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LEAD POLLUTION IN THE
NEW ZEALAND ENVIRONMENT

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NEIL IAN WARD

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ABSTRACT

Section I: The optimum conditions for the determination of lead by atomic absorption spectrophotometry were investigated. Using the analysis line $2170\text{\AA}$, vegetation and soils could be analysed with satisfactory reproducibility. Lead concentrations in solution were determined in some cases at levels ten-fold higher than normal environmental (background) levels.

The productivity of various analytical techniques used, in particular sample preparation, were shown to affect the analysis of lead in vegetation (leaves, barks, ring-cores) and soil samples.

Section II: The effects of lead from motor-vehicle exhausts on trees growing along a busy thoroughfare in Palmerston North, New Zealand, were investigated. Analysis of tree samples (leaves, bark, trunk cores) and of soils, showed that the distribution of emitted lead was influenced by the direction of the prevailing wind. Lead levels were higher on the sides of trees facing the traffic. Measurements of lead concentrations in leaves, bark and soils, showed considerable accumulation in the vegetation at distances of about 5m from the main traffic movement.

An investigation was carried out to determine the seasonal variation in lead content of tree leaves and dust samples along the thoroughfare and in the Palmerston North Square. It was found that only a gradual seasonal increase in the lead content occurred in leaves from the initial time of development to exfoliation. High lead levels in young leaves indicated a rapid accumulation of lead. A comparison of the lead content of Whatman filter papers and of leaves exposed to motor-vehicle exhausts, showed a

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significant difference associated with the type of surface retention mechanism. Dust samples from the Palmerston North Square showed no direct pattern of seasonal variation.

Section III: The lead content of soil and vegetation along part of a State Highway passing through an uninhabited area of New Zealand was investigated. The region studied was 20 km from the nearest town and was traversed by a single highway carrying an average of 1200 motor vehicles per day (1973). The topography was fairly flat, about 1000 m above sea level, and the light volcanic soil supported vegetation less than 1 m in height.

Analysis of soil and vegetation samples showed that elevated levels of lead occurred within 100 m of the edge of the highway. Close to the highway the decrease of lead levels in vegetation was approximately exponential, with the excess over background levels being halved about every 10-20 m. Accumulation of lead in soils, even within 10 m of the highway, was significant only down to a depth of 5 cm. It is estimated that the total amount of lead in excess of background soil values, contained within 250 m of the roadway and within 6 cm of the surface, represented a significant proportion of the total lead emitted by all vehicles that have traversed the highway since the introduction of lead tetra-alkyls into motor fuel.

Section IV: Lead concentrations in vegetation and soils were measured in the vicinity of the Tui Mine, Te Aroha, New Zealand. Lead levels in leaves of Beilschmiedia tawa reflected dispersion of wind-borne material around an ore treatment plant. Vegetation

growing over an ore body show very high lead concentrations accumulated by the root systems. This mode of uptake could be easily differentiated from air-borne deposition by the much lower proportion of the metal burden, which was removable by washing. Analysis of trunk core sections showed again a dissimilar pattern between air-borne deposition and accumulation of lead via the root system. With air-borne accumulation, trunk-cores showed a significant increase of levels towards the outside of the trunk. When accumulated via the root system, lead concentrations were appreciably uniform through the entire trunk.

Section V: Sweet-corn plants (husks, leaves, stalks, kernels, cobs) and soils in the vicinity of a Hastings-Napier highway were analysed for lead fallout from motor vehicle exhausts. The distribution of lead was influenced by the direction of the prevailing wind and by traffic volume. Lead levels in inedible parts of the plants (leaves, husks, stalks and cobs) were ten-fold higher in plants near the roadway than in plants taken from background areas. Edible portions (kernels) were relatively low in lead. Extraction studies showed that a considerable portion of the total lead burden was present as a superficial deposit removable by washing with water. The evidence favoured air-borne lead rather than soil-borne lead as the main contributor to elevated levels of this element in plant tissues.

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GENERAL INTRODUCTION

In recent years with the increased concern about pollution of the environment, no trace element pollutant has been studied more extensively than lead. The discovery of increasing lead levels (Murozioni et al, 1969) in Greenland snow ($20 \mu\text{g.t}^{-1}$, $120 \mu\text{g.t}^{-1}$ and $210 \mu\text{g.t}^{-1}$ between 1750, 1950 and 1965); the "survey of lead in the atmosphere of three urban communities" (U.S.H.E.W., 1965) and the reported mean blood lead level of a control group of Manchester children of 0.31 ppm (ranging from 0.02 to 1.05 ppm) compared with the lower mean blood lead poisoning level of 0.40 ppm (Gordon et al, 1967) has catalysed the exponential interest of lead concentrations in air, water, food, soil and blood.

Lead is a relatively minor constituent of the earth's crust, occurring at levels of about 15 ppm (igneous rocks). In its natural state, lead is found mainly as galena (PbS). The lead content of the oceans is only about 0.001 ppm (as a Pb^{2+} ion) due to scavenging by ocean sediments where it accumulates as the sulphide or sulphate. Fresh waters can have up to 0.02 ppm.

Natural lead levels in soils can range from 1 to 100 ppm depending on the nature of the substrate from which the soils are formed. Vegetation (expressed on a dry-weight basis) averages around 2-3 ppm lead (70 ppm on an ash-weight basis). The natural level of lead in the air is about $0.8 \mu\text{g.m}^{-3}$.

With the continuing discharge of lead into the air and water, the rate of increase of lead concentrations in the environment has accelerated. It is estimated that about 180,000 tonnes of lead are mobilised naturally each year throughout the World as a result of weathering processes. In contrast to this there are two major sources of lead 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 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.

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 Martin, 1972) have shown that measurable effects of lead pollution in soils extended to at least 10 km 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 air-borne 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 16 km from the source. Such results showed clearly that smelting works represent a potential source of very serious lead pollution, although much more localised than other sources (motor-vehicle exhausts).

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) showed lead levels of up to 2-5 ppm (drinking water), 250-6680 ppm (soil), 4 ppm (vegetables) and 200 ppm (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 operations restricted to areas well away from population centres. However, dust from opencast operations and ore treatment plants could scatter large amounts of lead from the mining area, 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 tetra ethyl lead (TEL) and tetra methyl lead (TML) are added to petroleum spirit in the range of 2-4 g of TEL per gallon. During driving, 25% to 75% of this lead is emitted into the atmosphere depending on driving conditions. Although most of this lead is ultimately deposited on the ground, the environmental air can often contain appreciable amounts of this pollutant. Cities like Los Angeles have a lead value of about $5 \mu\text{g.m}^{-3}$ (Hall, 1972) although lead levels of $71.3 \mu\text{g.m}^{-3}$ have been recorded during peak traffic periods on Los Angeles freeways (U.S.H.E.W., 1966). About 80% of particulate lead (Habibi, 1970) (the main form), from petrol combustion is less than 0.9μ in mean diameter (Robinson et al, 1967). Therefore, lead emitted from motor-vehicle exhausts is particularly suited for retention by biological components (leaves, barks, etc.) and human tissues (lungs).

Lead pollution of the atmosphere, soils and vegetation along major highways as a result of motor-vehicle exhaust emissions (Warren and Delavault, 1960; Cannon and Bowles, 1962; Atkins, 1969; Singer and

Hanson, 1969; Chow, 1970; Smith, 1971), showed distributions that were influenced by the wind direction and by general traffic movement patterns along the highway. The effect of lead pollution reduced rapidly within a relatively short distance of major highways.

The overwhelming contribution of lead alkyl pollutants emitted as motor-vehicle exhaust emissions into the environment is reflected in the annual consumption of tetra ethyl lead in such countries as the United States (181,000 tonnes in 1968) and in the United Kingdom, where the amount of lead used in the manufacture of petrol additives increased by 11.9% in the first 10 months of 1972 over the amount used in 1971 (Chow, 1973). The most insidious effect of this form of lead pollution is the general raising of the lead threshold in the atmosphere as a whole throughout the World.

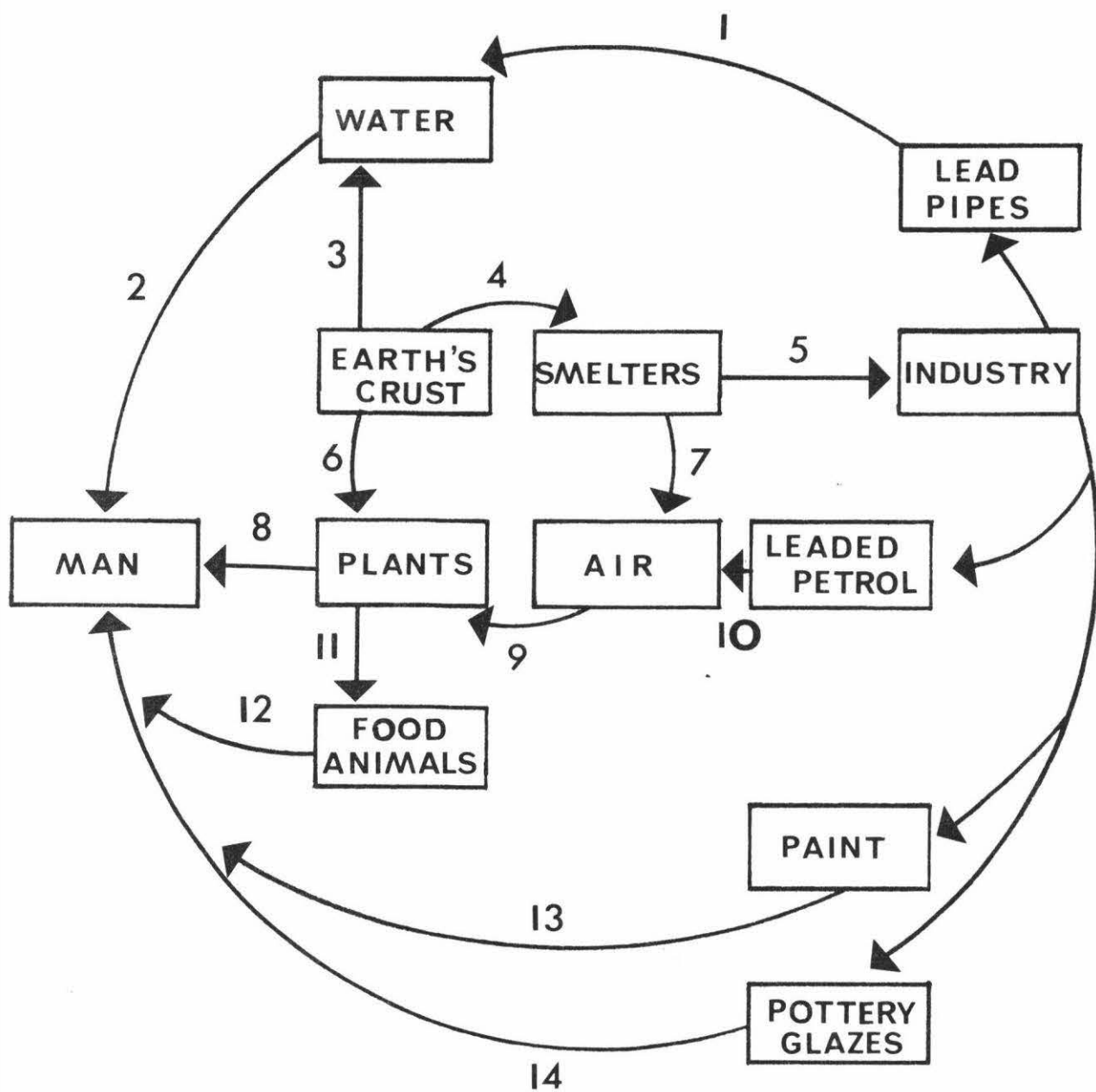
The only other sources of lead pollution worthy of mentioning are the release of soluble lead from glazed earthenware surfaces (Gilfillan, 1965; Klein et al, 1970) into the liquids contained in the vessel and lead poisoning, particularly in children, from lead in paint pigments (Copeland, 1971). Such sources play only a minor role in the addition of lead to the environment compared with those already mentioned.

It is clear that Man's efforts have seriously upset the natural cycle of lead in the environment as shown in Fig. O.I.

With 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.)

Fig. O.I. 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 produces pig lead.
6. Uptake of lead plants via root systems.
7. Smelter fumes pollute air.
8. Contaminated plant food eaten by humans.
9. Polluted air, deposits lead on vegetation.
10. Leaded petrol pollutes air via motor-vehicle exhausts.
11. Contaminated vegetables eaten by food animals.
12. Food animals eaten by humans.
13. Children ingest lead from paint flakes.
14. Lead glazes contaminates foodstuffs eaten by humans.



Inorganic lead (Pb^{2+}) is a general metabolic poison and enzyme inhibitor. Young children are particularly affected and can suffer mental retardation and semi-permanent brain damage (Vigliana and Zurlo, 1951; Harrison et al, 1969; Catton et al, 1970). 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.

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 a). 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 range from 0.2 to 0.8 ppm lead. Many investigations have shown blood levels exceeding these values in suburban and large city communities such as Manchester (Gordon et al, 1967,) and Philadelphia (Ludwig et al, 1965). Other methods of evaluating lead poisoning other than blood are by using hair or urine samples (Kopito et al, 1967; Kehoe, 1969). 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.

As a result of the evidence given on environmental lead pollution and the necessity for serious consideration of the immediate future when such high lead levels are found in other countries, it was considered necessary to determine the extent of lead pollution in the New Zealand environment. As far as is known, no investigations of this nature have previously been carried out in New Zealand.

Lead as an environmental pollutant in New Zealand is associated mainly with mining operations and as motor-vehicle exhaust emissions.

Lead was first mined in the Coromandel region of New Zealand near Te Aroha in 1884 with a view to supplying flux for smelting the Waiorongonui 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 Champion and Raukaka. An average assay of the primary ore (Williams, 1965) showed levels of 7.01% lead, 16.68% zinc and 0.62% copper. 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 a). Geological investigations (Henderson and Bartrum, 1913; Cochrane, 1969; Weissberg and Wodzicki, 1970 b) have shown that the metallic lode body is basically quartz-pyrite, sphalerite, chalcocypymite 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 paniculatus, Hedycarya arborea, Brachyglottis repanda and Schefflera digitata.

An aerial view of the Tui Mine, Te Aroha, is shown in Plate O.I. Reference positions are shown in Fig. IV.1.

Following the crushing procedure the base-metal ores were concentrated by a flotation process into copper and lead-zinc concentrates. These concentrates were then exported for smelting since no such industry

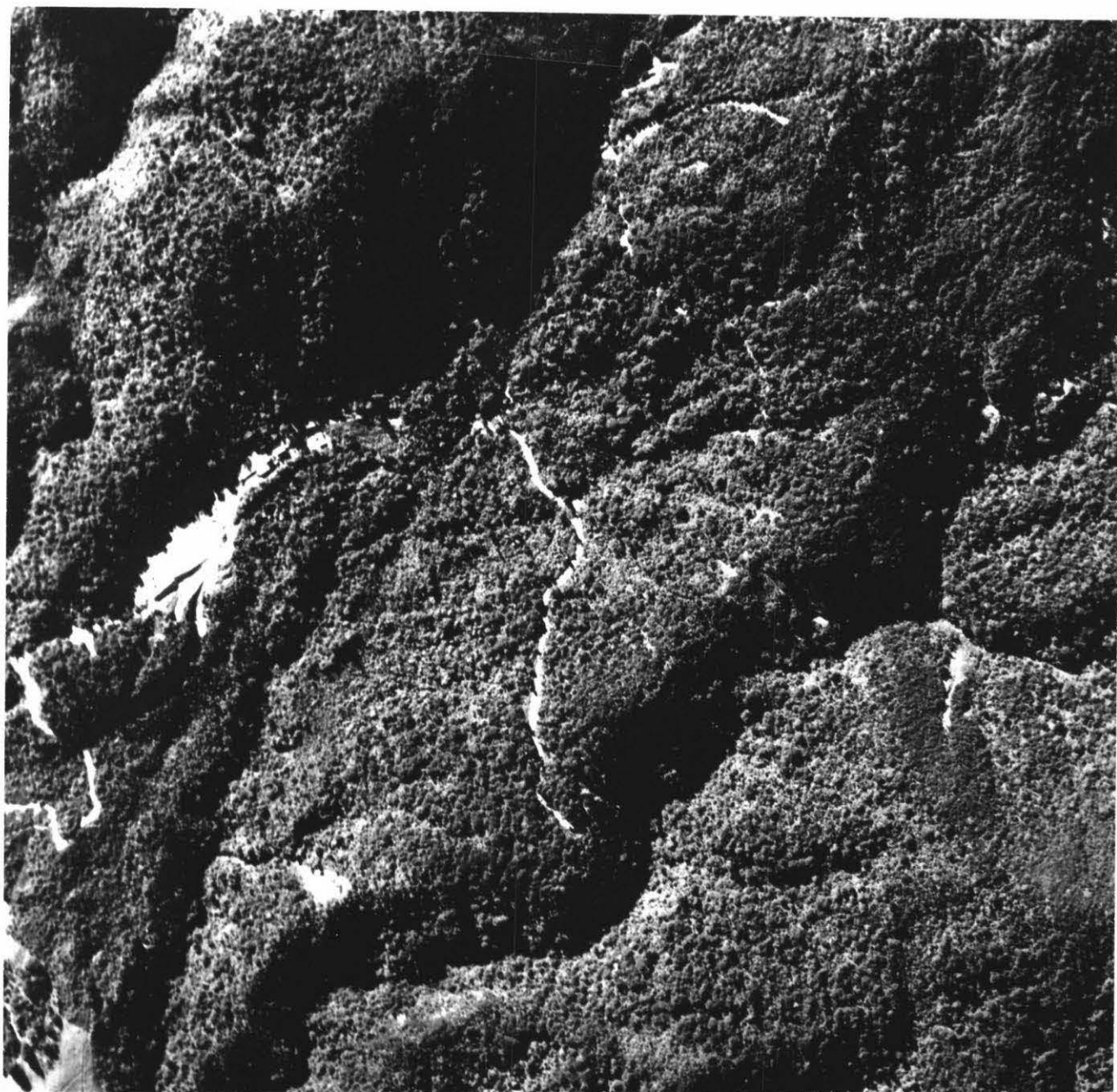


Plate O.I Aerial view of the Tui Mine, Te Aroha

has been established in New Zealand. The flotation process used may also present a major source of environmental dispersion by lead in the form of soluble lead in the water.

In contrast to a study of lead levels in soils and vegetation as a result of the air-borne exposure from the Tui Mine ore-treatment plant, experiments were proposed to determine the lead uptake and accumulation in vegetation (B. tawa) growing over a base-metal deposit at Te Aroha, (the Raukaka Lode). Similar investigations have shown lead values of up to 1% in the wood ash of B. tawa (Nicolas and Brooks, 1969). The results of these investigations are reported in Section IV.

In view of the serious nature of motor-vehicle exhaust emissions as a major source of lead pollution, three regions in New Zealand were considered for study of lead levels and distribution effects in the New Zealand environment.

Although Palmerston North's (population 54,300) main thoroughfares have not yet reached the levels of traffic density found in metropolitan areas in some parts of the world, it is considered that a main thoroughfare, Fitzherbert Avenue (shown in Plate O.II) having a traffic flow of 11,500 vehicles per day, should give a typical representation of lead levels from motor-vehicle exhaust emissions of any major New Zealand city. This site is particularly suitable for such studies due to: the regular position of trees along each side of the thoroughfare at distances of 2-5 m from the emitted lead leaving the motor-vehicle; the relatively constant traffic flow, and a characteristic prevailing wind direction.

With the rapid increase in the number of motor-vehicles in Palmerston North in recent years, the pattern of annually-emitted lead may be estimated



Plate O.II Fitzherbert Avenue, Palmerston North

by the lead levels in tree trunk-core sections. Similar investigations were prepared to determine the seasonal variation in lead content for vegetation and dust samples along the thoroughfare and in the Palmerston North Square. The results of these investigations are reported in Section II.

Fewer studies have been carried out in regions of low traffic density. The other two regions investigated in New Zealand were along a State highway situated in the centre of the North Island (as shown in Plate O.III) having a relatively low traffic volume of 1200 vehicles per day (results reported in Section III), and a highway situated near Taradale, Hawkes Bay, which connects Hastings (population 31,500) and Napier (population 42,900) having a daily traffic volume of about 6,000 vehicles.

It was proposed that the latter investigation could determine the patterns of lead concentrations of sweet-corn under New Zealand conditions and be able to examine the effect of various factors such as traffic density and the direction of the prevailing wind upon the lead levels within the plant. The results of these investigations are reported in Section V.

In conclusion, the main outlines of this work can be summarised as follows:

1. To develop sensitive and reproducible procedures for the determination of lead in vegetation and soils; and investigate the analytical techniques of sample preparation.

2. To investigate the distribution and accumulation of lead in soils and vegetation in the vicinity of the Tui Mine ore-treatment plant (air-borne lead pollution) and in vegetation growing over a base-metal deposit, the Raukaka Lode (soil-borne lead pollution), compared with natural lead levels from "background" areas.



Plate O.III National State Highway No.1, central
region, North Island

3. To investigate the lead content of soils and tree vegetation bordering a main thoroughfare in Palmerston North, New Zealand, and to show the influence on distribution by the wind direction and general traffic movement patterns along the thoroughfare. The effects of seasonal variation in lead content in vegetation and dust samples were also investigated.

4. To study the distribution and accumulation of lead discharged from motor-vehicle exhausts along a New Zealand State Highway in an area of low traffic density and determine lead levels in predominant plant species and in particular soils.

5. To determine the levels of lead contamination of sweet-corn and consider whether the main source is from air-borne emissions from motor-vehicle exhausts or obtained directly via the root system. It was also hoped to examine the extent of contamination within the plant as a function of such factors as wind direction and distance from the highway.

SECTION I
ANALYTICAL METHODS

A. INTRODUCTION

A literature survey of the analytical techniques in use for the determination of lead in chemical and biological systems showed that only colorimetry and especially atomic absorption spectrophotometry had any likelihood of fulfilling the requirements of speed, sensitivity and reproducibility.

The main colorimetric method used for the determination of lead is based on a dithizone extraction (Stanton, 1966). Dithizone is a reagent of 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 520 nm and obey the Beer-Lambert Law up to about 3 ppm 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 rock and soil samples) may give some precipitation of calcium phosphate that may occlude lead and cause low recovery values. The main disadvantage of the dithizone technique is that it is a non-specific extraction procedure which permits the determination of a number of trace elements in a sample with a single separation. In particular, the presence of copper, iron and zinc (Thompson and Nakagawa, 1960), which although don't react with dithizone in ammonical 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.

The development of atomic absorption spectrophotometry has proved to be an eminently suitable method for lead, especially due to the rapid determination of low concentrations of the metal. The use of atomic

absorption techniques is discussed in the next part of this section.

The superiority of atomic absorption spectro photometry over classical wet analytical methods is shown in such advantages as:

- (i) prior chemical separation of constituents is not required with preparation limited to placing the sample in solution.

- (ii) high degree of reproducibility.

- (iii) versatility, is illustrated by the ability to determine between 60 and 70 metallic elements, in concentrations that range from trace to macroquantities.

- (iv) the elimination of chemical separations of constituents allows for rapid analysis.

Finally, attention should be drawn to Flameless Atomisation using the carbon rod atomiser as an accessory to the AA5 (Varian Techtron) spectrophotometer. The development of the carbon rod atomiser has greatly facilitated the speedy analysis of blood and low metal content samples. Some of the advantages compared with conventional flame analysis are:

- (i) lower detection limits

- (ii) higher sensitivity

- (iii) minimized sample handling

- (iv) further increases in sensitivity and decreases in detection limit by preconcentration of the sample on the rod

- (v) prior chemical pretreatment of the sample is minimized. The sample can be ashed on the rod in seconds

- (vi) much smaller samples are required

B. ATOMIC ABSORPTION TECHNIQUES

1. Review of techniques

In recent years the increased interest in environmental lead pollution has stimulated the use of atomic absorption spectrophotometry. Techniques for determining the levels of lead in varying sample types are well documented for: blood and urine (Wallis, 1962; Berman, 1964; Reynolds and Aldous, 1970), metals and alloys (Elwell and Gidley, 1961; Dagnall *et al.*, 1966), gasoline (Robinson, 1961; Trent, 1965; Wilson, 1966), worn lubricating oil (Burrows and Heerdt, 1965; Means and Ratcliff, 1965), electroplating solutions (Shafto, 1964), wines (Zeeman and Butler, 1962) and hair (Noller and Smythe, 1972).

The development of such atomic absorption techniques is shown in the various applications of such methods for the determination of lead concentrations in blood and urine (Rose and Willden, 1971; Norval and Butler, 1972), metals and alloys (Tsukahara and Yamamoto, 1972), gasoline and petroleum materials (Campbell and Palmer, 1972) and water effluent samples (Sprague and Slavin, 1964; Biechler, 1965; Galle, 1971).

The principal interest shown in atomic absorption spectrophotometry in the past 5 years has been centred around the determination of lead in such materials as blood, water, soil, air and vegetation. Natural lead concentrations in the environment have been estimated using techniques (Wedepohl, 1956) which give in accurate detail the distribution of lead in a variety of rocks and minerals.

Lead concentrations in soil have been investigated with many techniques (Swaine and Mitchell, 1960; Chow, 1970; Motto *et al.*, 1970; Langerwerft and Specht, 1970). The various methods differ mainly in the choice of sample decomposition (Stanton, 1966) and solution mediums used for analysis. (These will be discussed

in more detail in Part C, Section I.)

Similarly, the determination of lead concentrations in vegetation have been subjected to many techniques (Warren and Delavault, 1962; Chow and Johnstone, 1965; Ter Haar, 1970; Schuck and Locke, 1970; Cannon and Anderson, 1971), mainly depending upon the type of digestion procedure.

2. Apparatus

Experiments were carried out on a Varian Techtron AA5 Atomic Absorption Spectrophotometer with an air-C₂H₂ flame and Varian Techtron hollow cathode lamps.

The fuel/oxidant mixture of acetylene/air is successful for lead which does form highly refractory oxides. This flame also gives an approximate temperature of 2450°K which is important in the production of free Pb²⁺ atoms and reduces the chemical effects of radicals and other substances present in the flame.

3. Preparation of standards

A stock solution was prepared which contained 1000 ppm of lead, from which working standards were prepared freshly for each day's analysis by successive dilutions to give standards of 100, 10, 5, 4, 2, 1 ppm.

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.

4. Preparation of samples

(a) Soil samples

All soil samples were dried for three days (at 60°C) and sieved (-60 mesh). Samples of soil (0.1 g) were digested with 10 cm³ volumes of a 1:1 mixture of concentrated nitric acid and hydrofluoric acid, and

taken to dryness in polypropylene beakers suspended in a water bath. The residues were redissolved in 5 cm³ of 2M hydrochloric acid prepared from the redistilled reagent.

(b) Plant and wood (bark and ring-core) samples

All bark, leaf samples and trunk-cores were oven-dried at 105°C, ignited at 450°C in a muffle-furnace and the ash was dissolved in 2M hydrochloric acid in the ratio of .05 g of ash to 5 cm³ of acid.

5. Detection limits

(a) Investigation of analysis line

The most sensitive lead lines are shown in Table I.1, with their relative signal intensity, sensitivity and recommended spectral band width (SBW).

All sample determinations for lead were measured using the most sensitive line 2170.0 Å, due to its high operational sensitivity.

(b) Sensitivity and detection values

The sensitivity for lead is measured in terms of the concentration giving 1% absorbance.

The most sensitive signal is obtained with the resonance line 2170.0 Å which has a sensitivity of 0.16 ppm.

The limits of detection for this study, in general, are not important, for the samples investigated have lead concentrations in solution which are 10-fold higher than normal environmental (background) values.

(c) Interferences

There are relatively few interferences in an air-acetylene flame for lead. Dagnall and West, (1964) made an extensive study of interferences from cations in a 1,000-fold excess over lead; (Ag, Ba, Bc, Bi, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, La, Li, Mg, Mn, Na, Ni, Sn, Sr), and concluded that there was no appreciable interference, although 10,000 ppm of iron enhanced 5 ppm of lead by

Table I.1
Lead Analysis Lines

<u>Wavelength</u> <u>Å</u>	<u>Sensitivity</u> <u>ppm</u>	<u>Relative</u> <u>Sensitivity*</u>	<u>Recommended SBW</u> <u>Å</u>
2170.0	0.16	1.00	9.9
2833.0	0.33	2.05	3.3
2614.1	5.8	36	3.3
2022.0	8.1	50.5	3.3
2053.2	55	344	3.3

* measured relative to the 2170.0 Å line

35%. At the high concentrations encountered in my work, interference effects are negligible.

The effects of scatter by incident light being deflected without being absorbed with the resulting spurious increase in the absorption signal, was detected by using the continuous spectrum of a hydrogen lamp at the same wavelength as the absorbing line (2170.0 Å). Any reading under these conditions was spurious absorbance and was subtracted directly from the absorbance of the lead line.

6. Reproducibility

(a) Samples

Table I.2 shows the results of replicate analysis of Te Aroha soils, National State Highway No. 1 plant (leaves and twig) samples and background samples.

The reproducibility of all sample analysis in this thesis is satisfactory, being less than 5% above 30 ppm.

Multiple analysis of each sample allowed a more accurate determination but decreased the speed of analysis.

(b) Standards

The variation in standard calibration curves was observed to be very slight as long as stock solutions were prepared fresh each day.

Solution ppm values were dependent upon the accuracy and reproducibility of analysis solution volumes. An accuracy to within $\pm 0.3 \text{ cm}^3$ in measuring volumes introduces an average variation of about 6% for most vegetation and soil samples. Such levels give a reasonable indication of a satisfactory reproducible technique. Values of $\pm 0.05 \text{ cm}^3$ in measuring 1 cm^3 solutions for ring-core ash for analysis introduces an average variation of about 5%.

In conclusion, the preparation of standards and solutions for the determination of lead is at a level of satisfactory reproducibility provided solutions

Table I.2
 Reproducibility of Te Aroha and
 National State Highway No.1 samples

<u>Sample</u>	<u>Number of</u> <u>Determinations</u>	<u>Range</u> <u>(ppm)±</u>	<u>Mean</u> <u>(ppm)±</u>	<u>Coefficient of</u> <u>Variation (%)</u>
<u>Plant leaves*</u>				
<u>Hebe odora</u>	20	340-350	344	3.9
<u>Cassina vauvilliersii</u>	20	450-469	458	4.5
<u>Plant background*</u>				
<u>H. odora</u>	20	80.0-82.5	81.25	2.1
<u>C. vauvilliersii</u>	20	87.5-92.5	90	2.3
<u>Plant twigs</u>				
<u>H. odora</u>	18	482-495	488	2.9
<u>C. vauvilliersii</u>	18	440-466	457	2.0
<u>Soil (Te Aroha)</u>	20	250-270	262	2.2
<u>Soil background</u>	20	38.5-40	39.6	1.8

* plant leaf samples unwashed

± leaf/twig samples ppm ash weight
 soil ppm dry weight

are fresh and prepared with close attention to measuring analysis volumes.

7. Instrumental operating conditions

Table I.3 gives the operating conditions used.

8. Conclusion

The methods described for analysis using an Atomic Absorption Spectrophotometer were very suitable for all determinations, giving good sensitivity and reproducible sample values. Variations due to various parameters involving the preparation of samples, gives the major variability of the data. An investigation into these parameters is described in the next section.

Table 1.3

Spectrographic Operating Conditions

Fill gas	Neon
Window	Quartz
Operating current	6 mA
Strike voltage	290 V
Operating voltage	200 V
Spectral bandwidth (SBW)	9.9 Å ⁰
Sensitivity	0.16 (air-C ₂ H ₂ flame)
Analysis line	2170.0 Å ⁰
Flame stoichiometry	oxidizing

C. DEVELOPMENT OF ANALYTICAL TECHNIQUES

1. Introduction

The various stages in the preparation of samples for analysis in particular the total lead content of the sample, fall into four categories: preliminary treatment, washing of sample, ashing (temperature decomposition), and acid digestion.

Each of these factors governs the efficiency with which any of the forms of lead contained within the sample is converted into available species for analysis. Matrix effects in different samples, showed that it was necessary to investigate each factor so that the highest reproducibility was obtained.

2. Sample preparation

(a) Preliminary treatment

Sample contamination and storage directly affect the concentrations of lead as well as absorption from external sources. All containers used for collection and storage, were polyethylene or polypropylene bottles having a negligible lead content. The water used for washing samples was checked for its lead content. The use of polypropylene containers for the acid digestion of soil samples eliminated any risk of lead contamination from the container.

(b) Washing of samples

The concentration of particulate lead in vegetation sampled in regions of high aerial fallout from industrial sources (Te Aroha crusher), or automobile exhausts (National State Highway No. 1 and Palmerston North), is totally dependent upon the proportion of lead removable by washing. Preliminary investigations (Little and Martin, 1972) of Elm, Ulmus glabra, leaves collected in the Avonmouth area near a Bristol smelter showed that between 30 and 85% of the total lead burden

on the leaves was removed by washing in deionised water. Within the natural environment such deposits on the surfaces of leaves may be removed by rain, wind, or sloughing of the cuticle wax (Moorby and Squire, 1963).

Further investigations (Little, 1973) subjected heavily contaminated leaves (due to aerial fallout of lead from a smelter) to several washing and extraction procedures. The conclusions obtained showed that a large proportion of the metal burden was found to be present as superficial deposits removed by washing and comprised water-soluble and insoluble deposits. The distribution of metals on, and in, the leaves varied significantly between different species.

As a result of these investigations, I considered initially two washing techniques on leaf samples of Hebe odora and Cassina vauvilliersii, subjected to contamination from the fallout of lead from automobile exhausts.

The leaf samples were washed with:

- (i) deionised-water (used to assess the water-soluble fraction)
- (ii) 2% detergent solution

Each sample was placed in a polypropylene bottle with 50 ml of solution and shaken for 1 hour on a reciprocating shaker. The aliquots of solution were obtained by vacuum filtration and prepared for analysis. Leaf samples were repeatedly washed three times with the appropriate solution which was added to the aliquots for analysis. Each leaf sample was prepared for replicate washings.

Table I.4 shows the proportion of lead removed by washing compared with unwashed Hebe odora and Cassina vauvilliersii leaf samples.

The washings with distilled deionised water removed only a small amount of the total lead content

Table I.4

The Mean % Lead Content Removed By Washing

	<u>ppm Pb</u> <u>Unwashed Sample</u>	<u>Mean ppm Pb</u> <u>Removed by washing</u>	<u>% Total Pb</u> <u>Removed by washing</u>
<u>H. odora</u>	340		
Deionised water		120	35.29
Detergent		230	67.64
0.2M HCl		320	94.11
Boiling deionised water		135	39.70
<u>C. vauvilliersii</u>	400		
Deionised water		130	32.50
Detergent		205	51.25
0.2M HCl		372	93.00
Boiling deionised water		140	35.00

of the leaf (water-soluble fraction) and showed that most of the lead had been either chemically bound in the plant by absorption and/or translocation; or physically bound in some component of the leaf (cuticle).

Washings with 2% detergent solution gave a considerable increase in the total % lead removed. Therefore, 50-60% of the lead has physically attached to the cuticular surfaces, but was not easily removed by water alone.

Also shown in Table I.4 are the values of two extended washing techniques:

- (i) acid; 0.2M HCl
- (ii) boiling deionised H₂O

As shown in Table I.4, over 90% of the lead content is removed with acid washing. Therefore, most of this metal is bound to the surface of the leaf by exchange phenomena or has been absorbed and translocated. Since such a small percentage of lead remains in the leaf after washing in acid, it seems probable that the acid is causing cellular and cuticular damage, releasing metal from cuticular binding sites and cell walls and membranes.

Boiling with distilled water will rupture the cell membranes, releasing intracellular metal, but lead may be bound to fragments or bound ionically to cell-wall binding sites (Martin and Juniper, 1970). Also it is noticeable that the total % lead removed by washing for the two species is significantly different especially that bound physically to the cuticular surfaces and removed by 2% detergent solution. Such factors as leaf surface area and density could account for this especially since Hebe odora has a higher percentage removed by washing and has the greater leaf surface area and vegetative density. Also the distribution of soluble and insoluble lead on and inside the leaf varied widely between the two species.

In conclusion, the superficial deposit removed by washing, comprises soluble and insoluble fractions of lead. The distribution and accumulation within the leaf, especially between different species, shows that washing with deionised water removes only a small part of the total lead content. For a reproducible analytical result, a standard washing procedure is obviously required.

(c) Ashing of samples

For atomic absorption analysis it is necessary for the sample to be in solution and for plant samples there are two main ways of achieving this:

(i) dry ashing at 450 to 500°C in a muffle furnace

(ii) wet ashing with mixtures of concentrated perchloric, nitric and sulphuric acids at approximately 100°C (Allen and Hamilton, 1952).

The choice between these two methods for lead, favours dry ashing since although lead is a relatively volatile metal, it is not removed to any appreciable extent when dry ashing is carried out below 500°C (Mitchell, 1964). Dry ashing at 500°C was also preferred to wet ashing, because in the latter procedure there is more risk of contamination from the reagents (which normally contain an appreciable amount of lead).

An investigation was carried out to determine the loss of lead by ashing at various temperatures as follows:

Samples (0.1 g) of leaves and twigs of Hebe odora and Beilschmiedia tawa, and a 1000 ppm lead standard added to Whatman (No.1) filter paper, were dry ashed at the temperatures of 200, 400, 500 and 600°C for 3 hours. The ash was dissolved in 2M hydrochloric acid and the results are shown in Table I.5.

From this Table I.5 it can be seen that at 500°C greater than 95% recovery was obtained. At higher temperatures the % recovery decreased due to the

Table I.5

Lead Content (ppm Ash weight) for Plant Samples
After Dry Ashing at Various Temperatures ($^{\circ}\text{C}$)

	200	400	500	600
<u>H. odora</u>				
leaves	20	100	220	170
twigs	40	70	110	90
<u>B. tawa</u>				
leaves	80	80	112	58
twigs	20	50	80	60
Standard				
value	200	600	988	800
% recovery	20%	60%	98.8%	80%

the volatilisation of lead.

Temperatures below 500°C, shown by the percentage recovery in plant ash values, indicate that incomplete ashing with the resulting incomplete dissolution on addition of the acid to the ash is likely.

In conclusion, a temperature of 500°C is most suitable for the highest percentage lead recovery of samples using the dry ashing method.

(d) Acid digestion of sample

The efficiency of decomposing a sample depends upon the ability of the subsequent treatment to convert the constituents into soluble components.

A 1:1 mixture of nitric acid (4M): hydrochloric acid is effective in decomposing all but the most refractory of silicates and gives a complete decomposition of all lead minerals.

In conclusion, all samples were acid digested using the above mixture. The substitution of the above acid mixture with aqua regia (hydrochloric:nitric acid 4:1) is unfavourable for samples with a very high organic carbon content. In general, sulphuric acid has been avoided for acid digestion of soil samples because of the possibility that lead sulphate may be co-precipitated with barium or calcium (Jeffery, 1968).

SECTION II
LEAD POLLUTION FROM
MOTOR-VEHICLE EXHAUSTS
IN
PALMERSTON NORTH

A. INTRODUCTION

Analysis of vegetation and soils to show the distribution and accumulation of lead as a result of petrol combustion and discharge from motor-vehicle exhausts along major highways has been investigated in several places in recent years. Warren and Delavault(1960) observed that lead levels in vegetation near major highways were inordinately high. Cannon and Bowles (1962) showed the accumulation of lead in vegetation collected at varying distances from major highways. The lead content of plant ash ranged from 100 to 700 ppm, depending on the distance, traffic volume, and direction of the prevailing wind.

Further studies have been carried out in Sweden by R nling and Tyler (1968), and in the U.S.A. by Singer and Hanson (1969). Lead concentrations have also been reported in vegetables by Cannon and Anderson (1971) and in Spanish moss by Martinez et al (1971).

With the rapid increase in the number of motor-vehicles on roads in New Zealand (from 505,000 to 911,000) between 1960 and 1970, and the increase of petrol consumption from 1050 to 1800 million litres during the same period, a considerable quantity of lead is now being emitted annually. The figure for 1970 may be estimated at 700 tonnes, based on a value of 0.7 g of lead per litre, together with the assumption that about 60% finds its way into the atmosphere. Recent figures for the U.S.A. indicate an annual consumption of lead alkyls of about 300,000 tonnes, of which about 180,000 tonnes appear in the atmosphere as emission from motor-vehicles (Stoker and Seager, 1972).

Although traffic densities in most places in New Zealand have not reached the levels found in metropolitan areas in some parts of the world, it is considered that the levels found in Fitzherbert Avenue, (Palmerston North) should apply to any

thoroughfares of a similar nature and traffic density, i.e. to major thoroughfares of small cities (e.g. 20-100,000 population) and to major suburban roads of larger cities. The traffic flow on the thoroughfare averages 11,500 vehicles per day over its length, with peak flows of about 1400 vehicles per hour.

B. LEAD IN TREES

1. Introduction

The effects of lead emission from motor-vehicle exhausts upon mature trees growing along major thoroughfares and highways have shown that the lead content increases with increasing traffic density and decreases with increasing distance from the roadway. Generally, lead contents are less than 50 ppm and frequently less than 10 ppm (Ault et al, 1970; Holtzman, 1970; Rühling and Tyler, 1968; Warren and Delavault, 1962).

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. Dep. Health, Educ., and Welf. 1970). Eighty-five % of the air-borne particles are less than 4 μ in diameter (Daines et al, 1970). Most of these are removed from the atmosphere within approximately 35 m of the roadway due to gravitational settling and impaction on various obstacles. As a result, the change in lead concentrations may be inferred from measurements of lead in tree rings (Schroeder et al, 1961).

Lead deposited in the annual rings of an elm tree growing about 50 m from a suburban street with light traffic showed the following trend: 1865-1879, 0.16 ppm; 1900-1912, 0.12 ppm; 1940-1947, 0.33 ppm; 1956-1959, 0.74 ppm; and 1960, 3.90 ppm. Presumably, the source of lead contamination in such areas could have been the soil or the air (Smith, 1971).

As a preliminary investigation, the lead content of bark samples from trees growing along Fitzherbert Avenue were determined to show any significant levels of contamination and the influence of traffic density and the direction of the prevailing wind. Bark and leaf samples were then collected to evaluate the distribution and contamination of the lead particulate burden. Changes in the lead concentrations were

determined in annual rings of trees sampled by ring-cores.

The results of these investigations are reported in this sub-section.

2. Sampling and analysis

Trees investigated

The following trees were studied: Acer pseudo-platanus L. (sycamore), Aesculus hippocastanum L. (horse chestnut), Fraxinus excelsior L. (ash), Quercus robur L. (oak), Platanus orientalis L. (plane), and Ulmus procera L. (elm).

Sampling procedures

Samples were taken from trees at various points along Fitzherbert Avenue, Palmerston North. Sampling sites are shown in Fig. II.1.

Samples of bark were taken at 1 m intervals from the east and west sides of each tree at various heights from the ground to 3 m. For some plane trees sampled, an inner bark sample was also taken.

Leaf samples were taken at approximately 4 m height and divided into washed and unwashed groups.

Trunk cores were taken by the use of an increment borer which was 1 cm in diameter. Each core was divided into estimated year groups (determined from annual ring growths) which were then analysed. Further samples, referred to as background, were taken from the west sides (windward) of trees in areas at a distance of more than 80 m from the nearest road.

Chemical Analysis of Vegetation

All bark and leaf samples (including trunk cores) were prepared for analysis as described in Section I.

3. Results and discussion

(a) Lead in bark of trees

Fig. II.2 shows mean values for the lead content (ppm) of ashed bark samples (71) taken from both sides of the road at a height of about 2 m from both sides of each tree, (adjacent and opposite to the roadway),

Fig. II.1. Map of Fitzherbert Avenue, Palmerston North, showing the location of trees sampled.

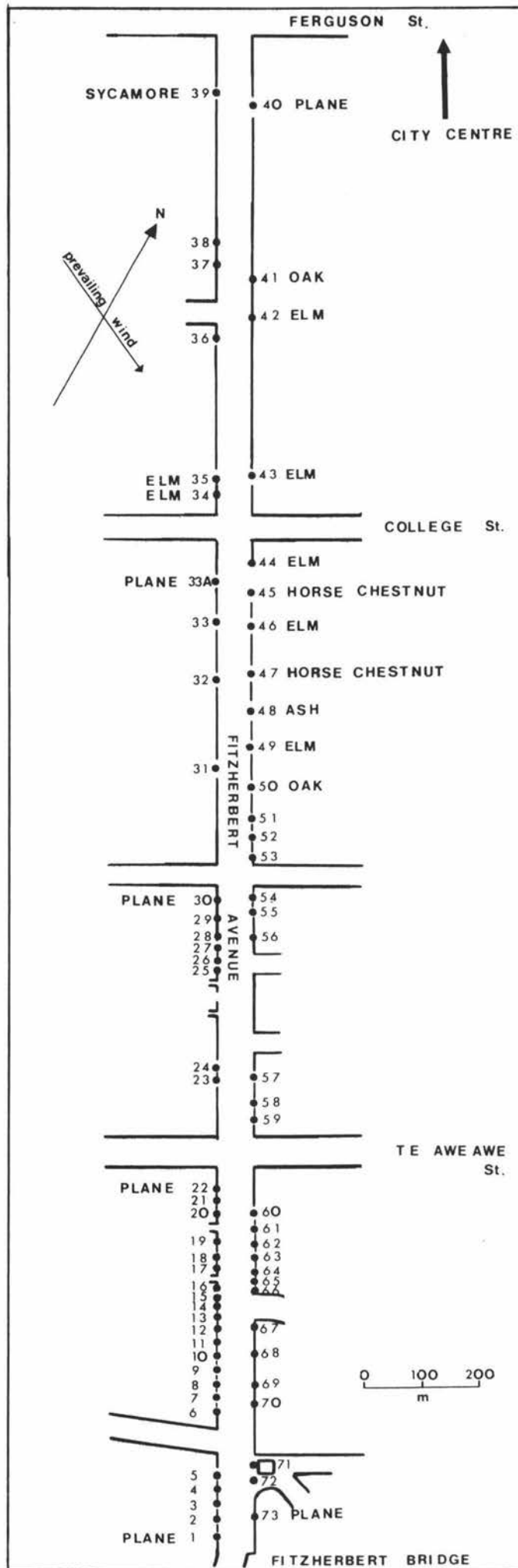
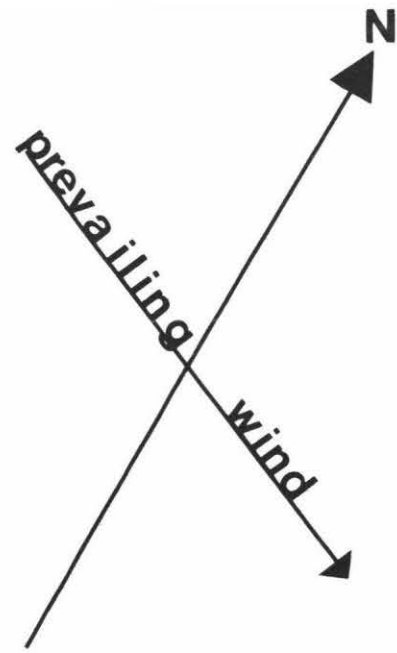


Fig. II.2. Idealised section (plan) across Fitzherbert Avenue, showing mean values for lead (ppm ash weight) in bark samples taken from opposite sides of trees.



750 TREE 840

FITZHERBERT
AVENUE

1080 TREE 770

and taken without regard to species differences. Background samples (17) averaged only 90 ppm. The prevailing wind is from the west-northwest direction. The 71 trees sampled, included two oaks, one sycamore, one ash, eight elms and two horse chestnuts. The remainder were planes.

Fig. II.2 shows that the lead contents of the sides of the trees away from the road were approximately the same for both sides of the road (750 ppm and 770 ppm for the west and east sides respectively). The sides facing the road showed a marked difference and samples on the east side contained 1080 ppm compared with 750 ppm. A t test showed that this difference was significant at the 97.5% level of probability and was to be expected in view of the prevailing wind direction. In general, the lead content of "Avenue" trees was ten times greater than those taken from background areas.

Having established that lead concentrations in bark were remarkably high, I then examined the vertical distribution of lead in the bark of the sides of plane trees facing the roadside. These data are shown in Fig. II.3.

There is a clear pattern of increase of lead values from ground level up to a height of about 1-2 m. Thereafter the levels decrease. These observations conform to a pattern of emitted lead leaving the vehicle at a height of about 0.25 m and rising to strike the bark of the trees at about the 2m level.

In order to examine the degree of penetration of lead from motor-vehicle exhausts, successive bark layers of plane trees were also analysed. There was a considerable difference in concentrations in the inner and outer barks as shown in Table II.1. From this table it is clear, at least for planes, that the absorption of lead in the bark is only superficial

Fig. II.3. Vertical distribution of lead (ppm ash weight) in bark samples of various trees:

- = outer bark of trees growing along Fitzherbert Avenue;
- ▲ = outer bark of trees growing in background areas;
- ◆ = inner bark of plane trees growing along Fitzherbert Avenue.

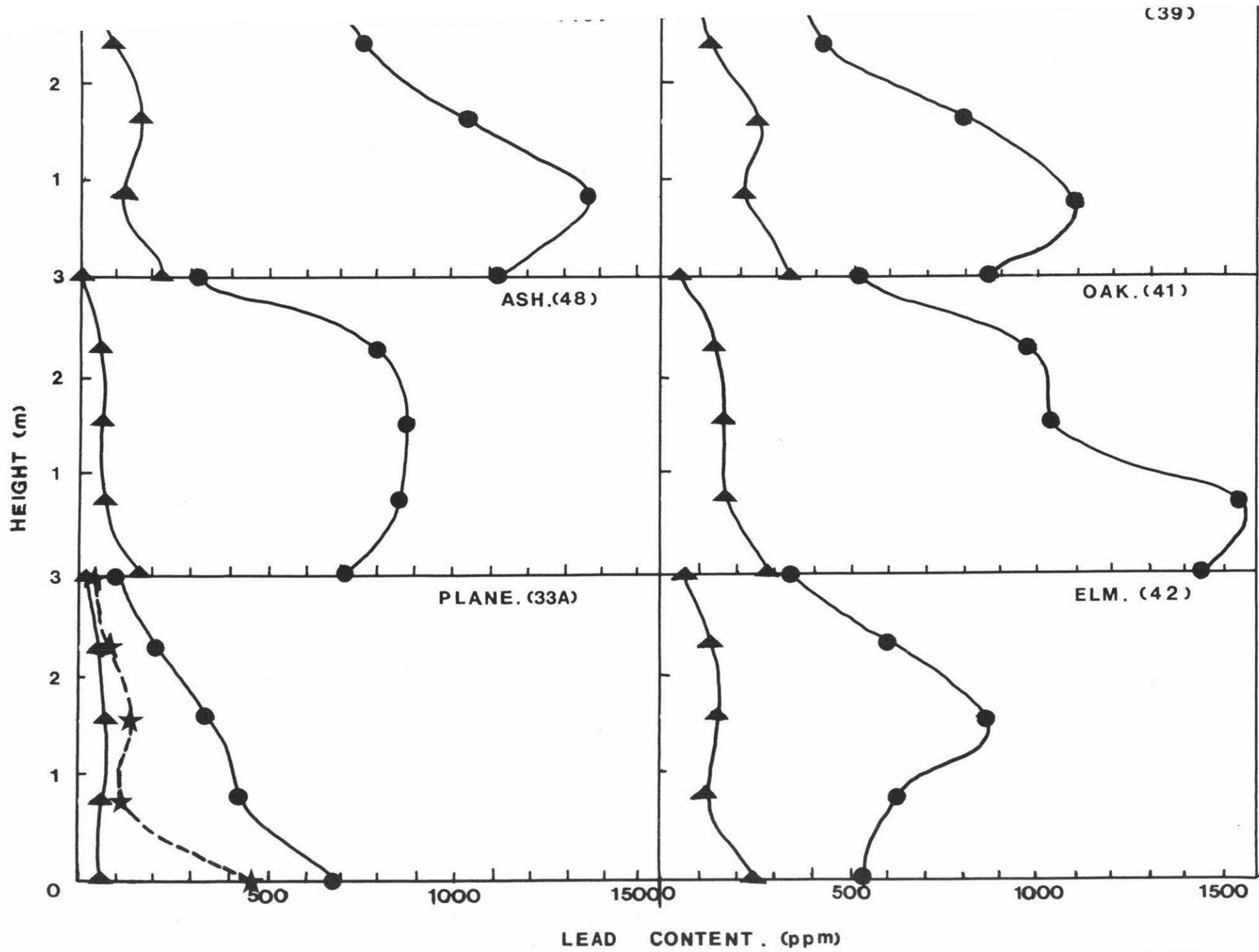


Table II.1

Maximum Lead Content (ppm ash weight) of
 Inner and Outer Bark Layers of Plane Trees growing
 Along a Major Thoroughfare in Palmerston North

<u>Position (Fig. II.1)</u>	<u>Lead in outer bark</u>	<u>Lead in inner bark</u>
1	810	130
22	580	80
30	760	100
33A	660	160
40	1800	450
73	1240	560
Background	80	50

and this element is probably removed from the tree as the outer bark peels off, falls to the ground, decays and enriches the lead content of the surface soil. Values for inner bark compared with outer bark are also shown in one of the plots in Fig. II.3.

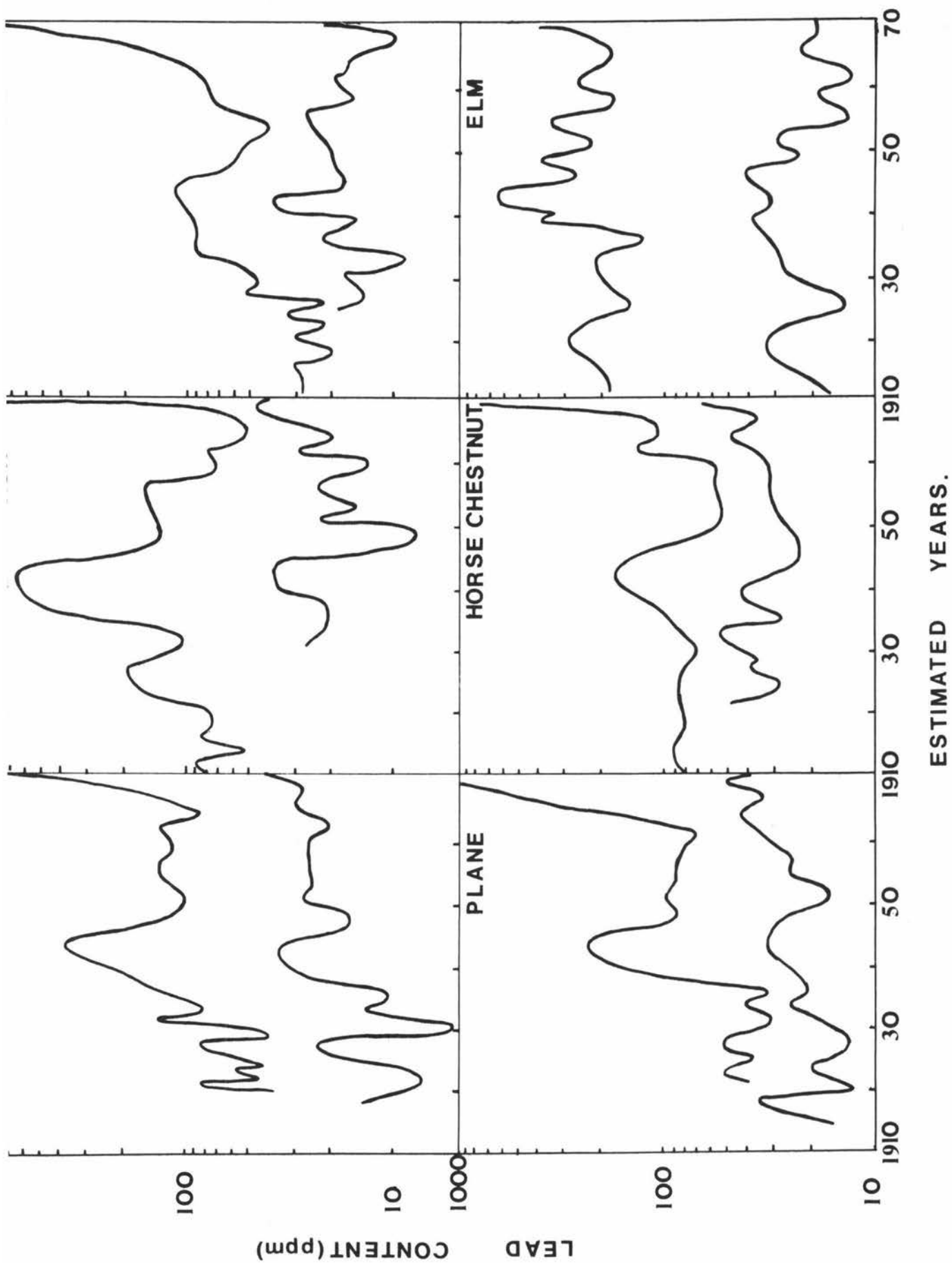
(b) Lead in annual rings of tree trunks

It is clear that the lead content of the surface soil is sufficiently high to permit appreciable lead absorption by the root system and its mobilisation into the trunk, branches and leaves. It is also possible that lead could diffuse from the outside of the trunk into the heartwood. However, because of the very sharp decrease of lead concentrations between the outer bark and inner bark of planes, it is considered that the most probable absorption pathway of lead is via the root system.

Fig. II.4 shows the lead content of annual rings. (ppm ash weight) plotted as a function of the age of each ring or group of rings. Examination of the pattern of the accumulation of lead shows a general increase since 1923 coinciding with the introduction of lead tetraethyl to petrol in New Zealand. There is a slight increase during the 1939-45 period with a marked decrease after 1946. This was probably due to the large amounts of poor quality petrol, high in additives, introduced into New Zealand during the war years. During 1945-46 there was a marked decrease in the amount of petrol available.

There was a steady increase in the amount of lead until the middle 1960's where the increase was extremely high. For plane No. 40 which is the most polluted tree, owing to its position at highest traffic density and exposure to the prevailing wind, there was an increase from 78 ppm ash weight (1961) to 1429 ppm (1971). This showed a great increase in

Fig. II.4. Lead content (ppm ash weight)
of annual rings of various trees:
upper line: from Fitzherbert Avenue;
lower line: from background areas.



accumulation and is largely due to the increase in the petrol consumed in Palmerston North (estimated from the number of motor-car registrations) which has doubled from 230 (1961) to 420 (1971) million litres.

(c) Lead in leaves of trees

The lead content of washed and unwashed ashed leaves is shown in Table II.2.

The values were in most cases at least five times background and correlated well with sites of maximum traffic density. Because the washed leaves were only slightly lower in lead than the unwashed samples, it is suggested that the lead is not present as easily-removable particulate matter. This is in agreement with findings of Cannon and Anderson (1971). Absorption is probably partly aerial absorption from motor-vehicle exhausts and partly indirect absorption via the root system.

Microscopic examination of intact samples of White pine needles sampled within 15 m of a 24,000 vehicle per day highway on the wind-borne side (Smith, 1970) revealed accumulations of large particulates near the fascicle sheath at the needle base and on twigs and buds where outer tissues were rough. In all probability, lead particles are initially impacted on needles and subsequently washed down the needles by precipitation.

- As shown by the lead content removable by washing plane leaves, such a postulate cannot be made directly for the Fitzherbert Avenue leaf samples, keeping in mind that pine needles are also particularly efficient accumulators due to their high surface to volume ratio and year-round persistence. The data presented here give a general indication of the magnitude and distribution of lead emission affected by the prevailing wind and regions of high traffic density.

Table II,2

Lead Content (ppm ash weight) of Washed and Unwashed Leaves of Various Trees Growing Along a Major Thoroughfare in Palmerston North. Background Areas are Included for Comparison.

Species	Thoroughfare trees		Background	
	Washed	Unwashed	Washed	Unwashed
Ash	440	440	80	90
Elm	680	860	60	80
Horse Chestnut	460	520	50	60
Oak	580	920	100*	130*
Plane	1020	1060	80	90
Sycamore	840	900	20	40

* Samples not true background (40 m from road)

C. LEAD IN SOILS

1. Introduction

Lead particulates suspended in the atmosphere will eventually fall to the ground as precipitation or dust. These lead compounds accumulate in the top-soil (Singer and Hanson, 1969; Chow, 1970) and is responsible for the high lead concentrations found in soils along highways and around centres of industrial fallout; smelters, mining activities and foundries. (Lagerwerft and Specht, 1970; Motto *et al*, 1970; Page and Garje, 1970; Warren and Delavault, 1971). By analysing contaminated soils in such regions, a relative estimate is achieved of the total aerial burden of lead presumed to originate both directly from the source (dusts, smokes and motor-vehicle exhausts) and indirectly from environmental and geographical conditions, such as wind direction, rainfall and climate (Goodman and Roberts, 1971).

The lead content of soils is of the order of its crustal abundance (15 ppm) because of the stability of this element in the geochemical cycle. Natural levels can range from 1 to 100 ppm depending on the nature of the substrate from which the soils were formed.

Soil samples from various metropolitan areas can contain lead levels ranging from 100 to 3000 ppm. Lead pollution patterns from motor-vehicle exhausts (Daines *et al*, 1970) have been found to be related to traffic volume, proximity to the highway, engine acceleration at constant speed, wind direction, and the amount of lead in the air.

The following data presented here show the lead levels in soils taken along Fitzherbert Avenue; an environment with relatively high mean wind velocities (17.0 km per hour) and with traffic densities which at peak periods (1400 vehicles per hour) are not as high as in many major European or North American cities previously studied.

2. Sampling and analysis

Samples of soils were collected at the base of trees by a core extractor (2.5 cm in diameter) to a depth of 20 cm, at a position within 1 m of the tree on the side facing the road. The cores were divided into 2.5 cm samples for analysis.

All soil samples were prepared for analysis as discussed in Section I.

3. Results and discussion

Lead in soils

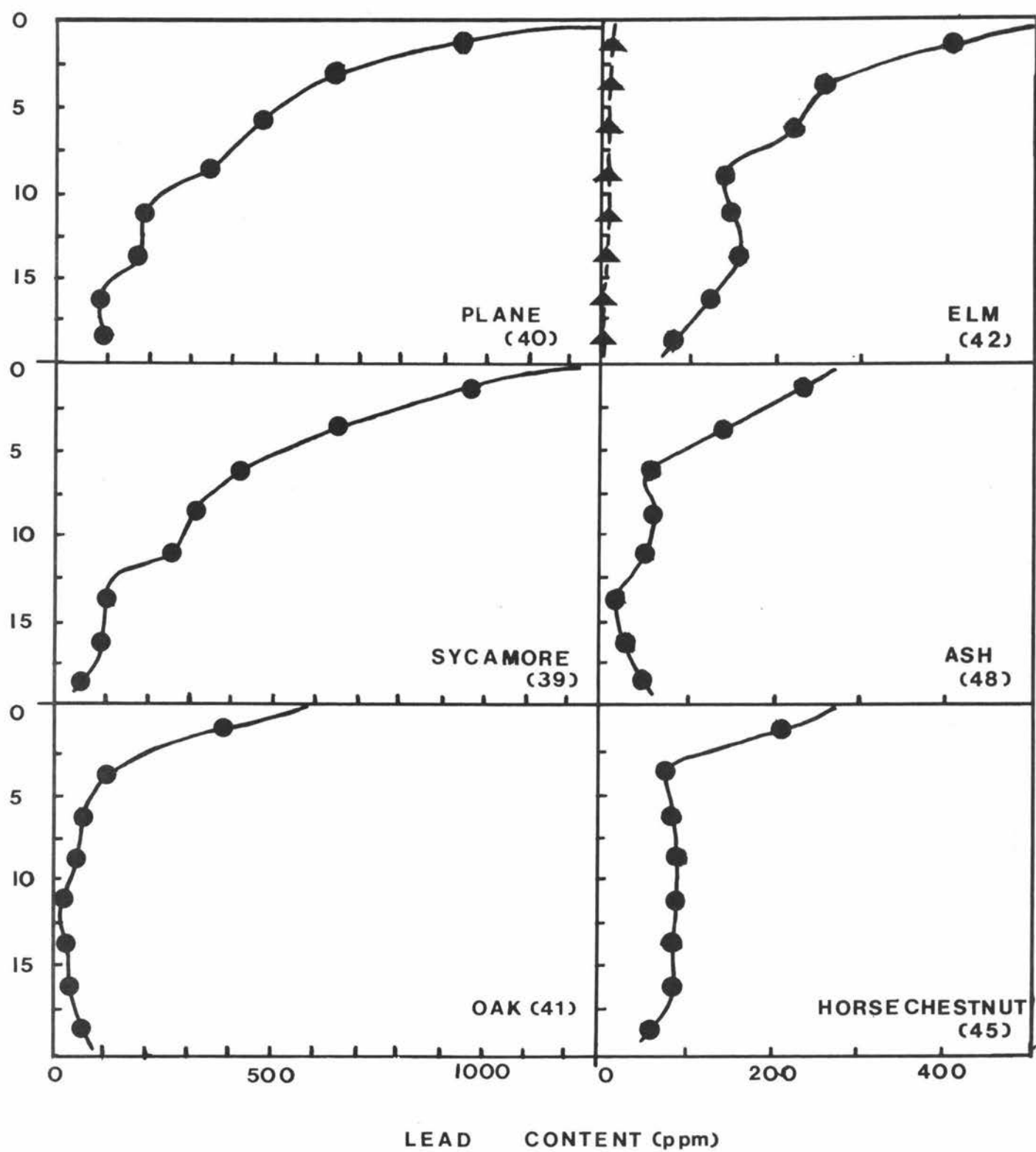
The distribution of lead in soils is shown in Fig. II.5. The difference between "Avenue" and background samples is large, showing accumulation at the surface and a decrease with depth. The value for plant No. 40 shows a high lead contamination at the surface of the soil (2985 ppm) compared with background (15 ppm). Even at lowest depths sampled (20 cm), a value of 130 ppm compared with 5 ppm (background) is obtained. This suggests some leaching of lead into the soil but accumulation at the surface as suggested by Chow (1970).

The magnitude and distribution of lead emission along Fitzherbert Avenue show quite clearly the effect of areas of high traffic density along the thoroughfare, (such as plane 40 and sycamore 39) situated near a major cross-road (Fergusson Street) and at a distance of 30-40 m from traffic lights. At such positions, vehicle engine acceleration and exhaust emissions are greatest, contributing a major factor to the amount of lead emitted into the air, (Daines et al, 1970). In contrast, the position of ash 48 is such that lead levels are lower as a result of reduced traffic volumes and constant engine emissions.

In conclusion, lead levels in the soil, although conservative compared with expected levels in urban areas of extremely high traffic densities (100,000 to

Fig. II.5. Vertical distribution of lead (ppm)
in profiles of soils taken from the
base of various trees:

● = soils from Fitzherbert Avenue;
▲ = soils from background areas.



50,000 vehicles per hour) found in some North American cities, give a general indication of the magnitude and distribution of lead emission for a moderately busy thoroughfare.

D. SEASONAL VARIATION OF LEAD IN LEAVES AND SOILS
ALONG MAJOR THOROUGHFARES IN PALMERSTON NORTH

1. Introduction

One of the factors that influence the uptake of trace elements by plants is the age variable of the various plant organs. There is some evidence for appreciable variation in the elemental content of plants of the same species but of different ages. Certain plant organs (leaves especially) show that the elemental content is influenced by seasonal factors.

The uptake of rare earths by the hickory tree (Robinson, 1943), showed variations for June 1st, July 1st and October 1st of 174 ppm, 634 ppm and 981 ppm for the same year. Similar observations have been made for the boron content in hickory trees (Robinson and Edgington, 1942) which doubled in the leaves between spring and fall. Seasonal variations have also been noticed for molybdenum (Barshad, 1951) and for copper and zinc (Warren and Howatson, 1947).

Other investigations have shown that seasonal differences in the concentration of elements in leaves occurs, especially with increases toward the time of development of the reproductive organs, (Molyuga, 1939; Chebaevskaya, 1960). The metal content of many deciduous leaves rises to a maximum just before ~~ex~~foliation; this is probably a convenient mechanism whereby plants can get rid of unwanted ballast elements. Guha (1961) examining 6 elements in leaves of 18 deciduous species showed convincingly the seasonal variations of elemental content.

The purpose of the investigations reported in this section was to determine the influence of seasonal variations on the total lead content of leaves from trees in Fitzherbert Avenue and dust samples taken

at similar positions, along with sites in the central city area, (Palmerston North Square).

In contrast, the lead content of Whatman paper filters was determined in relationship to the time of exposure to motor-vehicle exhaust emissions at similar seasonal periods.

2. Sampling and analysis

Samples of leaves were taken from trees 39-42, 45 and 48 (and background areas) as shown in Fig. II.1. These were from the tree species indicated earlier in Section II. The first sampling corresponded to a time of two weeks growth (from the bud stage) with successive sampling occurring from the same branch and height every month. Special attention was focussed on the relative size of the leaves sampled, to enable a uniform collection of totally exposed (seasonal) leaves.

All leaf samples were prepared for washing and analysis as described in Section I. Results were expressed as ppm Pb (ash weight).

Whatman (5.4 cm diameter) filter papers were placed at a height of 1.5 m above the road surface on the outer bark of trees 39, 40 and 73. They were placed in a position of maximum surface area exposure to motor-vehicle exhaust emissions. Filters were collected every month, and prepared for analysis using the same technique as for leaves (no washing). Results were expressed as $\mu\text{g Pb per cm}^2$ (filter paper), over a period of 6 months sampling.

The seasonal variations in the lead content of dust were determined by collecting dust samples at the side of the road, at depths of 0-2 cm and at 6 positions within the Palmerston North City area; Fitzherbert Bridge (Eastern extension of Fitzherbert Avenue), Fitzherbert Avenue-Fergusson Street corner,

and the four corners of the Palmerston North Square. Samples were taken monthly and prepared for analysis, and analysed as described in Section I. Results were expressed as ppm Pb (dry weight).

3. Results and discussion

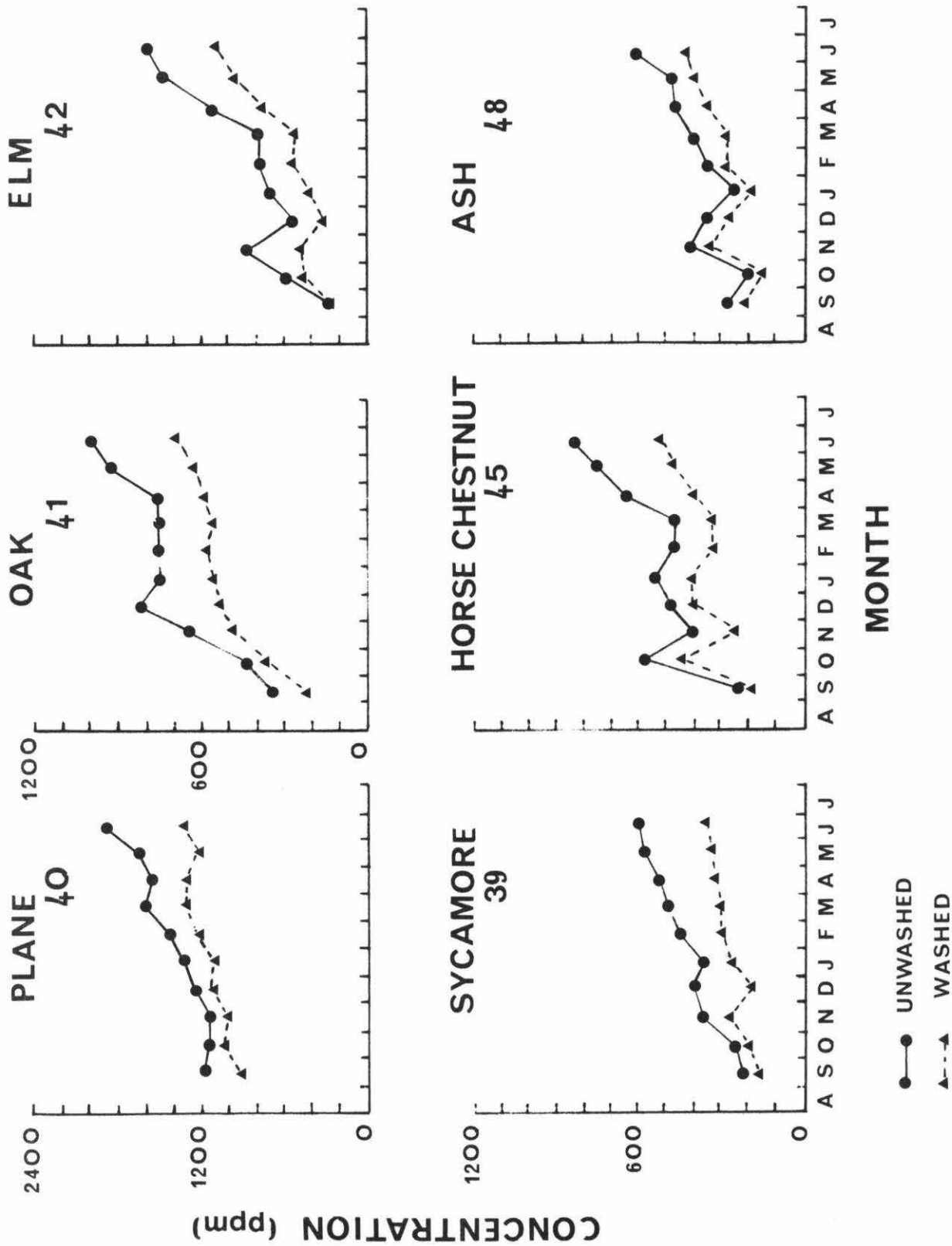
(a) Seasonal variation of lead in leaves

Fig. II.6 shows mean values for the lead content (ppm) of washed and unwashed ashed leaves as a function of seasonal variation (expressed in months). Samples were analysed without regard to the number of leaves ashed and expressed in concentration units (ppm) for that month.

There is a clear pattern of gradual seasonal increase in lead concentration from the time of first sampling after two weeks growth in September to ex-foliation in June and July. Similar patterns were noticed by Chebaevskaya, (1960) and Guha (1961). These observations conform to a pattern of increased lead content at a higher level than would have been expected to compensate for leaf growth alone. Such levels associated with an increasing leaf surface area could increase the degree of exposure leading to absorption and accumulation of lead within the leaf. Also with the increasing age of a leaf, the degree and time of absorption of lead into the leaf is dependent upon the weight factor. Differences in concentrations may only be superficial as a result of dilution of lead with the increasing weight of the leaf associated with constant lead absorption.

It is noteworthy that such high lead levels occurring within leaves after only two weeks of development, indicate a rapid accumulation of lead followed by an equilibrium between absorption and growth. Although no direct conclusion can be drawn from this, it is suggested that such factors as the degree of absorption by buds, and leaf growth

Fig. II.6. Seasonal variation in lead content
(ppm ash weight) in leaves from
various trees.



mechanisms (especially within the first few weeks of development), could influence the degree of penetration and accumulation of lead within the leaf.

The values for washed leaves show no direct pattern of seasonal variation compared with unwashed leaves, although fluctuations may be a result of rainfall, and other climatic factors.

The effect of the prevailing wind from the west-northwest direction and traffic density are shown in the considerable difference in lead concentrations for plane 40 compared with the other trees sampled. In general, background values fluctuated from 20-80 ppm lead (ashed weight) over the seasonal period showing no correlation with seasonal increases in the lead content of leaves.

Having established that lead levels in leaves followed a pattern of gradual seasonal increase, the lead content of individual leaves was determined ($\mu\text{g Pb per leaf}$) and expressed as a function of the surface area of the leaf (cm^2) as shown in Fig. II.7.

The pattern of accumulation of lead with increasing leaf surface area shown as a straight line relationship, suggests that absorption is probably a direct result of aerial absorption from motor-vehicle exhausts. The gradient of the straight line gives an indication of the lead content ($\mu\text{g Pb per cm}^2$) per leaf. The value obtained for each tree sampled is shown in Table II.3. The values obtained show a steady pattern influenced by the amount of lead absorbed and is a function of the position of the tree, traffic density, and exposure to the prevailing wind.

(b) Seasonal variation of lead in filters

Fig. II.8 shows the lead content ($\mu\text{g per cm}^2$) of exposed Whatman filter papers (attached to trees at a height of 1.5 m along Fitzherbert Avenue), as a function of the time of exposure (expressed in months).

Fig. II.7. Lead content (ug lead ash weight per leaf) as a function of the surface area per leaf (cm²).

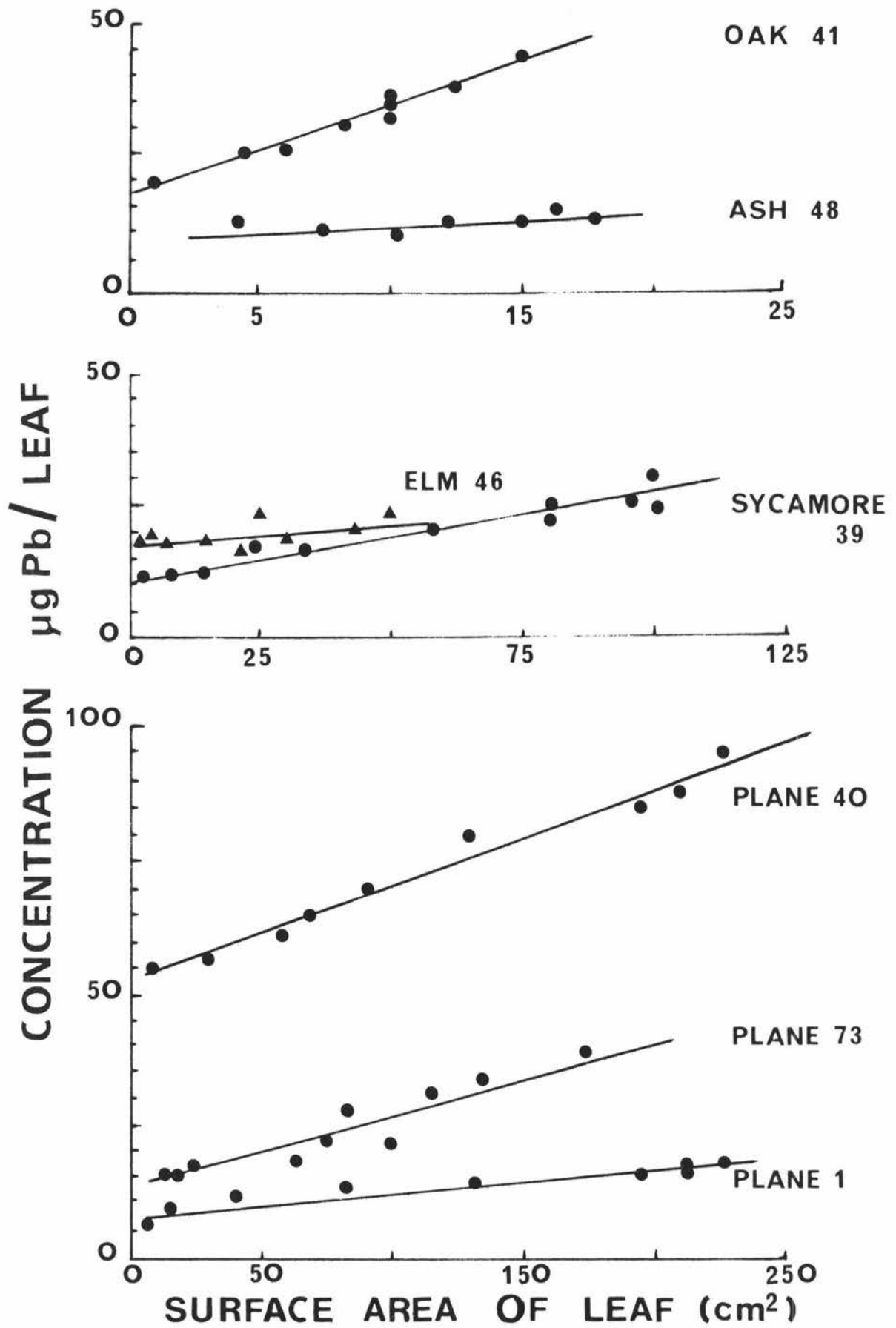


Fig. II.8. Lead content ($\mu\text{g per cm}^2$) of exposed filter papers attached to various trees, as a function of the time of exposure (months).

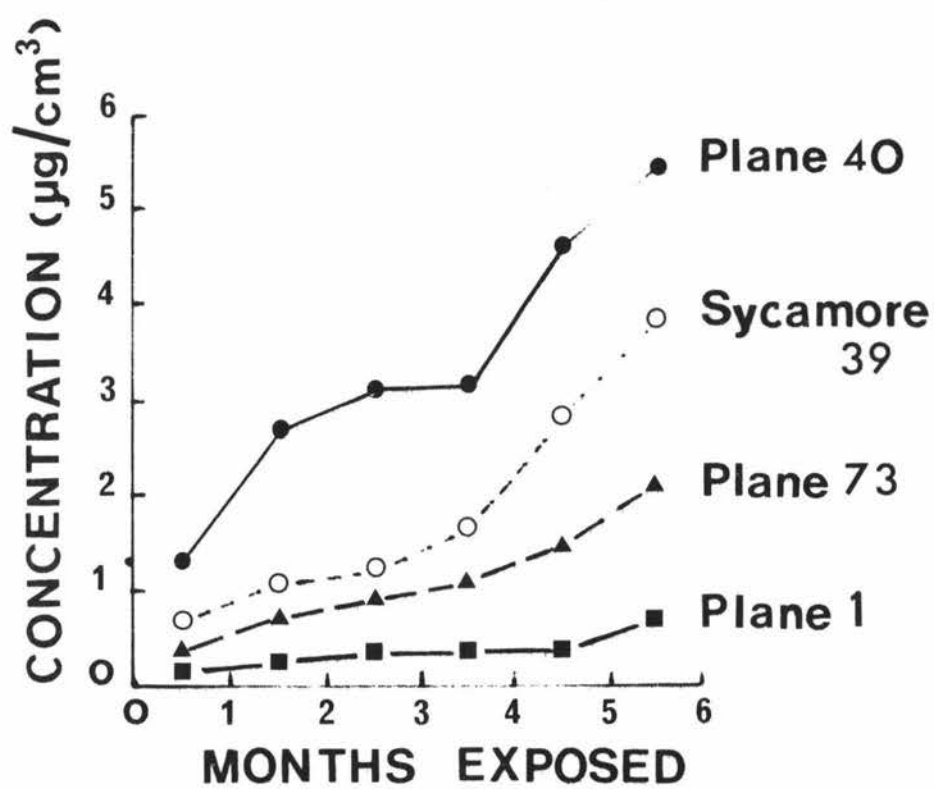


Table II.3

Mean Lead Content ($\mu\text{g}/\text{cm}^2$) of Exposed Leaves and
Filter Papers taken along Fitzherbert Avenue.

<u>Sampling site</u>	<u>Mean Lead Content ($\mu\text{g}/\text{cm}^2$)</u>	
	<u>Filter</u>	<u>Leaf</u>
Plane No. 40	3.380	0.175
Sycamore 39	1.890	0.150
Plane 73	1.100	0.130
Plane 1	0.330	0.055

Examination of the pattern of the accumulation of lead gives direct evidence of air-borne lead absorption as the major source influencing lead levels found in plant vegetation. As previously shown, the degree of accumulation is dependent upon the position of the tree relative to traffic density and the exposure to the prevailing wind. Filters sampled in background areas showed negligible lead content with the time of exposure.

The mean (6 months) lead content ($\mu\text{g}/\text{cm}^2$) for filter papers at each sampling position are shown in Table II.3 as a comparison to those levels derived from exposed leaves.

It is clear that the lead content of leaf samples is considerably lower than for filters. Overall there is a ten-fold factor in the lead content between planes 40 and 1 for the filters compared with only a three-fold factor for the corresponding tree leaves. It is suggested that such differences are due to the varying retention mechanisms between leaves and filter papers. The degree of penetration of lead from motor-vehicle exhausts is higher for filters than for leaves. As shown by Smith (1971), the capacity of particulate filters is dependent upon the particulate burden.

The significant difference between lead levels in filters and the associated leaves is dependent upon the nature of the lead contamination and the uptake mechanism. For leaves, if the lead salts are impacted on the outside of the leaf surface in an insoluble form, they probably remain on the outside of the epidermis. If, however, they are deposited in a soluble form (e.g. lead chloro-bromide) or are rendered soluble after impact, they are probably taken into the leaf through stomates and other openings, (Primault, 1958; Koeppe and Miller, 1970). The differences in such pore openings and surface

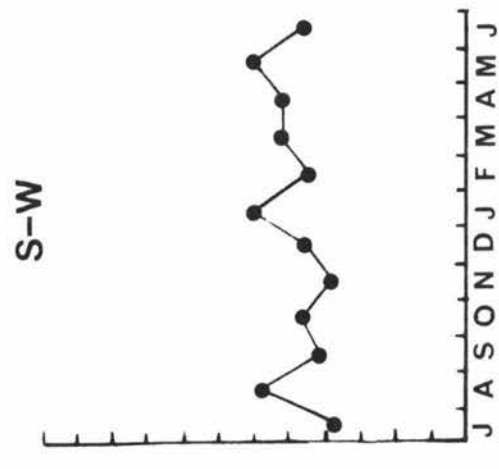
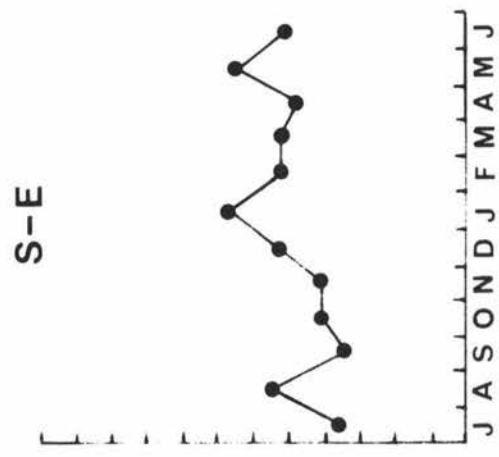
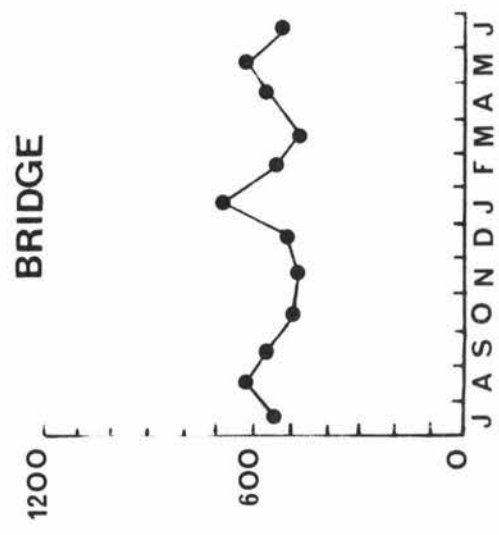
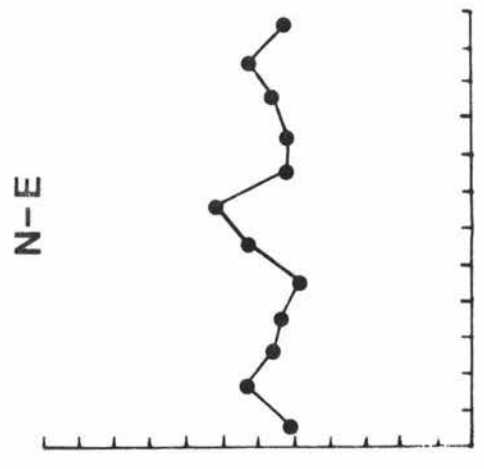
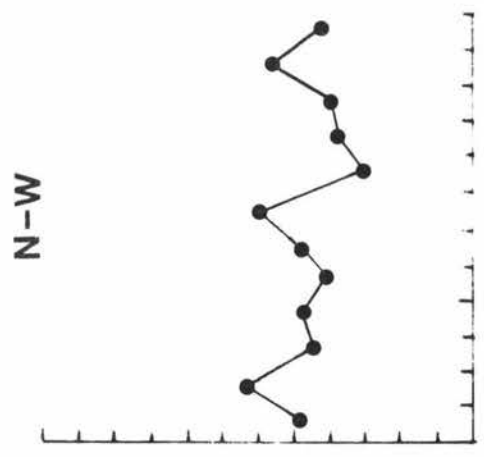
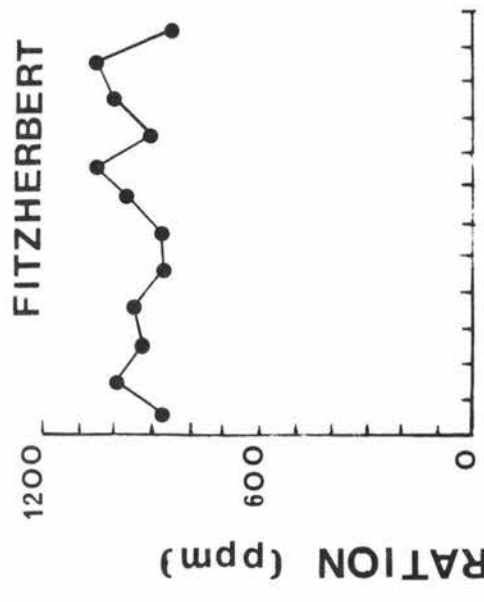
retention mechanisms give rise to the wide difference of lead concentrations between leaves and filters.

(c) Seasonal variation of lead in dust samples

Fig. II.9 shows the lead content (ppm) of dust samples collected along major Palmerston North thoroughfares, as a function of seasonal exposure (expressed in months).

There is no clear pattern of seasonal variation in lead values. The general data variation is most likely due to minor differences in climatic factors like rainfall, and external sources of lead from aerosols and dusts (other than from motor-vehicle exhaust emissions). Differences in traffic density at public holiday periods may contribute to a minor increase in the lead content, especially during January. There is no significant influence in the lead levels associated with the direction of the prevailing wind as shown in the similar patterns for Palmerston North Square samples taken at each corner (NW, NE, SE and SW). This is probably due to varying wind directions produced within a main built-up area. The effect of traffic density at a particular sampling site is only significant for those samples taken at the Fitzherbert Avenue-Fergusson Street corner.

Fig. II.9. Seasonal variation in lead content (ppm)
of dust samples in Palmerston North.



MONTH

SECTION III
LEAD POLLUTION ALONG A
NEW ZEALAND STATE HIGHWAY
WITH
LOW TRAFFIC VOLUME

1. Introduction

In recent years there have been many investigations into the distribution and accumulation of lead discharged from motor-vehicle exhausts. Most of these studies have involved analysis of soils and vegetation taken at various distances from the centre of traffic flow along major urban or inter-city highways. Lead levels of 100-3000 $\mu\text{g/g}$ have commonly been reported both in soils and in the ash of plants taken near roads carrying a high volume of traffic, e.g. more than 10,000 vehicles per day (Warren and Delavault, 1960; Cannon and Bowles, 1962; Ruhlung and Tyler, 1968; Singer and Hanson, 1969; Chow, 1970; Smith, 1972; Impens et al, 1973).

Fewer studies have been carried out in regions of low traffic density. Page and Ganje (1970) found that no significant lead had accumulated in soils over a period of about 40 years in areas of California that had a low density of motor-vehicles (≤ 80 per square mile), provided that samples were taken more than a mile from a major highway. Where the vehicle density exceeded 580 per square mile, general surface-soil levels were found to have increased from about 16 $\mu\text{g/g}$ to 31-52 $\mu\text{g/g}$ over the same period. It was concluded that the more excessive accumulations of lead in soils caused by heavy traffic exhaust emissions are localised near the point of discharge.

The present work consists of a detailed study of lead distribution near a New Zealand State Highway in an area where the traffic volume is relatively low (1200 vehicles per day), far removed from urban or industrial centres, agricultural operations, and other highways. The lead content of soils was measured as a function of both distance from the highway and depth, and the lead content of predominant plant species was also investigated.

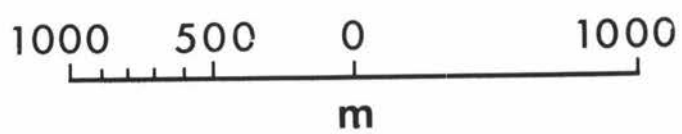
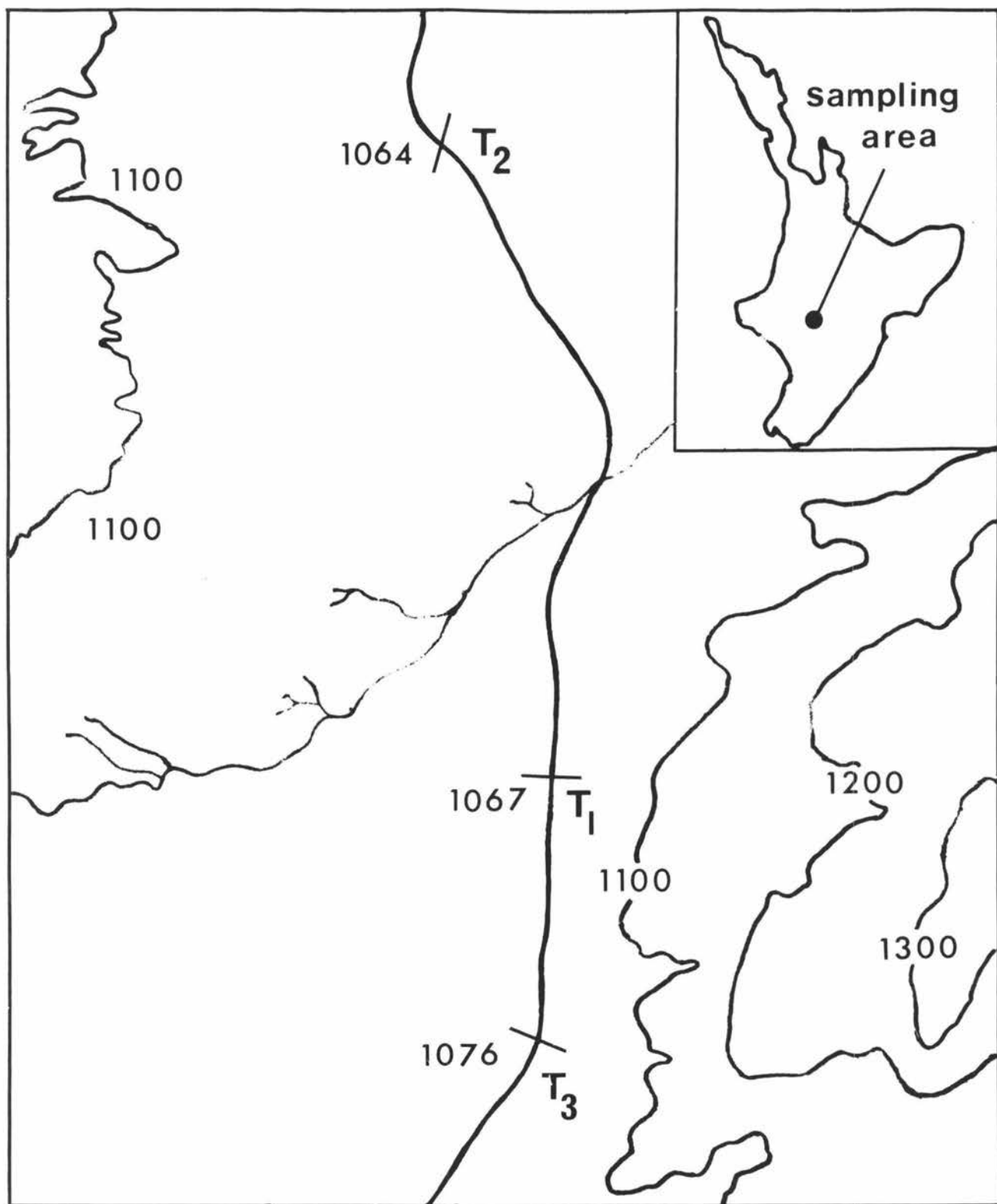
2. Study area and methods

The area selected for study is situated on New Zealand State Highway 1, in the centre of the North Island, about 20-25 km north of the town of Waiouru. The highway here traverses a volcanic plateau at an elevation of 1000-1100 m. The site is particularly suitable for this study for the following reasons:

- (i) there is no permanent habitation within 20 km;
- (ii) the highway runs in a general north-south direction across relatively flat terrain;
- (iii) to the east, the nearest public highway is more than 80 km away, separated by ranges of mountains up to 1700 m high, while to the west and north-west, highways and settlements are 25-30 km distant and are separated from the study site by the volcanic cones of Ruapehu (2797 m) and Ngauruhoe (2291 m);
- (iv) the volcanic soil supports vegetation consisting largely of tussock grasses, mosses, and small shrubs less than 1 m in height;
- (v) the area has not been used for agricultural operations and should therefore be completely free from lead-containing agricultural chemicals. The area has an average annual rainfall of 1426 mm, and a westerly wind is slightly predominant.

Samples of soil and vegetation were taken from three transects perpendicular to the direction of the highway at different points as shown in Fig. III.1. The species of vegetation studied were Cassinia vauvilliersii L. (cottonwood) and Hebe odora L. (koromiko). Vegetation close to the road near Transect 1 was first examined by taking samples of 10 specimens of C. vauvilliersii within 1-6 m of the edge of the road on each side, and a further 10 specimens in the 7-12 m range. H. odora was similarly sampled on the west side of the road, but was not sufficiently abundant on the east side.

Fig. III.1. Map showing study area; elevations in metres above sea-level; sampling transects shown as T_1 , T_2 , T_3 .



The effect of increasing distance from the roadway was studied in more detail by taking samples of each species at regular intervals (5 m or 10 m) over about 150 m of each transect on each side of the road. At each vegetation sampling site a sample of the top 2.5 cm of soil was also taken.

In a preliminary study of soil profiles near the road, cores of 10 cm depth were divided into 2.5 cm fractions. Because no significant elevation of lead levels was found at depths greater than 5 cm, subsequent work made use of 6 cm cores subdivided into 1 cm fractions. All soil cores were taken with a core extractor of diameter 2.5 cm.

Vegetation samples were divided into unwashed and washed portions for analysis, the washing being carried out by agitation in about 20 l of slowly-running water. Only the leaves were analysed.

Vegetation and soil samples were prepared for analysis and analysed as described in Section I. All concentrations were expressed in $\mu\text{g Pb per g}$ of soil or plant ash.

3. Results and discussion

(a) Lead in vegetation

The lead content of plants growing close to the road near Transect 1 is shown in Table III.1 each value being the mean from 10 different plants. In all cases the washed samples contained 70-90% of the lead levels of the unwashed samples, indicating that a significant, but not predominant, fraction of the lead is in the form of easily-removed particulate matter. This observation parallels that of Impens et al, (1973) who found that 10-20% of the lead of beet leaves collected 10-35 m from Belgian highways could be removed by washing.

Average values for H. odora are generally 60-65% of those for C. vauvilliersii at the same location,

Table III.1

Lead Content of Ash of Plants growing Close to
Highway Near Transect 1.

<u>Species</u>	<u>Distance/m</u>	<u>Side of road</u>	<u>Mean Pb ug/g ash</u>	
			<u>Unwashed</u>	<u>Washed</u>
<u>C.vauvilliersii</u>	1-6	East	826	584
	7-12	East	350	306
<u>C. vauvilliersii</u>	1-6	West	506	410
	7-12	West	392	294
<u>H. odora</u>	1-6	West	308	244
	7-12	West	250	184

which may indicate a lower adhesion of particulate matter to H. odora and a lower tendency for this plant to take up lead from the soil. The higher surface/weight ratio of leaves of C. vauvilliersii is probably an important factor also. The highest lead levels in the washed plants, and the largest amounts of easily-removed lead, are found in C. vauvilliersii in the first 6 m on the east side of the road, into which the prevailing wind blows. It is noteworthy, however, that a significant effect of wind direction on vegetation lead levels does not appear to extend more than 6 m from the edge of the highway.

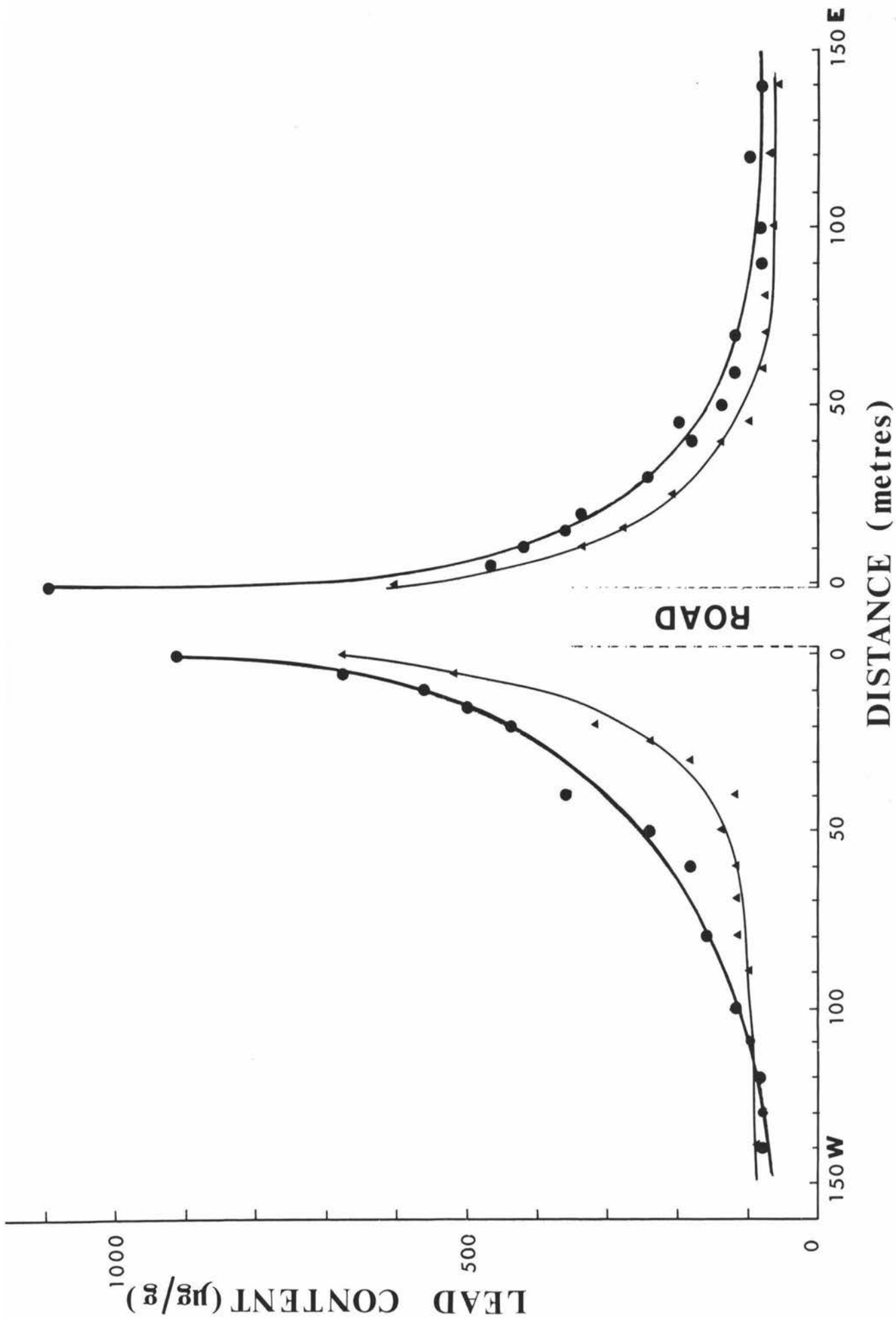
Fig. III.2 shows the variation of lead content with distance for each of these two species over the length of a transect. Only the curves for unwashed specimens are shown; levels in washed samples were generally about 80% of these values. Corresponding curves for other transects are very similar, the main variations being in the levels found at the sampling points closest to the highway. Maximum lead levels (at the road verge) for the ~~three~~ transects were in the range 640-1100 $\mu\text{g/g}$ (C. vauvilliersii) and 300-680 $\mu\text{g/g}$ (H. odora).

'Background' values for both species (at distances of 120-150 m) were 50-90 $\mu\text{g/g}$, and a clear pattern of increasing lead levels is observed on approach to within 50 m of the highway.

The lead values (after subtraction of background) gave a close fit to curves showing an exponential decay with distance for about 50 m on either side of the roadway. The interval in which this 'excess lead' decreased by 50% was in all cases between 10 m and 20 m. It is noteworthy that a similar analysis of the data of Motto et al., (1970) on lead in roadside grasses, gives the same result, even though their data are derived from several different localities of much greater traffic volume.

Fig. III.2. Lead content of leaves of plants,
as a function of distance from the
highway:

● = Cassinia vauvilliersii
▲ = Hebe odora.



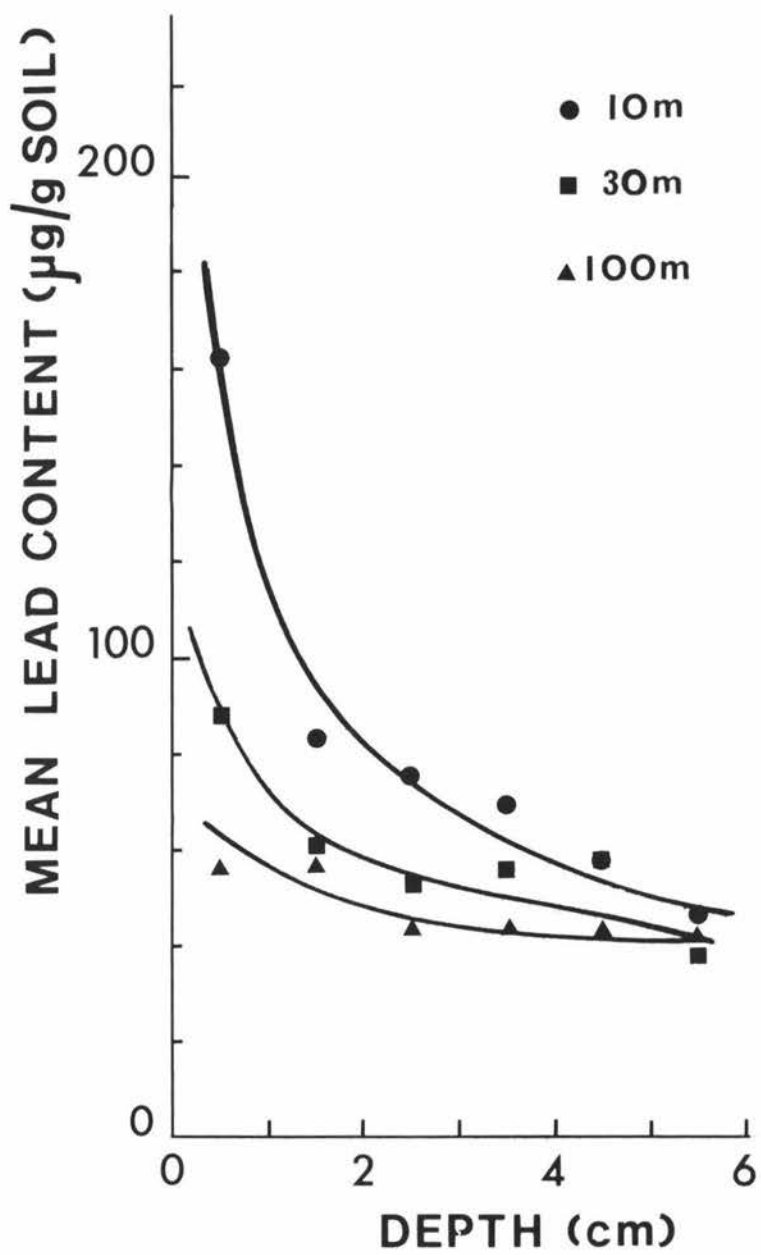
(b) Lead in soil cores

The lead concentrations in the 10 cm soil cores taken only 3 m from the edge of the sealed surface of the road at Transect 1 indicated clearly that significant elevation of lead levels did not occur below 5 cm. This observation supports those of several previous investigations. Chow (1970) showed that along the Baltimore-Washington Parkway (56,000 vehicles per day) the soil lead levels at distances of 7-30 m from the highway were distinctly elevated in the 0-5 cm layer, but 'background' levels were found in the 5-10 cm and 10-15 cm layers. Motto *et al.*, (1970) show soil profiles indicating limited downward movement of lead in soils close to New Jersey highways carrying 12,000-55,000 vehicles per day. Page and Ganje (1970), in their study of soil lead levels at distances of more than a mile from major highways, found that even in regions of high traffic density the lead concentration in the 2.5-15 cm layer was close to the background. Evidence for deeper penetration of lead of automotive origin has been found only under rather specific conditions: Vandenabeele and Wood (1972) showed that the combined effect of low temperature and presence of sodium chloride diminished the ability of an alluvial soil to retain lead in the topmost layer.

It is clear, therefore, that any detailed study of the decrease of soil lead concentrations with depth must make use of closely subdivided cores. In the present work, 6 cm cores were divided into 1 cm fractions. The results on profiles at various distances on each side of the highway at Transect 1 showed little difference between the two sides; mean values are plotted in Fig. III.3.

With soil lead data available as a function of both depth and distance it is possible to estimate the total 'excess lead' (above background) in the area

Fig. III.3. Lead content of soils, as a function of depth, at various distances from the highway.



under study. The background level was taken as 42 $\mu\text{g/g}$, being the mean of 22 measurements on soil samples taken at depths 7 cm near the road and at depths 33 cm at distances of more than 100 m.

Co-ordinates are defined as follows: x - distance from roadway; y - distance parallel to the roadway; z - soil depth. The bulk density of the soil (dried at 60° C) was found to be 0.53 g cm^{-3} , enabling total masses of lead to be calculated from the concentration data. For example, increments of soil measuring 1 metre in both the x and y directions and 6 cm in depth contained 2.63 g Pb at $x = 10$ m, 1.87 g Pb at $x = 30$ m, and 1.52 g Pb at $x = 100$ m, the background contribution being 1.33 g.

The total excess lead contained in such increments from $x = 0$ to $x = \infty$ (i.e. per metre of road length) can be found by integration, either graphically or by fitting a suitable function to the experimental points.

By graphical integration to $x = 250$ m a value of 69 g is found for the total lead in the soil on each side of the highway, per metre of roadway length.

An alternative approach consists of plotting the values of excess lead in the volume increments of 1 m x 1 m x 6 cm as a function of distance, and finding an integratable function which fits the data closely. Such a function is

$$M(x) = M(0)e^{-k\sqrt{x}}$$

in which $M(x)$ is the excess mass of lead in the increment at distance x . This provides a better fit than functions based on e^{-ax} , as the decrease with distance beyond about 50 m is less sharp than would be expected from an exponential plot passing through the points at closer distances. The best-fit curve to the above equation has $M(0) = 2.65\text{g}$, $k = 0.266 \text{ m}^{-\frac{1}{2}}$, and

$$\int_0^{\infty} M(x)dx = 74 \text{ g}$$

in good agreement with the result from graphical integration.

In principle, a third possibility consists of fitting to exponential curves the decrease of excess lead concentration with both distance and depth, giving an equation of the form

$$C(x,z) = C(0,0) e^{-k_1 x} e^{-k_2 z}$$

where $C(x,z)$ is the lead concentration in excess of background, expressed in $\mu\text{g Pb/g soil}$. The integration to give the total excess lead on each side of the roadway per metre of its length takes the form

$$M = C(0,0) \rho \int_0^\infty e^{-k_1 x} dx \int_0^\infty dy \int_0^\infty e^{-k_2 z} dz$$

where ρ is the bulk density of the dry soil in g cm^{-3} and x, y, z are in metres.

$$\text{Hence } M = \frac{C(0,0)\rho}{k_1 k_2}$$

The data of the present work, however, do not fit this form of function sufficiently well for k_1 , k_2 and $C(0,0)$ to be determined reliably.

It is of interest to compare the estimate of the excess lead in the soil (approximately 70 g on each side of the road, per metre of its length) with a calculated total lead emission in the area by all the traffic that has used the road over a period of more than 40 years since the use of lead tetraethyl in petrol became widespread.

The following quantities have been estimated:

average vehicle fuel consumption:	0.10 l km^{-1}
average Pb content of fuel:	0.7 g l^{-1}
average Pb exhausted:	0.4 g l^{-1}

The last estimate is based on the data of Habibi (1970) who studied the percentage of lead actually exhausted from vehicles as a function of speed. An estimate of

55-60% lead exhausted at the speeds of 50-60 mph generally used in the area of the present study, is consistent with the findings of Habibi.

Hence each vehicle exhausts an average of 0.04 g Pb per kilometre of distance travelled along the highway, i.e. 40 μ g per metre. Vehicle volume counts have been kept on this part of the highway by the New Zealand Ministry of Works and Development since 1957, allowing a reliable estimate to be made of the total number of vehicles that have traversed the highway since that time. Extrapolation back to 1930 has been carried out by assuming that the growth curve of the use of this highway has been parallel to the growth curve of vehicle registration in New Zealand. The estimated total traffic flow since 1930 is 6.0×10^6 ($\pm 1.0 \times 10^6$) vehicles, and the total exhausted Pb is therefore estimated to be 240 g along each metre of the road. Comparison of this figure with the calculated excess in the soil, i.e. 140 g along each metre of the roadway, indicates that the major part of the automobile lead can be accounted for by the present-day soil-lead elevations in the top 6 cm of soil within about 250 m of the road. The amount of lead contained in (or on) the vegetative cover of the area at any given time is very much smaller than that which has accumulated in the soil.

The balance of the exhausted lead will have been lost from the area of study in the form of

- (i) primary exhaust carried more than 250 m from the road,
- (ii) secondary removal as wind-blown dust,
- (iii) washing of particulates and leaching of soluble lead to depths greater than 6 cm.

There is no evidence to suggest that the last of these processes is important, since the lead levels approach background at depths of only a few centimetres, even when surface levels are much higher than

those reported here. Furthermore, it has been indicated that soluble lead moves only with great difficulty in most soils (Keaton, 1937).

The lead not accounted for in soil retention has therefore probably been lost from the study area by processes (i) and (ii). Although most studies show that concentrations of lead in surface soils and vegetation decrease rapidly with distance to a 'background' level, the concentration of air-borne particulate lead does not decrease nearly as rapidly. This is apparent from work such as that of Daines et al, (1970) who found that, for several different traffic densities, levels of air-borne lead at 500 feet from the roadway were 30-50% of the levels at 30 feet. It is observed that a region of slow decline in air-borne lead levels is reached at about 250 feet from the highway. There is therefore a minor, but significant, proportion of the exhausted lead which persists in the atmosphere and is dispersed over distances much greater than those within which augmentation of natural soil and vegetation levels can be observed.

SECTION IV
LEAD POLLUTION AROUND
THE TUI MINE,
TE AROHA,
NEW ZEALAND

1. Introduction

The distribution and accumulation of air-borne heavy metals from industrial sources has been widely reported in recent years. Most interest has been concentrated on soil and vegetation contamination by zinc, lead, copper and recently cadmium. (Martin and Hammond, 1966; Ender, 1969; Costescu and Hutchinson, 1971; Little and Martin, 1972; Buchauer, 1973; Marchant, 1974). Other environmental components studies 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 (Buttersworth et al, 1972; Burkitt et al, 1972).

Elevated levels of heavy metals have been connected predominantly with emissions from smelting complexes. (Abdullah, et al, 1972; Burkitt, et al, 1972; Buttersworth et al, 1972) and to a lesser degree from mining activities (Chisnall and Markland, 1971; Markland and Vallance, 1971; Crudgington et al, 1973).

The principal object of this study was to obtain some estimates of the total aerial burden in soils and vegetation, of lead presumed to originate directly from a base-metal mine and ore treatment plant at Te Aroha, New Zealand, and to compare the data with the amount and mode of distribution of lead accumulations in plants growing directly over the ore deposits, where the metal is accumulated via the root systems.

2. Study area

The Tui mine is situated about 3 km north-east of the township of Te Aroha and is at an altitude of about 600 m on the west side of the southern extension of the Coromandel Peninsula Range on the flank of Te Aroha Peak (952 m). The Coromandel Peninsula is situated 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 propylitized andesite of the Miocene period. There are two mineralised reefs known as Champion and Raukaka. The Raukaka Lode has been traced for a strike length of about 600 m and a dip of 60° S.E. The Champion Lode has been traced by surface outcrops for a strike length of over 450 m and has a dip to the north-east.

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

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

The flora consists of a typical New Zealand broad-leaf, evergreen forest with tall species such as Beilschmiedia tawa ("tawa") being dominant. Smaller trees and bushes such as Brachyglottis repanda and Schefflera digitata ("five finger") are common beneath the forest canopy.

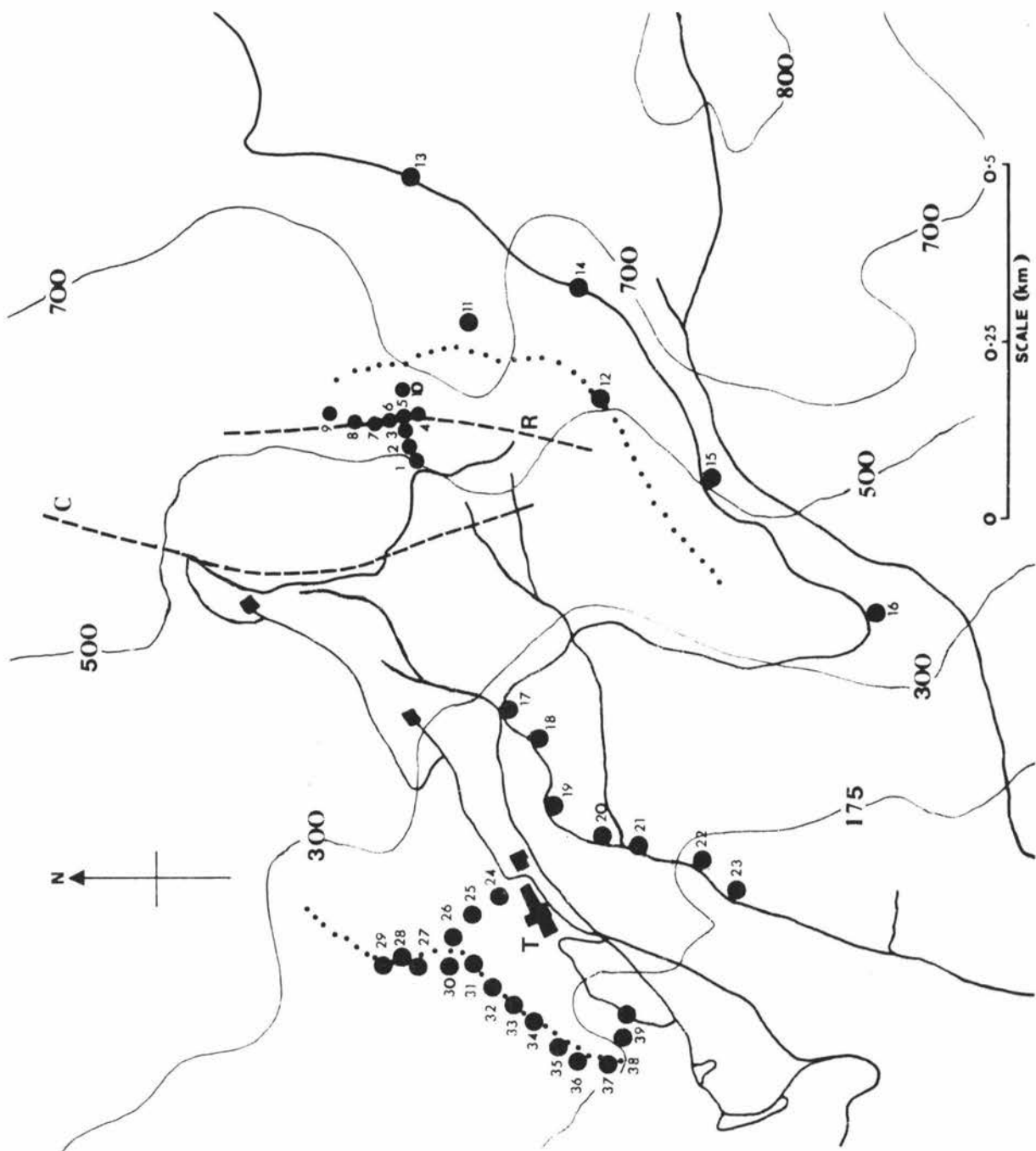
The soils are classified as yellow-brown earths and vary in depth from over 200 cm on the gentler slopes to almost nothing on the steeper hillsides. A soil survey of the area has been carried out by Weissberg and Wodzicki (1968).

3. Methods and materials

Samples were collected in three major regions as shown in Fig. IV.1: samples 1-12 Raukaka Lode area; 13-23 Valley-Road area (background); and 24-39 treatment plant;.

At each sampling point, leaves (B. tawa and S. digitata) were taken from heights varying between 1 and 3 metres from the ground, and soils were taken within 5 cm of the surface. Trunk-core samples

Fig. IV.1. Map of Tui Mine area showing sampling sites. The Champion (C) and Raukaka (R) lodes are shown as broken lines. The ore-treatment plant is shown as (T).



(6 mm diam.) of B. tawa were taken at sampling sites 3, 5, 12, 13, 17, 22, 26, 33 and 36.

Foliage and soil samples were prepared for analysis as described in Section I. Plant foliage results were expressed as ppm ash weight.

B. tawa trunk-core samples were dried for 3 days at 60°C and divided into 2.0 cm lengths which were ashed at 450°C and dissolved in 2M hydrochloric acid (1-2 cm³). Trunk-core data were reported in terms of ppm dry weight.

During analysis, corrections for non-atomic absorption were made where necessary by use of a hydrogen lamp at the same wavelength as the absorbing line of lead.

4. Results and discussion

(a) Soil

The lead content of soils across the Raukaka Lode is shown in Fig. IV.2. Because the data were log-normally distributed, they are shown with logarithmic co-ordinates in the figure.

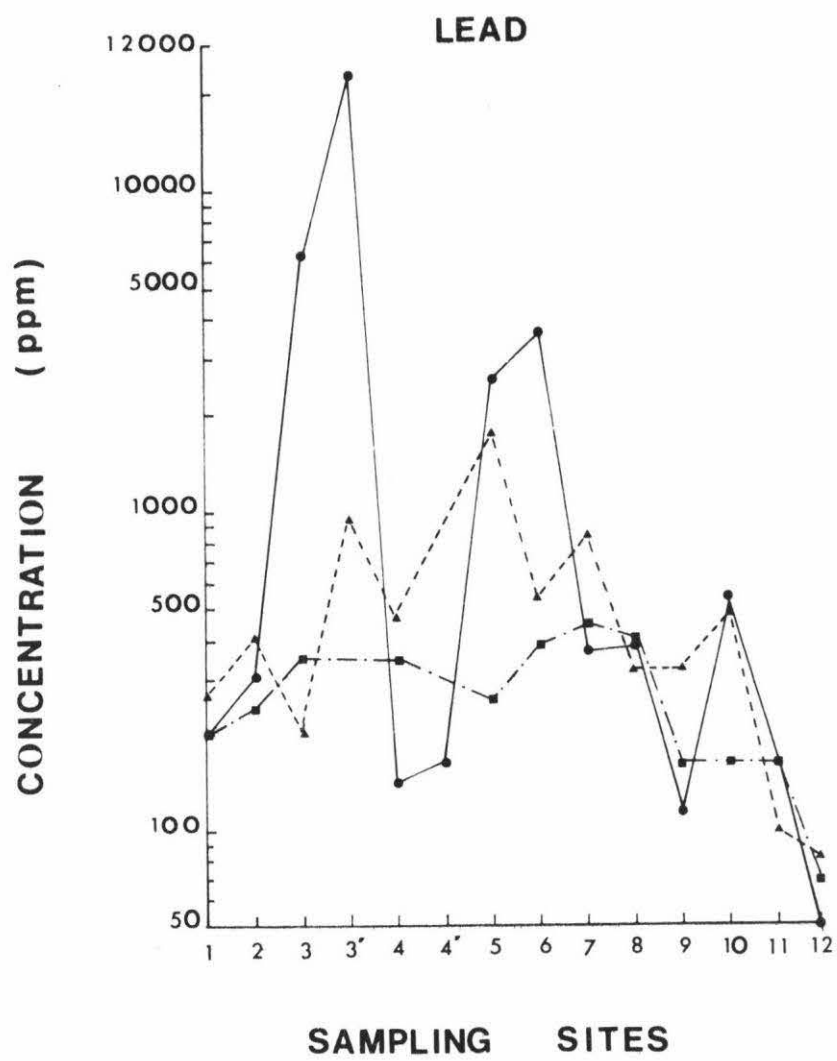
The highest lead levels occurred at the base of the Raukaka Lode outcrop, situated at sampling site 3'. In this area the metal content of the soil sampled to the south (3') was two-fold higher than that to the north (3) of the outcrop. Samples along the direction of the lode showed variable lead concentrations with the highest levels at sites 6 and 10. The lead content for the Raukaka Lode ranged from: 47-12,500 ppm. Background values for this area were about 20 ppm lead.

Samples from the vicinity of the Valley Road area (sites 11-23) showed metal contents ranging from 39-460 ppm for lead. Values within this area should have presumably been nearer to background levels, but sites 15, 16 and 20 to 23 showed high elemental

Fig. IV.2. Lead levels in soils and vegetation
in a transect across the Raukaka

Code:

- = soil;
- ▲ = B. tawa;
- = S. digitata.



concentrations comparable to the west and east sides of the Raukaka Lode. Such levels were probably due to road construction with contaminated rocks, and wind-borne dust deposition from mining activities adjacent to the treatment plant.

The distribution of lead, as air-borne dust particles around the treatment plant is shown in Fig.IV.3. The soils in this area are derived from non-mineralised country rock, and elevated concentrations of base metals must have been due to deposition of air-borne 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 150 m. Highly-contaminated soils, as a result of direct deposition of wind-borne dust from the treatment plant, occurred within 30 m of the source. The range of lead concentration in soils adjacent to the plant was 20-270 ppm.

(b) Vegetation

Elemental levels in ashed leaves of Beilschmiedia tawa and Schefflera digitata are also shown in Fig.IV.2. Accumulation of lead shows a pattern similar to that of the corresponding soils.

Background values in the ashed leaves of B. tawa from the Valley Road area were 60 ppm lead.

In the vicinity of the treatment plant (Fig.IV.3), there was a pattern of lead concentrations in ashed leaves of B. tawa which was similar to that already noted in soils. The highest metal accumulations were within a 100 m radius of the source, although even at greater distances, values above background were obtained. Distributions seemed to depend mainly on the direction of the prevailing wind. Elemental levels

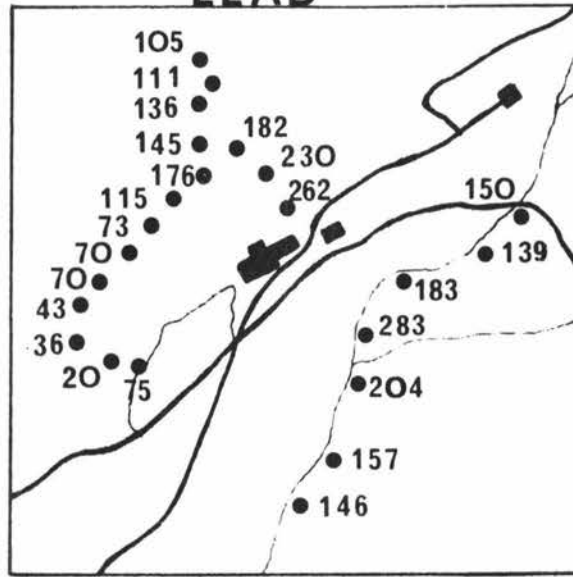
Fig. IV.3. Lead levels in the vicinity of the
ore-treatment plant:

above = soils;

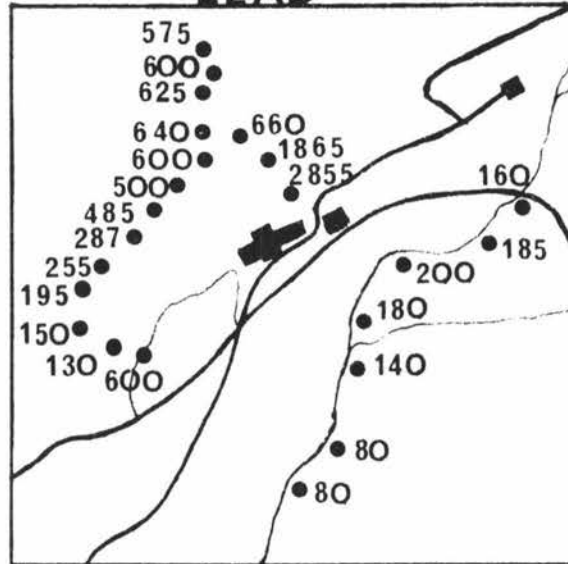
below = B. tawa leaves.

For scale and sample site identification
see Fig. IV.1.

LEAD



LEAD



at sites 38 and particularly 39 were higher than expected because these specimens grew within 10 m of the settling pond. It is suggested that absorption from the root-system may occur at these sites as shown by only 8-15% of the metal burden being removable by washing the leaf surfaces.

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

Inspection of the table shows three dissimilar patterns. Near the treatment plant, 68% of the total lead content was removed by washing. This suggests the accumulation of deposits of inert material upon the leaves and has been reported previously by Little and Martin (1974) for fallout from a smelter.

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 lead in leaves were appreciably higher than in samples taken from near the treatment plant, the percentage removable by washing was four or five times lower.

The samples from the background area showed that a very high percentage of the total lead burden was removable by washing. It is suggested that even these 'background' samples contain an appreciable component of aerial fallout, and that true background samples will probably be found at considerably greater distances away from the mine and treatment plant.

Table IV.1 also includes data on the plant/soil ratios (concentration in plant ash divided by the concentration in the soil) for lead in leaves of B. tawa from all three localities. Under natural conditions (e.g. on the Raukaka Lode), this ratio is usually less than unity. Where fallout is

Table IV.1

Mean Percentage Lead Content Removed by Washing
Beilschmiedia tawa Leaves

<u>Location</u>			
	<u>Treatment Plant</u>	<u>Raukaka Lode</u>	<u>Background</u>
Lead			
Removed by washing	68%	20%	88%
Plant/Soil Ratio	5.30	0.25	2.48

extensive the value is usually above unity and bears an inverse relationship to the percentage removable by washing.

(c) Trunk core samples

The concentration of lead (ppm dry weight) in 2 cm lengths of 6 mm diameter cores of B. tawa are shown in Fig. IV.4 and are expressed as a function of distance from the centre of the trunk.

The conversion factor for expressing data on an ash weight basis is 7.9.

Inspection of Fig. IV.5 shows that two main patterns of uptake emerge. Samples from near the treatment plant show elevated lead levels 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 lead levels towards the outside of the trunk, decreases progressively with increasing distance from the treatment plant.

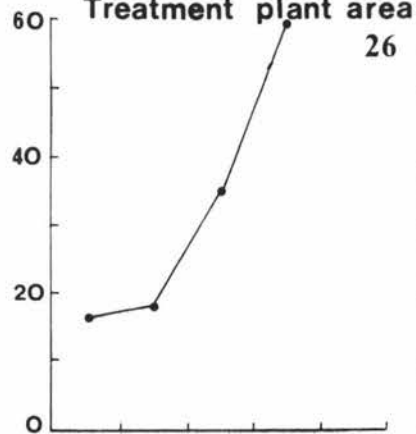
Uptake patterns of lead levels in trunk cores seem to reflect the mechanism of uptake. Where accumulation is via the root systems, distributions are relatively uniform, whereas aerial fallout results in higher levels towards the exterior of the trunk. This accumulation is probably due to absorption via the bark which in the case of Beilschmiedia tawa is comparatively thin.

5. Conclusions

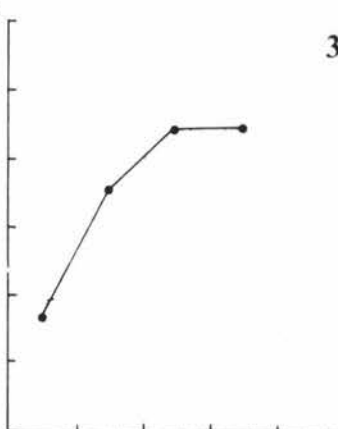
It is clear that there is a widespread distribution of air-borne lead from dust particles emanating from the ore treatment plant at the Tui Mine. It is also evident that trees growing over the ore bodies contain natural levels of lead in amounts even greater than those derived from wind-borne sources.

Fig. IV.4. Lead levels in trunk cores (ppm dry weight) of Beilschmiedia tawa expressed as distance from centre of trunk. Numbers refer to sampling sites shown in Fig. IV.1.

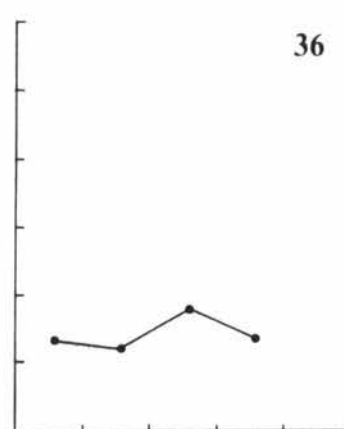
Treatment plant area



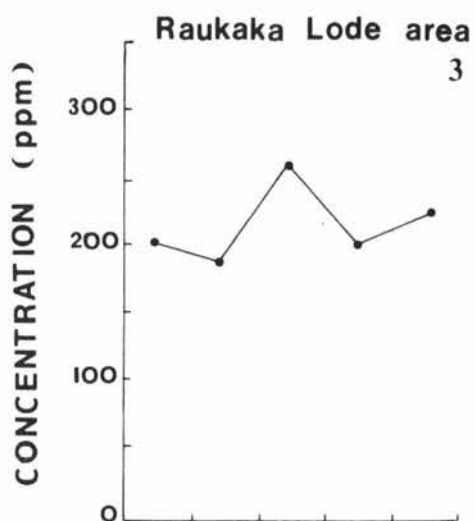
34



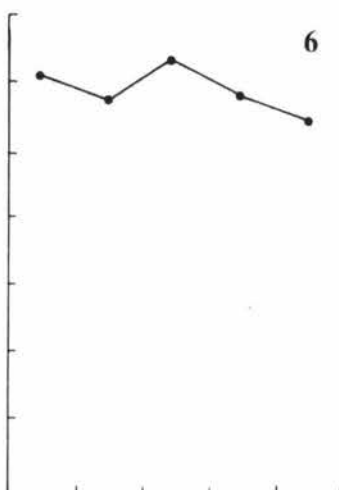
36



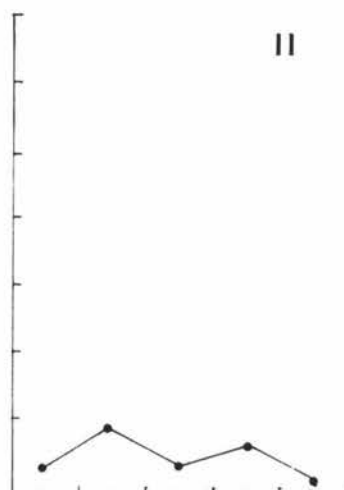
Raukaka Lode area



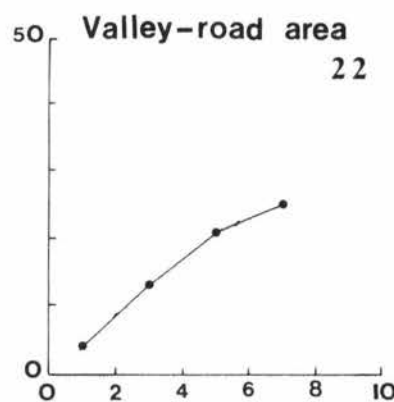
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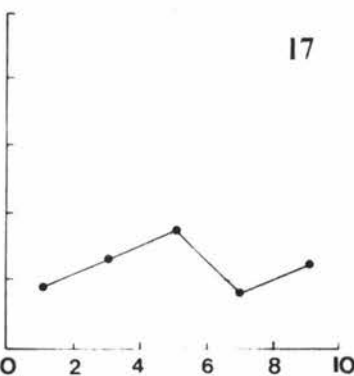
11



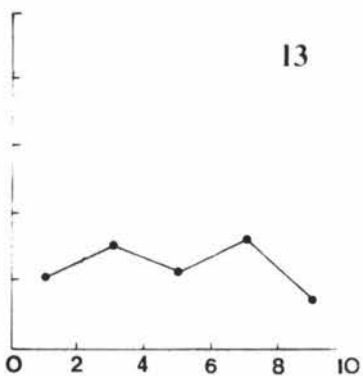
Valley-road area



17



13



DISTANCE (cm)

The differentiation of uptake mechanisms shows quite clearly that lead concentrations due to accumulation via the root system are significantly higher than those associated with air-borne deposition in such areas as the vicinity of smelters, ore treatment plants and highways (motor-vehicle exhaust emissions).

Future investigations to assess the overall environmental impact of such operations at Te Aroha, especially from air-borne deposition from the ore treatment plant, upon the population centre of Te Aroha would give a more detailed insight into the degree of concern with which lead pollution should be considered within the human environment.

SECTION V
LEAD FROM MOTOR-VEHICLE EXHAUSTS IN
SWEET-CORN PLANTS AND SOILS
IN
HAWKES BAY

1. Introduction

The deposition of air-borne lead from motor-vehicle exhausts, has been studied extensively in natural vegetation, edible crops and soils. Warren and Delavault (1960), Cannon and Bowles (1962), Kloke and Riebartsch (1964), and Dedolph et al, (1970), observed that lead levels in vegetation growing near a highway were considerably higher than in natural localities. Lead levels were found to be dependent on traffic volume and the prevailing wind direction.

Further studies on lead levels in edible crops (Prince, 1957; Warren and Delavault, 1962; Motto et al, 1970; Schuck and Locke, 1970; Ter Haar, 1970) showed that inedible parts of most crops (corn husks, wheat and oat chaff, soy-bean hulls and the outer leaves of cabbages) had lead levels two or three-fold greater near highways than in background areas. In most cases, lead contamination of the edible parts was negligible except in the case of lettuce leaves (Ter Haar, 1970).

Because food is the main source of Man's normal lead intake (Kehoe, 1947, 1961a, 1961b, 1961c, 1964; Schroeder and Balassa, 1961) and because human food is derived directly or indirectly mainly from plants, the effect of air-borne lead contamination on plants is very important. Several investigations have also been carried out on soils (Tatsumoto and Patterson, 1963; Chow and Johnstone, 1965; Martin and Hammond, 1966; Singer and Hanson, 1969; Chow, 1970) with particular emphasis on the contribution of lead in soils, to the overall lead burden in the vegetation.

Sweet-corn is an ideal subject for lead studies because direct aerial fallout is confined mainly to the leaves, stalks and husks. Kernels and cobs which are protected by the husks from aerial fallout, may well derive their lead from other sources such as

absorption from soils via the root system or translocation of air-borne lead from leaves. Sweet-corn is moreover an important food crop in New Zealand, with an annual consumption of at least 1000 tonnes. Because of consumer demand for fresh supplies and because of excessive transport costs, this cereal (unlike wheat or oats) tends to be grown near centres of population and hence is much more subject to contamination from lead fallout derived from motor-vehicle exhausts.

The purpose of this study was to determine the patterns of lead contamination of sweet-corn under New Zealand conditions and to examine the effect of various factors such as traffic density and the direction of the prevailing wind upon the lead levels within the plant.

2. Sampling area and methods

The area investigated was situated near Taradale on the main Hastings-Napier highway in Hawkes Bay. Transects were taken over two sections of the highway. The first section was opened in 1969 and at present has a daily total of 5,070 vehicles with a cumulative total of 6,800,000 vehicles to the end of June 1974. The other section was opened in 1973 and has a daily total of 3,875 vehicles with a cumulative total of 1,090,000 vehicles to the end of June 1973. Before construction of this highway, the area consisted of farmland with a negligible volume of traffic in the vicinity. Rainfall in the area is 570 mm per annum and the prevailing wind is N.E.W.

Samples of sweet-corn (stalks, leaves, and husks) were taken at a height of 1.5 m in the plant and were selected from specimens growing at 10 m intervals in two separate transects crossing the highway. The transects ran parallel to the direction of the

prevailing wind. Cob and kernel samples were also taken at intervals of 30, 60 and 90 m from each side of the highway.

Soil samples (1-2 cm in depth) were taken from the base of each corn sample (i.e. every 10 m). Further soil samples at positions of 10, 30, 60 and 100 m on each side of the highway, were taken to a depth of 6 cm by use of a 2.5 cm diameter core extractor. Background samples of soils and corn were taken from a site more than 2 km from the nearest major road.

Sweet-corn and soil samples were prepared for analysis and analysed as described in Section I.

Half of the sweet-corn samples for each plant part were divided into three groups for washing. One group were washed thoroughly in running water and then shaken with deionised water for two hours. The other two groups of sweet-corn leaves were treated with a more vigorous washing procedure involving shaking for two hours with 2% detergent and for the same period with 4M hydrochloric acid.

Sweet-corn cobs and kernels were analysed in replicates of five. All other samples were analysed in duplicate. For low lead concentrations, background corrections were made by use of a hydrogen lamp.

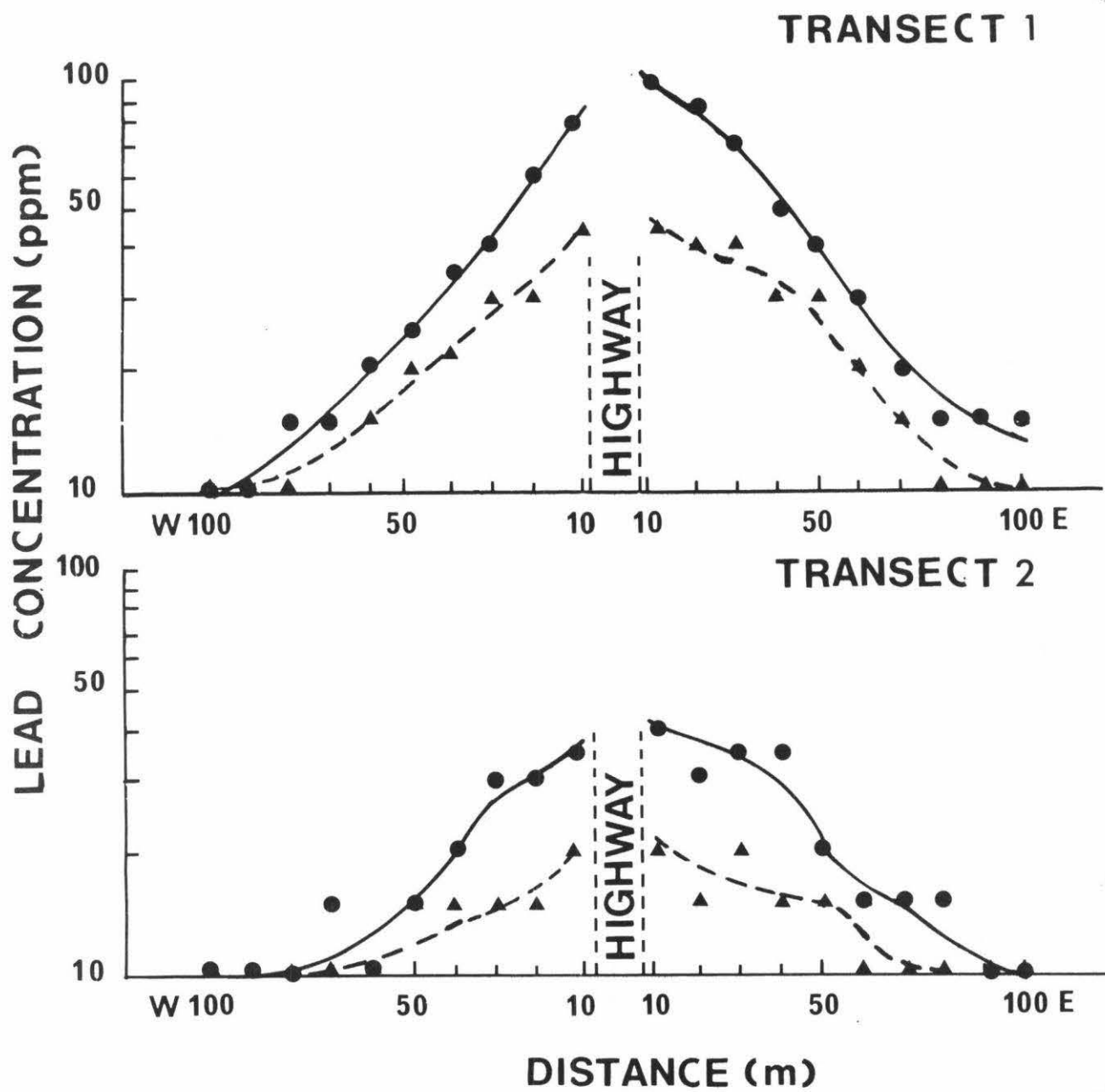
pH measurements were made on aqueous extracts produced by shaking 1 g of soil with 10 cm³ of deionised water for a period of 24 hours.

3. Results and discussion

(a) Lead in sweet-corn husks and stalks

Fig. V.1 shows mean values for the lead content (ppm) of ashed sweet-corn stalks (washed and unwashed) taken on both sides of the highway for the two transects. In general, the lead content of samples taken from near the highway was five to ten times

Fig. V.1. Lead (ppm ash weight) in sweet-corn stalks sampled from two transects across a major highway:
● = continuous lines, unwashed samples;
▲ = broken lines, washed samples.
Background values were 10 ppm.



greater than for background samples. The lead content decreased rapidly with increasing distance from the road and reached background values at a distance of 80-100 m. Washing removed more than half of the lead from samples growing near the roadway and the percentage removable by washing decreased rapidly at distances greater than 60 m. This indicated surface contamination of the plants, by motor-vehicle exhaust emissions.

Analogous data for husks are shown in Fig. V.2 and give the same pattern as above although the lead accumulation is appreciably greater than for stalks. As before about half of the lead in husks is removable by washing.

Since husks and stalks are the most exposed parts of the plant, and because so much of the lead can be removed by washing, it would seem that the lead is of aerial origin rather than having been obtained via the root system. Further evidence of the aerial nature of the lead contamination is afforded by the greater accumulation of this element on the leeward (eastern) side of each east-west transect (see Fig.V.1 and V.2).

(b) Lead in sweet-corn leaves

Table V.1 gives data for washed (deionised water) and unwashed sweet-corn leaves. The data show that a large proportion of this lead burden is readily removed, particularly for samples taken near the roadway.

The superficial lead contamination removable by washing in water is probably not physiologically harmful to the plant (Hooper, 1973; Little, 1974). However, the difference between the amounts removed by deionised water and by 2% detergent represents the fraction physically attached to the cuticular surface of the leaves.

Fig. V.2. Lead (ppm ash weight) in sweet-corn husks sampled from two transects across a major highway:

● = continuous lines, unwashed samples;

▲ = broken lines, washed samples.

Background values were 20 ppm.

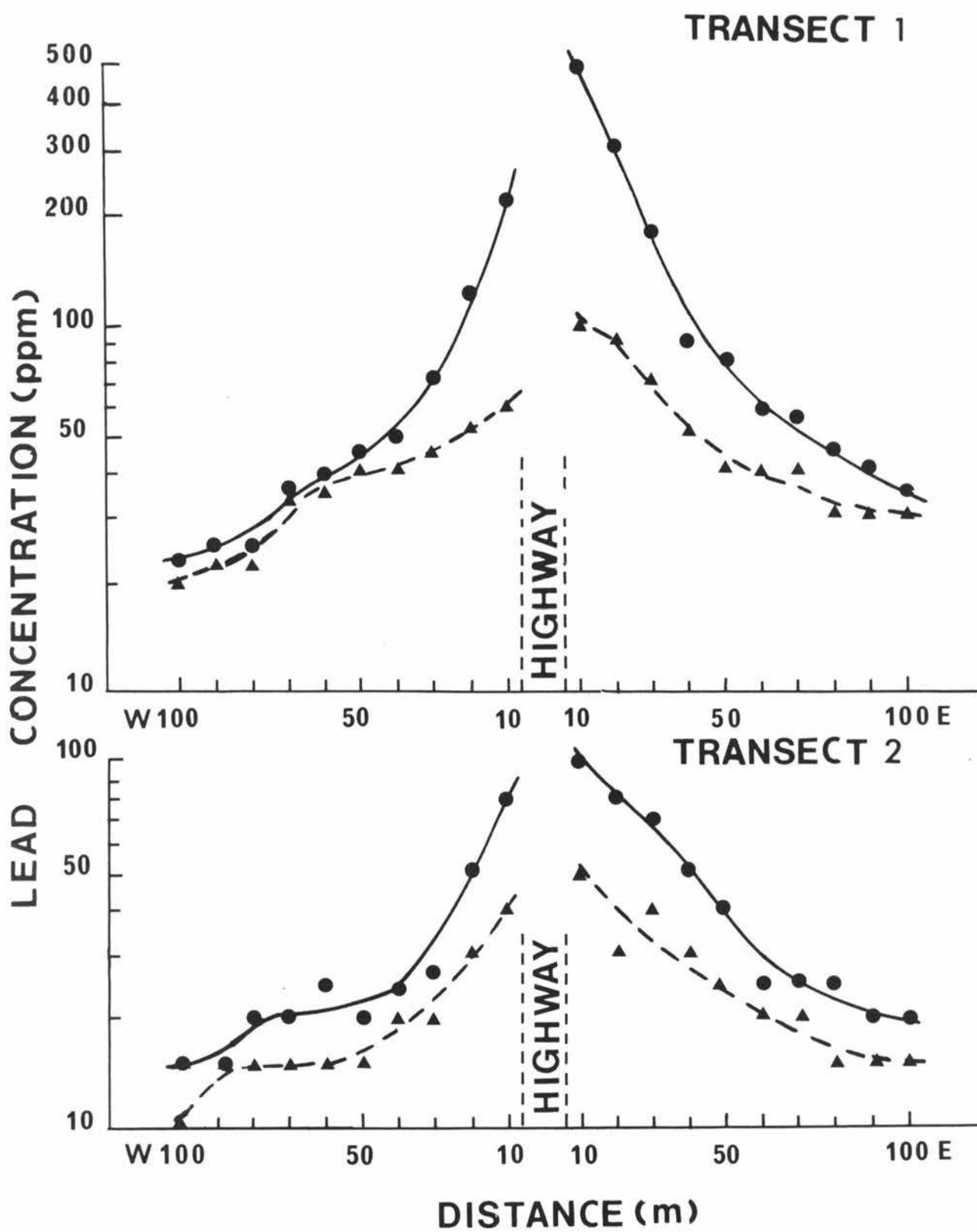


Table V.1

Percentage of Lead in Sweet-Corn Leaves which is
Removed by Washing with Various Agents

<u>Distance from</u> <u>road (m)</u>		<u>Deionised Water</u>	<u>2% detergent</u>	<u>4 M hydrochloric</u> <u>acid</u>
Transect 1	10 W	47.5	62.8	94.6
	30 W	42.8	50.0	68.0
	90 W	27.2	28.0	45.2
	10 E	57.6	75.8	96.7
	30 E	45.3	62.0	74.0
	90 E	35.7	48.0	48.0
Transect 2	10 W	45.8	58.0	92.8
	30 W	35.7	52.0	73.0
	90 W	11.1	38.0	46.2
	10 E	46.6	60.8	92.6
	30 E	38.8	54.2	64.8
	90 E	16.6	37.5	48.0
Background		8.2	12.8	18.0

After absorption by the leaf through the cuticle, lead may be bound to the cuticular membranes and cell walls by intracellular ionic binding (Little, 1974). Since such a large proportion of the lead is removed by washing with 4M hydrochloric acid, it seems probable that this treatment is causing cuticular and cellular damage.

With all three washing procedures, there is a general trend towards a lower percentage of removable lead for increasing distances from the highway.

The particle size of airborne lead (Lee and Patterson, 1968; Daines and Motto, 1970) from motor vehicle exhausts is such that much of it could pass through open stomata and be deposited within the leaf. The degree to which it is absorbed into the leaf cell membranes and intracellular components is only partially reflected by the percentage removed by washing with deionised water. The remaining metal appears to be actually incorporated into the cuticle and cell walls of the leaf.

Clearly, the process of lead accumulation, and absorption from aerial deposition is very complex. Such variables as rainfall, microclimate and exposure time of the plant to the contaminant are highly significant in determining the total lead content.

For comparison, the technique of washing samples (Hebe odora and Cassia vauvilliersii leaves) was discussed in Section I.

(c) Lead in sweet-corn cobs and kernels

The distribution of lead in the edible and inedible parts of the sweet-corn is of great importance to the human diet. Table V.2 shows lead levels in the ash of washed (deionised water) and unwashed cobs and kernels. In all cases, the edible kernels have a lead content less than half that of the cobs. The same trend is found if the data are expressed on a

Table V.2

Lead Concentrations (ppm ash weight) in Sweet-Corn
Kernels and Cobs

<u>Distance from road (m)</u>		<u>Cobs</u>		<u>Kernels</u>
		<u>Washed</u>	<u>Unwashed</u>	<u>(unwashed)</u>
Transect 1	10 W	12	15	7
	30 W	9	10	4
	90 W	7	8	2
	120 W	4	4	0.5
	10 E	15	20	10
	30 E	10	12	6
	90 E	8	9	3
	120 E	4	6	1
Transect 2	10 W	6	8	4
	30 W	4	4	2
	90 W	2	2.5	1
	120 W	2	2	1
	10 E	8	10	6
	30 E	4	5	2
	90 E	2	2	1
	120 E	1	1.5	0.5
Background			1	0.5

N.B. Factors for converting concentrations from an
ash-weight to a dry-weight basis are:

0.028 for cobs and 0.031 for kernels

dry-weight basis because the ash weight-dry weight conversion factors are almost identical (see Table V.2). The lower lead content of kernels is fortunate from the viewpoint of human health and it is interesting to consider possible reasons for this difference. The lead content of the cobs is unlikely to be derived from aerial fallout because not only can this lead not be removed by washing, but the cobs are shielded from aerial lead fallout by the husks and kernels. Since the pathway from leaf to cob is considerably shorter than the pathway via the root system, it is probable that lead in cobs represents a component obtained via absorption on the leaf surfaces. There is moreover the fact that most plants are able to restrict uptake of lead via root systems, a mechanism that is usually very effective unless lead concentrations in the soil become inordinately high (Hammett, 1928; Nicolls et al, 1965; Mitchell and Reith, 1966; Brooks, 1972).

The contribution of lead in sweet-corn to the human diet can be calculated fairly readily. From data provided by Spilsbury (1971), it can be assumed that the average consumption of sweet-corn kernels is about 1 kg (fresh weight) per person per annum. This represents a dry weight of about 400 g. On the basis of a maximum value of 0.5 ppm dry weight (5 ppm ash weight), this yearly intake represents 200 μ g or 0.55 μ g per day. Schroeder and Balassa (1961) have assumed a daily intake of 200-400 μ g and therefore the above figure of 0.55 μ g represents a maximum increase of only 0.27%. This calculation has also assumed that only sweet-corn growing near a highway was involved in the human diet; a situation not likely to exist in practice.

(d) Lead in soils

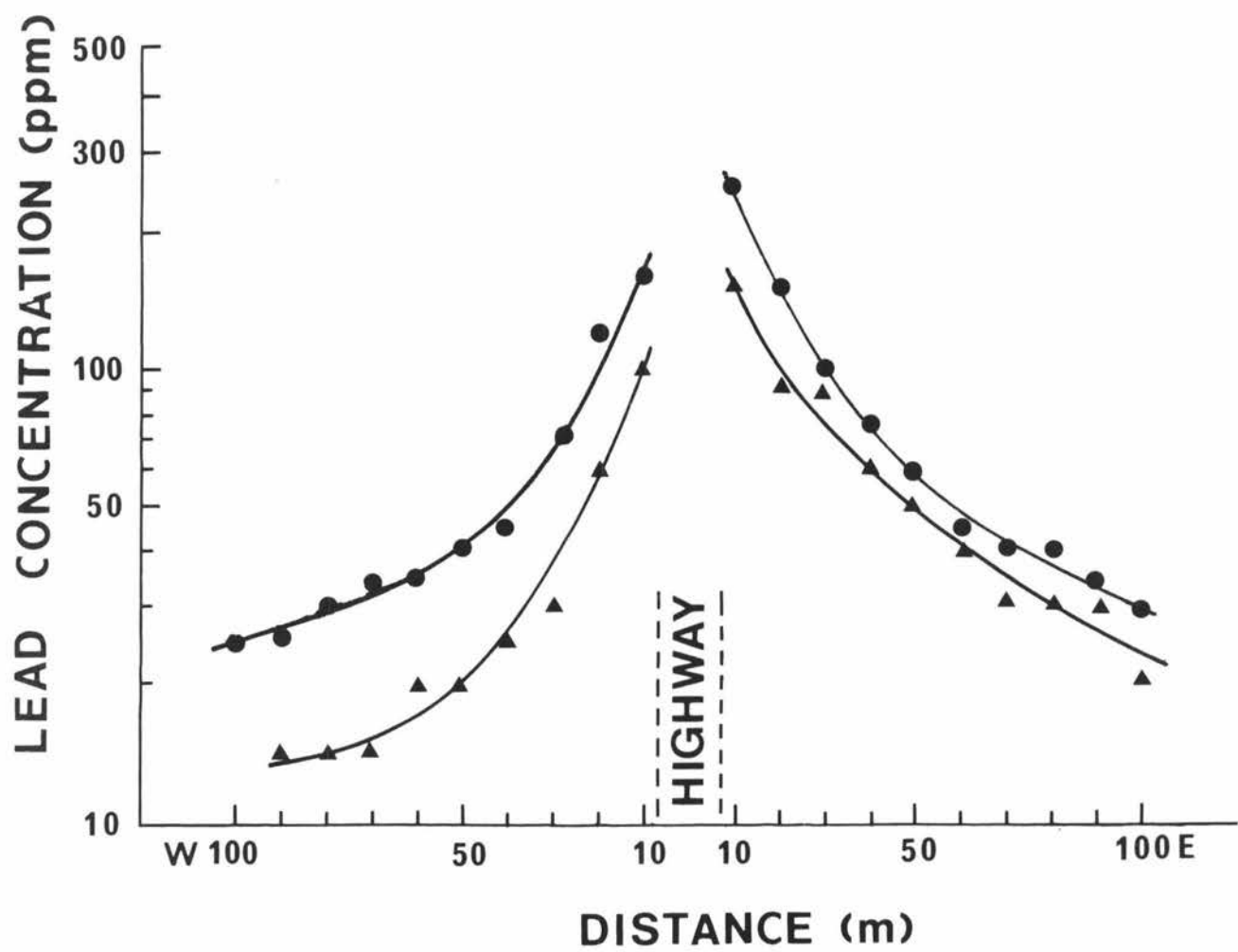
The distribution of lead in the soils of the two transects is shown in Fig. V.3. The lead values show

Fig. V.3. Lead (ppm dry weight) in soil samples taken from two transects across a major highway:

● = transect 1;

▲ = transect 2.

Background values were 15 ppm.



the effect of the direction of the prevailing wind. Integration under the curves in Fig. V.2 showed that on the eastern (leeward) side of the road, in transect 1, 61.7% of the total lead burden for that side is found within 30 m of the highway. The corresponding figure for the western (windward) side is 49.3%. At 60 m, the corresponding values are 85.8% and 68.1% respectively. For transect 2, the respective values are 60.8% and 47.4% for the 30 m interval and 84.3% and 63.1% for the 60 m interval.

The pattern of lead distribution in soils closely follows that of uptake by sweet-corn plants. The close similarity between the two patterns implies either aerial fallout or uptake of lead from the root systems as discussed above.

Table V.3 shows pH values for some of the soils studied. There is evidence for a small but significant decrease of pH with increasing distance from the highway. As the mobility of lead decreases with increase of pH, this will have the effect of counteracting to some extent, uptake of lead via roots systems for plants growing close to the highway.

Soil profiles for unploughed sites close to the roadway (≤ 10 m) are shown in Fig.4 and show a decrease of lead levels with increasing depth of sample. Below about 5 cm values approach normal background levels. Data for other sites further from the road are not given because it was considered that disturbance from ploughing would render the data meaningless.

4. Conclusions

The main conclusions of this work are given with the reservation that they apply specifically to this particular location and may not be indicative of results to be expected in areas of different conditions of climate and traffic density.

Fig. V.4. Lead (ppm dry weight) in soil profiles
taken within 10m of a major highway:

● = transect 1;

▲ = transect 2.

LEAD CONCENTRATION (ppm)

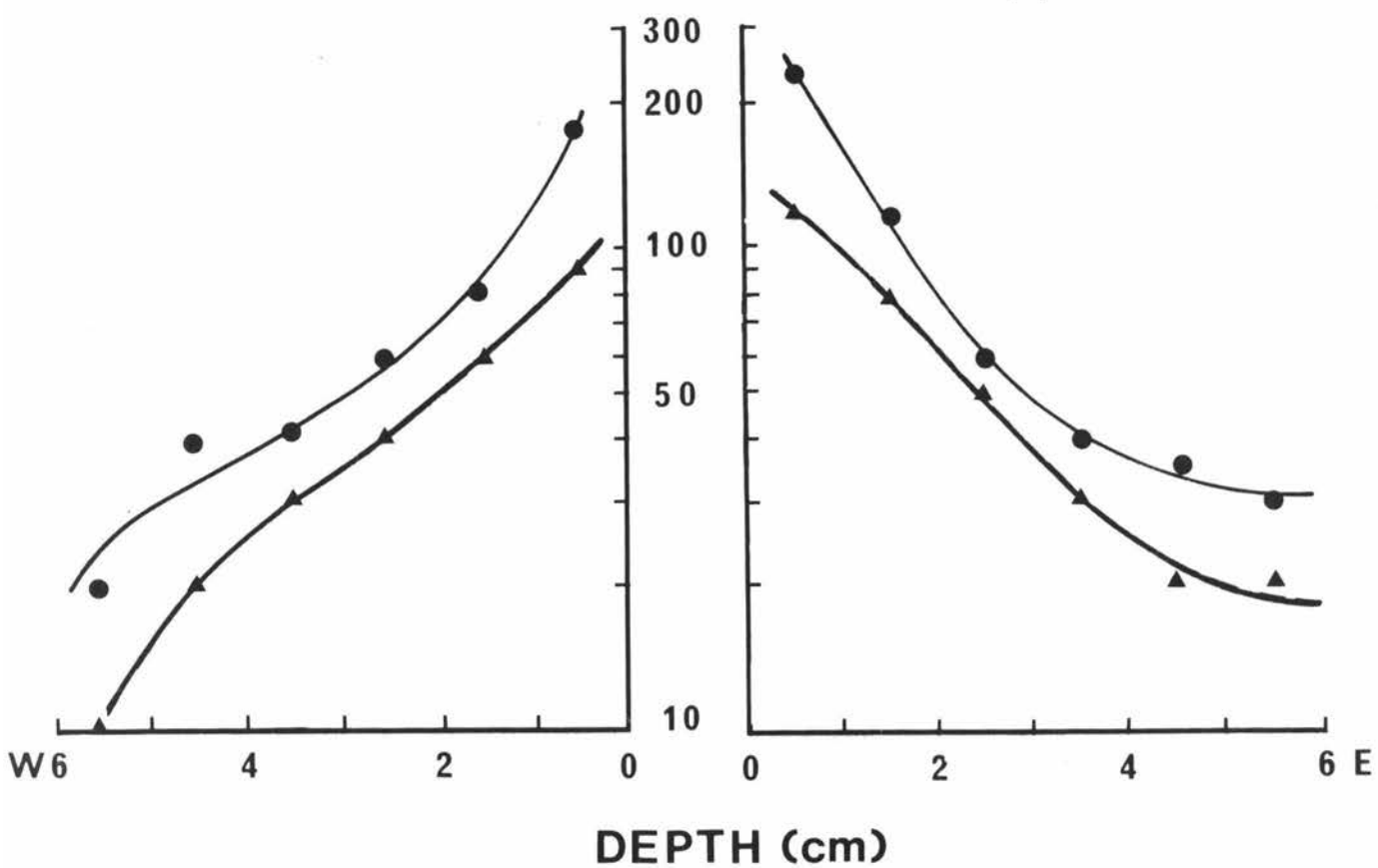


Table V.3

pH of Soils in Transect 1 Across Highway

Distance from road (m)	pH	
	East	West
10	7.8	7.9
20	7.7	7.5
30	7.0	7.0
40	6.6	7.0
50	6.8	7.4
60	6.6	7.3
70	6.6	7.2
80	6.6	7.0
90	6.8	6.6
100	6.4	6.4

It is concluded that most of the lead burden of the sweet-corn plants was derived directly from airborne emissions from motor-vehicle exhausts and was not obtained indirectly via the root system.

The extent of contamination of plants and soils was a function of the direction of the prevailing wind and the distance of the site from the highway.

Traffic density also seemed to have an influence on the lead levels in soils and plants.

Present levels of lead in sweet-corn kernels do not seem to present a very serious danger to public health because the edible kernels contain appreciably less lead than other parts of the plant and moreover sweet-corn samples growing close to major highways must of necessity form a relatively small proportion of the New Zealand crop.

Although present-day levels may not pose a particularly serious health hazard, the situation should not be viewed with too much equanimity, since if this process is allowed to continue for a very long period, it is not difficult to envisage a serious situation developing at some time in the future.

SUMMARY
AND
GENERAL CONCLUSIONS

The aims of this thesis, as mentioned in the General Introduction, were summarised as follows:

1. To develop sensitive and reproducible procedures for the determination of lead in vegetation and soils; and investigate the analytical techniques of sample preparation.

2. To investigate the distribution and accumulation of lead in soils and vegetation in the vicinity of the Tui Mine ore treatment plant (air-borne lead pollution) and in vegetation growing over a base-metal deposit, the Raukaka Lode (soil-borne lead pollution), compared with natural lead levels from "background" areas.

3. To investigate the lead content of soils and tree vegetation bordering a main thoroughfare in Palmerston North, New Zealand, and to show the influence on distribution by the wind direction and general traffic movement patterns along the thoroughfare. The effects of seasonal variation in lead content in vegetation and dust samples were also investigated.

4. To study the distribution and accumulation of lead discharged from motor-vehicle exhausts along a New Zealand State Highway in an area of low traffic density and determine lead levels in predominant plant species and, in particular, soils.

5. To determine the levels of lead contamination of sweet-corn and consider whether the main source is from air-borne emissions from motor-vehicle exhausts or obtained directly via the root system. It was also hoped to examine the extent of contamination within the plant as a function of such factors as wind direction and distance from the highway.

The results presented in Sections I to V of this thesis show that the above aims have been achieved.

The analytical section (Section I) showed that atomic absorption spectrophotometry could be successfully used to analyse lead concentrations in vegetation (leaves, barks, ring-cores) and soils, at levels sometimes 10-fold higher than normal environmental (background) values. The procedure followed, provided satisfactory reproducible results.

The productivity of the various analytical techniques investigated showed that sample preparation, in particular the washing, ashing and acid digestion of samples, directly influenced the determination of the total lead content of the sample.

The findings reported in Sections II, III and V give a general indication of the magnitude and distribution of lead pollution in New Zealand as a result of motor-vehicle exhaust emissions. The patterns which have emerged show quite clearly how lead distribution is affected by the prevailing wind.

Lead accumulation is influenced by the traffic density of the region as shown by the significant variation in lead levels in Fitzherbert Avenue, Palmerston North (11,500 vehicles per day), National State Highway No.1 (1200 vehicles per day) and the Hastings-Napier Highway (6000 vehicles per day).

The other major findings from the investigations of lead pollution from motor-vehicle exhaust emissions were:

(i) Lead accumulation is affected by the side of the tree sampled (i.e. facing or away from the highway), the height above ground level and bark layer sampled.

(ii) Lead levels in vegetation gave a close fit to curves showing an exponential decay with distance for about 50 m on either side of the highway.

(iii) Significant elevated lead levels do not occur below a depth of 5 cm in the soil at distances of 7-30 m from the highway.

(iv) Comparison of an estimated total exhaust Pb (based on total traffic flow since 1930 on National State Highway No.1), with the calculated excess of lead in the soil, indicated that the major part of the motor-vehicle lead can be accounted for by present-day soil lead elevations in the top 6 cm of soil and within about 250 m of the highway.

(v) The distribution and accumulation of lead in ring-cores indicated the increased contribution of lead from motor-vehicle exhausts.

(vi) The seasonal variation of lead content in leaves (and filter papers) showed a pattern influenced by the amount of lead absorbed as a function of the position of the tree, the surface area of the leaf and climatic factors, representing direct evidence of air-borne lead absorption.

(vii) The distribution of lead in the parts of the sweet-corn showed the trend of lower lead levels in edible parts (kernels) compared with inedible parts (husks, cobs and stalks). Such levels represent an estimated lead contribution of 0.27% from edible parts to the human diet daily.

(viii) The pattern of lead distribution in the sweet-corn plant showed that most of the lead burden was derived directly from air-borne emissions from motor-vehicle exhausts and not obtained indirectly via the root system.

The effect of lead pollution from mining activities as the other major source of lead pollution in New Zealand is clearly shown in the findings reported in Section IV.

The widespread distribution of air-borne lead from dust particles emanating from the ore treatment plant at the Tui Mine occurred at levels lower than those derived from soil-borne lead in trees growing over the ore-bodies of the Raukaka Lode.

The degree of absorption or fixation of lead into B. tawa leaves and ring-cores showed quite clearly the differentiation of uptake mechanisms. Washing procedures showed three dissimilar patterns: samples from the Raukaka Lode involved accumulation predominantly via the root systems, shown by a predictably low elemental component removable by washing with water; samples from background areas showed a very high percentage of the total lead burden removable by washing (appreciably aerial fallout); and samples near the treatment plant having nearly 70% of the total lead content removed by washing, suggesting accumulation of inert material upon the leaves as air-borne lead fallout.

The significant association of air-borne lead deposition as a major source of the total lead burden of plants and soils in such areas as the vicinity of the Tui Mine ore treatment plant, is shown with similar findings for motor-vehicle exhaust emissions, based on washing procedures.

It is concluded that the total lead content, either derived directly from air-borne emissions (motor-vehicle exhausts and mining activity deposition) or indirectly as soil-borne lead which passes into the plant via root systems; is increasing in the New Zealand environment.

Such present-day levels may not pose a serious pollution problem, but if lead levels are allowed to continue for a very long period, it is not difficult to envisage lead pollution levels as shown in other countries.

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