HEAVY METAL POLLUTION IN THE NEW ZEALAND ENVIRONMENT

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

— p153: The Hidden Structure:
<u>The Assent of Man</u>
J. Bronowski.

ABSTRACT

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

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

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

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

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

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

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

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

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

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

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

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

There was no evidence to suggest that lead is 'excreted' from the body organs or blood into the wool. Although washing removes a significant percentage of lead from the wool of sheep exposed to motor vehicle emissions, lead particulates adhere and become incorporated into the wool fibres, especially in the outer 2-4cm of wool.

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

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

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

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

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

Section V:

The seasonal variation in lead content of Lolium perenne L.

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

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

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

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

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

Section VIII: The effect of lead on seedlings of _Lolium perenne_ L. (perennial ryegrass) and _Trifolium repens_ L. (white clover) was investigated by a series of pot trials involving a sterile silica sand substrate with varying amounts of added lead. Limiting amounts of lead were found after 14 weeks in all organs of both species for substrates containing over 1000 µg/g lead. These values were about 60 µg/g and 100 µg/g (dry weight basis) for leaves and roots of ryegrass. For clover, values of 80 µg/g, 85 µg/g and 100 µg/g were found in leaves, stolons and roots respectively. In both cases, significant uptake did not occur until 12 weeks after germination.

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

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

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

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

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

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

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

TABLE OF CONTENTS

page.

page.

After page.

LIST OF FIGURES

After page.

After page.

After page.

page.

LIST OF TABLES

After page.

LIST OF PLATES