors are the mean dry-weight/ash-weight ratios for each of the three groups of samples.

The degree of element uptake by bryophytes was influenced partly by their habitat and partly by the locality of the collection site. For plants collected at Te Aroha, elemental concentrations in all species tended to be approximately the same for the mineralized and treatment plant areas and the concentrations of these elements in plants collected as 'background', showed values which were ten times lower.

The similar concentrations of heavy metals in bryophytes for mineralized and treatment plant areas, contrasted with the much lower values for substrates in the latter compared to the former area, gives an indication of a different mode of uptake (Figures X1-4) by these plants. In the former, uptake was presumably dominated by passive ion-exchange through the rhizoid-soil interface as suggested by Ruhling & Tyler (1970a). In the region of the "dusty" treatment plant, uptake was presumably dominated by surface absorption via aerial transport of the ore concentrate. Apart from these two processes, other mechanisims such as active transport and surface absorption may well play a part.

Transfer of ions from substrate to bryophyte was apparently more efficient for epiphytic than for terrestrial bryophytes in the mineralized areas. This is apparent because bryophyte accumulations were about the same despite a much lower elemental content of the substrate of the epiphytes. A similar pattern for both moss types was also evident for the background areas.

Fissidens rigidulus accumulated cadmium and lead relative to its environment. Further, it possessed approximately the same zinc but less copper. This variable behaviour is probably a function of a difference in ion exchange capacity of this species

Table X.1

Ranges and Means of Heavy Metal Concentrations, Expressed in μg/g Dry Weight, in Hypnum cupressiforme from the Maratoto and Te Aroha Mining Areas in New Zealand (10 plants from each part of the two localities). Values for the Same Species From Sweden are Included for Comparison and Represent Means of 10 Specimens From the Background Locality With the Lowest Heavy Metal Concentrations.

Location		Elemental Concentrations				
		Ag	Cd	Cu	Pb	Zn
New Zealand	Mineralized areas (range)	0.16-0.60	0.80-4060	18-34	160-202	112-156
	Treatment plants (Range)	0.01-0.10	1.20-3.40	15-34	74-125	126-167
	Background areas (range)	0.01-0.02	0.10-0.80	6-14	8-14	12-23
	Background areas (Mean)	0.015±0.003	0.41±0.21	10.1±2.4	10.6±2.0	17.2±3.3
Sweden, Lowest background (mean)[*]		-	0.68±0.03	6.8±0.5	42±8	82±13
New Zealand and Swedish values		-	P<0.001	P<0.001	P<0.001	P<0.001

[*]Data from Rühling & Tyler (1971)
 S** very-highly significant difference

	Cd	Cu	Pb	Zn
t=	t= -4.0 S**	t= +4.3 S**	t= -12.1 S**	t = -15.1 S**

relative to each metal (Whitehead and Brooks, 1969).

The pattern of silver concentrations at Maratoto (Figure X.6) was somewhat different from that of Te Aroha. Although data for the mineralized area were similar (i.e. similar concentrations of silver in all bryophytes but lower levels in the epiphyte substrates), concentrations of silver in bryophytes collected near the treatment plant were considerably lower than for specimens from the mineralized area. This is probably a reflection of the much lower scale of operations at this plant where production of concentrate was very much less than at the Te Aroha treatment area. It is also clear that absorption of silver by the aquatic bryophyte was relatively low in the mineralized and treatment plant areas.

Elemental concentrations in Hypnum cupressiforme from New Zealand are summarized in Table X.1. The mean background levels are compared with the lowest mean values obtained by Rühling & Tyler (1971) for the same species in Sweden. A t-test showed that background levels were lower in New Zealand for cadmium, zinc and lead, and higher for copper. These differences, though statistically significant, were relatively small for copper and cadmium, and extremely large for the other two elements where mean values were about four times higher in Sweden for lead and zinc. If consideration is taken of the highest background values found in the Swedish sources then the differences become even greater and the Swedish concentrations exceed by factors of about 4, 2, 15 and 9, the New Zealand values for cadmium, copper, lead and zinc. The lower concentrations in the New Zealand specimens must surely reflect the much lower general level of industrialization in this country. For the same reason, this and other mosses should be in New Zealand, more positive indicators of heavy metal contamination than in industrialized areas of Europe.

5. Conclusion.

Cadmium, copper, lead, silver and zinc were determined in bryophytes from two mining areas in New Zealand. The following conclusions were made:

(i) Near the "dusty" treatment plant at Te Aroha, all bryophytes had high metal concentrations compared with the substrate, and indicated foliar uptake of airborne contaminants compared with presumed uptake by passive ion-exchange at the rhizoid - soil interface in the mineralized areas;

(ii) uptake of silver near a treatment plant at Maratoto was at considerably lower levels than from the mineralized area. Silver absorption by the aquatic bryophyte _Fissidens_ _rigidulus_ was relatively low in the mineralized and treatment plant areas;

(iii) background concentrations of all elements except copper in _Hypnum_ _cupressiforme_ were lower than in the lowest background values obtained for Swedish specimens of this species.

SUMMARY

AND

GENERAL CONCLUSIONS.

In Section I, the development of various analytical techniques associated mainly with the determination of lead in whole blood was outlined. The carbon rod atomizer method adopted on the basis of an investigation into the disadvantages of flame atomic absorption spectrophotometry and an evaluation of other analytical methods for whole-blood lead analysis, required a 1:1 dilution of whole blood samples with Triton X-100 (an alkyl phenoxy polyethoxy derivative of ethanol) before sample application (1 µl) to the atomizer. After determining the optimium instrumental parameters, maximum absorbance was obtained with a reproducibility of < 5%, with the addition of Triton X-100 in the lead concentration range of 0.1-1.0 µg/ml. The presence of such additives as double-distilled water, nitric-perchloric acid, conc. ammonia solution, and 1000 µg/ml Na Cl solution, resulted in a considerable reduction in absorbance. The effect of EDTA and heparin (whole-blood anti-coagulants) in reducing the absorbance of lead was eliminated by the addition of Triton X-100.

The potential of animal blood sampling combined with the subsequent measurement of whole-blood lead levels using the CRA, led to an extensive survey of the lead levels in whole blood of New Zealand domestic animals (Section II.) and sheep exposed to motor vehicle emissions (Section III.) In summary, cats, dogs, and sheep showed no significant differences in lead levels according to age, whereas larger ruminants such as cattle (t = 4.67 for 250 degrees of freedom) and horses (t = 5.81 for 256 d.f.) showed a very-highly significant (P< 0.001) difference between those animals younger than 18 months compared with all other age groups. Cattle also showed a very-highly significant difference between the sex groups, male and female - neutered animals. The major finding of this section was the very-highly significant difference (t = 3.1 for 80 d.f.) between sheep dogs and pedigree dogs from city areas. It is emphasized that the whole-blood lead level of a domestic animal is very much dependent upon the eating/drinking habits of the animal and the type of environment in which it lives. Therefore the lower lead levels measured in the whole-blood of rural dogs is surely a reflection of reduced access to

pollution from motor vehicle emissions, since other forms of pollution such as lead from piping and paints would presumably not be greatly different in both types of environment. This was also reflected in the whole-blood lead levels of dogs living within the vicinity of service stations and which reached 7.40 µg/ml compared with normal lead levels of 0.25 µg/ml.

The lead levels of whole-blood, organs, muscle tissue and bones of sheep exposed to motor vehicle emissions indicated that the lead burden is acquired partially by direct inhalation of airborne lead from exhaust emissions and partially indirectly by consumption of contaminated forage. Although it is difficult to establish which mechanism is the more important, it is apparent that both contribute to the accumulation of lead in the lungs (as a result of direct inhalation) and in the kidney cortex and liver (by digestion). Accumulation of lead in these latter organs presents a minor health hazard as a result of the use of offal in the preparation of pet food (Hankin et. al., 1975) which is some-times consumed by humans. A more significant hazard is the direct consumption of contaminated livers or kidneys by humans where, assuming an acceptable daily intake of 0.4mg of lead (W.H.O, 1972) by adult humans, a single serving of 200g of liver containing 20 µg/g lead would supply the maximum permissible elemental intake for a period of 10 days. With animal production and meat quality in mind, it is fortunate that muscle tissue shows the smallest concentrations of lead in absolute terms. Bones, because of their high proportion of total body weight represents the greater reserv-oir of lead within the animal.

Although there is no evidence to suggest that sheep 'excrete' lead from the body organs into the wool, a very-highly significant correlation (P< 0.001) was obtained between the lead content of the outer 2 cm of wool (as a result of lead particulates adhering and becoming incorporated into the wool fibre) and the lead content of the whole blood. Therefore it is suggested that it could be possible to use easily sampled wool material in place of whole blood to assess the lead burden of sheep.

The indication that part of the total lead burden in these sheep is acquired by direct inhalation of airborne lead particulates from motor vehicle exhaust emissions led to a more detailed study of the distribution of lead from motor vehicle emissions and its effect on roadside soils and pasture species (Section IV and V). Enhanced levels of not only lead but also cadmium, chromium, copper, nickel and zinc were measured in soils and pasture species along the Auckland Motorway and correlated well with traffic densities (ranging over 12,000 - 63,500 vehicles/24 hours). The highest accumulations of heavy metals were found in <u>Trifolium repens</u> L. (white clover) and the lowest in paspalum grass, with <u>Holcus lanatus</u> L. (yorkshire fog) indicating the best correlation with traffic density. The apparent build-up of cadmium, chromium, copper, nickel and zinc in soils and vegetation along motorways probably originates from mechanical wear and tear of motor vehicles (in particular car tyres - Cd, Zn; lubricating oils - Cd, Cu, Zn; chrome-plating - Cr, Ni; and the various components of engines and chassis - Cr, Cu, Ni), which deposits these metals in the fine dust of the roadway and from there to soils and vegetation. Evidence that the source of heavy metal pollution along such motor-ways was aerial deposition from motor vehicles was reflected in the reduction in elemental concentration with depth in soil profiles and the removal of about one-third of the aerial burden of each element by washing of the pasture species. The influence of the predominant winddirection upon the distribution of lead from motor vehicle emissions was indicated by the exponential decrease of lead content in <u>Lolium perenne</u> L. (perennial ryegrass) and <u>Trifolium repens</u> L. (white clover) with distance from a moderately busy (< 5000 motor vehicle/24 hours) New Zealand state highway, north of Bulls. The seasonal variation in lead content of these two pasture species may be a result of the density and leaf area index of a particular species, the influence of "road-splash" from passing motor vehicles (especially during the autumn and winter at sites close to the side of the highway) and the seasonal variations in the prevailing winddirection. Generally the lead content of the leaves exceeded that of the roots. It was also

observed that agricultural activities such as ploughing may
prevent the accumulation of high lead levels in the upper most
5cm of soil and thereby reducing the availability of lead to the
supported pasture.

In order to obtain a total assessment of the various types
of lead pollution in the New Zealand environment other than that
from motor vehicle emissions, investigations were carried out on
the heavy metal distribution from a base metal mine, Te Aroha
(Section VI) and lead pollution from a battery factory and smelter,
Te Papapa(Section VII). Airborne cadmium, copper, and zinc as
dust particles emanating from the ore-crushing treatment plant at
the Tui Mine were widely spread into the immediate environment.
Beilschmiedia tawa (Benth. & Hook f.) trees growing over the ore
bodies contained natural levels of these base metals in amounts
even greater than those derived from windborne sources. Analysis
of B. tawa tree ring-core sections showed that with airborne
accumulation derived from particulate emissions associated with
the ore-crushing treatment plant, the highest elemental levels
occurred towards the outside of the trunk. In contrast, when
elements were accumulated via the root system, (as with those
trees growing over the ore bodies) concentrations were appreciably
uniform through the entire trunk.

The significant effect on vegetation and soils of airborne
particulates from the ore-crushing treatment plant was studied in
a nearby pasture. During a period of 12 months after mining
operations had ceased at the Tui Mine, an overall decrease in
the elemental burden had occurred. In surface soils, there had
been about a 40% reduction of copper and lead, and 25% of cadmium
and zinc. The elemental concentration in soils as a function of
depth indicated that there was less differentiation after 12
months at the surface and at a depth of 5 cm, indicating a steady
loss of pollutants from the surface soil after the completion of
mining activities. There was no specific pattern for all pasture
species although overall the initial heavy metal burden at the
more heavily contaminated parts of the pasture (which were well
above background levels) showed a significant decrease after 12

months especially at those sites closest to the source of
pollution. If this reduction of the heavy metal contamination of
surface soils and pasture species, probably as a result of down-
ward leaching through the soil profile and by downslope movement
continues, the elemental concentrations in plants and soils
should ultimately approach background values. However this may
not occur within the vicinity of the Te Papapa battery factory and
smelter where extensive lead deposition as airborne particulates
and the products of weathered batteries resulted in lead levels
approaching 12.4% dry weight in surface soils and 0.84% dry weight
in some pasture species adjacent to the smelter. The magnitude of
the lead burden was reflected in very high lead levels in soil
profiles even at a depth of 12cm as a result of contamination from
the battery factory, smelter and stored batteries. There is clearly
a limit to the degree of physical adsorption of lead particulates
upon vegetation, since the greater percentage of the lead burden
of vegetation is removable by washing at sites of maximum
accumulation of lead. In contrast with these lead levels measured
in roadside soils and vegetation at a nearby thoroughfare, the
lead contamination from this industrial complex is more extensive.
However, this industrial lead pollution has only a local effect
whereas that from motor vehicle emissions is more universal in
distribution.

The accumulation of lead by pasture species and feed crops
is clearly a significant health hazard. Although it is assumed by
many workers that lead accumulation from motor vehicle exhausts
is largely by airborne particulates adhering and becoming incor-
porated into the aerial components of vegetation, there is ample
evidence for accumulation of lead via soil systems. Therefore, to
what extent is uptake by root systems from the soil responsible
for the high concentrations of lead in roadside vegetation?
Lead accumulation by aerial parts of <u>Trifolium</u> <u>repens</u> L. (white
clover) and <u>Lolium</u> <u>perenne</u> L. (perennial ryegrass) can total about
10% of the lead content of the soil and is somewhat greater for
white clover than for ryegrass. For plants growing in substrates
containing 5000 and 10,000 µg/g lead, values in all organs of both

species were the same as for the 1000 μg/g substrates and indicate
(as already mentioned for those soils near the Te Papa battery
factory and smelter), that a limiting value for lead in plant
organs does in fact exist. Elevated lead concentrations in soils
also affected the plant height of both species. Concentrations
exceeding 500 μg/g in the substrate (values typical of most
roadsides of major thoroughfares) are sufficient to reduce plant
heights by one half. White clover seed germination is also reduced
by high lead levels.

In assessing the degree of environmental contamination by
lead within the vicinity of the ore-crushing treatment plant at
the Tui Mine, Te Aroha, comparison with another heavy metal,
silver was made in a similar mining environment at Maratoto.
Silver in soils showed elevated levels near the treatmentplant.
(due to aerial fallout), and also in natural vegetation growing
over the ore deposits. Airborne particulate deposition of silver
from ore trucks resulted in elevated levels in pasture soils and
vegetation within 4 meters of the treatment plant access road.
Partial silver contamination in these pastures was also derived
from deposition of mineralized stream sediments as a result of
flooding. The silver content of stream sediments and waters though
anomalous near the deposits and treatment plant, showed a progress-
ive decrease with increasing distance from the source. The
significance of the distinctly different mechanisms of uptake in
leaves and tree ring-core samples of Beilschmiedia tawa (Benth.
& Hook f.) already noted for lead was evident also for silver;
either by aerial fallout or by natural uptake via root systems.

To summarise, heavy metal pollution (in particular lead) from
mining activities does not appear to present such a large problem
as motor vehicle exhausts or smelting operations. This is mainly
because of the lack of a gaseous component, the limited dispersion
of such elements as cadmium, copper and silver, and because of the
sparsity of population in these mining areas. However, animals
grazing on farmland within the vicinity of these ore-crushing
treatment plants and mining activities at Te Aroha and Maratoto
would be subjected to elemental concentrations in the pasture

approaching 2.5 µg/g cadmium, 12 µg/g copper, 20 µg/g lead, 0.3 ⌐ ᵃ µg/g silver and 30 µg/g zinc (dry weight) compared with normal levels of 0.05 µg/g cadmium, 2.0 µg/g copper, 2.0 µg/g lead, 0.06 µg/g silver and 6.0 µg/g zinc (dry weight). Poisoning of cattle and ponies as a result of grazing on farmland containing high lead levels has been reported by Chisnall & Markland (1971).

Another method of indicating the influence of pollution from industrial sources such as mining activities (Lounamaa, 1956) and smelters (Goodman and Roberts, 1971) is the use of analysing bryophyte samples. Because of the difficulty of obtaining true background values for heavy metals in bryophytes from industrial Europe it would be of interest to obtain comparative values from a relatively unpolluted country such as New Zealand, in particular for such a bryophyte as Hypnum cupressiforme (Hedw.) which has been studied extensively by other authors overseas. Similar conclusions to those for Beilschmiedia tawa (Benth & Hook f.) located at the mining areas of Te Aroha and Maratoto were observed in that all bryophytes had high metal concentrations compared with the substrate near the ore-crushing treatment plant and indicated foliar uptake by airborne particulates. In contrast in the mineralized areas, the presumed uptake was by passive ion-exchange at the rhizoid-soil interface. Silver absorption by the aquatic bryophyte Fissidens Rigidulus (Hook f. et. Wils.) was relatively low in the mineralized and treatment plant areas. The ability to use bryophyte samples in New Zealand to determine background concentrations was shown in Hypnum cupressiforme (Hedw.) where all elements studied, except copper were lower than in the lowest background values obtained for Swedish specimens of this species.

Overall, what conclusions can be drawn about the potential health hazard presented by deviant heavy metal (in particular lead) levels in the New Zealand environment? There can be no doubt that human industry has increased the mobilization of lead (and other heavy metals) into the New Zealand environment. The use of lead alkyls in petrol constitutes the major source of lead in the soil and pasture along major thoroughfares and the atmosphere of cities.

The investigations into the effect of motor vehicle exhaust emiss-
ions upon sheep, reported in this work, emphasize the potential
health problems that human inhabitants living near motorways in
large cities or connected with employment in the petrol industry
could be subjected too. Thomas et. al. (1967) reported that the
blood lead levels of men in a population living near the San
Bernardino (Alhambra - Los Angeles, U.S.A.) freeway, was 0.227
µg/ml. The mean value for men living near a coastal area (con-
sidered to be a natural-lead leveled environment) was 0.16 µg/ml.
The difference between these two groups was statistically signif-
icant (P< 0.006). The corresponding values among women were 0.167
and 0.099 µg/ml (P< 0.0006). In a study of the lead concentrations
in the atmosphere and population of Japan, Tsuchiya et. al. (1975)
reported on the whole-blood lead and urinary δ -aminolevulinic
acid levels of over 3000 policemen. They concluded that the pl--
of work or residence was statistically significant, with blood
lead levels increasing with urbanization. Moore et. al. (1976)
confirmed this in a study of the total blood lead levels of a
group of 48 petrol vendors in the greater Hobart area, Tasmania.
The concentrations of lead in the blood of petrol vendors (0.329
µg/ml) were significantly higher than those of a comparison group
of 47 clerks and students (0.143 µg/ml).

Therefore any future work on lead in the New Zealand environ-
ment could well be centred on establishing the total lead burden
of humans by studying the whole-blood lead and urinary δamino-
levulinic acid levels of persons living near the Auckland Motorway
and the various effects of lead uptake by inhalation of motor
vehicle emissions as a function of urbanization and employment
(for example; taxi drivers, service station attendents and street-
cleaners) in a large New Zealand City like Auckland. Comparative
studies have already been reported by Mencel & Thorp (1976)in
Sydney.

There is sufficient evidence to justify the conclusion that
other than the Te Papapa battery factory and smelter, the mining
activities investigated in this work do not present any potential
health problems to humans other than those employed or living
within the vicinity of the mining areas (which at both Te Aroha

and Maratoto is very small). Increased dissemination of lead and
the other heavy metals associated with these mining activities;
in particular cadmium and silver (both of which are very toxic),
may only occur through the re-opening of operations and increased
housing development within the vicinity of the mining areas
(especially at Te Aroha). Pollution from the Te Papapa battery
factory and smelter although causing very elevated lead levels is
only significant within the immediate area, which is predominantly
industrial.

It is concluded that the total lead content derived from
airborne emissions (motor vehicle exhausts and industrial
depositions) is increasing in the New Zealand environment. Besides
lead, elevated levels of cadmium and copper as a result of motor
vehicle emissions along major motorways may also indicate a future
source of concern for human health. Such present-day levels of
these heavy metals may not pose a serious pollution problem, but
if elemental levels are allowed to continue rising for a very long period,
it is not difficult to envisage pollution levels approaching the
magnitude in other countries.

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