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 2170A°, 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

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 $\mu g.t^{-1}$, 120 $\mu g.t^{-1}$ and 210 $\mu g.t^{-1}$ 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 $\mu g.m^{-3}$.

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 $\mu g.m^{-3}$ (Hall, 1972) although lead levels of 71.3 $\mu g.m^{-3}$ 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 0.9 μ 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.

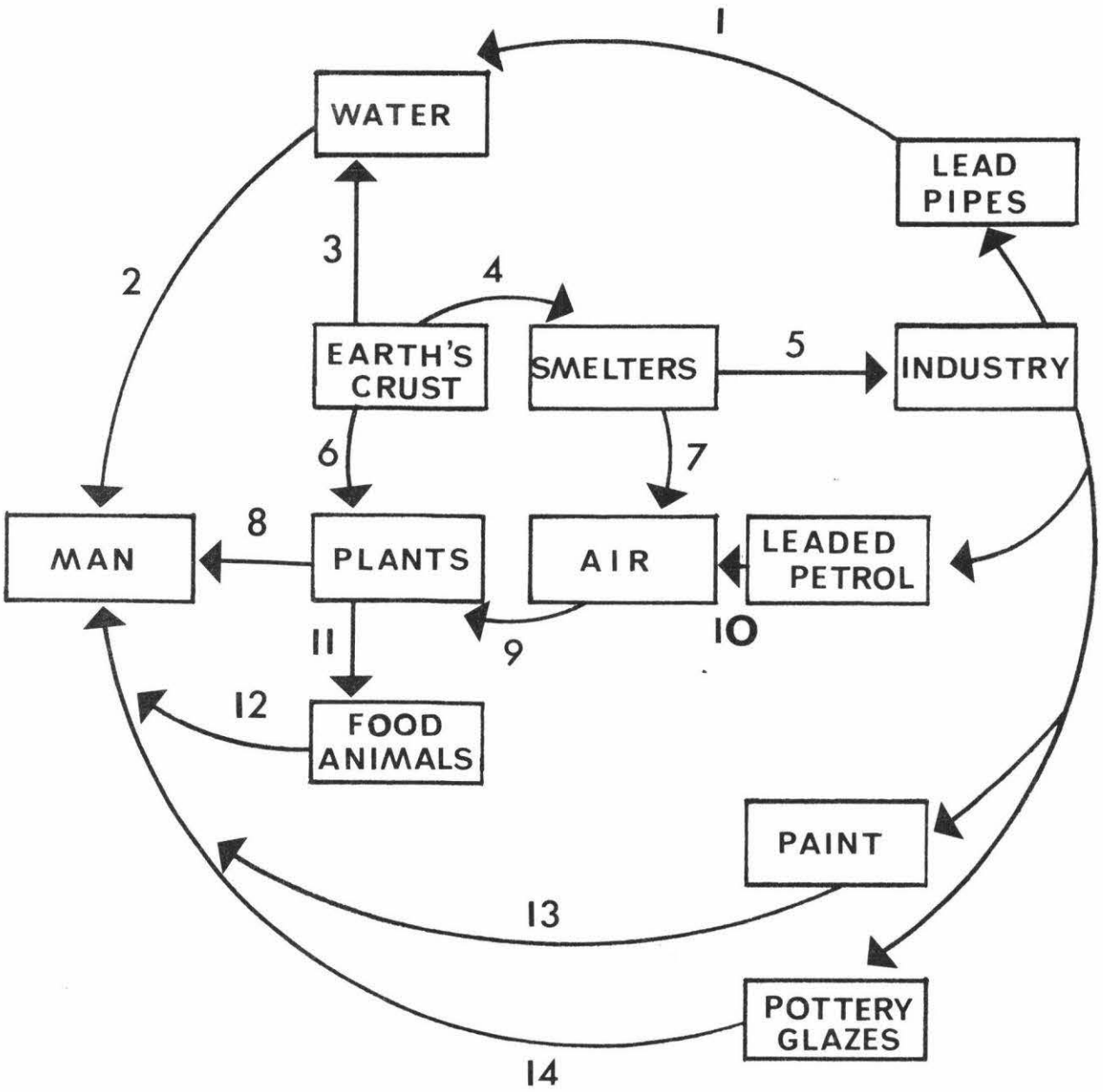
The only other sources of lead pollution worthy of mentioning are the release of soluble lead from glazed earthenware surfaces (Gilfillan, 1965; Klein et al, 1970) into the liquids contained in the vessel and lead poisoning, particularly in children, from lead in paint pigments (Copeland, 1971). Such 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. 0.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 smeltering 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.


1
WATER
LEAD PIPES
2
3
4
EARTH'S CRUST
SMELTERS
5
INDUSTRY
6
7
8
MAN
PLANTS
AIR
LEADED PETROL
9
10
11
12
FOOD ANIMALS
PAINT
13
POTTERY GLAZES
14

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 Waiorongomai 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, cholcopymite and galena. Quartz is the main gangue material.

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

An aerial view of the Tui Mine, Te Aroha, is shown in Plate 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

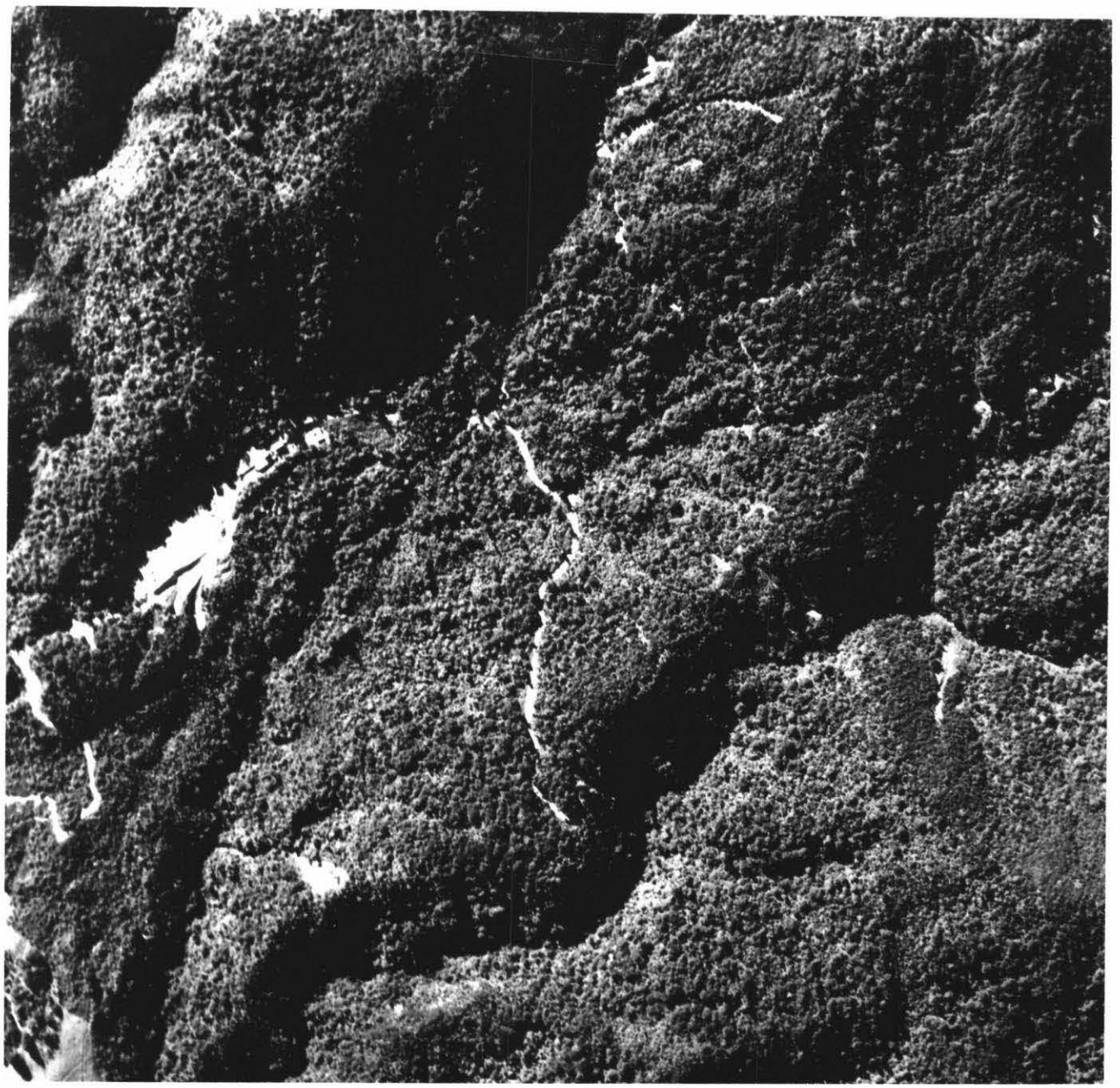


Plate O.I Aerial view of the Tui Mine, Te Aroha

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 0.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.

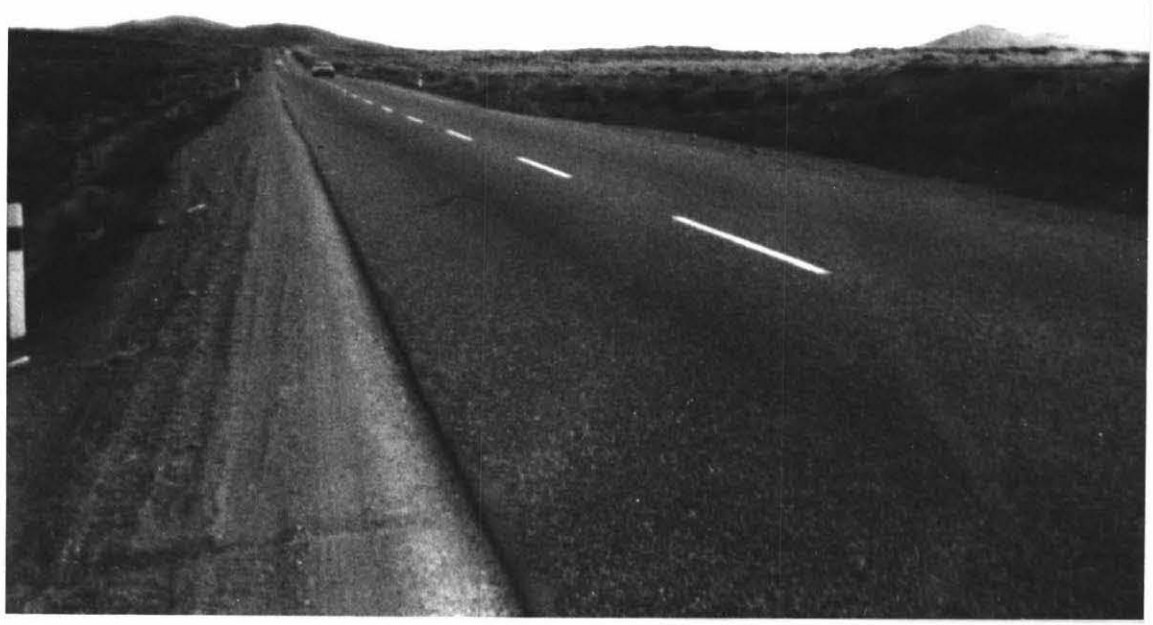


Plate O.III National State Highway No.1, central region, North Island

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.