A STUDY ON THE EXTENT TO WHICH LEAD AND CADMIUM FROM MOTOR VEHICLES HAVE CONTAMINATED ROADSIDE SOILS AND VEGETATION IN NAIROBI AND KIAMBU, KENYA. '

BY

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This thesis is my original work and has not been presented for a degree in any other University.

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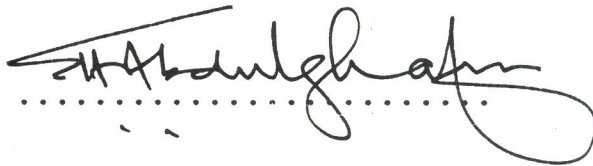
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Dedicated

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LIST OF ABBREVIATIONS

FM - Fresh mass

DW - Dry weight

AAS - Atomic Absorption Spectrophotometer/
Spectroscopy

UNEP - United Nations Environment Programme

USDA - United States Development Agency

EPA - Environmental Protection Agency

FAO - Food and Agricultural Organisation

DNA - Deoxyribonucleic acid

WHO - World Health Organisation

ABSTRACT

The lead and cadmium concentrations in roadside soils and grass from six sites in Nairobi and four sites in Kiambu were determined by atomic absorption spectrometry. Results showed that both soil and grass contained the metals studied. Linear regression analysis between concentrations of metals in the samples and traffic volumes of sites revealed, the two were strongly correlated, thus indicating that motor vehicles form a major source of lead in the roadside. For cadmium there was no significant correlation between concentration and traffic volume. The cadmium concentrations did not show any clear variation with distance away from the roads.

The roads were chosen with traffic volumes ranging between 40 and 1412 motor vehicles per hour. The regional distribution of lead in roadside soils and grass show high levels of contamination occurring mainly in the highly urbanised parts where most of the traffic is concentrated.

In Urban Nairobi the soil lead concentrations ranged between 30.6×10^{-3} ppm and 350 ppm while the plant lead concentrations ranged between 7.71×10^{-3} ppm and 45.8 ppm. Cadmium concentrations ranged between 0.110 ppm and 0.387 ppm in soils and between 0.092 ppm and 0.249 ppm in plants.

In rural Kiam soil lead concentrations ranged between 8.91×10^{-3} ppm and 74.4×10^{-3} ppm, while in

plants the range was between 2.88 X 10^{-3} ppm and 33.0 X 10^{-3} ppm. Cadmium concentrations ranged between 0.200 ppm and 0.694 ppm in soils and between 0.140 ppm and 0.340 ppm in plants.

The variation of lead concentration with distance varied in two ways. For sampling transects with barriers there was a decrease away from the road and then an increase towards the barrier. For open sampling transects the variation was exponential like. The soils were classified and their pH determined in order to investigate the possible role pH plays in lead and cadmium retention in soils and also in the metal uptake in grass. However, there were no observable relationships between the pH and metal concentrations on the roadside soils and grass.

An evaluation of the implications of the introduction of lead and cadmium into the environment especially their introduction into the food chain has been covered.

CHAPTER ONE

INTRODUCTION

Trace elements are the main source of metal toxicity problems in the environment, since most organisms are not adapted to deal with them when they occur locally at high concentrations. Trace element analysis is necessary for the understanding of environmental hazards related to heavy metal pollution. Trace elements can be categorised into two classes; Essential elements and non-essential elements. Essential trace elements are those that are necessary for specific physiological functions in organisms (Mertz, 1981; Rainbow, 1985). Non-essential trace elements do not have any biological functions in living tissues, they are acquired and accumulated as environmental contaminants.

Excessive levels of trace metals occur naturally or due to anthropogenic sources. Once available they are not easily detoxified and thus accumulate. The metals pollute the environment either by direct toxicity, interference with the respiratory and photosynthetic balance or by impairment of the diversity and stability of an ecosystem.

Lead and cadmium are among the most hazardous elemental pollutants. They are known to have cumulative effects, so that even small quantities consumed may show effects later in life (Lucas, J.,

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1975). In the recent years there has been increasing concern about the possible toxic effects of these metals in plants and animals. The ability of plants and soil to accumulate these elements has been used to investigate and monitor their levels in the environment.

In Kenya the number of registered motor vehicles has been increasing steadily. This has led to a high concentration of traffic, not only in urban areas, but also in rural areas where the main activity is agriculture. The increase in traffic density may result to high lead and cadmium levels in nearby roadside soil and vegetation.

Lead pollution arising from motor vehicle exhaust fumes has been amply studied in the developed world in recent years. The addition of tetramethyl or tetraethyl lead to petrol is one of the cheapest ways of increasing its octane number. Only a fraction of the lead content of petrol is emitted to the atmosphere in motor vehicle exhaust. Hirshler and Gilbert (1964) have estimated a 70 to 80 per cent discharge to the environment. Data concerning lead emission to the atmosphere are discrepant, on a per vehicle basis (Smith, 1976; Cantwell et al., 1972; Ter, Haar and Boyard, 1971). The average lead content in petrol is calculated to be 0.19 g/l (Ward et al., 1975).

The lead burden of the environment is related to the vehicular traffic density as shown by Daines *et al.* (1980), Motto *et al.* (1970), Shuck and Locke (1970), Gange and Page (1972) and Wheeler and Rolfe (1979), have found that lead levels in soil and vegetation increase with an increment in traffic density.

Other factors that affect lead content in the ecosystem near the roads are, the distance from the road, the predominant wind direction, the local topography and the season of the year. Motto *et al.* (1970) have pointed out that most of the effect of lead discharge from motor vehicles is confined within a zone 33 metres wide from the road edge, however Ward *et al.* (1975) suggested a strip having a width of 100 metres.

Cadmium pollution due to abrasion of motor vehicle tyres, (wear of galvanized parts and some motor oils) has not received much attention as expected. Cadmium is primarily derived from motor vehicle tyres, whose cadmium content varies between 20 and 90 μg/g (Lagerwerff and Specht, 1970). Cadmium may also be a by-product of combustion of certain fuels (Porfi'ev *et al.*, 1970; 1971; Krayushkin *et al.*, 1965).

The dynamics of cadmium transport to soil and vegetation differ from those of lead. Cadmium reaches the soil mainly in runoff water and not through an

aerial route. Ward *et al.* (1977) have found a significant correlation between traffic density and cadmium levels in the soil and vegetation of the median strips of the roads.

In order to investigate the influence of traffic density on lead and cadmium levels in roadside soil and vegetation, several sites were selected with varying traffic densities in Nairobi and Kiambu.

1.1.0   LEAD IN THE ENVIRONMENT

Lead is a fairly abundant element in the earth's crust and is present in all parts of the environment. Its effect as a hazardous metal has been recognised since early civilization. The metal being easily smelted has been used by man for making tools and vessels for either cooking, eating or wine storage. In modern times lead has played a major role in occupational diseases among smelters, miners, automobile finishers, storage battery workers and spray painters (UNEP, 1980). This has led to a lot of research work on lead as an environmental pollutant.

1.1.1   LEAD IN SOILS

The terrestrial abundance of lead indicates a tendency for lead to concentrate in the acid series of magmatic rocks and argillaceous sediments in which the common lead concentrations range from 10 to 40 ppm, while in ultramafic rocks and calcareous sediments its

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range is from 0.1 to 10 ppm. Mineral sources of lead are galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$).

The natural lead content of soils is strongly related to the composition of the bedrock, and lead is reported to be the least mobile among the heavy metals. Although the lead species can vary considerably from one soil to another, it may be concluded from the results given by Norrish (1975), Riffaldi et al. (1976), Tidball (1976) and Schnitzer and Kerndoff (1986) that lead is associated mainly with clay minerals, manganese oxides, iron and aluminium hydroxides and organic matter. However some soil lead may be highly concentrated in calcium carbonate particles or in phosphate concentrations.

The solubility of lead can be greatly decreased by liming. A high soil pH may precipitate lead as hydroxide, phosphate or carbonate, as well as promote the formation of lead-organic complexes.

The characteristic localisation of lead near the soil surface in most soil profiles is primarily related to the surficial accumulation of organic matter. The greatest lead concentrations are also often in the organically rich top horizons of uncultivated soils, as was reported by Fleming et al.(1968). Therefore organic matter is considered as the important sink of lead in polluted soils.

The fate of the anthropogenic lead in soils has recently received much attention because this metal is hazardous to man and animals from two sources; the food chain and soil dust inhalation. The steadily increasing amounts of lead in surface soils, both arable and uncultivated, have been reported for various terrestrial ecosystems (Hughes *et al.*, 1980). The accumulation of lead in surface soil exposed to various pollution sources at some sites has already reached a value as high as about 2% of dry soil material. The levels of lead in soils that are toxic to plants are not easy to evaluate, however several authors have given quite similar concentrations, ranging from 100 to 500 ppm.

Studies on lead compounds in contaminated soils have been reviewed by Hildebrand (1974), Olson and Skogerboe (1975) and Harmsen (1977). The main lead pollutants emitted from smelters occur in mineral forms (e.g. PbS, PbO, $PbSO_4$, $PbO.PbSO_4$), while lead in automobile exhausts is in the form of halide salts {e.g. $PbBr$, $PbBrCl$, $Pb(OH)Br$, $(PbO)_2PbBr_2$}. Exhaust lead particles are unstable and readily convert into oxides, carbonates and sulphates. Because lead enters the soil in various and complex compounds, its reactions may differ widely among areas.

Several observations of the lead balance in various ecosystems show that the input of this metal greatly exceeds its own output. Hansen and Jjell

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(1978) estimated that the annual increase of lead in Danish agricultural soils was 3.7% of its total amount in soil. The contamination of soils with lead is mainly irreversible and therefore a cumulative process in surface soils will continue even if the inputs are low. The accumulation of lead in surface soils is of great ecological significance, because this metal is known to greatly affect the biological activity of soils. This topic has been reviewed by Tyler (1975), Anderson (1976), Doelman and Hanstra (1979), Hughes *et al.* (1980), who showed that increased levels of lead in soil are likely to limit enzymatic activity of microbiota and as a consequence, markedly increase the accumulation of incompletely decomposed soil organic matter, particularly those materials that do not decompose readily such as cellulose.

Niyazova and Letunova (1972) reported a strong tendency of soil microflora to accumulate lead at a very high rate that was proportional to the metal content of soils. Consumers such as earthworms also at times concentrate lead from the soil substrata, which greatly contributes to a secondary deposition of lead in surface soils.

1.1.2   LEAD IN PLANTS

Although lead occurs naturally in plants, it has not been shown to play any essential roles in their metabolism. Broyer *et al.* (1972) concluded that if

lead was necessary for plants its concentration at the level of 2 to 6 ppm should have been sufficient.

Zimdahl (1975) and Hughes *et al.* (1980) have shown that lead, although not readily soluble in soil, is absorbed mainly by root hairs and is stored to a considerable degree in cell walls. When lead is present in soluble forms in nutrient solution, plant roots are able to take up great amounts of this metal, the rate increasing with increasing concentration in the solutions and with lime. The lead content of plants grown in mineralised areas is in general highly correlated with the lead concentration in soil, although this relationship differs among the organs of the plant.

The translocation of lead from roots to tops is greatly limited. Zimdahl (1975) reported that only 3% of the lead in the root is translocated to the shoot. Apparently most of the lead in soil is unavailable to plant roots. Cannon (1976) and Zimdahl and Koeppe (1977), Wilson and Cline (1966) showed that only 0.003 to 0.005% of the total lead in soils may be taken up by plants, this uptake, however varies significantly over the concentration ranges currently present in soils and with various forms of lead that occur in soils. There is evidence that lead is taken up from soils by roots, at both low and high lead concentrations and that this process is strongly governed by soil and plant factors.

Airborne lead, a major source of lead pollution, is also readily taken up by plants through foliage. Much controversy exists in literature on the question of how much lead is actually taken into foliar cells.

A number of studies have shown that lead deposited on the leaf surface is absorbed by these cells. Although it has been suggested that most of the lead pollution can be removed from the leaf surfaces by washing, there is likely to be a significant translocation of lead into plant tissues (Isermann, 1977). Zimdahl and Koeppe (1977) have shown that under certain conditions lead is mobile within the plant. It is generally agreed, however that lead from soil source is not readily translated to the edible portions of plants. The main process responsible for lead accumulation, in root tissue is the deposition of lead especially as lead pyrophosphate, along cell walls. Malone *et al.* (1974) identified the deposits in cell walls outside the plasmalemma as lead precipitates and lead crystals. Similar lead deposits observed in roots, stems and leaves suggest that lead is transported and deposited in a similar manner in all tissues of the plant.

Although there is no evidence that lead is essential for the growth of any plant species, there are many reports on the stimulating effects on plant growth of some lead salts, mainly $Pb(NO_3)_2$ at low concentrations. Moreover, other reports have described

inhibitory effects of low lead levels on plant metabolism. Several reports describe the toxic effects of lead on processes such as photosynthesis, mitosis and water absorption, however the toxic symptoms in plants are not very specific (Kabata and Kabata, 1988).

Although even very low lead concentrations may inhibit some vital plant processes, lead poisoning has seldom been observed in plants growing under field conditions. The two possible explanations are; the relatively low lead concentration in soil and a low lead availability even in contaminated soil conditions.

The interference of lead with other trace elements has been reported only for zinc and cadmium. The stimulating effect of lead on cadmium uptake by plant roots may be a secondary effect of the disturbance of the transmembrane transport of ions. The zinc-lead antagonism adversely affects the translocation of each element from roots to tops.

The interference of lead with calcium is of metabolic importance, since lead can mimic the physiological behaviour of calcium and thus inhibit some enzymes. The beneficial effect of liming on reducing lead absorption by roots is governed by soil type. In soils where lead-organic complexes are formed, Ca^{2+} cations do not significantly limit the availability of lead.

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A favourable phosphorous regime is known to reduce the effects of lead toxicity. This interference is due to the ability of lead to form insoluble phosphates in plant tissues, as well as in soils. Sulphur is also known to inhibit the transport of lead from roots to shoots. Jones *et al.* (1973) reported that sulphur deficiency in soils increases markedly the lead movement into plant tops.

The great variation of lead content of plants is influenced by several environmental factors, such as the presence of geochemical anomalies, pollution, seasonal variation, and genotype ability to accumulate lead. Nevertheless natural lead in plants growing in uncontaminated and unmineralised areas appears to be quite constant, ranging from 0.1 to 10 ppm and averaging 2 ppm (Alloway, 1968; Cannon, 1976).

The ability of plants to absorb lead from two sources, soil and air, is of major environmental significance, even though lead is believed to be the metal of least bio-availability and the most highly accumulated metal in root tissues. Several plant species and genotypes are adapted to grow in high lead concentrations in the growth media; this is reflected by anomalous amounts of this metal in plants.

The highest bio-accumulation of lead generally is reported for heavy vegetables (mainly lettuce) grown in surroundings of non-ferrous metal smelters where plants are exposed to lead sources of both soil and

air. In this locations highly contaminated lettuce may contain as much as 0.15 % (DW), (Roberts *et al.*, 1974).

1.1.3   LEAD: FOOD CHAIN AND HEALTH

Lead pollution and its health effects are matters that deserve serious attention. With the steady increase of motor vehicles using leaded petrol in Kenya, there is no doubt that the lead level in the environment will also increase as a result of auto-exhaust emissions. Although the present levels may not be directly harmful to human health, the concentration of lead is steadily increasing in food chains. This could ultimately produce toxic dose to man and other organisms which feed on large quantities of food contaminated with lead.

Lead can be taken by man through air, water or food. The atmospheric contribution to the total lead intake in an average man depends on his working and domestic environment. McMullen (1977) reported 0.01 mg/m^3 for urban areas and 0.002 mg/m^3 for non-urban areas.

It has been found that the lead content of crops growing within a short distance from the motorway increased with time as the plant grew to cover larger ground (McClean and Shield, 1977; Davies *et al.*, 1972). Grazing livestock in the vicinity of heavily used roads exposes the animals to lead from exhaust

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fumes. Graham and Kalman (1974) established that lead content of forage grass from sites at varying distances from the roads were sufficient to pause a threat to grazing animals. Ingestion of such grass by livestock may provide an additional increment of lead in man's diet.

Several studies have shown high lead levels in animals habiting roadsides heavily used by motor vehicles. Lead from automobile exhaust poisoned roadside populations of deer mice (Marian and Faura, 1975). In a study on seven different tissues from deer mice, Welch and Dick (1975) found that increased traffic density and higher fraction of exhausted lead had contributed to higher environmental lead levels and higher tissue levels. Ward et al. (1979) found significant lead concentrations in organs of sheep grazing adjacent to busy highways. Lead levels determined in the organs was a result of automobile exhaust emissions. These results suggest that offal animals grazed adjacent to highways stand a high risk of lead pollution, which subsequently finds its way into the food chain.

TABLE 1; THE DISTRIBUTION OF LEAD IN THE BODY (Lucas, 1975)

Bone	7.0-11	ppm
Liver	2.0	ppm
Kidney	1.0	ppm
Brain, heart and muscle tissue	0.01	ppm

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The average concentration of lead in human beings ranges between 1.5 and 7.1 mg/kg. Lead is mainly deposited in the bones, where it replaces the calcium. More than 95% of the body burden is stored in the bone as tripolyphosphates.

Even though there is no evidence in literature concerning biological necessity of lead in living organisms, experiments on animals have shown that even minute quantities interfere with respiratory pigments, energy production and membrane function. Lead affects the formation of blood by retarding normal maturation of red blood cells in the bone marrow and also by inhibiting the synthesis of haemoglobin by interfering with deltaminolevulinic acid (δ-ALA) and coproporphyrin (Lucas, 1975).

In lead poisoning δ-ALA and coproporphyrin are excreted in the urine in excess. The normal daily coproporphyrin values in urine vary between 0.005 mg/l and 0.015 mg/l as compared to 0.098 mg/l in lead poisoning, δ -ALA dehydrogenase is inhibited when organic lead levels in blood are between 0.2 and 0.4 mg/kg (Hernberg et al., 1970; Miller et al., 1970). In a survey done in America on lead blood levels, it was found that blood levels were in the range of 0.15 to 0.70 mg/kg and averaged about 0.3 mg/kg.

Lead poisoning effects mainly involve blood-forming mechanism, gastrointestinal tract and in the advanced stage, the nervous system. The effects in

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adults are different from those on children. In the early stages of poisoning, adults become anaemic, restless and easily distracted. Children develop stomach pains, constipation and heartburn. The most serious manifestation of lead poisoning is the involvement of the nervous system which accounts for a wide range of neurologic symptoms ranging from drowsiness to coma and epileptic convulsions. After prolonged excessive lead absorption, paralysis of the eye muscles and the extensor muscles occur (UNEP, 7th February, 1984).

The minimum lethal dose of inorganic lead for man has been estimated at between 300 and 700 mg/kg and blood levels of 0.8 mg/l. Lead poisoning involving a physicians family, reported in America in 1969, revealed that six members of the family experienced fatigue, poor appetite, vague pains in the stomach and vomiting. Unexplained personality changes were also observed in both the children and the parents. Their lead blood levels was found to be 1.94 mg/l (Walbott, 1978).

Lead poisoning can cause permanent injury or even early death. In a survey in Chicago, out of 405 children with chronic lead poisoning, only 257 recovered completely, the remaining ones had permanent mental retardation and recurrent epileptic seizures. Pregnant women are more vulnerable to lead poisoning, which cause abortions and premature births. Lead also

causes sterility in women. These harmful effects of lead on women prompted the restriction of employing females in lead based industries (UNEP, 7th February, 1984).

Lead contaminated soil invariably has been found to contribute significantly to children's risk of blood level elevation. A study carried out in Charleston, South Carolina showed that, the soil lead levels around 37 poisoned children were significantly greater than the levels of 170 randomly selected sites in the city (Fairey and Gray, 1970). A study carried out by Rabinowitz and Bellinger (1988) established that as the mean soil lead concentration rose from 225 ppm to 1800 ppm in the study area, the mean blood levels of the inhabitants rose from 0.17 to 0.30 mg/l.

Lead in surface soil and dust accounts for most of the lead exposure in young children. Children up to the age of six years are a population at increased risk for lead exposure and its related adverse effects, because of their behaviourial characteristics. Mielke *et al.* (1983) estimated that 40 to 50 % of reported lead poisoning in the USA were a result from sources in the environment such as soil, plants, water, roadside dustfall and indoor dust. Guidelines published by United States Development Agency (USDA) and Environmental Protection Agency (EPA) indicate that lead levels in garden soils ranging from 500 to 1000 mg/kg can be a potential

health hazard for children that may ingest the soil (Mielke *et al.*, 1984).

1.2.0   CADMIUM IN THE ENVIRONMENT

Cadmium is an extremely toxic element for plants, animals and man. Although the earliest recorded incident of cadmium poisoning occurred in 1858, as a result of occupational exposure, numerous outbreaks of acute cadmium food poisoning occurred up to 1945 because food was allowed to come into contact with cadmium-plated containers (Fulkerson *et al.*, 1973).

However cadmium emissions from various high temperature sources (smelting of certain ores), incineration, combustion of certain fossil fuels and the continuing incorporation of cadmium into products of domestic and industrial use have shifted concern to the health effects of environmental cadmium.

Increased cadmium concentration on highways result from the wearing out of automobile and truck components (tyres, galvanized metal) as well as from the combustion of petroleum distillates and their additives.

1.2.1   CADMIUM IN SOILS

The abundance of cadmium in magmatic and sedimentary rocks does not exceed 0.3 ppm, and this metal is likely to be concentrated in argillaceous and shale deposits. Cadmium is strongly associated with

zinc in its geochemistry, but seems to have a stronger affinity for sulphur than zinc and exhibits also a higher mobility than zinc in acid environments.

The main factor determining the cadmium content of soil is the chemical composition of the parent rock. The average content of cadmium in soils lie between 0.07 and 1.1 ppm. However, the background cadmium levels in soils apparently should not exceed 0.5 ppm, and all higher values reflect the anthropogenic impact on the cadmium status in top soils.

Forbes *et al.* (1976) and Street *et al.* (1977) have revealed in their studies that cadmium activity in soil is strongly affected by pH. In acid soils, the organic matter and sesquioxides may largely control cadmium solubility and in alkaline soil, precipitation of cadmium compounds is likely to account for cadmium equilibria. Cadmium is most mobile in acidic soils within the range of pH 4.5 to 5.5, whereas in alkaline soils cadmium is rather immobile.

1.2.2   CADMIUM IN PLANTS

Although cadmium is considered to be a non-essential element for plants, it is effectively absorbed by both the roots and leaf systems. Soil pH is the major soil factor controlling both total and relative uptake of cadmium. Kitagashi and Yamane

(1981) reported that the relative uptake by rice seedlings was greatest with the pH range 4.5 to 5.5.

Although soil characteristics, other than pH, can also cause differences in cadmium absorption by roots, soluble species of cadmium in soil are always easily available to plants. Although an appreciable fraction of cadmium is taken up passively by roots, cadmium is also absorbed metabolically (Smeyers-Verbeke *et al.*, 1978). Chaney and Hormic (1977) reviewed plant response to increased levels of cadmium in soil and showed a great difference in the ability of various plant species to absorb this metal. Cadmium can be easily transported within a plant in the form of organometallic complexes.

A great proportion of cadmium is known to be accumulated in root tissues, even when cadmium enters the plant via foliar systems (Kabata-Pendias, 1978). Although the roots of several species can take up large amounts of cadmium from the growth medium, the translocation of cadmium through the plant may be restricted because cadmium is easily held mainly in exchange sites of active compounds located in the cell walls. The most important biochemical characteristic of cadmium ions is their strong affinity for sulfhydryl groups of several compounds. In addition cadmium also shows an affinity for other side chains of protein and for phosphate groups.

Dabin *et al.* (1978) and Braude *et al.* (1980) reported that cadmium was likely to be concentrated in the protein fractions of plants. This fact is very important in food production problems. Cadmium toxicity results from the metal disturbing enzyme activities. Cunningham *et al.* (1975) and Baszynski *et al.* (1980) reported inhibition of the formation of anthocyanin and chlorophyll pigments in plants that were treated with cadmium.

Overt symptoms induced by elevated cadmium content of plants are growth retardation, root damage, chlorosis of leaves and red-brown coloration of leaf margins or veins. The phytotoxicity of cadmium, beyond interfering with normal metabolism of some micronutrients, shows inhibitory effects on photosynthesis, disturbs transpiration and carbon dioxide fixation, and alters the permeability of cell membranes. Cadmium is also known to inhibit the DNA-mediated transformation in microorganisms and to interfere with symbiosis between microbes and plants as well as to increase plant predisposition of fungal invasion (Mennear, 1979).

The cadmium content of plants is, however, of the greatest concern as a cadmium reservoir and as the pathway of cadmium to man and animals. Thus, tolerance and adaptation of some plants species to higher cadmium levels, although important from the environmental point of view, create a health risk.

Plants are simultaneously exposed to a variety of pollutants and thus their integrated effects most often are different from the effect of cadmium only. Several elements are known to interact with cadmium in both the element uptake of plants and in biochemical roles. Zinc, for example reduces the uptake of cadmium by both root and foliar systems. Chaney and Hornick (1977) reported that when the cadmium/zinc ratio in plant tissues is limited to 1%, the cadmium interacts with copper, manganese, nickel, selenium, phosphorus, and calcium in plant uptake.

1.2.3   CADMIUM;   FOOD CHAIN AND HEALTH

In man and animal nutrition, cadmium is a cumulative poison, therefore, its content in food and feed plants has been widely studied. Although plants have no metabolic requirement for cadmium, most plants readily take up cadmium from their surroundings. Absorbed cadmium is quite mobile in plants and is generally not excluded from edible portions such as fruits or seeds, however roots normally contain the highest levels. Two key food grains, rice and wheat are particularly capable of absorbing cadmium from the soil (Kabata-Pandias, 1988).

A comparison of the cadmium contents of the plant foodstuffs produced under uncontaminated conditions of various countries shows the highest cadmium concentration in spinach leaves (0.11 ppm FM) and

lettuce leaves (0.66 ppm DW),(Kabata-Pendias, 1988).
When plants are grown on contaminated soil, however,
cadmium is very likely to also be concentrated in
roots.

Because cadmium is readily available to plants
from both air and soil, its concentration rapidly
increases in plants grown in polluted areas. A few
data collected from several countries show that both
industrial and agronomic practices may create a
significant cadmium supply to plants. The highest
concentration of cadmium in polluted plants were
always reported from roots and leaves, whereas cadmium
seems to be excluded from seed crops. The highest
cadmium values reported for wheat grains (14.2 ppm)
and brown rice (5.2 ppm) were less than amounts of the
metal accumulated in root and leaf tissues of these
plants (Kabata-Pendias, 1984).

The most serious case of environmental hazards of
cadmium occurred in Japan after world war II. Exposure
to cadmium occurred through the ingestion of rice
grown on fields irrigated by industrially polluted
water (UNEP, 1980). The affected subjects developed a
syndrome that began with renal dysfunction and
eventually resulted in painful bone changes (Friberg
et al., 1974). The mysterious disease, then called
itai-itai kyo, occurred most commonly among post-
menopausal women above 45 years of age, who delivered
several children. Cadmium was reported to interfere

with calcium and vitamin D metabolism (Piscator and Larsson, 1972).

The main sources of cadmium in the diet are organ meats such as liver and kidney, aquatic animals such as molluscs and crustaceans and cereal grains such as wheat. Dairy products, potatoes and fruit make lesser contributions. FAO/WHO experts recommend a provisional tolerable weekly intake of 400-500 µg cadmium.

Cadmium interacts with many nutrients to produce altered rates of absorption and responses. Some components that interact with cadmium include zinc, copper, mercury, selenium, calcium, cobalt, protein and chelating agents. The main clinical signs and responses of primary cadmium toxicity in animals are anaemia, retarded gonadal development or degeneration, enlarged joints, scaly skin, liver and kidney damage, reduced growth and mortality rate that relates directly to the concentration of cadmium fed. (Cousins et al., 1973; Pond and Walker, 1972; Nearthery and Miller, 1975).

Cadmium ions absorbed from the intestine become bound to metallothionein or other transport proteins (Nearthery and Miller, 1975). Chicken, sheep, cattle, pigs and horses have all been shown to produce metallothionein in response to excess intake of cadmium (Evans et al., 1970). Kidney and liver tissues may accumulate sufficient cadmium concentrations in cadmium exposed animals to pose concern regarding the

consumption of animal derived foods. However, milk and muscles, the main animal protein foods are very low in cadmium concentrations even in poisoned animals.

That cadmium accumulates in the body, its concentration increasing with age was reported in a study on rats by Matsubara-Khan and Machida(1975). Inhalation of cadmium oxide dust can occur in certain occupation and can lead to severe pulmonary changes including emphysema. An occupational exposure, for example of 0.008 mg/m^3 for 25 years can cause cadmium poisoning (Hodges, 1977). Cadmium can lead to very rapid sterilization of animals because of its toxicity to testicles and sperm cells. Cadmium and its compounds have been proved to produce malignant tumors in rats, but it is not certain whether they are carcinogenic and teratogenic to humans.

Several studies revealed that cadmium leads to high blood pressure in rats, rabbits and dogs and is probably associated with heart diseases in humans. The induction of hypertension in cadmium fed animals has been reported (Schroeder and Buchman, 1962, 1967; Schroeder et al., 1970). The toxic action of cadmium seems to involve the replacement of zinc in certain enzymes by cadmium, resulting in inhibition of their proper functioning (Pulves, 1977).

In humans, absorbed cadmium is more highly concentrated in the plasma than in the red blood cells, except in persons with elevated exposure, where

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the situation is reversed. Plasma cadmium rapidly deposits in the liver, prostate and the kidneys. In time, most of the cadmium is redistributed to the kidneys. Renal cadmium levels increase up to age 50, and levels of accumulation are approximately dependent on cumulative exposure. The critical renal cortex concentration of cadmium which produces chronic kidney damage is estimated to be about 200 mg/Kg wet weight. Normal urinary excretion of cadmium by typical adult human is usually less than 2×10^{-3} mg/day. Renal tubular dysfunction might be expected when urinary excretion exceeds $2.0-2.5 \times 10^{-3}$ mg/day; renal pathological effects probably occur at urinary levels of 5×10^{-3} mg/day. Increased urinary excretion of beta-2-microglobulins is probably the earliest indicator of cadmium-induced renal tubular dysfunction. Nutritional deficiencies (zinc, iron, calcium) may predispose individuals to adverse effects from dietary cadmium levels below the $250-350 \times 10^{-3}$ mg/day estimated to give a level of cadmium in the renal cortex of 200 mg/Kg, the critical concentration for kidney damage.

1.3.0   OBJECTIVES OF THE PROJECT

1.3.1   AIM

To conduct a detailed study on the extent to which lead and cadmium from motor vehicles have contaminated soils and vegetation in selected areas in Kenya.

1.3.2   OBJECTIVES

i)   To investigate the relationship between motor vehicle exhaust emissions (by estimating traffic density) and occurrence of lead and cadmium on roadside soils and vegetation on chosen roads in Nairobi and Kiambu.

ii)   To investigate lead and cadmium concentration in relation to distance from the chosen stations.

iii) To determine the acidity/alkalinity of the soil samples.

iv)   To evaluate, environmental implications of lead and Cadmium from motor vehicles especially their introduction into the food chain.

1.3.3   SIGNIFICANCE OF THE PROJECT

Lead and cadmium are toxic trace elements. Both may be derived from motor vehicles. Several studies indicate that lead derived from combustion of lead antiknock compounds (tetraethyl and tetramethyl lead) in motor vehicles form a major component of the global lead cycle. Automotive lead is a major contributor to the high lead levels in the surface waters and sediment, especially in the vicinity of roads with heavy traffic. Cadmium concentration near highways result from the wearing out of automobile and truck components (tyres, galvanised metal), as well as from the combustion of petroleum distillates and their additives.

Apart from accumulation by plants, animals and human beings, lead and cadmium deposited on soils and vegetation may be removed and translocated elsewhere by action of run-off water and wind and may eventually reach rivers and lakes, thus polluting other parts of the ecosystem.

Several studies showing the toxic effects of lead from motor vehicle exhaust fumes on vegetation, animals and humans located close to highways have been well documented (Patterson, 1965; Rabinowitz and Wetheril, 1972; Andrew, 1972; Welch and Dick, 1975). Ward *et al.* (1977) found a significant correlation between traffic density and cadmium levels in the soil and vegetation of the median strips of roads. Toxic effects of cadmium on plants and animals have also been well documented (Mennear, 1979).

However most of these studies have been carried out in the developed world. Some of the results obtained have led to laws being enacted to minimize or eliminate environmental pollution. Few such studies have been conducted in the developing world, particularly in Africa, thus leaving a vacuum on the related information. It is therefore necessary to document the extent and magnitude to which lead and cadmium have contaminated roadside soils and vegetation in Kenya, as this will help in monitoring and managing environmental pollution from these two trace elements.

In Kenya some studies have been done on the concentration of heavy metals in environmental samples, rivers, lakes and the Indian ocean (Wandiga, 1981; Kinyua, 1982; Wandiga *et al.*, 1983; Ochieng, 1987). This project is therefore an attempt to establish the contribution of the tremendous increase in traffic density on Kenyan roads to the levels of lead and cadmium, in soils and vegetation, particularly in high motor traffic density areas.

CHAPTER TWO

2.1.0   ANALYTICAL TECHNIQUES

Several reliable methods for monitoring trace metals in the environment exist. Walsh and Beaton (1973) discussed the new atomic absorption techniques, such as atomic fluorescence and electrodeless atomic absorption spectroscopy. Methods of analyses like X-ray fluorescence, polarography, neutron activation analysis and spark source mass spectroscopy have been described (Pinta, 1973).

Atomic absorption is a viable analytical technique for measuring trace elements, because of its high specificity and relatively high sensitivity when compared with other methods, (Slavin, 1968). Atomic absorption spectroscopy has been widely used for trace element analysis in environmental samples. Good reviews of flame and non-flame atomic absorption techniques have been published by Christian (1965, 1969), Segar and Gili (1973) and Van Ormer (1973).

In this chapter only flame atomic absorption spectroscopy is discussed. One of the main advantages of atomic absorption spectrophotometry as an analytical method is that absorption by atoms takes place within very narrow spectral regions and only those involving the ground state are normally observed, yielding extremely simple spectra, thus there is very little possibility of coincidence of lines and therefore very little spectral interference (Welz, 1976).

2.1.1.   THEORY OF ATOMIC ABSORPTION SPECTROSCOPY

The determination of elements by atomic spectroscopy is based on the principle of absorption or emission of radiation by free atoms. (fig.1)

E $\uparrow$

E_n(Excited state)

E_m(Ground state)

(a)   (b)
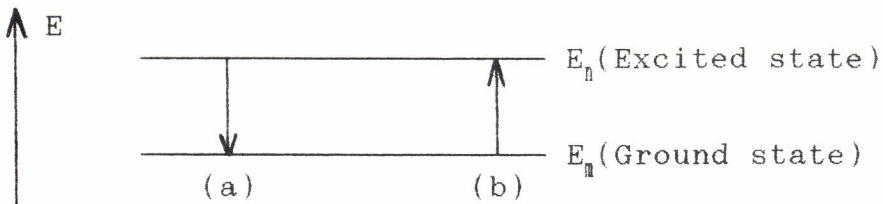
Fig. 1   ABSORPTION/EMISSION

(a) Emission of line of frequency, v.

(b) Absorption of the same line.

For the excitation of a ground state atom, R to $R^{\ddagger}$.

$$R + h\gamma \rightleftharpoons R^*$$ (1)

where h is Planck's constant and V is the frequency, the absorption or emission of light is associated with the process of transition of atoms from one steady state to the other. The type of transition between the steady states will be dependent on the magnitude of the energies involved.

For the steady states m and n with energies E_m and E_n, respectively, absorption of light will take place when $E_n > E_m$, following the transition from m to n, while the transition n to m, results in the emission of light.

The frequency V_{mn} for m to n transition will be inversely proportional to Planck's constant, so that,

$$v_{mn} = \frac{E_n - E_m}{h} \qquad (2)$$

Einstein's quantum theory of radiation suggests that between levels of steady states m and n, three types of transitions may take place;

(i) Emission (n———>m), transition from an excited state, to a lower energy state, due to external radiation of the same frequency V_{nm},

(ii) Spontaneous emission (n———>m), transitions from the excited state to lower energy state, and,

(iii) Absorption (m———>n), transition from a lower energy state to a higher one due to external radiation with frequency V_{mn}. This is the basis of atomic absorption spectroscopy.

Absorptions involving ground state atoms result in the production of resonance lines characteristic of the element. However, the proportion of population of excited atoms to ground state atoms at a given temperature is governed by the Boltzmann distribution;

$$\frac{N_n}{N_m} = \left(\frac{g_n}{g_m}\right) \exp^{-(E_n - E_m)/KT} \qquad (3)$$

where;

N_n = number of atoms in excited state.

N_m = number of atoms in ground state.

g_n and g_m = statistical weights of excited and ground states respectively ($g=2J+1$, where J is the rotational quantum number).

E_n and E_m = Energies of excited and ground states respectively.

$E_n - E_m$ = Excitation energy.

K = Boltzmann's constant ($1.3806*10^{-23}$ JK^{-1})

T = absolute temperature.

At a fixed value of g_n/g_m, the ratio N_n/N_m increases with temperature for a particular element at a particular spectral line.

Absorption by atoms takes place within very narrow spectral regions, of the order of a hundredth of an angstrom, and in the laboratory, only those involving the ground state are normally observed, yielding extremely simple spectra. This accounts for one of the main advantages of atomic absorption spectrophotometry as an analytical method; there is very little possibility of coincidence of lines and therefore very little spectral interference (Welz, 1976). For an atomic gas consisting of a population of atoms in thermal equilibrium capable of absorbing a

quantum of energy hv, containing a radiation of frequency V and intensity I_0, passing through the atomic gas, the absorption of the incident radiation by neutral atoms is given by;

$$A = \log\left(\frac{I_o}{I}\right) \qquad (4)$$

The resulting emission I does not compensate the absorption I_0 because it is omnidirectional. The absorption can be measured by classical spectrophotometric procedures. It permits the quantitative determination of the elements introduced into the atomizing source. A relation exists between I_0 and I that depends on the absorption; fig.(2)

$$N = N_m + N_n$$
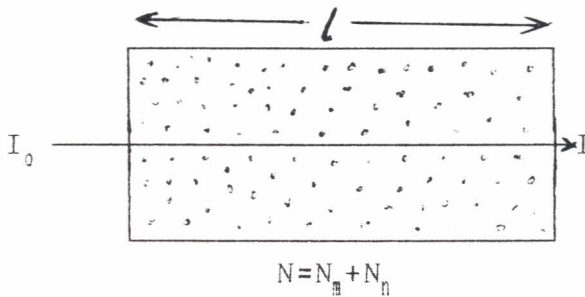
Fig. 2   ABSORBANCE

$$I = I_0 e^{-(k_\nu N_0 l)} \qquad (5)$$

where;

I_0 = Intensity of incident beam

I = Intensity of transmitted beam

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K_γ = Absorption coefficient at the

       frequency, v

N_0 = atomic population with a concentration

  of N_0 atoms per cm^3 in path.

FIG 3   BLOCK DIAGRAM OF THE ATOMIC ABSORPTION SPECTROPHOTOMETER
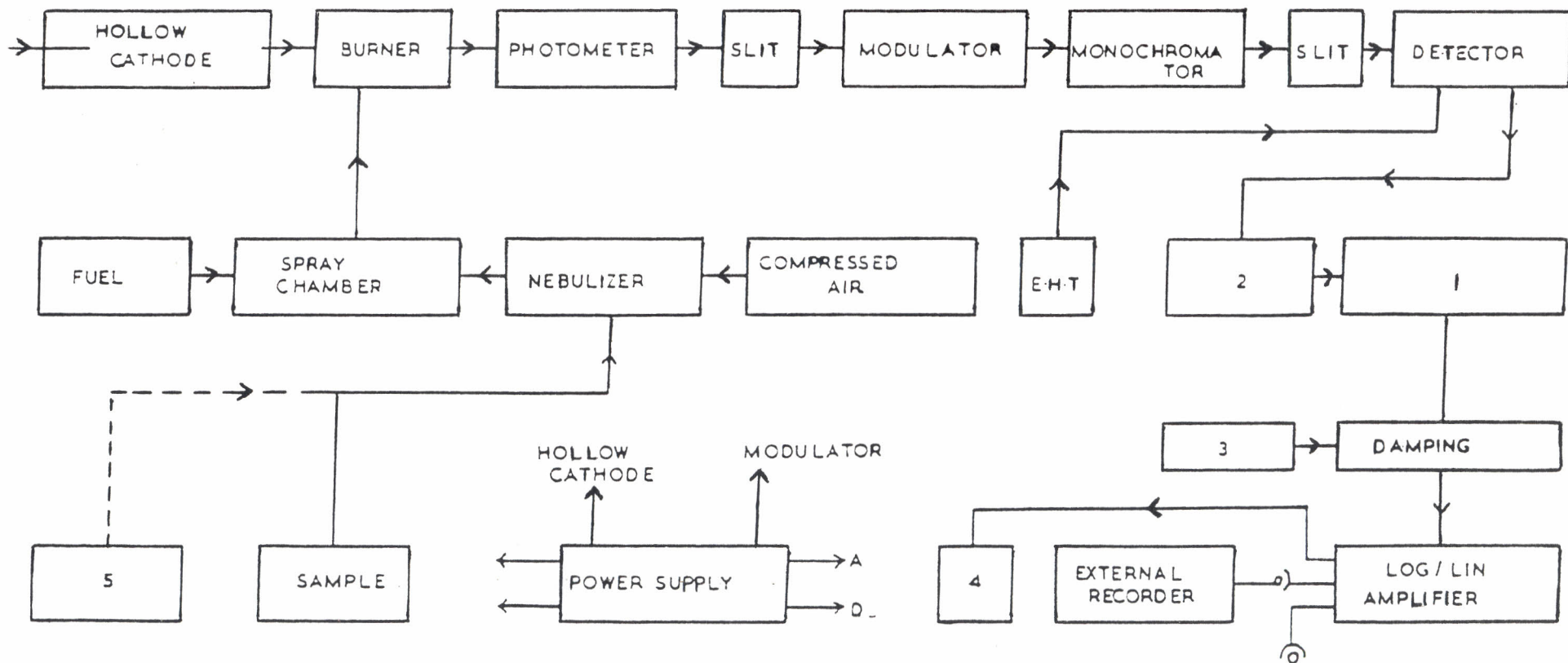
1	SYNCHRONOUS RECTIFIER	4	DIRECT READING GALVANOMETER
2	AMPLIFIER	5	AUTOMATIC SAMPLE CHANGER
3	ZERO SUPPLY	A	AMPLIFIER

D   DETECTOR

2.2.1   INSTRUMENTAL PRINCIPLES

The basic components of an atomic absorption spectrophotometer are shown in fig. 3.

(i) A light source which emits the spectral line characteristic of the element under study.

(ii) A method to produce atomic vapours of the sample being analysed.

(iii) A wavelength selector (monochromator) which isolates the desired resonance line,

(iv) The electronic system comprising a detector, amplifier and read-out.

The light source in most AAS measurements is the hollow cathode lamp, whose cathode incorporates the element being determined. The radiation is passed through the flame and the resonance lines are partially absorbed by the ground state atoms of the same element, if they are present in the sample. By comparing the intensities of the light transmitted by the flame before and after the introduction of the sample, the instrument indicates the amount of light absorbed, which is a measure of the concentration of the element in the sample.

Atomization takes place at the nebulizer - burner stage. For flame AAS, the fuel oxidant mixture, in the proper ratio, is ignited to produce temperatures of up to 3000 K. Chemical radicals and other substances present in the flame will produce chemical effects

during the analysis and therefore a proper choice of the mixture is important.

Fuel gases include, propane, hydrogen and acetylene, while oxidants commonly used are nitrous oxide and compressed air. Air-acetylene is a proper choice for those elements which do not form refractory oxides on introduction to the flame. The use of nitrous oxide as the oxidant gas was suggested to improve the sensitivity of those elements which form refractory oxides. The sample uptake into the nebulizer is made possible by the creation of low pressure at the end of capillary tube by the flow of the carrier gas or oxidant. In the spray chamber, the introduced sample forms an aerosol with the fuel mixture before reaching the burner.

For the flameless AAS, formation of vapour takes place at the desired low temperature without the ignition fuel. This technique became popular in the early seventies when Osland (1970) and Braun and Husbands (1971) developed procedures for the determination of mercury.

When the hollow cathode lamp is used, several non-absorbing lines may be produced by the cathode metal or the lamp fill gas. To achieve the desired resolved spectral line, a monochromator is used. Additional characteristic features of the monochromator is to isolate the measured resonance line from the molecular emission and other background

continuum which originate in the flame, this explains the reason why it is placed before the detector.

The resolution of the monochromator and the detector depend on the amount of light reaching them. Slits function to allow controlled amount of light reaching the monochromator. The amount of this light is dependent on the slit width selected, which in turn depends on the wavelength, nearness to the resonance line of other lines by the source, the intensity of the resonance line and background emission from the flame. Transition elements, which include trace heavy metals require narrower slits because they have other lines near the resonance line due to complex emission spectra. The slit-width can also be increased to improve the electronic gain during operation, especially with low intensity source.

The detectors are normally photomultipliers made of photosensitive materials, usually alloys of alkali metals with antimony, bismuth and/or silver.

The read-out system may consist of a meter or be simply a digital scale, both calibrated linearly with absorbance. The detector output is proportional to the energy falling on it and this is proportional to the transmittance.

2.2.2 INTERFERENCE IN MEASUREMENT OF ABSORBANCE SIGNAL

The presence of some substances (metal ions or other species) in the flame may be detected in the instrument and this may lead to suppression or enhancement of absorbance signal as compared with standard absorbance reading of standard solutions, in which no interferents are present , for the element under study. These foreign substances cause interference with signal output. There are two types of interferences, spectral and non-spectral.

Spectral interferences (Lovett, 1975) arise from coincidence of spectral lines emitted by radiation situated close to the spectral line under study. However, AAS is highly specific for a given element and as such there are very few known examples of actual spectral interference.

Non-spectral interferences are grouped into two; physical and chemical. Physical interferences refers to incomplete volatization of the solid particles of the samples formed in the flame, variations in the physical properties of the solutions or matrix effects (Welz, 1976; Price, 1972) and scatter and background absorption.

Chemical interferences (Cooke, 1973) include stable complex formation and metal ionisation. Most AAS laboratory guides deal with these effects at

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length, and this too, is another advantage of atomic absorption over other methods of analysis.

2.2.3 INTERPRETATION OF THE ABSORBANCE SIGNAL

Absorbance is directly proportional to the absorption coefficient, which is characteristic of the particular element under study. There are two major methods of obtaining quantitative data by interpretation of the absorbance signal. These are;

(a) the standard curve method,

(b) the standard addition method.

The standard addition method (Welz, 1976; Klein, 1977) suffers the disadvantage of being time consuming and lengthy, while the standard curve method for which a plot is made of absorbance Vs standard concentration of the element in solution is affected by matrix effects, but if proper correction is made to reduce the matrix concentration (Welz, 1976), the standard curve is the most commonly accepted method of quantization in atomic absorption spectrophotometry. Both methods are however based on the fact that a proportionality exists between absorbance, A, and concentration, C, so that,

$$A = KC \qquad (6)$$

where K is the constant of proportionality.

2.3.0   pH MEASUREMENTS

2.3.1   THE GLASS ELECTRODE

The glass electrode was used for pH measurements. It consists of a pH-sensitive glass containing a chloride solution of known pH, and an internal reference electrode, usually calomel. The glass is a partially hydrated aluminosilicate containing sodium or calcium ions and often small amounts of lanthanide ions. It is reactive to hydrogen ions in the sense that an ion can join an oxygen site at the same time that another, on the opposite surface leaves, thus maintaining electrical neutrality in the glass. An equilibrium is easily established with hydrogen ions in the inner and outer solutions, producing a potential:

$$E = K + \frac{RT}{F} \ln \frac{(H^+)_{inner}}{(H^+)_{outer}} \qquad (7)$$

K in this expression includes the difference between the characteristic potentials of the inner and outer reference electrodes, the liquid-junction potential, and a small, unpredictable contribution known as the asymmetry potential, possibly due to physical strains in the glass.

By introducing the definition of pH, (7) can be rewritten (at 25°C) as,

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$$E = K + 0.0591 (pH_{outer} - pH_{inner}) \qquad (8)$$

In any given electrode the pH of the inner solution is the constant, so it can be combined with K and the subscript dropped, to give,

$$E = K' + 0.0591 pH \qquad (9)$$

In a practical pH meter, the constants K' is taken into account in the calibration procedure, whereby the electrode assembly is immersed in a standard buffer and the indicator arbitrarily made to show the correct value. The glass electrode is characterised by a pH of zero potential, the point where the inner and outer solutions are of the same pH.

Potassium Chloride solution serves as an electrostatic shield for the high-resistance glass electrode. One short coming of the glass pH electrode is that an erroneously high reading is obtained in the presence of a large concentration of an alkali metal, the so called sodium error. The correction to this is covered by the Nernst-Eisenman equation (Ewing, 1985).

2.3.2 INSTRUMENTATION

A pH meter is a voltmeter that contains an amplifier that senses the signal voltage and produces a proportional meter deflection or numerical (digital)

indication. The resistance of a glass electrode may be as high as 10^8 ohms, and if the error is to be held at 0.1 per cent, the input resistance of the amplifier must not be less than 10^4 ohms. This is easily achieved with modern solid-state amplifiers.

A line-operated laboratory pH meter has three controls on its panel, and may have a fourth. These are;

(i) Switch with standby and operate positions.

(ii) A calibration or standardization adjustment, which amounts to a zero offset with which to adjust the meter to read the correct value when the electrodes are immersed in a standard buffer.

(iii) Temperature compensator that permits alteration of the sensitivity to account for the temperature dependence of the Nernsts potential.

(iv) A scale selector, that allows the instrument to cover the whole pH range (0 to 14).

CHAPTER THREE

3.0.0   MATERIALS AND EXPERIMENTAL TECHNIQUE

3.1.0   DESCRIPTION OF STUDY AREAS

For Nairobi Stations refer to Figs. 4 and 5. For the Kiambu Stations refer to Figs. 4, 6 and 7.

3.1.1   STATION N1 (Museum Hill Round-about)

Soil and grass samples were collected at a transect perpendicular to the round-about on a flat terrain at distances of 2.5, 5.0, 10.0, 20.0, and 30.0 m from the road. The direction of the wind was perpendicular to the transect. The study area had been cultivated before, though at the time of sampling it was all covered with vegetation. There was a high plant fence about 5.0 m from the 30 m sample point. The average number of cars per hour was 1412. Sampling was done on a dry day, during the short rains in November, 1990.

3.1.2   STATION N2 (Waiyaki Way)

Soil and grass samples were collected on a transect perpendicular to the road at distances of 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0 and 60.0 m. The direction of the wind was perpendicular to the transect. The terrain was flat from the road up to the 10.0 m sample point, where there was a sharp downward
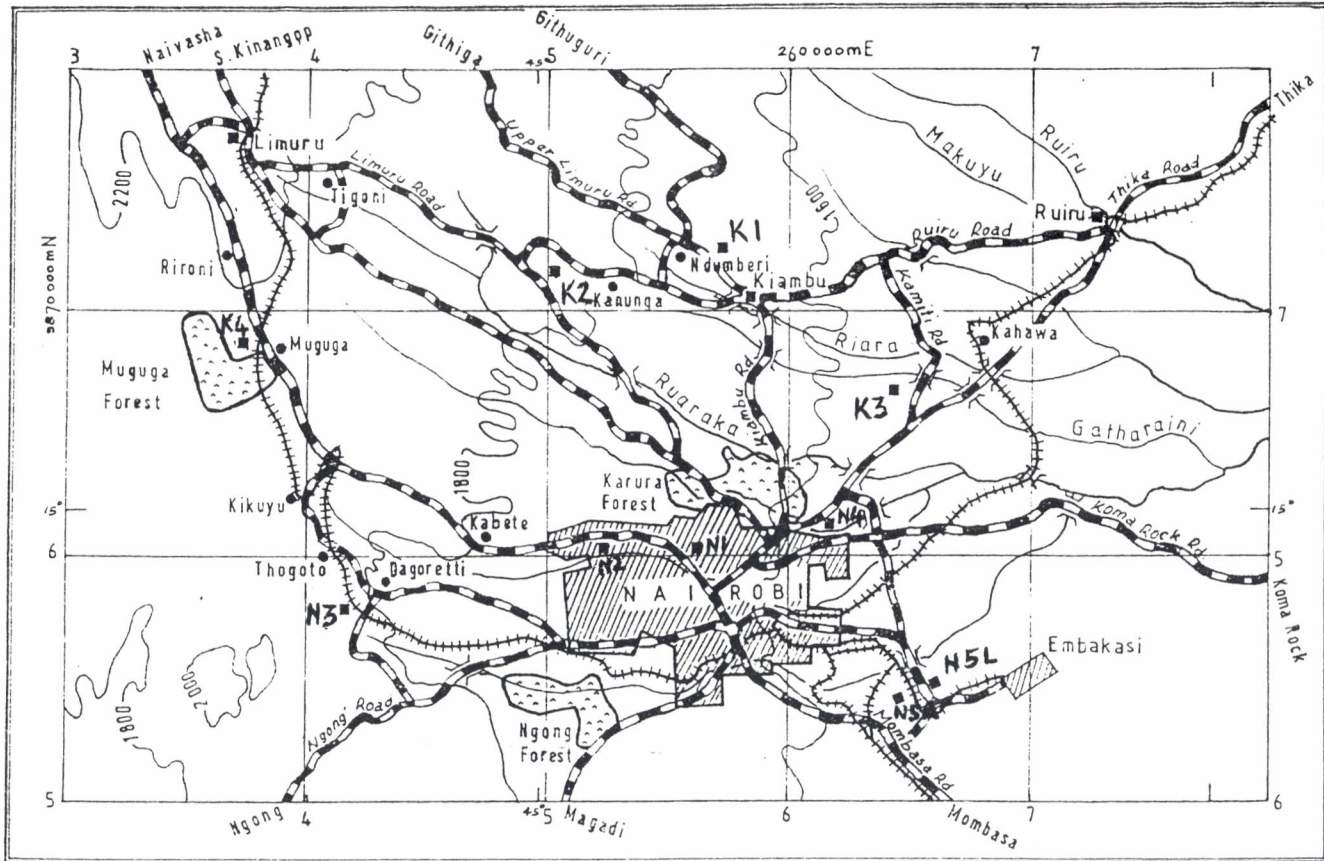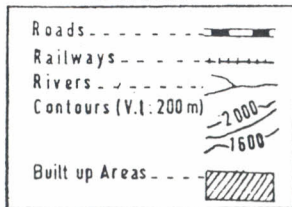
Fig.4 Map of Nairobi and Kiambu showing all sampling sites

NAIROBI

SCALE 1:70,000
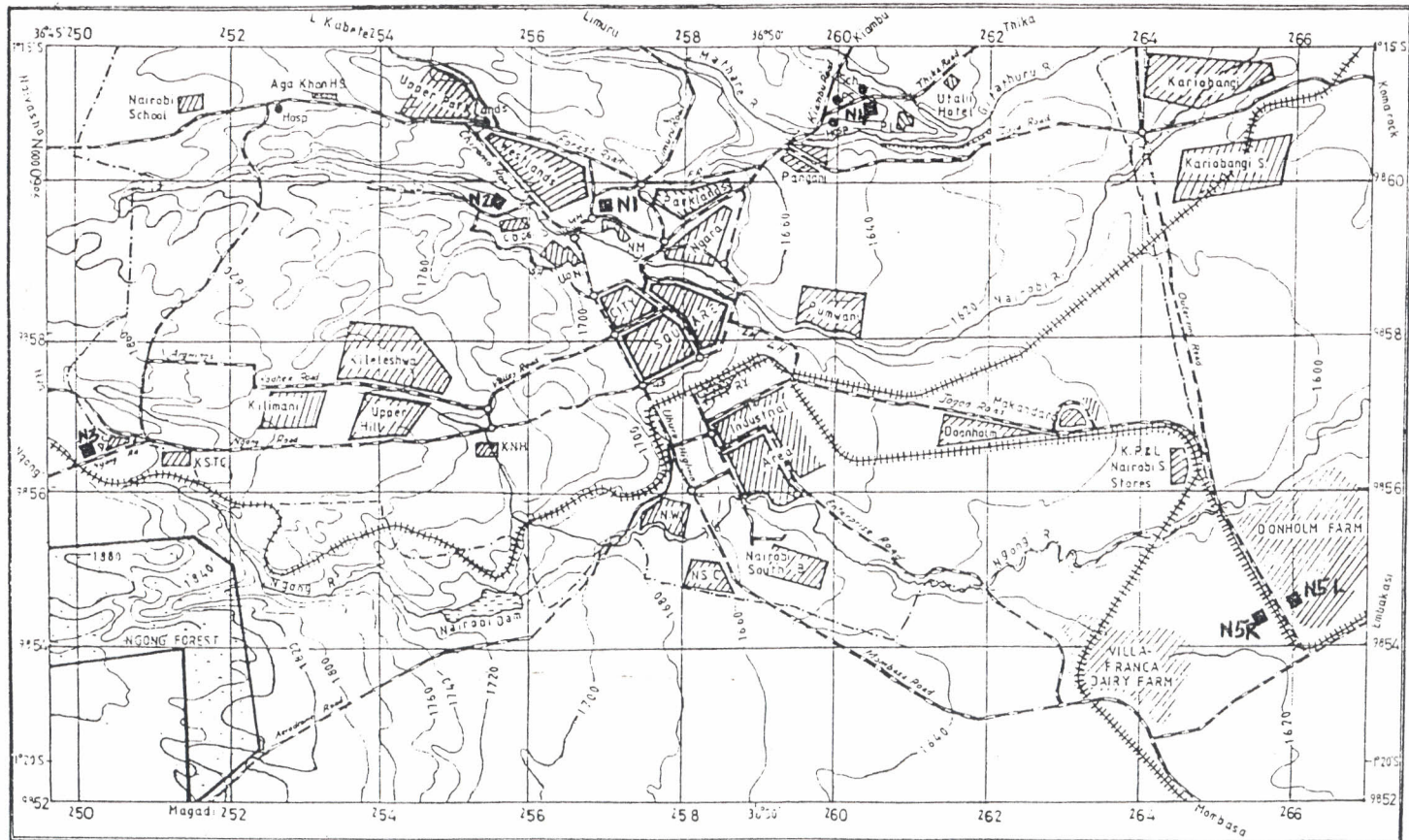
Adapted from sheet 148/4 Nairobi, series (Y 731)
Cartography by Kimiti S.K.

N

Reference

Roads	
Railways	
Boundary (Provincial)	
Rivers	
Contours (V.I 20m)	1600 / 1640
Built up Areas	

Abbreviations

K N H	Kenyatta National Hospital	U o N	University of Nairobi	CD	Chiromo Drive
K P & L	Kenya Power & Lighting	N.M.	National Museum	MH	Museum Hill
KSTC	Kenya Science Teacher's College	cbps	College of Biological & Physical Sciences	F.R	Forest Road
NSC	Nairobi South 'C'	RY.	Railway Yard	LH	Landhies Road
NW	Nairobi West	PL	Police Lines	HS	Haile Selasie Avenue
DC	Dagoretti Corner				

Fig. 5 Map of Nairobi showing the sampling sites

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KIAMBU

Limuru 250 252 254 Githunguri 56 258 36°50' 260 262 264

9874

Upper Limuru Road

1740

1700

Kibubuti Estate

Kamiti

1660

Ruiru

Limuru

R a i n
K2

1860

Kanunga

Kiambu-Ndumberi Rd
Ndumberi K1

Riabai

Ruiru Road

9872

Boma Road

Ndumberi

Kamiti Prison Farm

1°10'

Kiambaa

Kanunga HS

Loreto Sch

Riara Sch

KIAMBU

Kiu Valley Rd

Kiu

Kamiti Road

KP
K3

9870

Karuri

Waguthu

Kaski

1820

1780

KGC
Riabai

1660

Kiu Rd

9870 000m N

1°10'

1700

250 Nairobi 252 254 256 258 Nairobi 260 264 266 Nbi

SCALE 1 : 100 000

Adapted from sheet 148/2 Nairobi, series (Y 731)
Cartography by Kimiti S.K.

Reference

Roads	_____
Boundaries; provincial	_ · _ · _
municipal	_ ·· _ ·· _
Rivers	dam
Contours (V.I. 40 m)	1660
Built up Areas	1620
Area Name	Riabai

| KGC | Kiambu Golf Club |
| KP | Kamiti Prison |

N

Fig. 6 Map of Kiambu showing the sampling sites

Scale 1:50 000
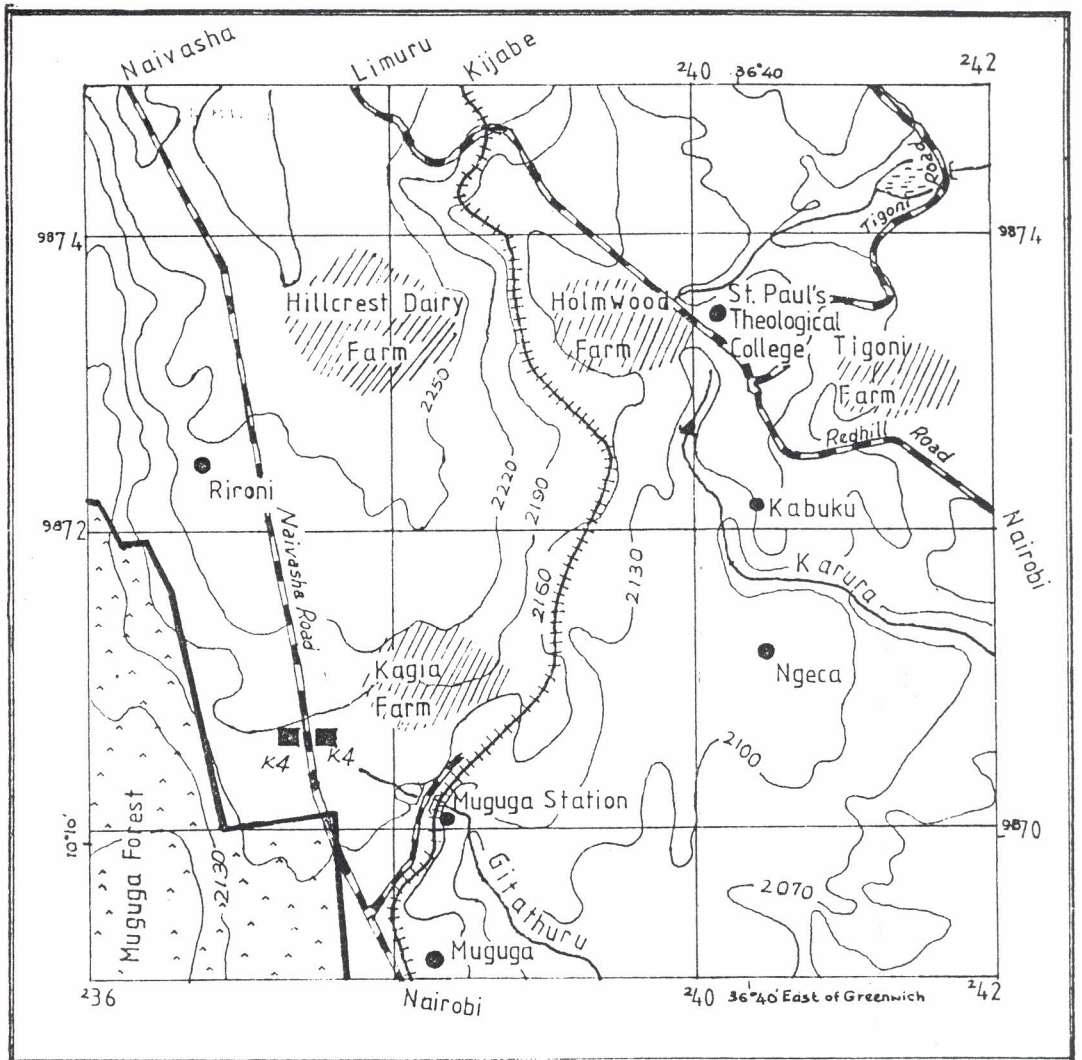
REFERENCE – Refer to map of KIAMBU

© S.K. Kimiti

Fig 7: Part of Kiambu map showing station K4 sampling site

slope, which gradually flattened out as one moved away from the road. Beyond the 60.0 m point there were double storey buildings. The number of average cars per hour was 1198. Sampling was done during the short rains in November, 1990.

3.1.3   STATION N3 (Ngong Road)

Soil and grass samples were collected on a transect perpendicular to the road at distances of 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0 and 100 m. The land was flat and was used as a playground as well as for grazing livestock. The number of average cars per hour was 1213. The direction of the wind was perpendicular to the sampling transect. Sampling was done during the short rains in December, 1990.

3.1.4   STATION N4 (Thika Highway)

Soil and grass samples were collected at a transect perpendicular to the road at distances, 0, 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, and 100 m. The road was on a slope which became steeper away from the road. The plant samples consisted of grass from the road up to 15 m. Beyond 15 m was a cultivated land and the plant samples here consisted of vegetables, sweet potato leaves and maize leaves. The wind was in the direction perpendicular to the sampling transect. The number of the average cars per

hour was 1440. The samples were collected during the dry season in January, 1991.

3.1.5   STATION N5 (Outer-ring Road)

Soil and grass samples were collected on both sides of the road at perpendicular distances from the road of 0, 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0 and 100 m. The direction of the wind was perpendicular to the road, from the left hand side to the right hand side. On the right hand side of the road sampling was done from 0 to 100 m, however, on the left hand side, there had been a fire and grass samples were collected only to the 10.0 m point. The terrain of the land here was flat. The land was sometimes used for grazing. The average number of cars per hour was 698. the samples were collected during the dry season in February, 1991.

3.1.6   STATION K1 (Kiambu-Ndumberi Road)

Soil and grass samples were collected at distances of 0, 2.5, 5.0, 10.0, 20.0, 30.0 and 40.0 m perpendicular to the road. The study area was an open portion to the road, with the other three sides fenced with plants. The road was on a hill, however the sampling points were on a flat terrain. The direction of the wind was perpendicular to the sampling transect. There was farming activities, around the sampling area, though on the sampling area there was

no sign of any recent activity. The average number of cars per hour was 140. The samples were collected during the dry season in March, 1991.

3.1.7   STATION K2 (Boma Road)

On this sampling site the road was on a hill. The sampling points were on a hill, perpendicular to and draining towards the road. Soil and grass samples were collected at distances of 0, 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0 and 100 m, perpendicular to the road . There were tall trees scattered around the sampling area and the land was used for livestock grazing. The average number of cars per hour was 53. The samples were collected during the dry season in March, 1991.

3.1.8   STATION K3 (Kamiti Road)

The sampling site was a large tract of land bordered on all sides with coffee plantations, except from the road. There was no evidence of apparent activities, though there had been a recent fire, and the vegetation looked quite green. The direction of the wind was along the sampling transect from the road. The average number of cars per hour was 40. Samples were collected during the dry season in March, 1991.

3.1.9   STATION K4 (Nairobi-Naivasha Road)

This sampling area was on a flat land scattered with tall trees. The land was mainly used for livestock grazing. Soil and grass samples were collected on a perpendicular to the road at distances of 0, 2.5, 5.0, 10.0, 30.0, 40.0, 50.0 and 60.0 m. The direction of the wind was perpendicular to the transect. The average number of cars per hour was 1180. The samples were collected during the dry season in March, 1991.

3.2.0   SAMPLING AND TRANSPORTATION

3.2.1   SOIL SAMPLES

Soil samples were collected at chosen stations, and distances given in the description of study areas. About 100 g of soil was collected randomly from each sampling point, using a stainless steel scoop. The soil was scooped up to a depth of 2 cm. The soil was then packed into labelled polythene bags and transported to the laboratory for further treatment.

3.2.2   PLANT SAMPLES

Plant samples were collected in a similar way to soil. A stainless steel knife was used to cut the grass (or plants), randomly at sampling points. About 80 g of the grass was packed into labelled polythene bags and transported to the laboratory for further treatment.

3.3.0   ANALYTICAL PROCEDURE

3.3.1   REAGENTS

All the chemicals used were of analytical reagent grade;

Nitric Acid, HNO_3	BERK SPENCER ACIDS LTD.
Hydrochloric Acid, HCl	BERK SPENCER ACIDS LTD.
Cadmium Chloride, $CdCl_2.2.5\ H_2O$	BDH CHEMICALS LTD.
Lead Nitrate, $Pb(NO_3)$	BDH CHEMICALS LTD.
Perchloric Acid, $HClO_4$.	Riedel-de Haen.

3.3.2 SOIL PRETREATMENT AND DIGESTION

Soil samples were oven dried at 105˚C for at least 24 hours in 100 ml beakers. The dry soil was sieved using a 1 mm sieve. The large particles which consisted mainly of stones and pebbles were discarded. The fine soil was then ground into a fine powder using a pestle and mortar.

To 1.000±0.005 g of dry soil in a boiling tube was added 6 ml conc. hydrochloric acid (HCl) and 2 ml conc. nitric acid (HNO_3). The boiling tubes were then placed in an aluminium hot block, which was heated on a hot plate at a temperature between 90 and 100˚C. The digests were heated with occasional stirring to near dryness, then allowed to cool.

About 20 to 30 ml of deionised water was added to the digest and the digest solution filtered through acid washed filter paper into a 100 ml volumetric flask. The filter paper was washed with deionised water and the filtrate was diluted to volume with deionised water. The filtrate was stored in preconditioned polypropylene bottles, ready for AAS analysis. The residue was discarded.

3.3.3 PLANT PRETREATMENT AND DIGESTION

Plant tissue samples were macerated and oven dried for at least 24 hours at 105˚C. Plant tissue samples were finely grounded using a pestle and mortar. To 1.000±0.005 g of dried plant tissues in 50

ml beaker, 5 ml conc. nitric acid (HNO_3) and 2 ml conc. perchloric acid ($HClO_4$) were added and the beaker covered with a watch glass. Pinta (1978) reported that $HNO_3/HClO_4$ mixture is most suitable for plant digestion. The sample was digested at a temperature of 90 to 100°C, to a final volume of 3-5 ml. About 10-15 ml of deionised water was added to the digest after cooling, and the digest solution filtered through acid washed filter paper into a 50 ml volumetric flask. The filter paper was washed with deionised water. The filtrate was diluted to volume with deionised water. The filtrate was stored in preconditioned polypropylene bottles ready for AAS analysis.

3.3.4   AAS ANALYSIS

Each sample was analysed in triplicate following the pretreatment and digestion methods already described. Blanks were analysed in triplicate for each Station (Separately, for plants and soil). The absorbance was recorded three times for each sample and the average taken.

3.3.5   DETERMINATION   OF   OPTIMUM   OPERATING CONDITIONS

In order to attain the best sensitivity, the absorbance of lead and cadmium were studied with respect to fuel composition, spectral band pass, wavelength, and the height of the light beam above the burner head. The sensitivity was checked by preparing

standards containing lead (20 mg/l) and cadmium (2.0 mg/l) as per manufacturers' recommendations.

3.3.6   ANALYSIS OF CERTIFIED REFERENCE MATERIALS

To check the quality and reliability of the results obtained by this method, certified reference materials distributed by the International Atomic Energy Agency (I.A.E.A.) were analysed as detailed below;

(i) S-5

For analysis, 0.50±0.01 g of the soil sample were accurately weighed in triplicate, and analysis carried out as previously described.(ref. 3.3.2)

(ii) S-7

For analysis, 0.50±0.01 g of the soil sample were accurately weighed in triplicate and analysed as previously described.(ref. 3.3.2)

3.3.7 CALIBRATION STANDARDS

STOCK SOLUTIONS (1000 ppm)

(i) LEAD

1000 ppm Pb ions in 0.5 M nitric acid (HNO_3), was prepared by weighing 1.6108 g of 99.5% lead nitrate [($Pb(NO_3)_2$] into a one litre volumetric flask and adding 31.70 cm^3 of 70% nitric acid (HNO_3). The solution was diluted to the mark by adding deionised water.

(ii) CADMIUM

1000 ppm Cd ions in 0.5 M hydrochloric acid (HCl), was prepared by weighing 2.0522 g of 99% $CdCl_2.2.5H_2O$ into a one litre volumetric flask adding 44.14 cm^3 of 35% hydrochloric acid (HCl), and diluting to the mark with deionised water.

The stock solutions were stored in cleaned, preconditioned polypropylene bottles. Immediate and working standard solutions were prepared by successive dilution.

Calibration standards were freshly prepared whenever required and were treated in the same way as the samples and carried through the whole procedure. For each metal analysis, solutions containing the concentrations detailed below were accurately prepared, additional to three replicate samples.

LEAD

Aliquots of the working solutions were used to prepare calibration standards containing 0.05, 0.1, 0.3, 0.5, 0.7, 1.0, 2.0, 3.0, 5.0, 10.0, and 20.0 ppm.

CADMIUM

Aliquots of the working solutions were used to prepare calibration standards containing 0.005, 0.01, 0.03, 0.05, 0.07, 0.10, 0.30, 0.50, 0.70, 1.00, 2.00 ppm.

3.4.0   METHODS

3.4.1   INSTRUMENTATION

3.4.2   ATOMIC ABSORPTION SPECTROPHOTOMETER

The Atomic Absorption Spectrophotometer used was Perkin-Elmer Model 2380 (Perkin Elmer Co. 1980). This is a microprocessor controlled Atomic Absorption Spectrophotometer which measures the concentration of metallic elements and provides integrated readings in absorbance and concentration. Single element hollow cathode lamps were used for the determination of the elements as per manufacturers' recommendations.

3.4.3   THE GLASS ELECTRODE

The glass electrode used was a combined electrode Model GK2401B, supplied by Radiometer Copenhagen. The combined glass/reference electrode feature; A wide temperature range; A symmetrical electrode chain based on Ag/AgCl cells, providing negligible light hysteresis, negligible light sensitivity and a fairly constant isopotential point even at great temperature variations. The pH range was 0 to 14 and the maximum flow of saturated KCl solution through the porous pin junction was 10 µl/h/10 cm water column.

3.4.4   THE pH METER

The pH meter 22, Type PHM220 supplied by Radiometer Copenhagen was used for pH determination. The pH meter is an electronic voltmeter that contains an amplifier that senses the signal voltage and produces a proportional meter deflection.

3.4.5   THE ALUMINIUM BLOCK

The Aluminium hot block, made according to specifications by Agemian *et al*., (1980), was used to digest soil samples. The block can accommodate 18 digestion tubes, which are placed in the hot block and heated on a hot plate to the required temperature.

3.4.6   LABWARE APPARATUS

All glassware was soaked for at least 24 hours in washing detergent, rinsed with chromic acid where necessary, then rinsed with running tap water and soaked in 10 % (v/v) Nitric acid (HNO_3) for at least 24 hours. The washing procedure was completed by rinsing the glassware when required for immediate use, with tap water and finally rinsing with deionised water and oven drying at 90°C.

3.4.7   SAMPLE BOTTLES - PRECONDITIONING

Polypropylene bottles were soaked in detergent solution for at least 24 hours, rinsed in tap water

and then leached in 10% (v/v) Nitric acid (HNO_3) for at least another 24 hours. The washing procedure was completed by rinsing the bottles when required for immediate use, with tap water and finally with deionised water and oven drying at 60°C.

3.4.8   pH DETERMINATION

2.000±0.005 g of dry soil sample were dissolved in 50 ml of deionised water. The soil paste was stirred and allowed to equilibrate for one hour, after which the solution was centrifuged and the pH determined using the pH electrode.

3.4.9   ESTIMATION OF TRAFFIC DENSITY

Car counts were taken for every sampling station. In the morning sessions car counts were taken between 9.00 and 11.00 am. In the afternoon sessions car counts were taken between 3.00 and 5.00 pm.

The average number of cars per hour was determined by taking the average over the four hours. The traffic flow during these times of the day are assumed to give an indication of the normal traffic flow. During the morning rush hour the traffic flow is usually high, while during the day and in the late evenings, traffic flow is usually low.

CHAPTER FOUR

4.0.0   RESULTS AND DISCUSSION

4.1.0   VALIDATION OF ANALYTICAL PROCEDURE

Evaluation of the analytical procedure was done by analysis of certified reference materials obtained from the International Atomic Energy Agency (IAEA). The validation of the analytical procedure was carried out by a comparative analyses of two certified materials, soil-5 and soil-7. The reproducibility of the analytical procedure was determined by the replicate analyses of soil and vegetation samples.

Measurements of concentrations are subject to systematic and random errors. The analysis of certified reference materials was done so as to allow for precision and accuracy to be assessed as summarised in Table 2 and Table 3.

Sensitivities were evaluated for each element from individual standard curves, examples of which are shown on figure 8 and figure 9. Only precision measurements were made for plant samples as there were no certified reference plant samples available, as in the case of soils to test the accuracy of the values.

4.1.1 PRECISION AND ACCURACY OF THE ANALYTICAL TECHNIQUE

TABLE 2; STANDARD SOIL-5 CONCENTRATION IN PPM (DW)

ELEMENT	REF. CONC.	EXPT'L CONC.	R.S.D. (%)	R.E. (%)
Pb	129±26	155.70±4.29	2.80	20.73
Cd	1.50	2.51±0.23	9.20	67.33

n=3, where n is the number of samples analysed.

TABLE 3; STANDARD SOIL-7 CONCENTRATION IN PPM (DW)

ELEMENT	REF.CONC.	EXPT'L CONC.	R.S.D. (%)	R.E. (%)
Pb	60	64.30±3.24	3.60	7.17
Cd	1.3	1.52±0.12	5.26	16.92

n=3, where n is the number of samples analysed.

The data shows good agreement between the certified and experimental values attesting to good accuracy of the analytical procedure. Relative standard deviation (R.S.D. %) values range from 2.80 % to 9.20 % for all samples analysed, demonstrating the good precision of the method.

4.1.2 OPTIMUM INSTRUMENTAL PARAMETERS

The AAS instrumental parameters that yielded the most sensitive and reproducible results are listed in Table 4.

TABLE 4; OPTIMUM INSTRUMENTAL PARAMETERS

	Cd	Pb
Lamp current intensity(mA)	4	10
Spectral band pass(nm)	0.7	0.7
Wavelength(nm)	38.3	283.3
Oxidant flowrate(l/min)	7.5	19.5
Acetylene flowrate(l/min)	1.0	1.3

Integration time: 0.5 seconds.

5 replicate readings.
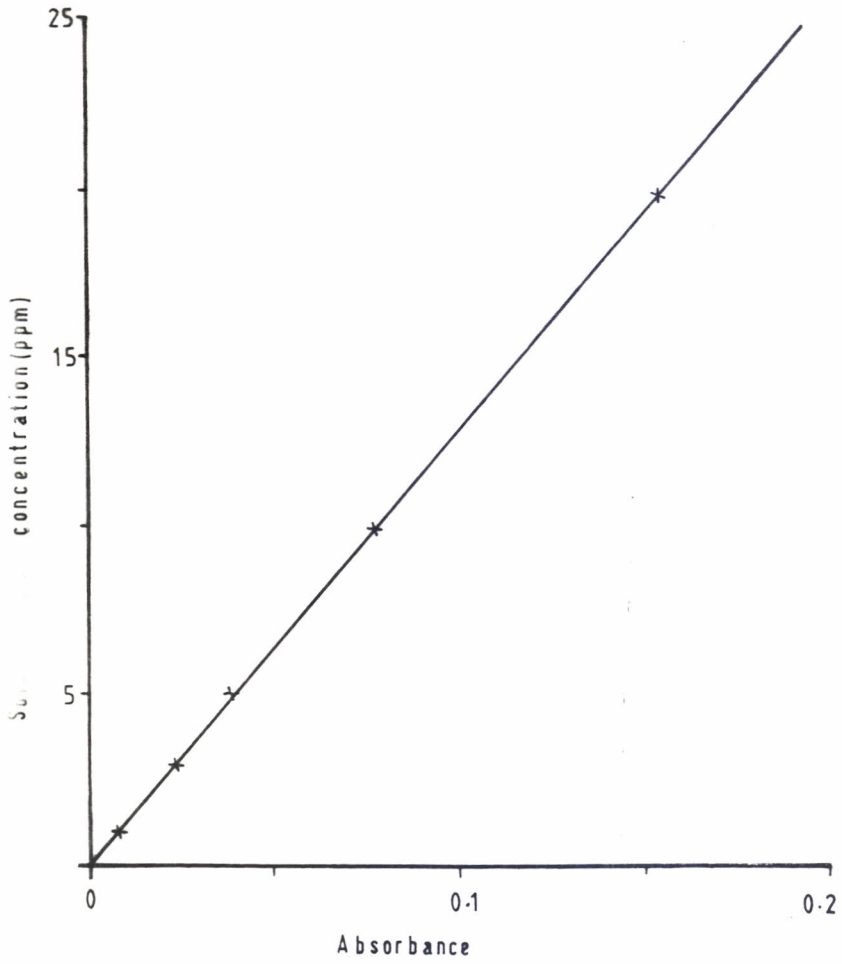
Fig. 8: Typical lead standard calibration graph
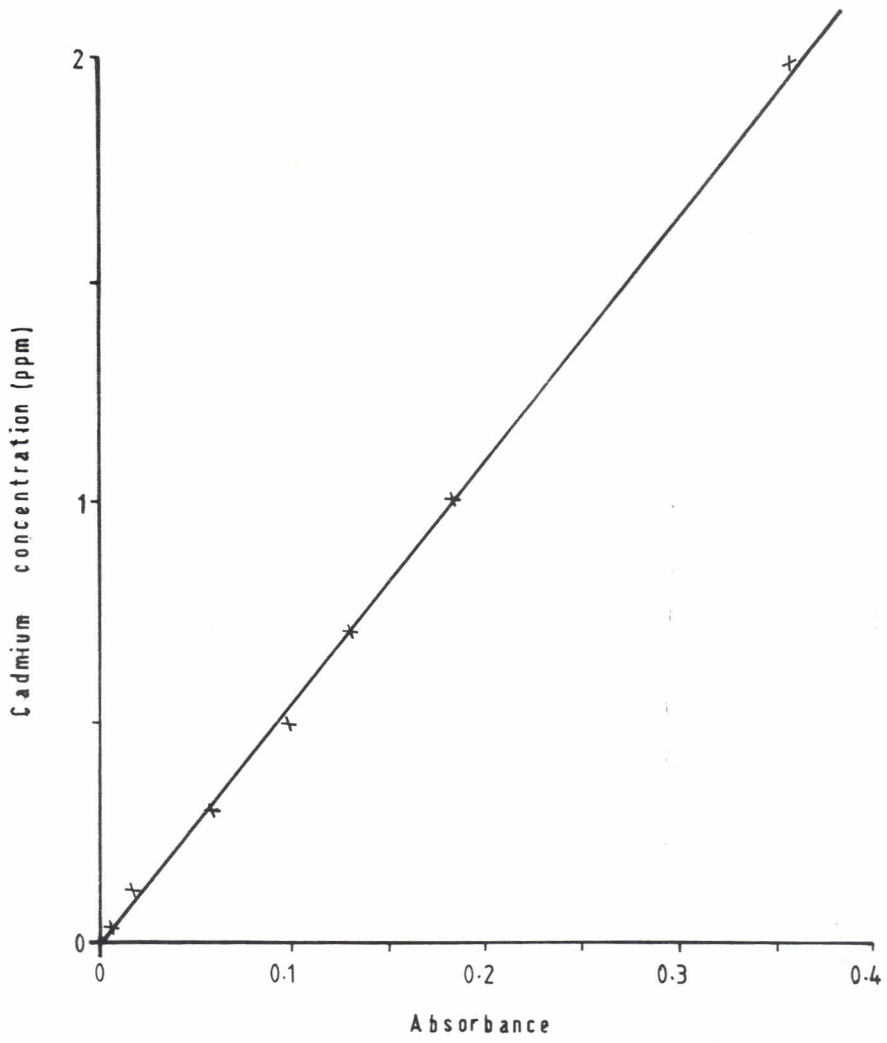
Fig. 9:   Typical cadmium standard calibration
graph

4.2.0   RESULTS

The results of analysis of roadside soils and vegetation for their cadmium and lead concentration as a function of distance from the road are presented on Tables 5 to 14. All the entries are averages of values for three determinations on each sample.

The lead data shows that 91% of the total number of samples analysed had relative standard deviations of between 0 and 10%. However all analyses had relative errors of below 45%. The low R.S.D. values obtained show commendable reliability.   T   h   e cadmium data shows that 87% of the total number of samples analysed had R.S.D.'s of between 0 and 5% and all the analyses had relative errors of below 48%. The low   R.S.D.   values   obtained   reflect   commendable reliability.

TABLE 5; STATION N1 MEAN [Pb] AND [Cd] IN ROADSIDE
SOILS AND PLANTS

Distance (m)	Soil pH	Pb (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
2.5	6.82	158.02 ±24.20	8.84 ±0.17	0.20 ±0.01	0.09 ±0.01
5.0	6.80	64.60 ±0.00	7.54 ±1.44	0.20 ±0.01	0.10 ±0.01
10.0	6.75	47.34 ±6.00	20.72 ±5.80	0.20 ±0.01	0.10 ±0.00
20.0	7.26	181.35 ±12.10	17.71 ±2.84	0.20 ±0.01	0.10 ±0.00
30.0	8.20	350.27 ±21.01	9.04 ±0.01	0.21 ±0.00	0.09 ±0.00

(n=3), where n is the number of samples taken per point.

It is noted that there is incongruency of lead concentration between soil and plants in Tables 5 and 6. These observations need further work for an explanation.

TABLE 6;   STATION N2 MEAN [Pb] AND [Cd] IN ROADSIDE
           SOILS AND PLANTS

Distance (m)	Soil pH	Pb (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
2.5	7.22	181.02 ±7.47	16.4 ±4.3	0.22 ±0.00	0.16 ±0.05
5.0	7.06	105.00 ±17.30	45.8 ±7.4	0.22 ±0.01	0.16 ±0.05
10.0	6.63	105.22 ±5.79	9.13 ±2.84	0.24 ±0.01	0.16 ±0.05
20.0	5.58	53.31 ±17.60	16.41 ±1.56	0.17 ±0.08	0.17 ±0.07
30.0	6.63	53.37 ±23.20	12.00 ±0.08	0.21 ±0.01	0.16 ±0.06
40.0	6.21	76.32 ±0.04	7.59 ±1.32	0.18 ±0.00	0.12 ±0.01
50.0	5.84	47.20 ±5.61	4.72 ±1.55	0.20 ±0.01	0.15 ±0.06
60.0	6.25	78.57 ±13.90	12.00 ±5.75	0.22 ±0.00	0.16 ±0.05

(n=3), where n is the number of samples taken per
point.

TABLE 7;   STATION N3 MEAN [Pb] AND [Cd] IN ROADSIDE
            SOILS AND PLANTS

Distance (m)	Soil pH	Pb $(\times 10^3)$ (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
2.5	7.26	41.89 ±0.43	30.27 ±0.40	0.14 ±0.00	0.10 ±0.00
5.0	6.87	34.61 ±2.06	30.20 ±0.26	0.13 ±0.01	0.10 ±0.00
10.0	6.74	33.37 ±0.30	30.45 ±0.03	0.12 ±0.01	0.11 ±0.01
20.0	6.82	33.83 ±0.25	29.82 ±0.06	0.13 ±0.02	0.10 ±0.00
30.0	6.32	33.78 ±0.17	29.73 ±0.05	0.11 ±0.01	0.10 ±0.00
40.0	6.37	32.72 ±0.01	29.50 ±0.30	0.12 ±0.01	0.10 ±0.01
50.0	6.06	32.63 ±0.18	29.34 ±0.14	0.12 ±0.01	0.10 ±0.01
60.0	5.84	31.82 ±0.18	29.39 ±0.11	0.12 ±0.01	0.10 ±0.01
100.0	5.64	30.61 ±0.01	29.60 ±0.42	0.11 ±0.00	0.10 ±0.00

(n=3), where n is the number of samples taken per
point.

TABLE 8;   STATION N4 MEAN [Pb] AND [Cd] IN ROADSIDE
            SOILS AND PLANTS

Distance (m)	Soil pH	Pb ($\times 10^3$) (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
0	7.48	108.51 ±7.07	68.88 ±0.00	0.23 ±0.00	0.21 ±0.00
2.5	7.5	90.44 ±1.08	66.70 ±1.15	0.24 ±0.01	0.21 ±0.00
5.0	6.27	64.78 ±0.01	65.43 ±0.93	0.23 ±0.00	0.21 ±0.00
10.0	6.46	64.47 ±1.01	60.10 ±0.18	0.22 ±0.01	0.23 ±0.00
20.0	6.05	63.43 ±0.44	60.62 ±0.30	0.22 ±0.01	0.22 ±0.01
30.0	6.12	62.66 ±0.59	61.19 ±0.08	0.22 ±0.01	0.22 ±0.01
40.0	5.76	62.44 ±0.54	61.95 ±0.04	0.23 ±0.00	0.25 ±0.00
50.0	5.44	62.53 ±0.10	60.69 ±0.42	0.23 ±0.00	0.25 ±0.00
60.0	5.53	62.03 ±0.12	60.73 ±0.54	0.22 ±0.01	0.25 ±0.00
100.0	6.26	63.76 ±0.24	60.32 ±0.22	0.23 ±0.00	0.25 ±0.00

(n=3), where n is the number of samples per point.

TABLE 9; STATION N5(RHS) MEAN [Pb] AND [Cd] IN ROADSIDE SOILS AND PLANTS

DISTANCE (m)	Soil pH	Pb ($\times 10^3$) (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
0	7.35	54.74 ±1.67	23.95 ±0.13	0.15 ±0.00	0.15 ±0.00
2.5	7.15	55.90 ±0.73	24.43 ±0.37	0.16 ±0.00	0.15 ±0.00
5.0	7.18	55.00 ±0.19	28.24 ±0.49	0.16 ±0.00	0.15 ±0.00
10.0	7.39	50.74 ±0.19	24.55 ±0.12	0.16 ±0.00	0.15 ±0.00
20.0	8.68	49.83 ±0.18	24.30 ±0.07	0.17 ±0.00	0.15 ±0.01
30.0	7.12	49.53 ±0.11	23.79 ±0.21	0.15 ±0.00	0.14 ±0.00
40.0	6.95	48.66 ±0.04	24.30 ±0.06	0.15 ±0.00	0.14 ±0.00
50.0	6.92	48.45 ±0.12	24.47 ±0.12	0.15 ±0.00	0.14 ±0.00
60.0	7.03	49.26 ±0.25	23.23 ±0.27	0.16 ±0.00	0.14 ±0.00
100.0	6.85	48.68 ±0.36	23.13 ±0.09	0.16 ±0.00	0.14 ±0.00

(n=3), where n is the number of samples per point.

TABLE 10; STATION N5(LHS) MEAN [Pb] AND [Cd] IN ROADSIDE SOILS AND PLANTS

Distance (m)	Soil pH	Pb $(\times 10^3)$ (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
0	6.7	55.20 ±2.81	7.85 ±0.03	0.39 ±0.01	0.18 ±0.00
2.5	6.9	52.71 ±0.29	8.05 ±0.11	0.37 ±0.01	0.17 ±0.00
5.0	6.99	51.09 ±0.11	7.71 ±0.13	0.35 ±0.00	0.17 ±0.00
10.0	8.05	50.32 ±0.09	7.89 ±0.01	0.36 ±0.01	0.17 ±0.00
20.0	8.35	47.69 ±0.19	ND	0.35 ±0.01	ND
30.0	8.22	47.76 ±0.22	ND	0.36 ±0.01	ND
40.0	7.82	47.61 ±0.26	ND	0.35 ±0.00	ND
50.0	8.13	46.89 ±0.24	ND	0.36 ±0.01	ND
60.0	8.13	46.72 ±0.14	ND	0.36 ±0.01	ND
100.0	7.98	47.00 ±0.07	ND	0.35 ±0.00	ND

(n=3), where n is the number of samples per point.

TABLE 11; STATION K1 MEAN [Pb] AND [Cd] IN ROADSIDE
SOILS AND PLANTS

Distance (m)	Soil pH	Pb (X10^3) (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
0	6.98	73.14 ±0.33	7.35 ±0.00	0.22 ±0.00	0.18 ±0.00
2.5	6.78	72.14 ±0.08	6.70 ±0.00	0.21 ±0.00	0.18 ±0.00
5.0	6.60	69.32 ±0.13	6.96 ±0.00	0.21 ±0.00	0.18 ±0.00
10.0	6.60	68.42 ±0.18	7.09 ±0.00	0.21 ±0.00	0.18 ±0.00
20.0	6.85	65.83 ±0.39	7.06 ±0.00	0.20 ±0.00	0.17 ±0.00
30.0	6.85	66.35 ±0.14	7.06 ±0.00	0.20 ±0.00	0.17 ±0.00
40.0	6.72	67.60 ±0.28	7.06 ±0.00	0.21 ±0.00	0.18 ±0.00

(n=3), where n is the number of samples per point.

TABLE 12; STATION K2 MEAN [Pb] AND [Cd] IN ROADSIDE SOILS AND PLANTS

Distance (m)	Soil pH	Pb ($\times 10^3$) (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
0	6.55	74.40 ±0.42	32.80 ±0.08	0.40 ±0.01	0.19 ±0.00
2.5	6.07	69.07 ±0.36	32.98 ±0.12	0.41 ±0.01	0.19 ±0.00
5.0	6.25	69.18 ±0.08	32.71 ±0.07	0.41 ±0.01	0.20 ±0.00
10.0	6.30	69.31 ±0.07	32.36 ±0.03	0.41 ±0.01	0.20 ±0.00
20.0	6.25	69.46 ±0.41	32.37 ±0.02	0.41 ±0.00	0.19 ±0.00
30.0	6.25	70.46 ±0.37	32.50 ±0.13	0.41 ±0.00	0.19 ±0.00
40.0	6.38	68.93 ±0.47	32.29 ±0.15	0.40 ±0.00	0.20 ±0.00
50.0	5.95	69.16 ±0.20	32.32 ±0.11	0.40 ±0.01	0.20 ±0.00
60.0	6.50	68.53 ±0.24	32.18 ±0.13	0.39 ±0.00	0.20 ±0.00

(n=3), where n is the number of samples per point.

TABLE 13; STATION K3 MEAN [Pb] AND [Cd] IN ROADSIDE
SOILS AND PLANTS

Distance (m)	Soil pH	Pb (X10^3) (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
0	7.05	19.19 ±0.30	3.89 ±0.14	0.69 ±0.00	0.34 ±0.00
2.5	7.02	14.91 ±0.30	3.71 ±0.02	0.69 ±0.01	0.34 ±0.01
5.0	6.81	10.36 ±0.31	3.31 ±0.00	0.69 ±0.01	0.34 ±0.00
10.0	7.12	9.20 ±0.02	3.31 ±0.01	0.69 ±0.01	0.34 ±0.00
20.0	6.95	9.75 ±0.28	3.30 ±0.00	0.69 ±0.01	0.34 ±0.00
30.0	7.02	9.19 ±0.24	3.31 ±0.00	0.68 ±0.00	0.34 ±0.00
40.0	6.69	9.50 ±0.25	2.88 ±0.00	0.69 ±0.01	0.34 ±0.00
50.0	7.04	8.91 ±0.28	3.45 ±0.28	0.69 ±0.01	0.35 ±0.00
60.0	6.94	9.32 ±0.09	3.74 ±0.01	0.65 ±0.00	0.34 ±0.00

(n=3), where n is the number of samples per point.

TABLE 14; STATION K4 MEAN [Pb] AND [Cd] IN ROADSIDE
SOILS AND PLANTS

Distance (m)	Soil pH	Pb (X10^3) (ppm)		Cd (ppm)	
		Soil	Plant	Soil	Plant
0	6.81	51.45 ±0.20	20.53 ±0.17	0.33 ±0.01	0.16 ±0.00
2.5	6.60	50.25 ±0.34	20.08 ±0.15	0.32 ±0.01	0.16 ±0.00
5.0	6.54	46.11 ±0.58	20.36 ±0.11	0.32 ±0.00	0.15 ±0.00
10.0	6.30	45.56 ±0.08	20.25 ±0.02	0.33 ±0.01	0.15 ±0.00
20.0	6.50	44.11 ±0.34	20.35 ±0.13	0.32 ±0.00	0.16 ±0.00
30.0	7.02	42.78 ±0.29	20.13 ±0.11	0.31 ±0.01	0.15 ±0.00
40.0	6.12	39.97 ±1.08	19.99 ±0.16	0.31 ±0.01	0.15 ±0.00
50.0	6.48	39.43 ±0.20	19.98 ±0.28	0.30 ±0.00	0.15 ±0.00
60.0	6.25	39.17 ±0.30	20.14 ±0.15	0.30 ±0.00	0.15 ±0.00

(n=3), where n is the number of samples per point.

TABLE 15; NAIROBI STATIONS CAR COUNT (cars/hour).

STATION	N1	N2	N3	N4	N5
CARS PER HR.	1412	1198	1213	1440	698

TABLE 16; KIAMBU STATIONS CAR COUNT (cars/hour).

STATION	K1	K2	K3	K4
CARS PER HR.	140	53	40	1180

TABLE 17; KIAMBU SOIL SAMPLES CLASSIFICATION

STATION	K1	K2	K3	K4
SOIL TYPE	sandy clay loam	clay loam	loam	clay

TABLE 18; NAIROBI SOIL SAMPLES CLASSIFICATION

STATION	N1	N2	N3	N4	N5R	N
SOIL TYPE	clay	clay	clay	loam	clay	cl

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4.3.0   DISCUSSIONS

4.3.1   LEAD CONCENTRATION IN SOILS

The concentration of lead in soil decreases in an exponential-like fashion with distance from the road for most of the stations as shown on figures 12 and 13. However, for Stations with barriers along the transects (stations N1 and N2), lead concentration falls to some minimum level and then rises again as the barrier is approached, as shown in figures 10 and 11. This trend may be attributed to reflection of lead particles on the barriers at the end of the transects.

Lead concentrations nearest to the road (0 to 5.0 m) invariably show the highest levels. The concentration then decreases up to distance of approximately 50 m, where nearly constant background levels are observed. Similar variations have been reported by Rodrigues et al.(1982).

Most of the areas exhibited a significant correlation between lead levels and vehicular traffic volume, however the overall correlation coefficient was 0.470. What appears to be an anomaly is the relatively high concentrations at K1 and K2 (73.10 X 10^{-3} and 74.40 X 10^{-3} ppm respectively) with low traffic (140 and 53 cars per hour respectively), as compared to K4 and N3 which have high traffic (1180 and 1213 cars per hour respectively), but low concentrations of 51.10 X 10^{-3} and 41.90 X 10^{-3} ppm respectively.

The low lead concentrations in soil at K4 and N3 may be attributed to other activities that take place on the two stations. Station N3 was a football field and was also used for grazing livestock. These kind of activities tend to reduce lead accumulation in the top soil. Station K4 was covered with scattered trees, which also obstructs the free dispersal of lead particles. Grazing may also be a factor in the low concentrations observed at this station.

There are several other factors like topology, windspeed, season, soil type, etc. which also contribute to the lead level in soils and plants. However, these other factors were not considered in this study and further research may show their contribution.

The soils analysed were mainly clay and lead ions become readily and firmly attached to clay particles and organic matter and maybe co-precipitated in insoluble complexes (Zimdahl and Skogerboe, 1977). This may be another reason for the low lead levels observed in this study.

To ascertain the influence of wind direction on the distribution of lead in the ecosystem, stations N5R and N5L were chosen because of their flat terrain, the absence of trees or buildings which could exert a screening effect for free lead dispersal. The predominant wind component blows from north-eastern to the south- western direction along the transects. It

is readily observed that the lead discharge concentrations of soil and grass are larger for the south-west side of the road. This constitutes evidence supporting an aerial route for the dispersion of lead through out the ecosystem near the roads.

Although the role of pH on lead levels has not been established in this study, it is known that high soil pH may precipitate lead ions as hydroxides, phosphates or carbonate as well as promote the formation of lead-organic complexes.
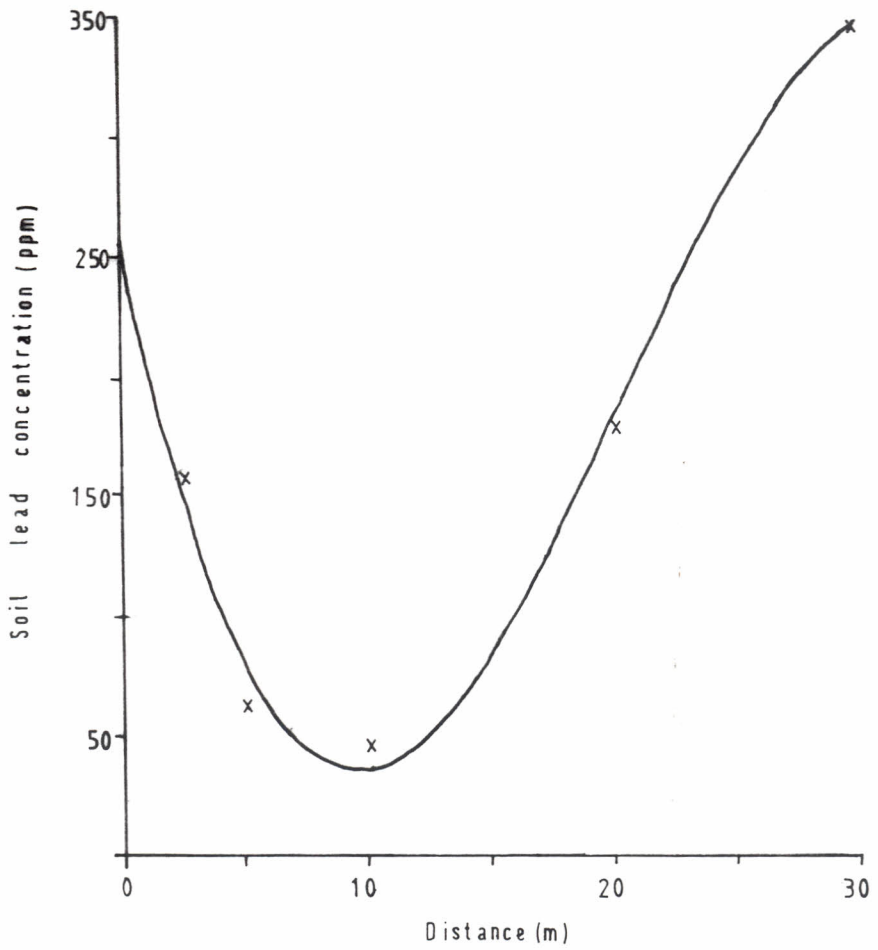
Fig. 10: Variation of lead concentration with distance for station N1 (*Museum Hill Roudabout*)
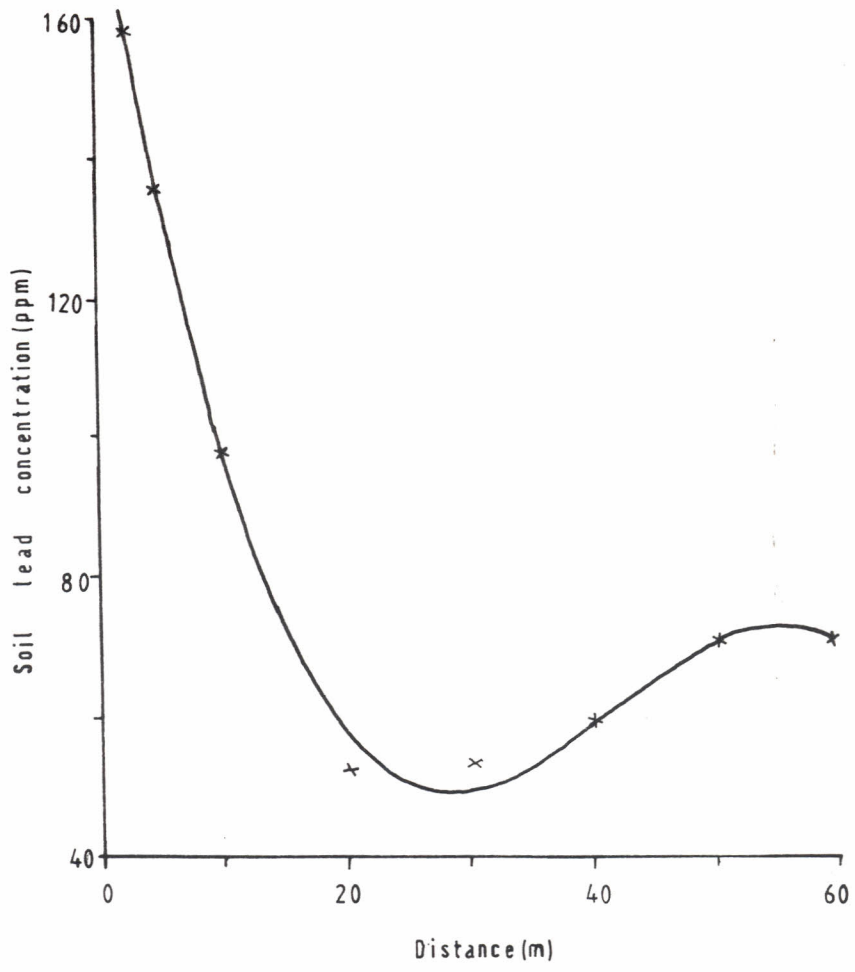
Fig. 11:   Variation of lead concentration with
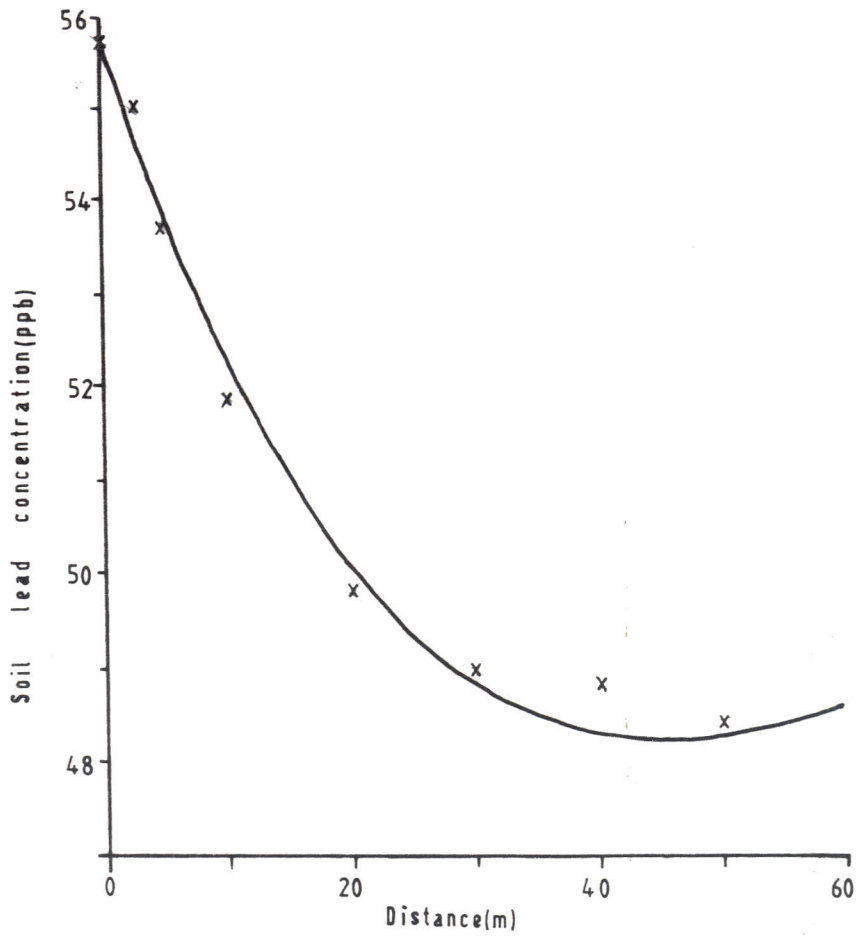   distance for station N2 (*Waiyaki Way*)

Fig. 12: Variation of lead concentration with
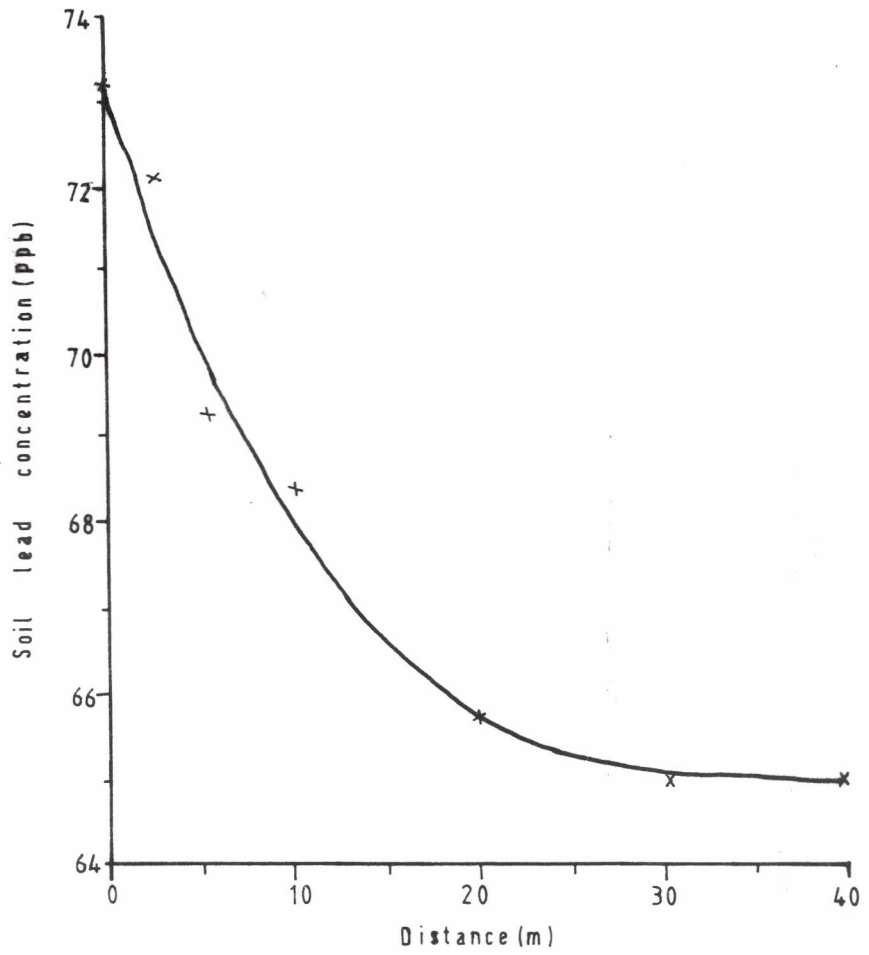distance for station N5R (*Outer Ring Road*)

Fig. 13: Variation of lead concentration with distance for station K1 (*Kiambu-Ndumberi Road*)

4.3.2   LEAD CONCENTRATION IN PLANTS

The lead concentration in plants were in all cases much lower than those found in soils. Lead concentration did not fall off rapidly with distance as had been observed with soils. In only three cases, was there a fall-off with distance (N2, N4 and K2). For N1, the lead concentration even increased with distance from the road. This may have been due to the many network of roads close to this sampling site and also the barrier situated approximately 35 m from the road, along the sampling transect, which was also responsible for the high lead levels close to the barrier.

The rest of the stations studied had no significant variation of lead concentration with distance. The concentrations appeared to be more or less constant for each of these stations. There was no significant correlation (R=0.395) of lead concentration in plants with traffic volume .

With the low lead concentrations in plants, it is most unlikely that even the heaviest contamination of roadside foliage with lead can cause any deleterious effects on plant growth. However, studies by Bazzaz et al.(1974) have shown that 20-50 ppm of lead causes reductions in photosynthesis and transpiration. It has also been reported that severe contamination of tree leaves (>4000 ppm) has not resulted in any detectable effects on the plant growth (Arvik and Zimdahl, 1974).

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Harmful effects have been observed at foliar concentrations of 6000 ppm, but such levels are far in excess of observed roadside levels. (Krause and Kaisser, 1977).

The great variation of lead content of plants is influenced by several factors, such as the presence of geochemical anomalies, pollution, seasonal variation, and genotype ability to accumulate lead. Nevertheless natural lead content in plants growing in uncontaminated and unmineralized arrears appear to be quite constant, ranging from 0.1 to 10 ppm and averaging 2 ppm (Alloway, 1968; Cannon, 1976).

The percentages of soil lead absorbed by plants in stations N1 and N2 range between 0.1 and 43.8%, showing how lead uptake by plants varies significantly over the concentration ranges currently present in soils. Airborne lead may also be taken up by plants through their foliage (Iserman, 1977), although much controversy exists in literature on the question of how much lead is actually taken into foliar cells.

In stations N3, N4 and N5(RHS), the percentages of soil lead uptake by plants appear to be very high, ranging from 43.6 to 100%. The anomalous amounts of lead metal in plants has been reported especially in areas where plants are exposed to lead sources of both soil and air (Roberts et al, 1974). The high lead concentrations observed in plants in the above

stations must therefore be due to atmospheric lead pollution.

Studies of lead uptake from roadside soils have in fact demonstrated remarkably little translocation to the shoots and to the edible portions of root crops. Concentrations of several thousand ppm of lead in soil often result in concentrations of no more than a few tens of ppm in plant shoots. As a general rule, harmful effects have seldom been detected in plants grown in soils containing less than 250 ppm lead in soil. (Hasset *et al.*, 1976)

When plants are grown in the field with adequate amount of fertilizer, the prevailing opinion is that soil lead concentrations of at least 1000 ppm must be present before effects are observed on plant growth. Indeed many studies near lead smelters have shown no observable effects of lead on plant growth even with soil lead concentrations greatly in excess of those recorded beside motorways.

However, the addition of lead rich highway dust to acid and calcareous soils has been reported to yield concentrations similar to those in roadside soils (140-1080 ppm) which produced significant growth reductions in acid soils with corn, beans, lettuce and radish at soil lead concentrations of greater than 140, 280 and 560 ppm respectively. It has also been noted that in calcareous soils, growth of corn and

beans was significantly impaired at >1080 and >560 ppm respectively (Page and Gange, 1972).

Thus it seems possible that the levels of lead currently found beside our busiest roads and motorways could be of very small significance to plant life.

4.3.3   CADMIUM IN SOILS

The cadmium levels in soil show some correlation (R=0.601) with traffic volume for all the stations, thus suggesting that traffic could be a source of cadmium on roadside soils. Stations K3, K2, N5L and K4 show relatively high levels of cadmium (0.69, 0.41, 0.39 and 0.33 ppm respectively). The rest of the stations exhibited an average of 0.20 ppm. The average content of cadmium in soils lie between 0.07 and 1.10 ppm. However, the background cadmium levels in soils apparently should not exceed 0.5 ppm, and all higher values reflect the anthropogenic impact on the cadmium status in top soils. The cadmium concentration in soils does not vary with distance away from the kerbside as was the case with lead. The cadmium concentration along each transect appears to be constant.

The low levels of cadmium observed in this study may be attributed to the relatively mobile nature of the metal in soil (Harrison et al., 1981), so that it would not accumulate to any appreciable extent in the top layer of soil. Cadmium activity in soil is

strongly affected by pH. It is most mobile in acidic soils, and this may explain the reason for the low cadmium concentration observed.

The presence of cadmium in phosphate fertilizers (P-fertilizers) constitutes a very diffuse source of cadmium contamination. Cadmium contents in P-fertilizers vary from 1-2 ppm for tertiary calciumphosphate to 50-170 ppm for superphosphate (Bolt and Bruggenwert, 1976). The relatively high concentrations observed in K2, K3 and K4 which are in rural agricultural locations may be due to the presence of P-fertilizers. Cadmium content of soil in non-polluted areas are usually below 1 ppm (Yamagata and Shigematsu, 1970).

Since apart from traffic volume many other factors also govern the dispersion of contaminants along the road, it is possible not to obtain correlations between traffic volume and concentration. Lau and Wong (1982),for example did not detect any correlation between metals in soil and the traffic volume.

4.3.4   CADMIUM IN PLANTS

The cadmium levels in grass are lower in all cases than the soil concentrations. The cadmium concentration again appears to be constant for each station (ie. does not vary with distance) thereby indicating that the contribution of traffic is minimal. There is some correlation (R=0.513) between the concentration in plants and traffic volume. The low correlation may occur as a result of several factors. The low cadmium input to the environment makes it more difficult to measure accurately the variations in the concentration of cadmium above background levels, and since cadmium is transported mainly through run-off waters, its distribution in the environment should follow a much less regular pattern than that of lead.

It is evident from the data that cadmium distribution is independent of wind direction, supporting the fact that the metal is mainly transported via runoff waters.

The low cadmium levels in plants is a reflection of the low levels found in soils. Street *et al.*,(1978) reported that lower pH enhanced solubility (and availability), resulting in higher uptake by plants. Hence the cadmium concentrations in plants in most of the cases points towards the low availability.

4.3.5   RELATIONSHIP BETWEEN TRAFFIC VOLUME AND
         CONTAMINATION ON ROADSIDE SOILS AND PLANTS
         BY LEAD AND CADMIUM

Stations N1 and N2 with the highest lead levels of 350 ppm and 181 ppm respectively are highly contaminated, since soil normally contains less than 20 ppm (Smith, 1976). However, the mean lead levels for soil in Nairobi was 88.54 ppm while that for Kiambu was 54.60 X 10^{-3} ppm, confirming the fact that Nairobi, where traffic was relatively large, with a mean of 1110 cars per hour has higher level of lead contamination than Kiambu (which is rural), with a mean of 353 cars per hour.

Soil tended to accumulate more lead than grass and the highest lead level found in soil was 350 ppm while for grass it was 20.70 ppm. The high mean soil lead of 88.54 ppm is not unusual bearing in mind, the generally high traffic volumes in Nairobi. Infact it is still much lower than the mean lead value of 1,545 ppm reported for Vancouver(Schmitt *et al.*, 1979) and 1564 ppm reported for Auckland(Ward *et al.*, 1977)

The lead levels in plants show the same trend. For Nairobi the mean lead level was 11.11 ppm while for Kiambu it was 16.14 X 10^{-3} ppm, attesting to the fact that high traffic volume contributes to high lead contamination in plants also.

The mean cadmium level in Nairobi soils was 0.229 ppm while that for Kiambu was 0.413 ppm. For plants the mean cadmium level was 0.160 ppm for Nairobi, while for Kiambu it was 0.219 ppm. It is apparent that the cadmium level in rural Kiambu is higher than in Nairobi for both soil and grass. This discrepancy between cadmium level and traffic volume may be a result of the use of P-fertilizers, which are a source of cadmium contamination in rural farming areas.

However the range of cadmium level in soil was in general agreement with similar studies in other places (Lagerwerff and Specht, 1970, Ward et al., 1977). Grass had lower cadmium concentrations than soils. Reports from other studies have shown that the levels of cadmium in roadside plants are generally low (Lagerwerff and Specht, 1970; Ho and Tai, 1985).

Ward et al.,(1977) found significant correlations between traffic density and lead and cadmium in surface soils from an Auckland motorway in New Zealand. However, such correlations between traffic volume and metal contamination, though present, often are not clear cut (Motto et al., 1970) since apart from traffic volume, many other factors also govern the release and/or dispersion of these contaminants along the road. Indeed, in some studies (Lau and Wong, 1982) no correlation was detected between metals including lead and cadmium in soils and the traffic volume.

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How well the levels of metal contamination in plants correlate with the traffic volume may also depend on the species concerned (Ward *et al.*, 1977).

CHAPTER FIVE

5.0.0   CONCLUSION AND RECOMMENDATIONS

5.1.0   CONCLUSION

Stations with high traffic volumes had high lead concentrations in both roadside soils and grass samples. It is evident from the results that the majority of stations in Nairobi, which is highly urbanised and where roads with high traffic flow are concentrated had relatively high levels of lead in both soils and grass samples. The converse was true for stations in Kiambu, which is predominantly rural and with low traffic flow.

Stations in Kiambu showed higher cadmium concentrations for both soils and grass samples, despite the lower traffic volume. This observation between cadmium levels and traffic volume may be attributed to the use of p-fertilizers which are known to be a source of cadmium contamination in rural agricultural areas.

In using soil and grass to monitor the extent of aerial deposition of roadside lead and cadmium, the roles played by these two materials are not identical. Soil tends to accumulate metals on a long-term basis since many metals in soil are not so mobile. This explains the overall higher contamination level of metals in soil and the reason for sampling the top layer.

The amount of metals in roadside grass generally represents a more recent accumulation since turnover of plant materials and meteorological influences prevent an uninterrupted build-up of metals. Thus by combining soil and plant in the study gives a better overall presentation of the contamination of lead and cadmium in the roadside ecosystem.

The concentration of lead in soils decreased in an exponential-like fashion with distance from the kerbsides for stations which did not have barriers along the sampling transects.

For lead concentration in grass, cadmium concentration in both soil and grass, there was no simple relationship between the metal concentration and distance away from the roadside. Infact cadmium concentration tended to be constant for soils and grass, though grass concentration were lower in all cases.

There was no observable relationship between the pH and metal concentration on the roadside soils and grass.

5.2.0   RECOMMENDATIONS

(1) To be able to understand the cause of the very low lead concentrations observed in this study, further research should be done to study;

 i) the effect of pH on retention of lead in top soils.

ii) the effect of meteorological influences on lead dispersal and retention in soils.

(2) Introduction of legislation to control lead emission and introduction of standards should be effected. The goal should be lead-free petrol or use of catalytic converters to reduce the amount of lead emitted.

(3) Apart from the study on accumulation of heavy metals in roadside soils and vegetation, bioaccumulation in animals and human body, affecting both physical and physiological parameters should be pursued. More studies should be done to ascertain the extent and level of these contaminants.

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