SOME STUDIES ON ENVIRONMENTAL POLLUTION CAUSED BY HEAVY METALS

A THESIS PRESENTED TO THE AHMADU BELLO UNIVERSITY IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE OF

MASTER OF SCIENCE IN
ANALYTICAL CHEMISTRY

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ABSTRACT

The levels of heavy metals, like lead, nickel, chromium and copper were determined in soil, vegetation and water samples taken from twelve state capitals of Nigeria, namely Lagos, Ibadan, Akure, Abeokuta, Kano, Ilorin, Makurdi, Maiduguri, Kaduna, Jos, Owerri and Sokoto. The samples were collected from along the sides of a major highway recording a reasonably heavy vehicle traffic volume.

The determination of metals was carried out using atomic absorption spectroscopy and colorimetric methods.

The levels of the metals in soil samples from Sokoto and Kano motor parks were also determined. The level of lead showed a distinct correlation with traffic volume.

In all the state capitals, the metal concentrations in soil samples were generally below permissible thresholds. However the lead values at Sokoto motor part and on leaves from Ibadan, Lagos, Kano, Maiduguri and Kaduna were sufficiently high to cause some concern. The nickel concentrations in water samples from Ibadan, Lagos, Kano and Kaduna were found to be high.

The two methods of analysis used were found to be statistically comparable

CERTIFICATION

We certify that this work was carried out by Mr. G. O. Adediran in the Department of Chemistry, Ahmadu Bello University, Zaria.

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DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other University or institution. Information derived from the published or unpublished work of others has been acknowledged in the text.



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DEDICATION

To Bola, my wife and Bola my daughter.

CHAPTER I

INTRODUCTION

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1-1 Environmental Pollution:

Environmental pollution has many possible definitions. A useful one is to regard environmental pollution as the presence in the environment of a substance or substances added directly or indirectly by an act of man, in such amounts as to affect humans, animals or vegetation adversely. The following are generally recognised to constitute environmental pollution:[1] The presence, in concentration higher than normal, in the natural water of dissolved or suspended foreign material such as silt chemicals or metallic elements constitutes water pollution. Air pollution arises when there are solid particles, liquid droplets or gaseous compound in the atmosphere which are not normally present or which are present in a concentration substantially greater than normal. One thing is common to all types of environmental pollution, they are caused by environmental pollutants.

1-1 Some Environmental Pollutants:

This term has been defined as any substance which changes the natural composition of the environment[2]. Most of the pollutants enter the environment as emission to the atmosphere or as discharges to water bodies.

These may be either in concentrated sources, such as from factory smoke, stack and sewage discharges, or in a diffused form such as from automobile exhaust[2]. Most of these materials eventually return to the earth surface as particulate fall-out or with rain. Among these pollutants are sulphur dioxide, nitrogen oxide, smoke, organic sulphur compounds and heavy metals.

1-3 Heavy Metal Pollutants in the Environment:

The main heavy metal pollutants in the environment include lead, nickel, copper and chromium. These heavy metal pollutants may cause air, soil or water pollution if their tolerance limits are exceeded[3].

Lead naturally occurs in the form of mineral deposit mainly as galena (lead sulphide), but enters the atmosphere through natural processes as a consequence of the activities of man[3]. Among these activities, the most important of them all is gasoline combustion. Production of gasoline antiknock additives, especially tetraethyl lead accounts for about 20% of the total lead consumed in the world[4]. When gasoline is burnt in an engine, the alkyl lead compounds decomposed and are emitted into the atmosphere as $NH_4Cl.2Pb\,ClBr$ and $2NH_4Cl.PbClBr$. These undergo photolysis and eventually

form PbO and $PbCO_3$. These oxides are in the form of particulates which are in the respiratory range and are fine enough to settle out within a short distance from the motor. This has been confirmed by Cantwell el al[6] who found that lead settled and was deposited relatively near the source. Other sources of lead alkyl compounds into the atmosphere include evaporation from gas tanks and during filling at service stations.

The street dusts represent an important source of lead input to surface water. Average lead concentration in dust of residential areas of 1636 µg/g and in commercial areas of 2413 µg/g have been reported[7]. Vegetation near the busy high ways have been studied and some lead contamination from exhaust fumes observed. This contamination effect is largely one of deposition with the outer leaves showing more lead than the inner leaves[8]. This decreases with distance from the highway as was observed by Donovan el al who studied pastures in relation to lead deposition and distance from the highway[9].

→ Lead is normally present in soils to the extent of 10 - 100 mg/kg, with more on the surface soil layer than in the lower horizons[10].

Nickel, another heavy metal pollutant, is emitted into the environment when gasoline is burnt though other sources such as paint and smelting industries contribute substantial amounts. In crude gasoline, nickel is present naturally and may range in concentration from hundredth of 1 ppm to about 0.01%[11]. Distillate fraction, particularly higher boiling gas oils used as catalytic cracking stocks, are apt to contain a considerable fraction of nickel.

Copper is added to fuel in form of copper chloride as a treating agent to remove mercaptans. Copper may also get into fuel as a contaminant resulting from contact with copper alloys used in valves, pumps, heat exchangers, both in and beyond the refinery[11]. When copper is emitted into the environment it settles down and gets adsrobed on negative surfaces in soils. The copper content of normal plants, even with high copper from exhaust of vehicles rarelly exceed 30 ppm unless damage has been done[12].

Chromium is widely distributed in soils and vegetation although, concentrations are generally low. As with other heavy metals, pollution may arise from the exhaust of the vehicle, though discharge of water products from electro-plating, manufacture of alloys and other industrial processes account for the major environmental

pollution from chromium[12].

1-4 Heavy Metals and Environmental Hazards

Many heavy metals may be beneficiary or even essential to human health, but when they exceed certain permissible amounts, they constitute environmental hazards. The heavy metals of interest which may constitute environmental hazards, when their permissible limits are exceeded will be discussed.

1-4.1 Lead:-

From above it can be seen that no man lives in a lead free environment.[12] All are exposed to lead in the environment, the exposure being largely determined by our living habits. Lead is a toxic substance which represents a health hazard even to the extent that it is taken up and retained by the body[12]. When the tolerance of the body is exceeded, the symptoms of plumbism, or lead poisoning are, abdominal cramps, headaches, constipation, loss of appetites fatigue, paralysis and ence-phalopathy[14]. No case of plumbism have been found in adults with blood - levels of below 80 µg/ 100 cm^3 or in children with blood - levels below 50 µg/ 100 cm^3 [14]. Other authorities believe that biological changes are exhibited at the lower exposures, and no

threshold exists below which no damage results[15]

1-4.2 Nickel:

The permissible exposure limit for nickel according to US federal standard automobile emission act 1970, is 0.001 ppm (0.007 mg/m^3)[16]. The route of entry of nickel into the body is by inhalation as particulate. Skin sensitization is most commonly seen toxic reaction to nickel and is seen frequently in the urban populace. This often results into chronic eczema "nickel itch". Element nickel, when deposited from inhalation is also carcinogenic, producing an increased incidence of cancer of the lung and nasal passages[16].

1-4.3 Copper

Copper may enter human body mainly through inhalation of dust or fumes. Chronic human intoxication occurs rarely but congestion of the nasal mucous membrane may occur. If copper particulates reach the gastroin - testinal tract, they may act as irritants, producing salivation, nausea, vomiting, gastric pain and diarrhea[16].

1-4.4 Chromium:

Like other heavy metal pollutants, the route of entry of chromium is by inhalation. Chromium compounds act as allergens which cause dermalities to expose skin[16].

They may also produce pulmonary sensitization. Chromium in the 3+ oxidation state are of low order of toxicity. In the 6+ state, it is an irritant. Acute exposure to dust of chromium particulates may cause coughing, wheezing, headaches and loss of weight[16].

1-5 Aims and Objectives of this Work

In recent years, concern has been expressed in many quarters over the level of heavy metals in the environment[17]. In case of lead in particular, there has been reports confirming possible adverse effects arising from exposure of the populace, especially children to the environmental concentration[18]. Nickel, when inhaled is carcinogenic while copper causes congestion of the nasal mucous membrane[18].

Combustion of petroleum is the main source of lead, chromium, nickel and copper into the environment, though other sources like metal smelting, municipal refuse are also important.[19]

A comprehensive study of the distribution of heavy metals in the Nigerian environment does not appear to be available. Thus, with the gradual increasing level of industrialisation and number of vehicles on our highways, this study has been undertaken to provide

some preliminary data on some of the metal pollutants, on which further systematic monitoring could be based. Hence the following analytical studies have been carried out.

(i) To establish the pattern and extent of environmental pollution caused by heavy metals.

(ii) To find out the possible sources of heavy metal pollutants in the environment.

(iii) To establish the possible effects of factors, such as traffic density, distance of samples from the motor highways, surface area of leaves and wind direction, on the amount of heavy metals in Nigeria environment.

(iv) To suggest possible control of the environmental pollution caused by heavy metals.

In order to achieve these objectives, soil samples were collected in one of the busiest highways, very close to the control post in some of Nigerian state capitals, namely, Lagos, Ibadan, Akure, Ilorin, Jos, Kano, Kaduna, Makurdi, Maiduguri, Sokoto and Owerri. The estimated traffic volume of each of these state capitals were also obtained from the traffic wardens.

Leaf-samples were collected at the outskirt of the state capitals, but on both sides of the busiest high-

way that lead into the city.

Water samples were collected from stagnant water, at about 3 and 20 metres away from the highway. Soil samples were also collected in Sokoto and Kano motor parks.

The soil samples were subjected to chemical analysis using atomic absorption spectrometer and colorimeter.

CHAPTER 2

ANALYSIS OF SOIL, VEGETATION AND WATER SAMPLES

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CHAPTER II

2-1 Estimated Number of Vehicles at the Location from where the Samples were Collected

Information regarding the number of vehicles plying the street where the samples were collected was obtained from the traffic warden on duty at the time of sample collection. The estimated number passing between $7^{\cdot 30}$ - $8^{\cdot 30}$ a.m., $3^{\cdot 30}$ - $4^{\cdot 30}$ p.m., $5^{\cdot 30}$-$6^{\cdot 30}$ p.m. were provided by the traffic warden. The figures were averaged to give a rough estimated of the number of vehicles passing per hour. The number of vehicles passing between the above mentioned hours were counted by me and treated as above. This is shown in table I.

Table I. Estimated number of vehicles in some of the Nigerian state capitals.

State Capital	Number given by Warden			Personal Counts			
	$7^{\cdot 30}-8^{\cdot 30}$	$3^{\cdot 30}-4^{\cdot 30}$	$5^{\cdot 30}-6^{\cdot 30}$	$7^{\cdot 30}-8^{\cdot 30}$	$3^{\cdot 30}-4^{\cdot 30}$	$5^{\cdot 30}-6^{\cdot 30}$	Average
IBADAN	1375	1351	954	1240	1349	674	1087
LAGOS	1456	1498	1230	1524	1409	700	1387
AKURE	950	1128	450	1042	1214	340	865
KANO	1390	1421	1004	1401	1473	1422	1432
JOS	1122	1106	802	1021	1102	782	968
MAIDUGURI	775	843	400	642	812	419	624
MAKURDI	672	452	204	584	743	304	543
ABEOKUTA	1282	1256	650	1124	1050	317	826
OWERRI	1140	1200	507	1094	1267	416	925
ILORIN	1040	1126	850	1231	1326	204	886
SOKOTO	1242	1238	604	1021	1096	109	793
KADUNA	1320	1310	980	1340	1467	280	1019

Table 2: Number of vehicles staying for 10 - 15 minutes during the hold-up

State Capital	Number	State Capital	Number
IBADAN	65	MAIDUGURI	55
LAGOS	190	MAKURDI	25
AKURE	45	ABEOKUTA	20
KADUNA	70	OWERRI	65
KANO	45	ILORIN	35
JOS	40	SOKOTO	20

2-2 Studies on distribution profile of heavy metals in the environment

The distribution profile of heavy metals (namely lead, nickel, chromium and copper) in the environment was studied using Samaru-Zaria and Kano-Zaria highway as case studies. In these studies, soil and vegetation samples were collected along these highways at 1 - 70 metres away from the highway on both left and right sides. The samples were analysed for heavy metals and the distribution pattern of the heavy metals with distance from highway studied as shown in tables 32 - 35. This distribution pattern determined the manner of the sample collection.

2-3 Collection of samples:

Sample collection is the most important part of the total process of analysis. It is an axiom that the reliability of analytical results obtained in the laboratory can never be more reliable than the sample upon which the tests are performed. With this as a guiding principle, coupled with the distribution profile of heavy metals in the environment the various samples were collected as follows:-

Soil samples:- Four transects, each at 6 metres away from the other were established from the traffic control post on both sides of the busiest street in each of the state capitals. Soil samples were collected at 3, 9 and 15 metres away from the highway (with a metal cylinder cover of length 19 cm) in each transect. The samples from the transects were combined and a representative portion of it was taken. The sample depth was 10 cm. All the samples were collected between July and September, except for Sokoto and Kano motor park samples that were collected in October. Polythene bags were used for the storage of the soil samples after collection. The highways of the corresponding state capitals from where the soil samples were collected are shown in table 3 below.

Table 3. STATE CAPITALS AND LOCATIONS FROM WHERE SAMPLES WERE COLLECTED

States	Capital	Locations Where Samples were Collected
OYO	Ibadan	University of Ibadan - Dugbe Highway
LAGOS	Lagos	Iddo - Badagary Highway
ONDO	Akure	Deji "
KWARA	Ilorin	Unity "
OGUN	Abeokuta	Sapon-Lafenwa "
KADUNA	Kaduna	Ahmadu Bello "
SOKOTO	Sokoto	" " "
PLATEAU	Jos	Rukuba Highway
KANO	Kano	Zaria "
BORNO	Maiduguri	Airport "
BENUE	Makurdi	Ali-Akilu Highway
IMO	Owerri	Douglas "

The soil samples from motor parks in Sokoto and Kano were collected at the centre and 1 to 20 metres away from the centre of the parks.

Vegetation samples:

Leaf samples were collected from trees of about two metres high. The leaves were collected from the

side of the trees that faced the busiest highway that leads into each of the state capitals at 2 and 20 metres from the highway on both sides of the road. The leaf samples were collected in perforated polyethylene bags and stored in the refrigerator. The surface areas of five leaves chosen randomly from each of the sample were measured and tabulated as shown in table 4.

Table 4. LEAF SURFACE AREAS IN cm^2

State Capital	1	2	3	4	5	Average cm^2
IBADAN	18.7	128.1	124.0	125.3	15.9	132.4
LAGOS	126	88.0	96	162	148.5	122.9
AKURE	126	80.7	90.7	65	67.5	86.1
ILORIN	60.4	40.7	62.4	61.5	67.4	58.3
KADUNA	74.2	11.4	24.5	32.6	16.3	30.6
SOKOTO	16.5	7.5	14.9	32	21.4	18.5
JOS	60.4	10.5	40.6	35.8	31.6	37.7
MAIDUGURI	10.8	12.7	8.3	8.5	5.6	9.2
MAKURDI	10.4	12.8	8.1	8.6	5.4	9.1
KANO	80.4	120	74.6	131	73.5	95.9
ABEOKUTA	51.4	42.4	44.6	42.8	40.1	44.3
OWERRI	114.2	98.1	79.1	120.2	174.	117.2

Water samples:

Water samples were collected in plastic containers of about 300 cm^3 from stagnant water bodies at about 2 and 20 metres from the highways.

2-4 DETERMINATION OF HEAVY METALS BY ATOMIC ABSORPTION SPECTROPHOTOMETER

Sample Pretreatment:-

Soil samples:

Prior to chemical analysis by atomic absorption spectroscopy, the soil samples were dried at 105°C for 3 hours in an oven. The dried soil samples were grinded and sieved to 60 mesh before being stored in sample bottles.

Vegetation samples:

Each leaf sample was divided into two portions, one part was carefully sponged with water containing detergent and then rinsed with de-ionized water to remove the surface contaminants. The second part was left unwashed. Both washed and unwashed were air dried, powdered and stored in polyethylene bags.

Water samples:

The water samples were filtered until they became clear. The cleared water samples were then concentrated

from about 500 cm^3 to 50 cm^3 and 10 cm^3 of concentrated hydrochloric acid was added to prevent the growth of the microorganisms.

Principle of Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is currently one of the most widely used method for the determination of heavy metals, especially those that occur at trace level in most of the environmental samples[12]. It is an analytical method based upon the absorption of radiation by free atoms in vapour state. Conversion (at least partial) of the sample into an atomic vapour is accomplished by spraying a solution into a flame. A hollow-cathode lamp containing the element to be determined is used as the light source. The atoms of this element in the flame absorb at precisely the same wavelength as that emitted by the light source. The decrease in intensity is measured using a monochromotor and detector system. This decrease is related to the concentration of the element in solution.

2-5 EXPERIMENTAL

Glasswares used:

All glasswares used were of pyrex and were washed clean and rinsed with warm nitric acid.

Reagents and Chemicals

All chemicals used are of analytical grade unless otherwise stated -

Lead Nitrate

Anhydrous Sodium Carbonate

Potassium Nitrate

Con. Hydrochloric acid (s.g. 1.18)

Nitric acid (1% V/V)

Hydrochloric acid (50% V/V)

Lead standard solutions

Stock solution - (100 ppm pb).

0.1599 g of lead nitrate was dissolved in 25 cm^3 of HNO_3 (1% V/V) and this was diluted to 1 litre with deionized water.

Working standards:

Lead standards in the range of 0 - 10 ppm were prepared by dilution of the stock solution with the inclusion of concentrated hydrochloric acid as appropriate to match the sample solutions.

Instrument used:

Perkin-Elmer atomic absorption spectrometer model sp 1900.

2-5-1 DETERMINATION OF LEAD

Preparation of sample solutions:-

Procedure for preparation of soil sample solutions:

Soil sample solutions were prepared by sodium carbonate fusion method. 0.5g of the soil sample was weighed into a clean silica crucible. To this was added 3.0g of anhydrous sodium carbonate and 0.3g of potassium nitrate. These were all mixed thoroughly and heated with Meker burner gradually at first, until the mass became quiescent. After 15 minutes, the sample was allowed to cool and washed with 10 cm^3 of deionised water into 50 cm^3 beaker. 10 cm^3 of hydrochloric acid (50% V/V) was added and boiled for three hours on a hot plate at the temperature of 90°C. The content was then filtered into 100 cm^3 standard flask and made up to the mark with deionised water.

Leaf sample solutions:

Procedure:

Dry ashing method was used for the preparation of the leaf sample solutions.

4.0 g portion of the washed leaf sample was weighed into a silica crucible. This was charred by a gas burner with a soft flame, taking care not to ignite the sample. The samples were put in muffle furnace and the temperature was gradually raised to 450°C and maintained between 450°C and 500°C for 5 hours. When a clean ash was obtained, the ash was cooled and 20 cm^3 of concentrated hydrochloric acid was added cautiously. This was boiled on water bath to dryness. The residue was dissolved in 20 cm^3 of hydrochloric acid (50% V/V) and made up to 100 cm^3 standard mark with deionised water. The unwashed leaf samples were similarly treated as washed leaf samples.

Water sample solutions:-

Procedure:

Filtered water samples were concentrated to 30 cm^3 in a 50 cm^3 volumetric flask and 5 cm^3 of hydrochloric acid (50% V/V) was added. It was then made up to the mark with deionised water.

Instrumental Conditions

Wavelength	-	217.00 nm
Slit setting	-	0.15 - 0.20
Flame	-	Air/acetylene flame

Air flow rate - 0.8 - 1.0 litre min^{-1}.

Procedure

The standard solutions were first aspirated into the atomic absorption spectrometer using the lead lamp. After this, the solutions were aspirated into the flame. The absorption intensifies were measured. A calibration curve was prepared from the standard solution intensity readings which was used to calculate the concentration of lead in ppm. These were converted into $\mu g g^{-1}$ using the equation below.

For soil and plant samples

$$Pb\ (\mu g g^{-1}) = \frac{C\ (PPM) \times \text{sample volume } (cm^3)}{\text{sample weight } (g)}$$

For water samples.

$$Pb\ (\mu g L^{-1}) = C\ (PPM) \times 10^3$$

The results of lead determination by atomic absorption spectroscopy are given in tables 5, 6 and 7.

2-5-2 Determination of Nickel

Reagents and chemicals:

All chemicals used were of analytical grade unless otherwise stated.

$Ni(NO_3)_2.6H_2O$ (Nickel Nitrate hexahydrate)

Potassium Pyrosulphate

Conc. Hydrochloric acid (S.g. 1.18)

Nickel standard solution (100 ppm Ni).

4.9530 g of $Ni(NO_3)_2.6H_2O$ was dissolved in deionised water and diluted to 1 litre.

Working Standard Solutions:

A concentration range of 0 to 10 ppm nickel was prepared from the stock solution by dilution and 1 cm^3 of hydrochloric acid (1% V/V) was added to match the sample solutions.

Preparation of sample solutions:

Soil samples:

Procedure:

0.5g of the soil was weighed into a borosilicate tube and 2.50 of potassium pyrosulphate was added. The mixture was heated over a burner until it melted and the heating continued for about 15 minutes. After cooling, 5 cm^3 of deionised water was added followed by 1 cm^3 of concentrated hydrochloric acid. This was boiled for two hours. The extract was filtered into 100 cm^3 volumetric flask and diluted to volume mark.

Leaf sample solutions:

The leaf sample solutions were prepared as for lead determination.

Water samples solutions:

Procedure:

The water sample solutions were also prepared as for lead determination.

Instrumental conditions

Wavelength - 232.00 nm

Slit setting - 10 nm

Flame - Air/acetylene flame

Air flow rate - 5.0 litre min^{-1}

Lamp current - 12 - 15 mA.

Procedure:

A wavelength of 232.00 nm was selected after which the air and acetylene flow rates were adjusted to 5.00 litre min^{-1} and 0.8 litre min^{-1} respectively. The hollow cathode lamp was allowed to stabilize. The standard solutions were first aspirated into the atomic absorption spectrometer using the nickel lamp. After this, the solutions were aspirated into the flame. The absorption intensities were measured. A calibration curve was prepared from the standard readings which was used to calculate the concentration of nickel in ppm. The concentration in ppm were converted to $\mu g g^{-1}$ and $\mu g L^{-1}$ for soil and water samples respect-

ively, using the equations in the lead determination.

The results of the nickel determination by atomic absorption spectroscopy are tabulated in tables 8, 9 and 10.

2-5.3 DETERMINATION OF CHROMIUM

Reagents and chemicals:

All reagents and chemicals used are of analytical grade unless otherwise stated.

Potassium chromate

Anhydrous sodium carbonate

Potassium nitrate

Hydrochloric acid (50% V/V)

Chromium standard solutions:

Stock solution (1000 ppm)

The stock solution was prepared by dissolving 3.7350g of potassium chromate in 250 cm^3 of deionised water. This was diluted to 1 litre in a volumetric flask with deionised water.

Working standard

A concentration range of 0 to 2 ppm chromium was prepared from the stock solution by dilution and 10 cm^3 of hydrochloric acid (50% V/V) was added as appropriate to match the sample solution.

Preparation of the sample solutions:

Procedure:

The soil, vegetation and water sample solutions were prepared as in nickel determinations.

Instrumental conditions:

Wavelength - 357.8 nm

Slit setting - 0.10 - 0.15 nm

Flame used - Air/acetylene

Air flow rate - 5.00 litre min^{-1}

Acetylene flow rate - 1.00 - 1.2 litre min^{-1}

Lamp current - 8 - 10 mA

Procedure:

A wavelength of 357.8 nm was selected and air/acetylene flow rates were adjusted as appropriate. The hollow cathode lamp was allowed to stabilize. The standard solutions were first fed into the atomic absorption spectrometer using the chromium lamp. After this, the solutions were aspirated into the flame and the absorption intensities measured.

A calibration curve was prepared from the standard readings which was used to calculate the concentration of chromium in ppm. These concentrations were converted into $\mu g g^{-1}$ for soil and leaf samples as in

nickel determination.

The results of the determination are as shown in tables 11 and 12.

2-54 DETERMINATION OF COPPER:

Reagents and chemicals:

Copper sulphate pentahydrate

Hydrochloric acid (50% V/V)

Copper standard solutions

Stock solution (100 ppm Cu)

0.3930 g of $CuSO_4.5H_2O$ was dissolved in water and made up to 1 litre.

Working standard:

A concentration range of 0 to 1.00 ppm copper was prepared by dilution of the stock solution.

Preparation of sample solution

Procedure:

As in chromium determination.

Instrumental conditions

Wavelength - 324.8 nm

Slit setting - 0.15 - 0.20 nm

Flame used - Air/acetylene

Air flow rate - 5.00 litres min^{-1}

Acetylene flow rate - 1.00 - 1.2 litre min^{-1}

Lamp current - 8 - 10 mA

Procedure

The wavelength of 324.8 was selected and all other instrumental conditions adjusted. The standard and sample solutions were aspirated using copper lamp as in the previous determinations. From the calibration curve, the concentrations of copper in the samples were obtained and converted into $\mu g g^{-1}$ for soil and leaf samples and $\mu g L^{-1}$ for water samples. The results of the determination are as shown in tables 13, 14 and 15.

2-6 DETERMINATION OF HEAVY METALS BY SPECTROPHOTOMETRIC METHOD

Principle

The variation of the colour of a system with change in concentration of some component forms the basis of spectrophotometric analysis[28].

This technique involves the determination of the concentration of a substance by measurement of relative absorption of light with respect to a known concentration of the substance. Light of a definite wavelength, usually constitutes the source of light, hence the use of photoelectric photometer to measure the light transmitted by the solution. This method of analysis is based on Beer Lambert law, which can be stated

mathematically as

$$\log \frac{I_o}{I_t} = \epsilon ct$$

$$\text{or} \quad A = \epsilon ct$$

where I_o = Intensity of incident light

I_t = Intensity of transmitted light

ϵ = Extinction coefficient

C = Concentration of the solution

t = path length

A = Absorbance

From this expression, absorbance or optical density is linearly related to the concentration of the substance if t and ϵ are constant.

2-6.1 EXPERIMENTAL

Glasswares used:

All glasswares used were of pyrex and were washed clean and rinsed with warm nitric acid.

Reagents and chemicals:

All reagents and chemicals used are of analytical grade unless otherwise stated.

Lead standards:

Stock solutions (100 µgPb)

0.1599 g of $Pb(NO_3)_2$ was dissolved in 20 cm^3 HNO_3 (1% V/V) and diluted to 1 litre with deionised water.

Working standards

The working standard solutions were prepared from the stock solution by dilution.

Dithizone solution:

Stock solution - 0.1% m/V in chloroform

Working solution

This was prepared by mixing 6 volumes of the stock solutions with 9 volumes of water and 1 volume of 5M NH_4OH.

The lower layer was rejected

Ammonium citrate (25% m/V)

Sodium Hexametalphosphate (10% m/V)

Nitric acid (1% V/V)

Ammonia solution (S .g. 0.880)

Chloroform

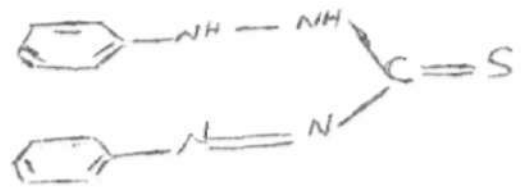
Ammonium sulphite - Cyanide solution.

Instrument used:

Spectrophotometer sp 20.

2-6.2 DETERMINATION OF LEAD BY DITHIZONE METHOD[30]

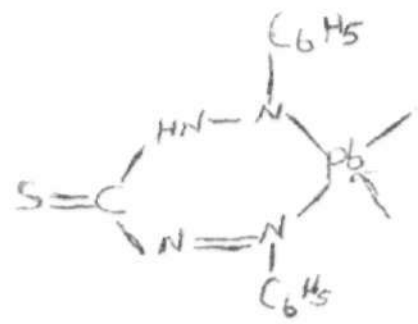
Dithizone is the reagent normally used for the spectrophotometric estimation of lead[30]. It has the structural formula



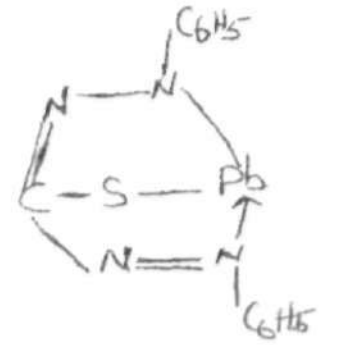
This organic reagent forms complexes with metals. The metal complexes are all soluble in chloroform or carbon tetrachloride which are all intensely coloured, usually red, yellow or brown.

The technique is to shake the extract solution for a minute or two with an excess of 0.1% V/V solution of dithizone in chloroform, where upon the metal which forms the complex goes into the organic layer. Though the reagent is unselective, its selectivity could be enhanced by control of the pH and by the addition of complex formers to the sample extract solution.

Two types of pb-dithizone complexes are possible, the keto and the enol form as can be seen below.



Keto form.



Enol form.

The keto complexes are formed under usual analytical condition.

In using this reagent for lead determination, the sample solution extracted is diluted and hydroxylamine is added to prevent oxidation of dithizone. Citrate and cyanide are added to mask interfering metals such as iron, copper and zinc. The pH as adjusted to 9 - 9.5 by the addition of NH_4OH.

Potassium, lead and Bismuth (if present) are extracted by dithizone in chloroform. The lead-dithizone complex in chloroform is destroyed by adding 1% (V/V) nitric acid. The complex is formed again and the lead amount determined spectrophotometrically.

Preparation of sample solution

Procedure:

The soil and leaf sample solutions were prepared as in the determination of lead by Atomic Absorption spectroscopy. The sample solutions were made up to 20 cm^3 and transferred into a 250 cm^3 connical flask.

Extraction:

First Extraction:

5.00 cm^3 of ammonium citrate solution was added followed by 10 cm^3 of sodium hexametaphosphate solution. The pH of the solution was adjusted to 9.0 -

9.5 by adding ammonia solution dropwise. This was cooled and 1 cm^3 of 10% KCN added, followed by 1 cm^3 of hydroxylamine hydrochloride. The whole was transferred into a separating funnel containing 10 cm^3 of chloroform. 0.5 cm^3 of dithizone working solution was added and the mixtures shaken for one minute. The extraction with dithizone solution was repeated until the lower layer was blue.

The chloroform layer was transferred into another separating funnel. About 3.0 cm^3 of chloroform was added and shaken with 0.2 cm^3 of dithizone working solution. The extraction with dithizone was repeated until chloroform washing was green. 10 cm^3 of HNO_3 (1% V/V) was added and shaken for one minute. The chloroform layer was rejected.

Third Extraction:

Exactly 5.0 cm^3 of the standard solution of range 0 to 40 ug Pb was pipetted into separating funnels, 10 cm^3 of HNO_3 (1% V/V) was added, followed by 30.0 cm^3 of Ammonium Sulphite - Cyanide solution. 10 cm^3 of chloroform was added followed by 0.5 cm^3 dithizone working solution and shaken for one minute. The optical densities of the chloroform layers were taken at 520nm. The

calibration curve was prepared from the optical density measurement of the standard solutions. All these readings were used to calculate the concentration of lead using the equation below

For soil and leaf samples.

$$Pb(\mu g g^{-1}) = \frac{C\ (\mu g) \times \text{sample volume } (cm^3)}{\text{Aliquot } (cm^3) \times \text{sample wt } (g)}$$

For water samples

$$Pb\ (\mu g L^{-1}) = \frac{C\ (\mu g) \times 10^3}{\text{Aliquot } (cm^3)}$$

The result of the determination is tabulated in table 16.

2-6.3 DETERMINATION OF NICKEL BY DIMETHYLGLYOXINE METHOD

Nickel may be determined spectrophotometrically by utilizing the formation of the well-known complex with dimethylglyoxine. The reaction is sensitive, but because of its low solubility, the complex is difficult to keep in solution. A number of metals, including copper, cobalt, iron and sometimes manganese, also react under the same conditions. The method used is based on that of Forster (1953)[29] and this included steps to remove the interfering metals.

Reagents and chemicals

Nickel standards

Stock solution (100 µg.Ni)

4.953g of Nickel Nitrate hexahydrate was dissolved in 100 cm^3 of deionised water and this was diluted to 1 litre.

Working standards

The stock solution was diluted 100 times and concentration range of 0 - 12 ug was prepared.

Dimethylglyoxine, (1% $^m/V$) in methanol

Hydroxylamine hydrochloride (1% $^m/V$)

Sodium citrate, (20% $^m/V$)

Ammonia (s. g. 0.880)

Ammonium Hydroxide (1 + 50)

Hydrochloric acid (1 + 30)

Chloroform

Hydrochloric acid (1 + 3)

Sodium tartarate (20% $^m/V$)

Potassium persulphate (4% $^m/V$)

Sodium hydroxide 5M

Sample solution preparation

Procedure

The soil and leaf sample solutions were prepared as for Atomic Absorption spectroscopy. Each solution

was made up to 20 cm^3 and transferred into a separating funnel.

Separating stage

To the extract solution in the separating funnel was added 2.0 cm^3 hydroxylamine hydrochloride solution (10% $^m/V$), followed by 5.0 cm^3 sodium citrate solution (20% $^m/V$). Ammonia was added until just pink to phenolphthalein and four drops added in excess. To all these, 2 cm^3 of dimethylglyoxine (1% $^m/V$) reagent was added and diluted to about 60.0 cm^3. This was extracted with 5.0 cm^3 of chloroform three times and all extracts combined. The combined extract was shaken with 5.0 cm^3 NH_4OH (1+50) and the aqueous layer discarded. The organic layer was shaken with 5.0 cm^3 of HCl (1 + 3) for one minute.

Colorimetric stage

20.0 cm^3 of standard solution was pipetted into 50.0 cm^3 volumetric flask to give a range of 0 - 12 μg nickel and 15.0 cm^3 of HCl (1 + 30) was included. To this, 2.0 cm^3 of sodium tartarate (20% $^m/V$) solution was added, followed by 10.0 cm^3 potassium persulphate solution (4% $^m/V$). 0.6 cm^3 of dimethylglyoxine was added followed by 25.0 cm^3 5M NaOH. This was mixed and diluted to volume, and left for 30 minutes.

The optical density was measured at 465 nm using water as the reference with spectrophotometer sp-20.

A calibration curve was prepared from the optical density readings of the standard solutions. The concentration of nickel in soil samples were calculated from the graph and expressed as $\mu g g^{-1}$ using the equation as in lead determination. The result of nickel determination by spectrophotometric method is shown in table 17.

2-6.4 DETERMINATION OF CHROMIUM BY DIPHENYLCARBAZIDE METHOD

Chromium in microgram amount can be determined spectrophotometrically by utilizing the deep red-violent colour formed by the oxidation of diphenylcarbazide ($CO(NH\text{-}NH\text{-}C_6H_5)_2$), by the dichromate ions in acid solution. The colour produced fades on standing and so measurements of the optical density are thus made as soon as the colour develops.

Reagent and chemicals

Chromium standards

Stock solution (1000 μg Cr)

0.2828 g of $K_2Cr_2O_7$ was dissolved in water and diluted to 1 litre.

Working standards (100 μg Cr)

The stock solution was diluted 100 times. Diphenylcarbazide (0.2% $^{m}/V$) in ethanol was prepared fresh.

Sample solution preparation

The soil and leaf sample solutions were prepared as for Atomic Absorption spectroscopy.

Procedure

A concentration range of 0 - 1.0 ug was prepared. Exactly 20 cm^3 of this standard solution was pipetted into 50.0 cm^3 graduated flask. To this, 10.0 cm^3 of 1M H_2SO_4 was added, followed by 2.0 cm^3 of methanoic solution of diphenylcarbazide (1% $^{m}/V$) containing 6 drops of concentrated H_2SO_4, per 100 cm^3. This was diluted to 500 cm^3 with deionised water.

The sample solutions were treated as for the standard solutions and the absorbance taken immediately with spectrophotometer sp 20 at the wavelength of 540nm.

The concentration of chromium in the sample was read from the calibration curve, and expressed in $\mu g g^{-1}$. The result of chromium determination is given in table 18.

CHAPTER 3

RESULTS OF THE ANALYSIS OF THE SOIL, VEGETATION AND WATER SAMPLES

Table Nos.	Content	Page
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13 to 24	AAS determination of amount of heavy metals in soil, leaf and water samples along the road sides of some state capitals.	46 - 56
25 to 27	Spectrophotometric determination of amount of heavy metals in soil, leaf and water samples along the road sides of some state capitals	57 - 59
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CHAPTER III

TABLE 5

AMOUNT OF LEAD (μgg^{-1}) WITH ESTIMATED STANDARD DEVIATION OF SOIL SAMPLES ALONG KANO - ZARIA ROADS USING AAS METHOD

KANO - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the Road
1	24.0±2.0	20.8±0.30
5	18.6±1.1	16.4±0.77
10	17.4±0.3	14.6±0.2
20	16.8±0.2	12.2±0.25
30	13.0±0.2	9.8±0.5
40	12.2±0.21	9.6±0.3
50	9.0 ±0.51	6.1±0.2
60	8.5 ±0.1	5.4±0.15
70	8.4 ±0.09	5.9±0.16
	8.4 ± 0.05	5.4 ± 0.16

SAMARU - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the Road
1	51.8±3.0	30.0±2.0
5	22.8±0.36	17.4±0.53
10	13.0±0.1	15.7±0.3
20	12.6±0.11	13.3±0.21
30	11.5±0.115	12.7±0.31
40	9.5±0.10	12.1±0.30
50	8.8±0.24	9.8±0.24
60	7.7±0.33	6.4±1.1
70	7.4±0.12	5.4±0.42
	7.75 ± 0.22	5.5 ± 0.4

TABLE 6

AMOUNTS OF LEAD ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATION OF LEAF SAMPLES ALONG KANO - ZARIA AND SAMARU - ZARIA ROADS USING AAS TECHNIQUE

KANO - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the Road
2	12.5±1.0	7.6±0.7
10	8.5±1.2	5.9±0.42
20	3.0±0.4	1.6±0.21
30	2.5±0.15	0.9±0.10
40	1.6±0.3	0.87±0.1
50	1.2±0.14	0.7±0.2

SAMARU - ZARIA ROAD		
Distance in metre	Left side of the Road	Right side of the Road
2	15.6±0.8	7.3±0.4
10	7.6±0.2	6.1±0.2
20	3.9±0.21	3.2±0.6
30	3.6±0.20	2.4±0.21
40	2.6±0.05	2.3±0.18
50	1.6±0.12	1.9±0.14

TABLE 7

AMOUNTS OF NICKEL ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATION OF SOIL SAMPLES ALONG KANO - ZARIA AND SAMARU - ZARIA ROADS USING AAS METHOD

KANO - ZARIA ROAD		
Distance in metre	Left side of the Road	Right side of the Road
1	17.8±2.6	16.3±0.4
5	12.8±0.4	19.4±0.31
10	9.6±0.1	14.7±0.1
20	14.4±0.3	14.4±0.5
30	12.3+0.5	15.0±0.6
40	9.3±0.1	9.3±0.5
50	8.0±2.6	8.2±0.8
60	8.7±1.2	8.3±0.3
70	9.2±0.3	8.0±0.4

SAMARU - ZARIA ROAD		
Distance in metre	Left side of the Road	Right side of the Road
1	15.6±0.34	13.0±0.64
5	15.2±1.01	12.4±0.28
10	13.5±0.3	10.4±0.20
20	12.6±0.2	10.8±0.33
30	10.7±0.21	10.4±0.24
40	9.8±0.42	10.5±0.27
50	10.1±0.9	10.2±0.25
60	9.7±1.2	9.8±0.24
70	8.2±0.9	9.9±0.21

TABLE . 8

AMOUNTS OF NICKEL (μgg^{-1}) WITH ESTIMATED STANDARD DEVIATION OF THE LEAF SAMPLES ALONG KANO - ZARIA AND SAMARU - ZARIA ROADS USING AAS TECHNIQUE

KANO - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
2	24.7±0.84	22.7±1.0
10	7.3±0.92	18.6±0.65
20	5.0±0.23	3.1±0.05
30	4.9±0.24	3.7±0.09
40	4.7±0.64	3.6±0.31
50	4.0±0.4	2.9±0.21

SAMARU - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
2	17.7±1.0	16.3±0.3
10	4.0±0.8	8.9±0.12
20	1.9±0.7	6.0±0.16
30	1.6±0.51	5.2±0.2
40	1.4±0.3	5.0±0.4
50	1.0±0.2	4.7±0.3

TABLE 9

AMOUNTS OF CHROMIUM ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATION OF SOIL SAMPLES ALONG KANO-ZARIA AND SAMARU - ZARIA ROADS USING AAS METHOD

KANO - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
1	15.7±0.58	16.0+1.2
5	11.9±0.31	11.3±1.1
10	9.4±0.5	5.8±0.73
20	5.7±0.61	3.3±0.64
30	6.6±1.1	3.7±0.57
40	6.8±0.9	3.3±0.52
50	3.4±0.53	2.7±0.26
60	3.0±0.1	2.3±0.16
70	2.51±0.2	2.1±0.14

SAMARU - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
1	15±2.6	13.7±0.6
5	12.1±2.0	9.3±0.85
10	12.0±0.16	9.4±0.7
20	9.7±0.6	7.7±0.52
30	6.0±0.04	6.3±0.6
40	5.8±0.7	6.2±0.16
50	5.6±0.52	4.9±0.52
60	5.3±0.64	4.8±0.5
70	4.6±0.31	5.1±0.71

TABLE 10

AAS DETERMINATION OF AMOUNTS OF CHROMIUM (μgg^{-1})
WITH ESTIMATED STANDARD DEVIATION OF THE LEAF
SAMPLES ALONG KANO - ZARIA AND SAMARU - ZARIA ROAD

KANO - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
2	9.5±0.8	22.7±0.4
10	7.5±0.6	18.6±1.2
20	5.0±1.2	3.1±0.78
30	5.1±0.8	3.4±0.2
40	5.7±0.54	3.0±0.1
50	4.9±0.4	2.4±0.31

SAMARU _ ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
2	17.7±1.2	14.4±0.6
10	4.0±0.73	7.2±0.45
20	1.9±0.62	4.4±0.28
30	1.4±0.42	4.2±0.24
40	1.5±0.7	3.8±0.18
50	0.9±0.3	2.9±0.3

TABLE 11

AMOUNTS OF COPPER (μgg^{-1}) WITH ESTIMATED STANDARD DEVIATION OF THE SOIL SAMPLES ALONG KANO - ZARIA AND SAMARU - ZARIA ROAD

KANO - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
1	6.4±0.5	3.4±0.3
5	4.5±0.65	2.6±0.14
10	4.0±0.71	2.8±0.2
20	3.2±0.21	1.9±0.3
30	3.0±0.14	1.8±0.25
40	2.8±0.09	1.6±0.14
50	2.7±0.51	1.0±0.11
60	2.6±0.4	1.2±0.09
70	2.7±0.26	1.1±0.13

SAMARU - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
1	4.17±0.7	2.3±0.3
5	2.63±0.4	2.18±0.4
10	1.45±0.9	2.9±0.21
20	1.39±0.61	2.10±0.14
30	1.25±0.4	1.24±0.09
40	1.30±0.62	1.23±0.07
50	1.32±0.51	1.13±0.09
60	1.29±0.61	1.04±0.12
70	1.25±0.42	1.12±0.16

TABLE 12

AMOUNTS OF COPPER ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATION OF THE LEAF SAMPLES ALONG KANO - ZARIA AND SAMARU - ZARIA ROADS

KANO - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
2	6.3±0.12	9.1±0.24
10	4.1±0.17	6.4±0.16
20	3.2±0.10	4.2±0.17
30	2.8±0.14	3.1±0.14
40	2.7±0.12	3.2±0.11
50	2.0±0.41	3.4±0.15

SAMARU - ZARIA ROAD		
Distance in metre	Left side of the road	Right side of the road
2	8.25±0.6	7.2±0.14
10	3.75±0.14	6.4±0.21
20	2.6±0.18	3.3±0.18
30	11.5±0.2	2.5±0.12
40	1.7±0.12	11.8±0.21
50	1.6±0.09	1.9±0.15

TABLE 13: AAS DETERMINATION OF AMOUNTS OF LEAD ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATION OF THE SOIL SAMPLES ALONG THE ROAD SIDES OF SOME STATE CAPITALS

	Distance in metre from left side of the road			Distance in metres from right side of the road		
	3	9	15	3	9	15
IBADAN	252.0±7.2	173±7.5	37.3±2.5	203±3.0	93 +12.5	34.3±5.1
LAGOS	377±2.6	279.6±4.5	31.0±1.0	177±11.3	135±1.0	36±3.6
AKURE	145.3±4.8	86.1±3.3	21.5±1.3	181.3±3.4	87.5±9.0	18.6±3.1
ABEOKUTA	157±3.0	55.6±2.5	31.5±3.1	170±1.4	90.3±4.5	37±3.5
ILORIN	147.6±2.7	89.2±5.3	41±3.6	181.3±3.0	79.3±4.0	28.0±3.0
KANO	269.3±5.5	154±5.5	81.1±3.1	260±2.4	169.5±5.8	77±3.2
MAIURDI	83.6±3.4	42±2.4	17.3±2.8	77±2.2	53.8±2.8	15.5±1.9
MAIDUGURI	65.8±2.7	39.3±1.3	26±2.8	71±2.8	35.2±2.8	16±2.6
KADUNA	273±4.3	157.3±4.2	35±3.3	185±3.3	86.4±2.2	38.2±4.4
JOS	221.6±3.8	94.8±3.7	37.3±4.1	171±2.4	82±2.5	32.0±1.9
OWERRI	140.0±1.0	92+4.5	31.6+3.1	160±1.7	92.6±5.2	24±4.0
SOKOTO	132.1±3.4	86.1±6.0	24.2±2.2	134±2.0	74.4±1.6	31.0+2.6

TABLE 14:

AAS DETERMINATION OF AMOUNTS OF LEAD ($\mu g g^{-1}$)
WITH ESTIMATED STANDARD DEVIATION OF LEAF SAMPLES
ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from left side of the road		Distance in metre from right side of the road	
	2	20	2	20
IBADAN	23.0±2.6	15.8±1.3	31.4±1.6	16.1±0.26
LAGOS	47.2±2.0	25.5±2.3	18.2±0.26	12.5±0.21
AKURE	44.8±1.1	17.3±2.1	32.1±2.3	27.3±1.9
ABEOKUTA	24.6±2.1	14.3±0.7	40.4±0.6	11.2±1.2
ILORIN	24.5±0.93	11.3±1.0	22.7±0.4	15.3±0.8
KANO	48.0±2.6	29.5±2.5	32.6±2.3	21.6±0.4
MAKURDI	27.0±1.8	18.4±1.9	19.1±0.4	9.0±0.2
MAIDUGURI	20.9±1.7	3.9±0.4	4.7±0.3	2.0±0.33
KADUNA	44.3±4.3	28.3±1.6	19.4±1.1	18.4±1.2
JOS	26.3±1.8	11.1±0.78	31.0±1.1	21.0±2.1
OWERRI	15.5±1.3	10.2±1.2	27.4±0.6	18.4±0.96
SOKOTO	19.4±1.8	9.2±0.4	16.5±2.0	9.1±0.6

TABLE 16

AMOUNTS OF LEAD ($\mu g\, L^{-1}$) IN WATER SAMPLES WITH ESTIMATED STANDARD DEVIATIONS ALONG THE ROAD SIDES OF SOME STATE CAPITALS USING AAS TECHNIQUE

State Capital	Distance in metre from the road	
	3	20
IBADAN	9.2±0.31	6.2±0.22
LAGOS	127 ±0.70	4.4±0.58
AKURE	9.8±0.30	2.3±0.55
ABEOKUTA	12.4±0.64	4.7±0.30
ILORIN	9.5±0.30	5.0±1.30
KANO	7.3±0.31	4.1±0.1
MAKURDI	3.8±0.31	1.2±0.21
MAIDUGURI	5.4±0.1	1.4±0.20
KADUNA	9.2±0.21	3.1±0.32
JOS	8.4±0.2	2.2±2.4
OWERRI	11.9±0.95	4.5±0.46
SOKOTO	8.6±0.42	4.8±0.2

TABLE 17

AAS DETERMINATION OF AMOUNT OF NICKEL ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATIONS OF THE SOIL SAMPLES' ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from left side of the road			Distance in metre from right side of the road		
	3	9	15	3	9	15
IBADAN	67 ±2.6	60.3±3.1	66.3±3.1	71.0±4.1	61.6±3.5	53.5±2.5
LAGOS	71.0±4.0	62.0±3.4	51.3±4.2	74.0±2.6	57.2±2.5	79.0±2.2
AKURE	87.0±3.2	39.8±3.2	37.0±4.1	61.0±2.4	42.0±2.6	49.3±2.1
ABEOKUTA	81.0±3.1	63.0±1.1	50.3±3.5	100.0±1.6	92.0±1.5	91.0±2.5
ILORIN	73.3±4.0	52.0±2.0	63.6±0.5	61.6±4.0	39.1±2.0	54.3±1.3
KANO	82.0±2.0	64.5±0.5	63.0±0.5	101.0±3.0	86.5±2.4	63 +1.4
MAKURDI	49.5±1.5	28.5±0.2	19.0±1.0	45.1±2.0	25.0±2.2	19.1±2.3
MAIDUGURI	34.0±2.0	23.0±1.2	11.5±0.8	33±1.0	24.1±1.0	15.5±1.9
KADUNA	91.3±3.1	93.0±1.0	66.3±2.0	84±2.4	69.3±1.5	66.1±1.7
JOS	92.0±3.4	79.1±2.6	75.0±4.1	36.6±3.4	94.6±2.7	56.1±2.0
OWERRI	86.0±2.0	73.3±2.3	51.0±2.6	47.6±2.1	37.5±1.5	55.2±1.4
SOKOTO	51.4±1.8	34.2±1.2	42.0±1.9	32.4±1.1	22.1±0.9	34.4±1.8

TABLE 18

AMOUNTS OF NICKEL ($\mu g g^{-1}$) IN LEAF SAMPLES WITH ESTIMATED STANDARD DEVIATIONS ALONG THE ROAD SIDES OF SOME STATE CAPITALS USING AAS TECHNIQUE

State Capital	Distance in metre from left side of the road		Distance in metre from right side of the road	
	2	20	2	20
IBADAN	2.2±0.26	0.7±0.02	1.1±0.15	0.5±0.01
LAGOS	1.3±0.1	0.52±0.05	1.9±0.1	0.91±0.03
AKURE	0.6±0.02	0.6±0.02	1.0±0.29	0.32±0.09
ABEOKUTA	0.94±0.2	0.37±0.02	1.1±0.14	0.63±0.04
ILORIN	1.0±0.26	0.45±0.1	1.6±0.26	0.72±0.06
KANO	1.5±0.115	0.53±0.04	0.73±0.02	0.39±0.01
MAKURDI	0.53±0.06	0.23±0.04	0.52±0.09	0.12±0.03
MAIDUGURI	1.3±0.15	0.51±0.11	1.2±0.01	0.18±0.04
KADUNA	1.03±0.14	0.46±0.01	0.61±0.08	0.30±0.01
JOS	0.9±0.1	0.31±0.12	1.1±0.20	0.26±0.05
OWERRI	0.53±0.14	0.32±0.01	1.5±0.072	0.26±0.03
SOKOTO	0.73±0.12	0.42±0.03	0.81±0.04	0.34±0.06

TABLE 19

AAS DETERMINATION OF AMOUNTS OF NICKEL ($\mu g L^{-1}$) WITH ESTIMATED STANDARD DEVIATIONS OF THE WATER SAMPLES ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from the road	
	3	20
IBADAN	390.6±1.62	127.3±3.2
LAGOS	940.0±1.73	460+2.6
AKURE	547.0±2.5	108.1±1.0
ABEOKUTA	957.1±2.1	453.0±2.9
KANO	377.0±2.5	190.4±1.0
MAKURDI	126.5±2.6	49.5±2.4
MAIDUGURI	88.5±2.9	38.0±3.7
KADUNA	433±2.6	84.6±2.4
ILORIN	904.6±3.7	450 +1.2
JOS	408 + 1.3	177.4±1.4
OWERRI	475.3+2.2	199.3±1.8
SOKOTO	264.7±1.9	132.1±2.0

TABLE 20

AAS DETERMINATION OF AMOUNTS OF CHROMIUM (μgg^{-1}) WITH ESTIMATED STANDARD DEVIATIONS OF THE SOIL SAMPLES ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from left side of the road			Distance in metre from right side of the road		
	3	9	15	3	9	15
IBADAN	14.0+0.58	11.1±1.1	10.8±2.8	8.5±0.5	3.6±0.6	2.0±0.3
LAGOS	15.0±1.0	8.0±1.2	8.1±0.36	13.6±0.5	8.2+0.47	1.7±0.5
AKURE	18.0±2.0	10.1±1.5	8.5±0.5	25.2±1.4	8.5±0.5	1.9±1.0
ABEOKUTA	33±1.0	13.0±1.1	7.6±1.5	16.0±2.0	1.7±0.3	1.6±0.24
ILORIN	9.0±1.0	8.1±1.3	1.1±0.1	12.1±1.8	7.9±0.95	1.5±0.9
KANO	19.0±0.7	14.0±1.5	1.6±0.6	19.2±2.1	7.8±0.90	2.1±0.5
MAKURDI	8.0±0.2	3.6±0.4	1.8±0.2	2.8±0.4	1.8±0.3	0.96±0.3
MAIDUGURI	1.0±0.4	0.93±0.2	0.8±0.1	1.2±0.36	1.3±0.28	0.87±0.17
KADUNA	19.5±1.1	13.3±1.1	7.0±1.1	16.4±1.2	7.3±1.3	4.6±0.6
JOS	18.0±1.9	14.4±2.1	9.4±1.4	15.3±2.0	10.1±0.8	8.0±1.0
OWERRI	18.9±0.9	14.0±1.0	7.0±1.3	14.2±2.0	10.5±1.0	8.0±0.7
SOKOTO	11.4±0.6	10.4±1.1	5.4±1.2	9.1±0.9	7.8±0.8	4.2±0.8

TABLE 21

AMOUNTS OF CHROMIUM ($\mu g g^{-1}$) IN LEAF SAMPLE WITH ESTIMATED STANDARD DEVIATIONS ALONG THE ROAD SIDES OF SOME STATE CAPITALS USING AAS TECHNIQUE

State Capital	Distance in metre from left side of the road		Distance in metre from right side of the road	
	2	20	2	20
IBADAN	15.5+0.15	4.8+0.13	10.1±0.3	4.1±0.23
LAGOS	10.4±0.37	7.0±0.36	12.0±0.35	4.0±0.26
AKURE	8.9±1.3	4.5±0.6	9.0±0.56	3.6±0.15
ABEOKUTA	5.1±0.65	2.0±0.3	6.7±0.31	5.2±0.26
ILORIN	7.2±1.1	4.2+0.15	4.7±0.62	2.5±0.14
KANO	4.6±0.51	3.8±0.56	7.5±0.41	2.0±0.32
MAKURDI	2.7±0.26	1.8±0.17	3.0±0.2	1.2±0.10
MAIDUGURI	4.5±0.51	2.3±0.1	2.8±0.14	1.5±0.11
KADUNA	13.0±0.5	8.7±0.61	9.6±0.32	3.1±0.12
JOS	6.7±0.48	4.9±0.59	6.8±0.54	2.7±0.22
OWERRI	3.0±0.43	1.9±0.18	3.9±0.21	1.6±0.11
SOKOTO	3.1±0.1	1.6±0.21	2.1±0.12	0.9±0.1

TABLE 22

AAS DETERMINATION OF AMOUNT OF COPPER ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATION OF THE SOIL SAMPLES ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from from left side of the road			Distance in metre from right side of the road		
	3	9	15	3	9	15
IBADAN	8.1±0.3	4.4±0.6	4.0±0.1	8.6±0.4	3.9±0.91	3.5±0.19
LAGOS	12.3±0.2	7.9±0.2	6.1±0.53	8.3±0.6	5.8±0.18	5.1±0.05
AKURE	8.1±0.29	4.0±1.0	4.0±0.8	12.9+0.67	8.4±0.4	7.7±0.19
ABEOKUTA	25.5±1.3	14.6±1.1	7.5±0.15	8.1±0.28	3.5±0.41	2.6±0.46
ILORIN	15.0±1.0	7.8±1.1	4.9±1.1	8.1±0.15	3.6±0.43	3.9±0.36
KANO	8.5±0.1	3.8±0.3	3.9±0.1	7.8±0.12	8.7±0.36	3.4±0.17
MAKURDI	6.5±0.51	8.3±0.31	7.8±0.54	7.8±0.43	3.0±0.07	2.7±0.33
MAIDUGURI	8.2±0.64	3.4±0.7	4.8±0.8	7.6±0.59	14.4±1.5	5.5±0.49
KADUNA	10.6±1.3	6.2±0.3	3.5±0.61	7.0±0.31	3.9±0.26	1.9+0.17
JOS	13.0±1.0	10.3±0.4	6.3±0.30	8.4±0.76	3.3±0.59	4.7±0.3
OWERRI	15.0±1.2	13.6±0.6	7.8±0.2	10.7±0.41	9.6±0.3	6.7±0.91
SOKOTO	9.4+1.0	8.0±0.5	5.4±0.1	7.9±0.20	6.4±0.2	5.2±0.4

TABLE 23

AMOUNTS OF COPPER ($\mu g g^{-1}$) IN LEAF SAMPLES WITH ESTIMATED STANDARD DEVIATIONS ALONG THE ROAD SIDES OF SOME STATE CAPITALS USING AAS TECHNIQUE

State Capital	Distance in metre from left side of the road		Distance in metre from right side of the road	
IBADAN	7.0±0.9	2.25±0.24	3.2±0.04	1.3±0.015
LAGOS	12.4±0.14	1.4±0.017	4.3±0.028	0.85±0.01
AKURE	13.9±0.29	7.4±0.06	8.3±0.54	5.9±0.21
ABEOKUTA	18.0±0.64	15.1±0.4	15.1±0.57	6.7±0.21
ILORIN	2.6±0.05	7.1±0.37	0.95±0.031	0.70±0.013
KANO	7.46±0.36	0.44±0.081	3.0±0.07	2.2±0.12
MAKURDI	0.88±0.34	1.3±0.04	0.26±0.01	0.31±0.09
MAIDUGURI	1.7±0.44	6.2±0.45	0.85±0.13	0.33±0.04
KADUNA	9.1±0.71	4.4±0.60	3.1±0.21	2.6±0.30
JOS	10.7±0.55	2.5±0.16	6.1±0.41	1.1±0.03
OWERRI	8.5±0.37	1.5±0.12	3.6±0.03	1.1±0.175
SOKOTO	3.2±0.25	0.9±0.08	1.2±0.02	0.27±0.18

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TABLE 24

AAS DETERMINATION OF AMOUNTS OF COPPER ($\mu g L^{-1}$)
WITH ESTIMATED STANDARD DEVIATION OF THE WATER
SAMPLES ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from the road	
	3	20
IBADAN	63.6±3.5	20.0±2.0
LAGOS	73.0±3.6	12.4±2.5
AKURE	62.0±2.0	13.2±1.1
ABEOKUTA	47.6±2.5	28.3±2.4
KANO	62.3±2.4	41.0±1.0
MAKURDI	61.6±1.5	49.0±1.2
MAIDUGURI	18.4±2.5	4.3±1.4
KADUNA	24.0±1.9	8.5±1.6
ILORIN	56.3±2.5	21.4±1.5
JOS	47.0±1.0	30.5±1.6
OWERRI	54.0±2.4	35.0±3.0
SOKOTO	48.4±1.3	23.1±3.0

TABLE 25

SPECTROPHOTOMETRIC DETERMINATION OF AMOUNTS OF LEAD (μgg^{-1}) WITH ESTIMATED STANDARD DEVIATION OF THE SOIL SAMPLES ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from left side of the road			Distance in metre from right side of the road		
	3	9	15	3	9	15
IBADAN	266.0±5.2	176.3±2.5	39.6±1.4	285±6.5	156.3±7.3	28.0±1.2
LAGOS	352±4.3	180.0±1.6	25.9±1.0	182.3±2.5	73.6±2.0	27.3±2.5
AKURE	142.0±3.0	90.3±2.0	37.0±1.0	179.6±1.5	99.0±2.6	48.0±1.0
ABEOKUTA	171.3±4.9	89.0±5.0	37.0±1.4	180.6±1.4	83.3±4.8	44.6±3.7
ILORIN	171.6±3.2	96.6±3.0	32.5±1.5	194.0±2.8	80.6±3.1	30.6±2.7
KANO	250±4.0	174.3±4.9	62.0±2.0	183.5±2.0	161.6±2.7	67.0±2.0
MAKURDI	92.0±4.3	70.6±3.0	18.6±2.1	65.3±3.6	54.0±2.5	13.3±1.6
MAIDUGURI	59.6±2.1	29.6±1.5	23.0±1.0	49.0±4.0	24.0±2.3	16.0±3.1
KADUNA	341.0±3.6	120.5±4.5	37.6±1.4	26.4±4.6	117.6±2.5	42.5±1.5
JOS	183.0±2.0	76.1±1.0	43.0±1.6	145.0±2.0	56.0±2.1	34.5±2.1
OWERRI	131.6±3.1	91.0±3.0	30.4±1.1	191.0±2.1	80.0±1.5	23.3±2.6
SOKOTO	147.0±1.9	121.0±2.5	33.6±3.2	91.3±3.1	66.0±2.0	26.0±1.9

TABLE 26

AMOUNTS OF NICKEL ($\mu g g^{-1}$) IN SOIL SAMPLES WITH ESTIMATED STANDARD DEVIATIONS ALONG THE ROAD SIDES OF ~~SOME STATE~~ EKET – IBENO + MOBIL ... CAPITALS USING SPECTROPHOTOMETRIC TECHNIQUE

State Capital	Distance in metre from left side of the road			Distance in metre from right side of the road		
	3	9 m	15 m	3	9 m	15 m
IBADAN	66.6±3.0	54.0±11.0	60.3±3.9	62.0±2.6	56.3±1.5	61.3±2.6
LAGOS	86.0±2.0	58.1±4.4	35.3±3.8	36.6±3.0	26.0±2.0	18.0±2.0
AKURE	75.3±3.2	46.1±1.7	28.4±2.0	72.3±1.5	40.1±2.0	33.0±6.3
ABEOKUTA	64.0±2.0	79.2±8.0	38.3±2.0	134.3±5.4	82.0±3.6	82.1±3.4
ILORIN	85.6±2.1	42.6±2.2	62.3±1.4	41.6±2.2	36.3±1.3	48.3±1.4
KANO	52.6±3.6	55.6±5.2	63.0±5.5	90.6±3.0	38.2±2.0	69.6±1.6
MAKURDI	43.3±4.1	25.6±1.5	15.4±2.8	58.3±2.6	16.0±2.1	23.3±3.0
MAIDUGURI	30.3±1.5	23.0±3.0	13.3±0.57	26.0±2.5	16.3±2.0	10.6±0.87
KADUNA	83.0±1.6	70.3±5.1	70.0±2.0	39.6±1.5	88.0±2.6	50.0±1.1
JOS	79.8±1.5	42.6±2.6	38.1±2.0	33.6±3.5	45.6±2.0	17.6±1.9
OWERRI	80.3±4.1	75.6±3.4	42± 2.4	42.4±2.6	31.3±2.8	49.6±2.1
SOKOTO	48.7±1.3	29.4±3.7	41.3±1.8	28.4±1.2	36.4±2.3	19.4±3.2

TABLE 27

SPECTROPHOTOMETRIC DETERMINATION OF AMOUNTS OF CHROMIUM ($\mu g g^{-1}$) WITH ESTIMATED STANDARD DEVIATION OF THE SOIL SAMPLES ALONG THE ROAD SIDES OF SOME STATE CAPITALS

State Capital	Distance in metre from left side of the road			Distance in metre from right side of the road		
	3	9	15	3	9	15
IBADAN	15.6±0.7	14.4±0.4	3.6±0.51	6.2±0.1	7.5±0.8	3.4±1.3
LAGOS	17.9±1.4	5.6±0.9	3.4±0.3	4.0±0.6	9.5±1.1	0.7±0.3
AKURE	11.9±0.1	2.7±0.5	2.8±0.9	3.5±0.12	1.6±0.8	1.0±0.6
ABEOKUTA	17.9±2.3	2.6±0.9	12.4±0.3	14.5±0.85	3.9±0.7	2.4±0.2
ILORIN	7.0±1.6	6.1±0.6	3.1±0.2	6.0±0.67	12.5±0.4	2.2±0.4
KANO	14.0±1.3	10.8±0.8	0.9±0.2	7.0±0.28	22.0±1.8	2.0±0.18
MAKURDI	3.0±0.1	0.76±0.1	1.2±0.3	0.96±0.3	3.3±0.6	1.5±0.7
MAIDUGURI	9.5±0.3	1.2±0.04	1.4±0.4	1.1±0.31	1.6±0.3	1.7±0.2
KADUNA	16.4±0.28	12.4±0.8	3.9±0.38	5.8±0.15	12.4±0.68	3.9±0.14
JOS	2.5±0.1	2.2±0.31	3.4±0.5	2.3±0.17	1.8±0.17	3.1±0.15
OWERRI	14.4±0.41	9.7±0.9	6.3+0.6	8.8±0.46	11.7±0.8	4.0±0.1
SOKOTO	9.7±1.3	11.1±2.1	2.1±1.2	6.8±1.0	10.1±1.2	3.8±0.9

T.BLE 28

AMOUNTS OF HEAVY METALS ($\mu g g^{-1}$) IN SOKOTO MOTOR PARK WITH ESTIMATED STANDARD DEVIATIONS

Distance from centre in metre	SOKOTO MOTOR PARK SOIL			
	Pb	Ni	Cr	Cu
0	713.3±1.7	28±1.0	34±4.0	19.0±0.4
1	600±8.0	23.0±1.3	26±3.8	13.5±0.6
6	164.3±6.1	25.0±0.9	30.4±3.0	17.25±1.5
12	142.0±10.1	23±1.0	26.6±1.1	14.4±0.1
20	1394 ±9.6	21±1.1	20.1±1.3	19.4±0.12

TABLE 29: AMOUNTS OF HEAVY METALS ($\mu g g^{-1}$) IN KANO MOTOR PARK WITH ESTIMATED STANDARD DEVIATIONS

Distance from centre in metre	KANO MOTOR PARK SOIL			
	Pb	Ni	Cr	Cu
0	266+5.1	13.0±0.4	14.6±1.1	18.0±0.3
1	289±3.1	12.0±0.32	13.3±1.5	16.24±0.12
6	274±42	13.1±0.51	16.6±1.1	14.7±0.21
12	327±5.5	16.0±0.14	15.1±0.9	9.0±0.14
20	242±4.2	17.9±0.5	13.3±1.1	8.25±0.18

CHAPTER 4

DISCUSSION AND CONCLUSION

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CHAPTER 4

4-1 HEAVY METALS DISTRIBUTION PROFILE ALONG SAMARU-ZARIA AND KANO-ZARIA ROADS

The highest amount of lead along Samaru-Zaria road was found to be 57.8 μgg^{-1} and 30.0 μgg^{-1} on the left and right side of the road respectively, at about 1 metre from the road as seen in table 5 and figure I. These amounts decreased to about 7.4 μgg^{-1} and 5.4 μgg^{-1} on the left and right sides of the road respectively, and remained constant at about 10 - 15 metres from the road. This would suggest that the background lead occured at about 15 metres from the road as seen in figure I.

The amount of lead in leaf samples followed the same pattern as for soil samples as seen in figure 4 except that the amount of lead was found to be smaller. The pattern of lead distribution, both on leaf and in soil samples for Kano - Zaria road, was found to be similar to that for Samaru - Zaria road, where the background lead of about 8.4 μgg^{-1} occured at about 14 metres from the road.

The soil samples of Samaru - Zaria road at about 1 metre from the road contained the highest amount of nickel amounting to 15.8 μgg^{-1} on the left

side and 13.3 μgg^{-1} on the right side. This decreased gradually to a background constant value of 10.2 μgg^{-1} on the left side and 10.4 μgg^{-1} on the right side of the road at about 19 metres away from the road.

The pattern of distribution of nickel in leaf samples followed the same trend except that the value became negligible at about 5 metres from the road. The same trend was observed in Kano - Zaria road soil samples.

Samaru - Zaria road has the highest amounts of chromium at about 1 metre from the road both left and right side, and these values were found to be 15.0 μgg^{-1} and 13.7 μgg^{-1} on the left and right sides respectively. The amounts decreased to a negligible value at about 20 metres from the road as seen in figures 3. The same distribution pattern was observed for chromium in soil and leaf samples along Kano - Zaria road as seen in figure 13. The amount of copper in soil samples along Samaru - Zaria road at about 1 metre from road was found to be 6.4 μgg^{-1} and 3.4 μgg^{-1}, left and right respectively. These values decreased to 3.0 μgg^{-1} and 1.9 μgg^{-1} at about 20 metres from the road.

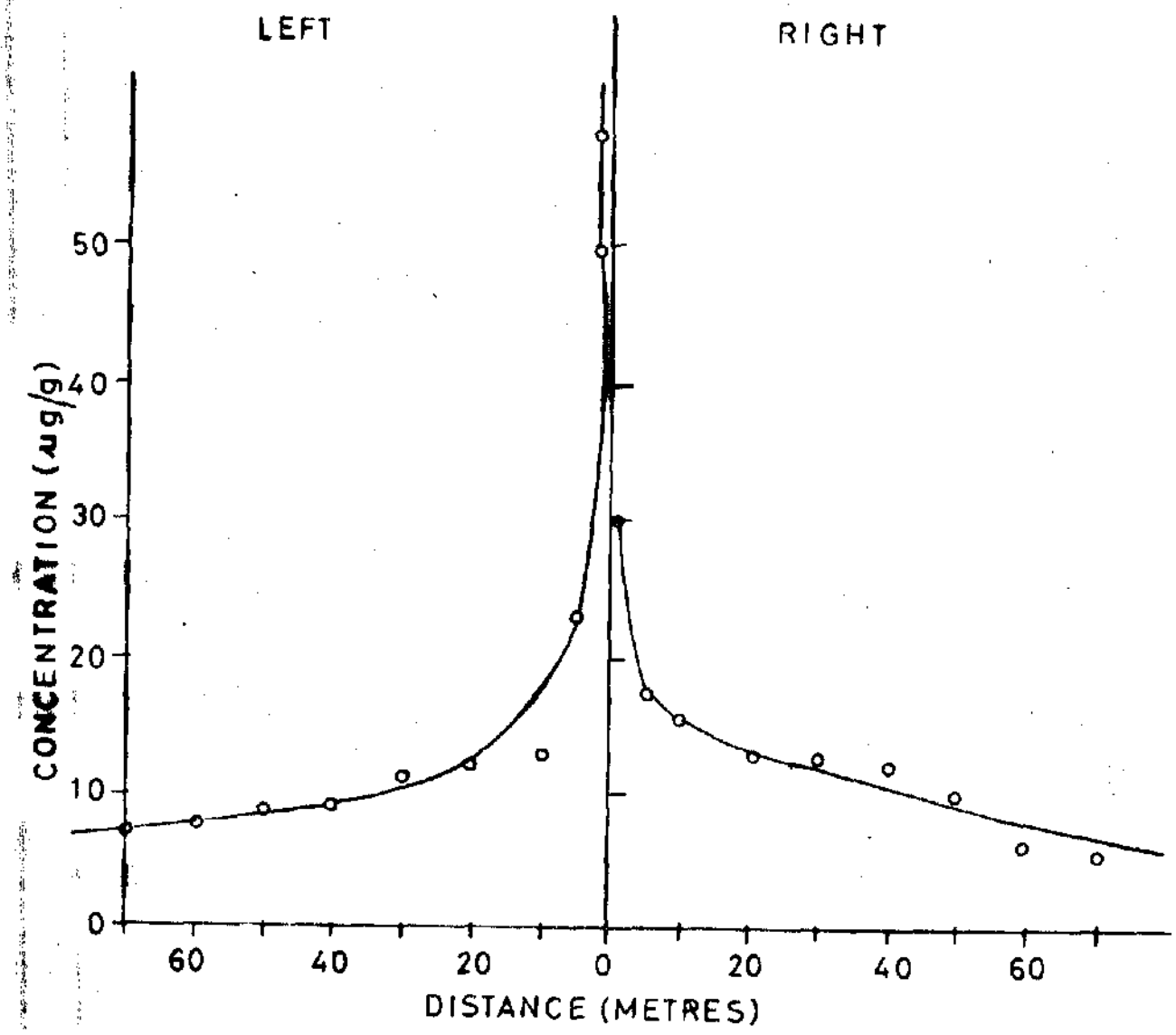
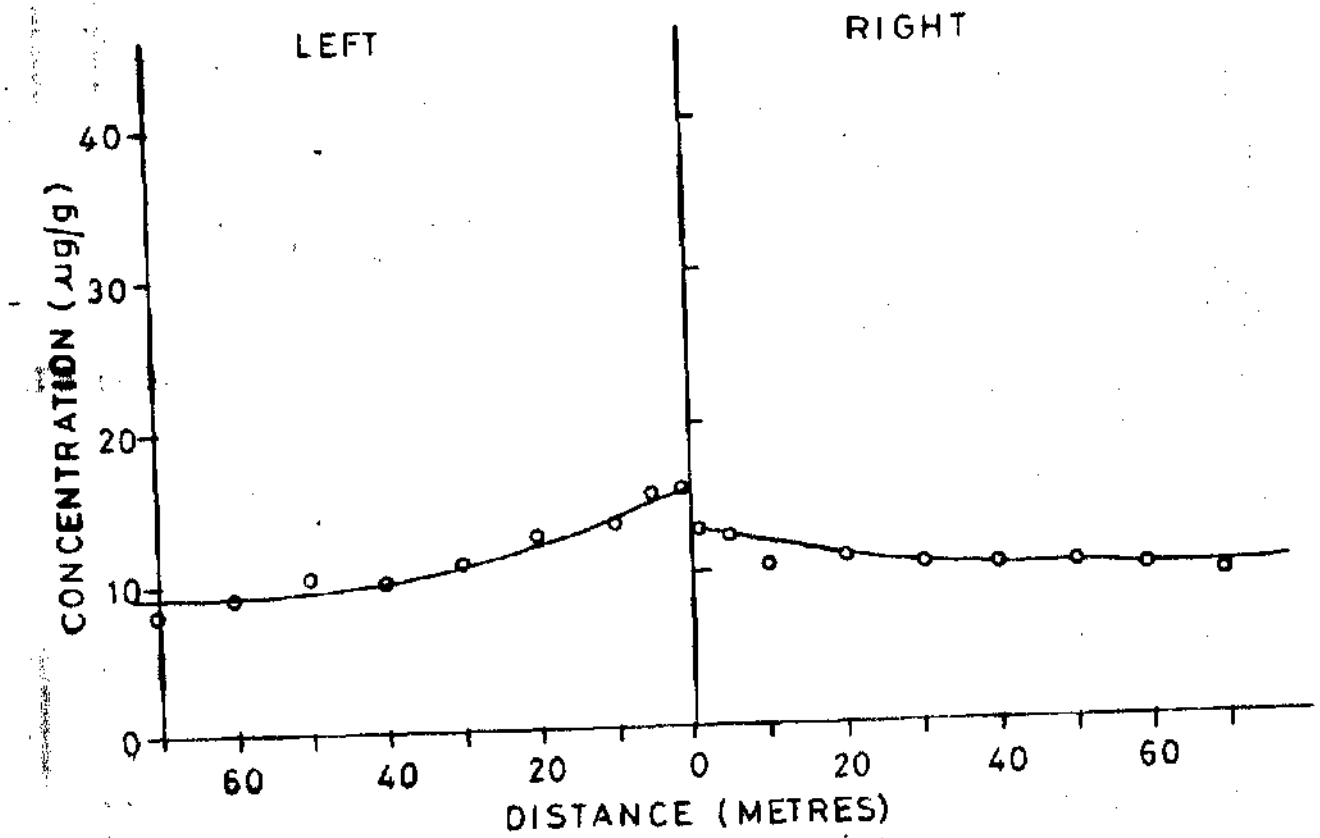


FIG. 1 : VARIATION OF LEAD CONCENTRATION IN SOIL SAMPLES WITH DISTANCE FROM SAMARU-ZARIA ROAD



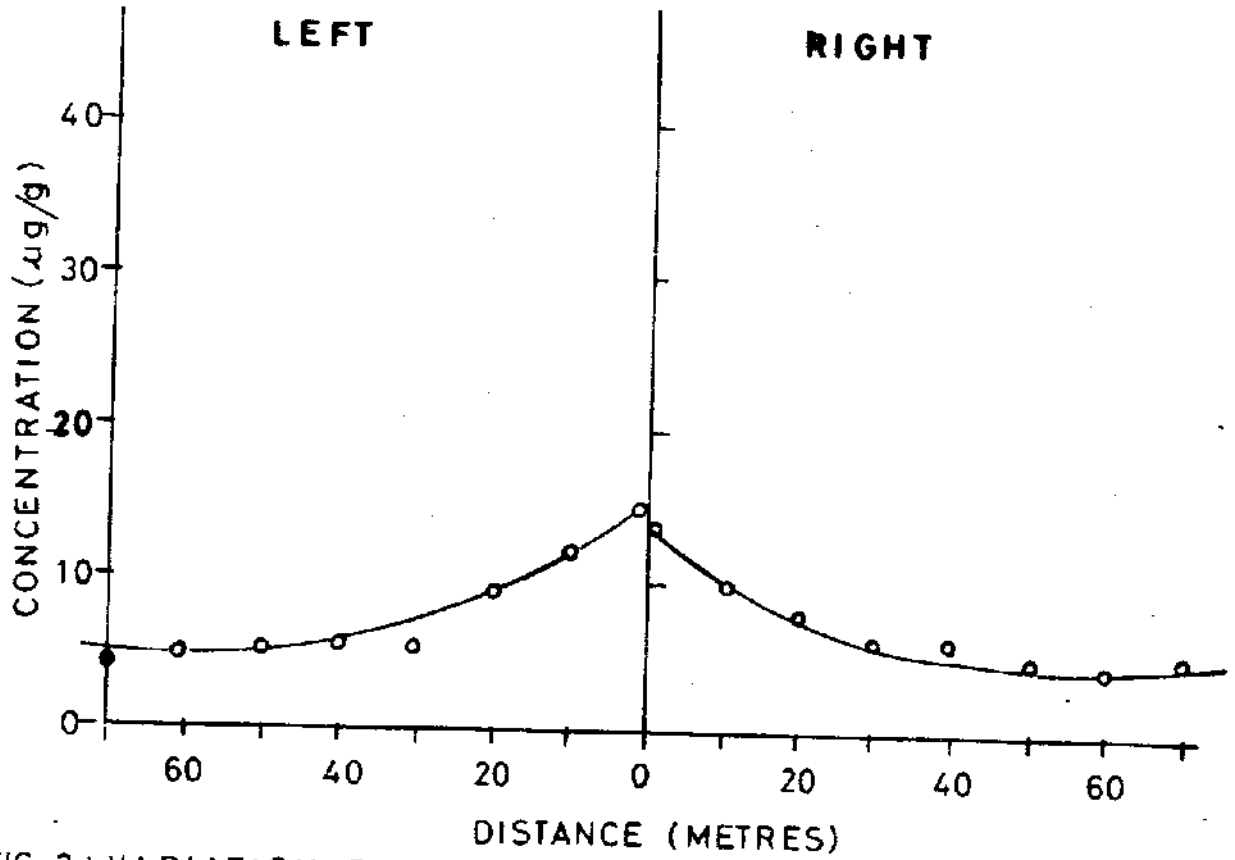


FIG. 3 : VARIATION OF CHROMIUM CONCENTRATION IN SOIL SAMPLES WITH DISTANCE FROM SAMARU-ZARIA ROAD

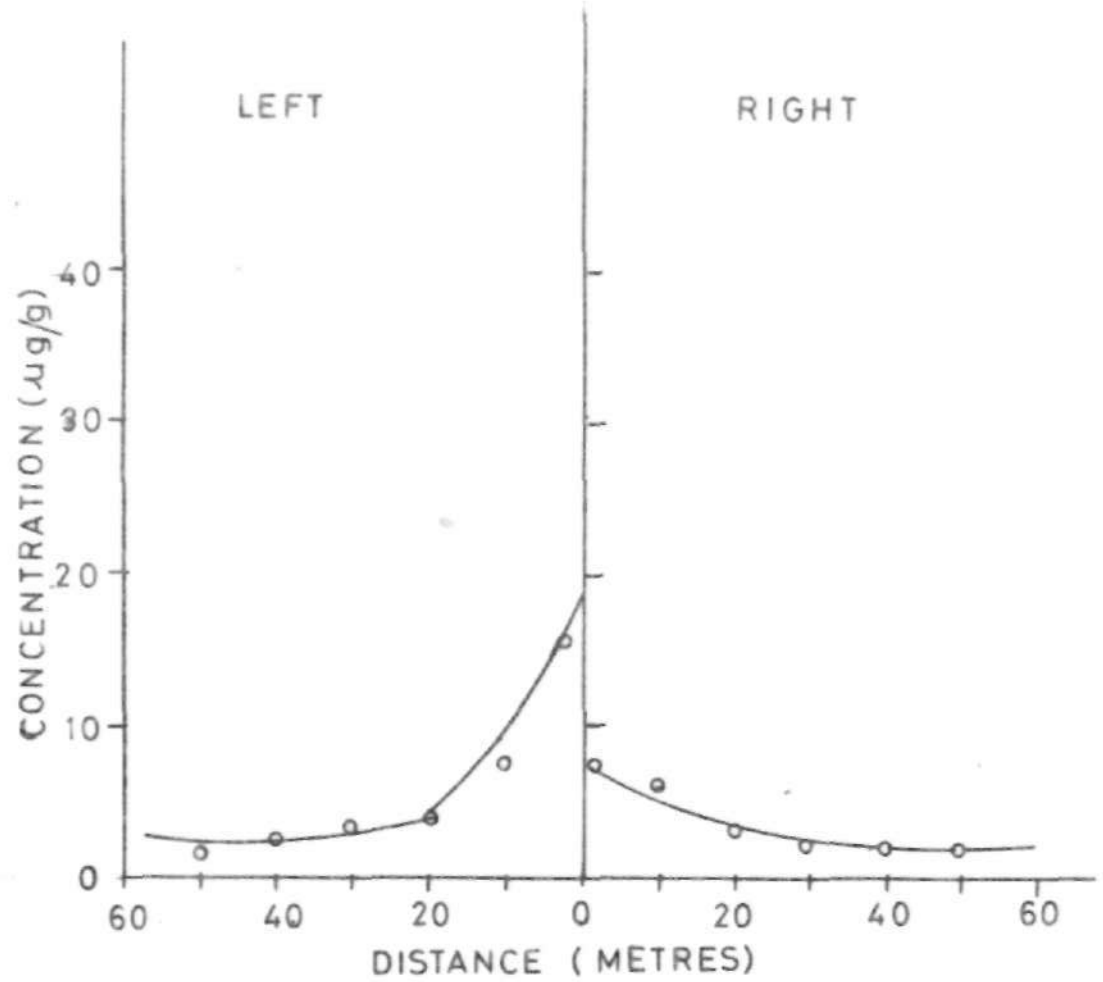


FIG.4: VARIATION OF LEAD CONCENTRATION IN LEAF SAMPLES WITH DISTANCE FROM SAMARU–ZARIA ROAD

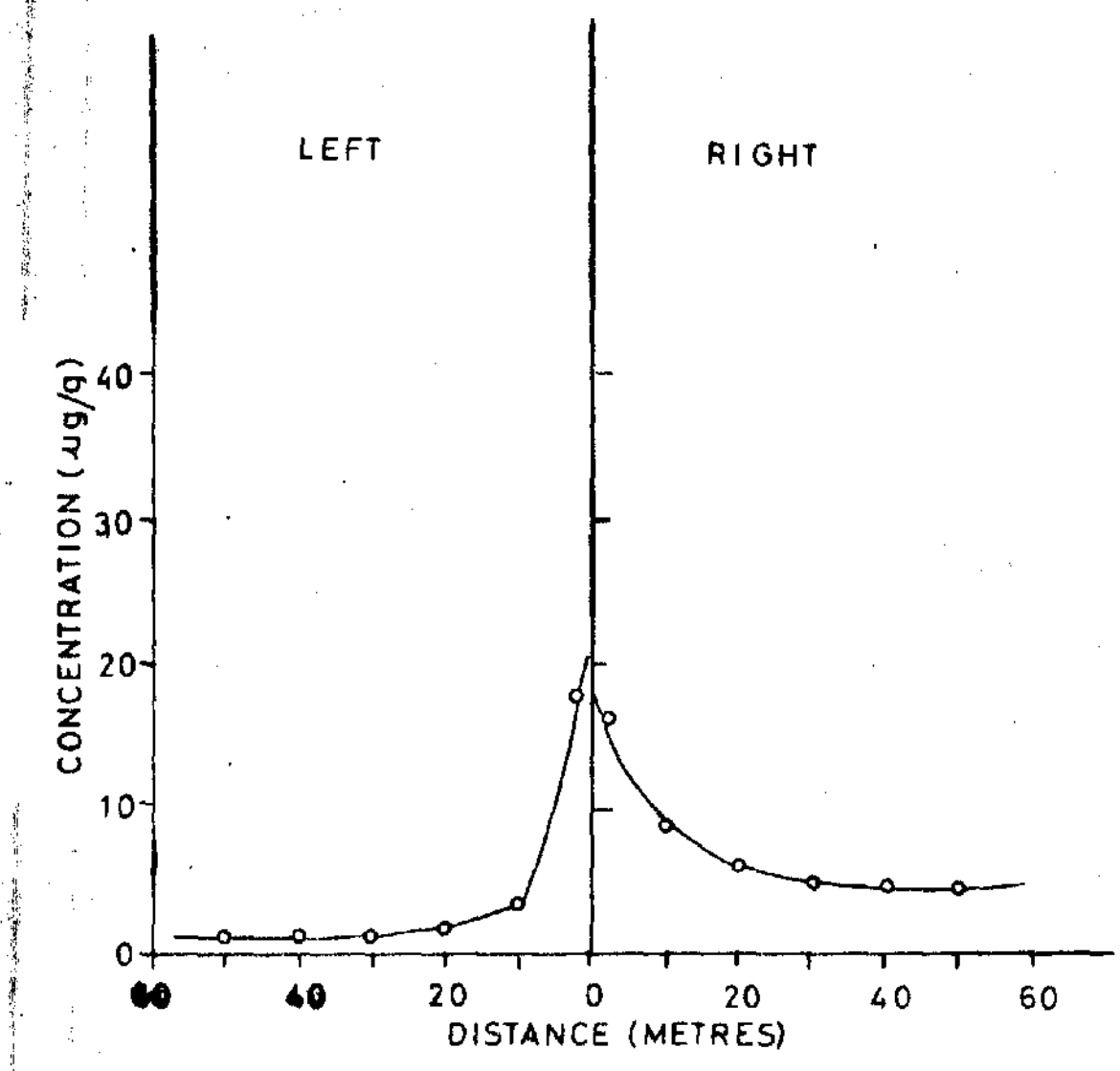


FIG.5 : VARIATION OF NICKEL CONCENTRATION IN LEAF SAMPLES WITH DISTANCE FROM SAMARU-ZARIA

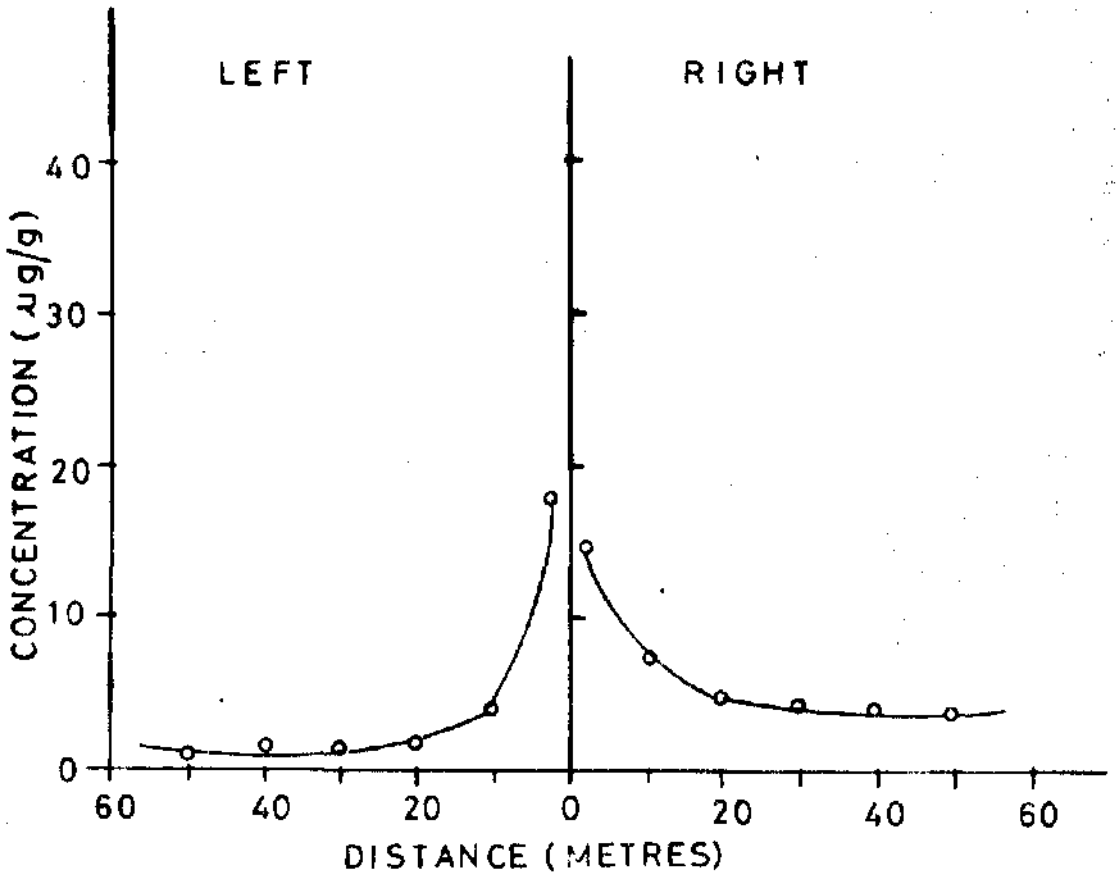


FIG. 6: VARIATION OF CHROMIUM CONCENTRATION IN LEAF SAMPLES WITH DISTANCE FROM SAMARU – ZARIA ROAD

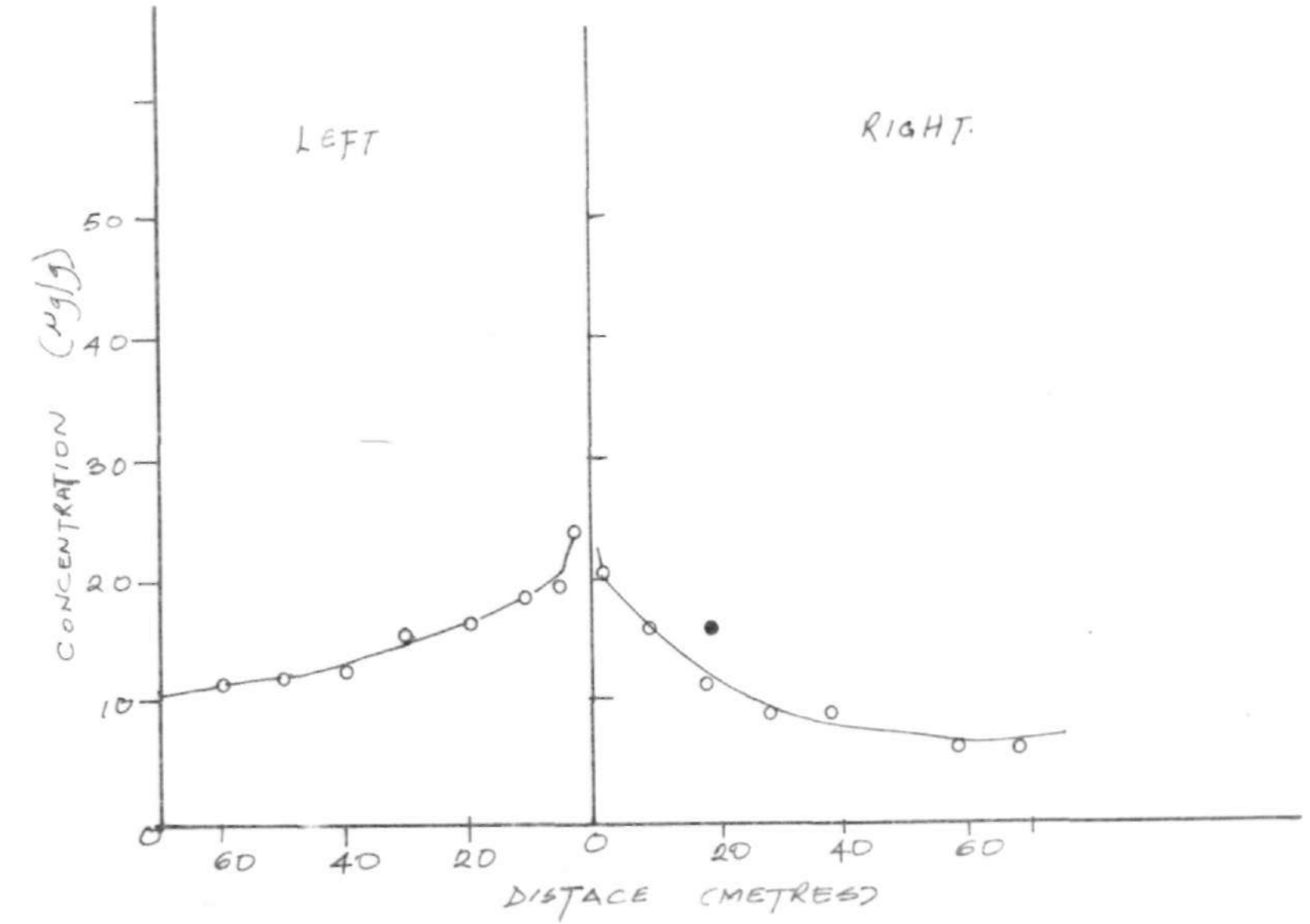


FIG 7 VARIATION OF LEAD CONCENTRATION IN SOIL SAMPLES WITH DISTANCE FROM ZARIA - KANO — ROAD.

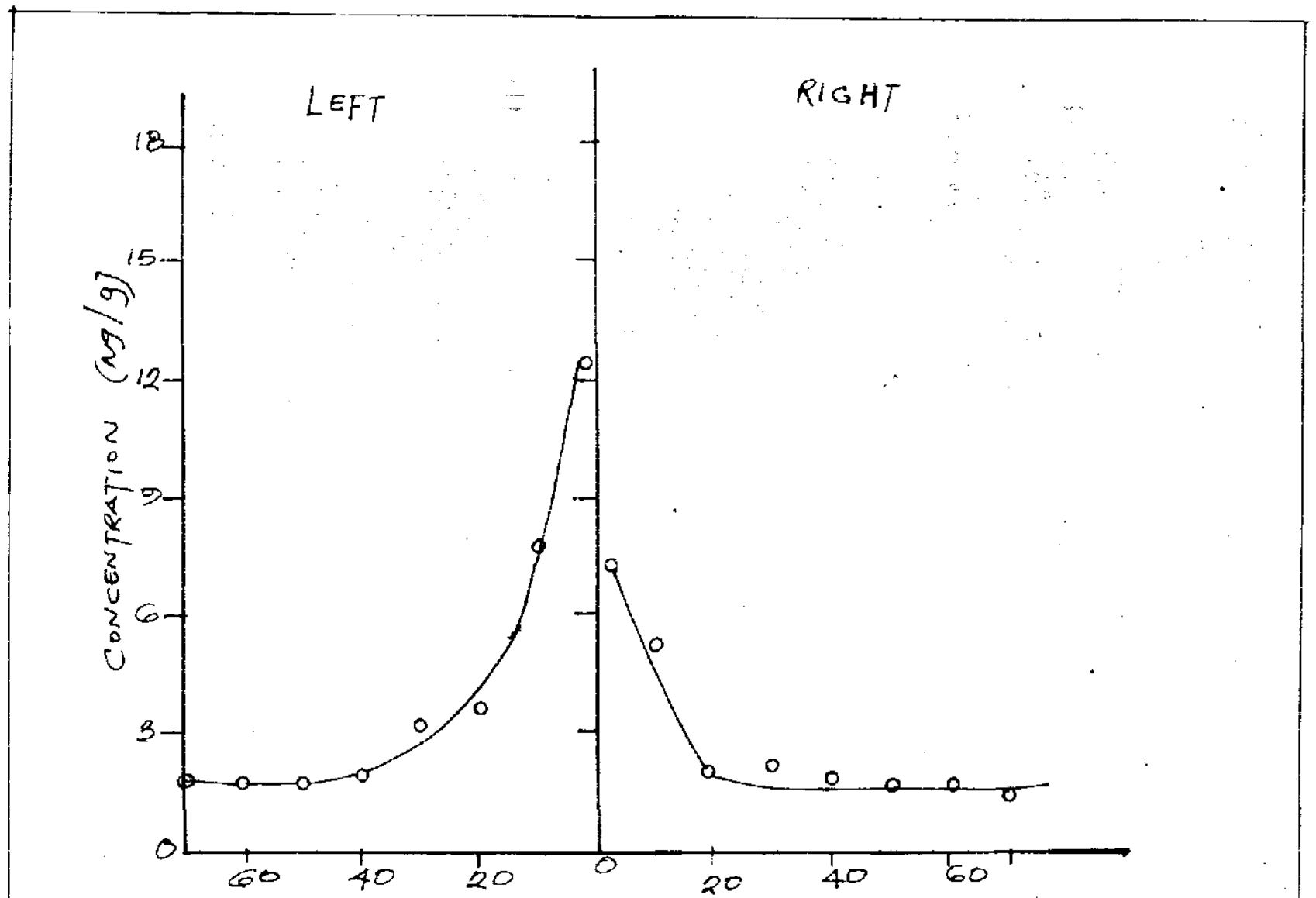
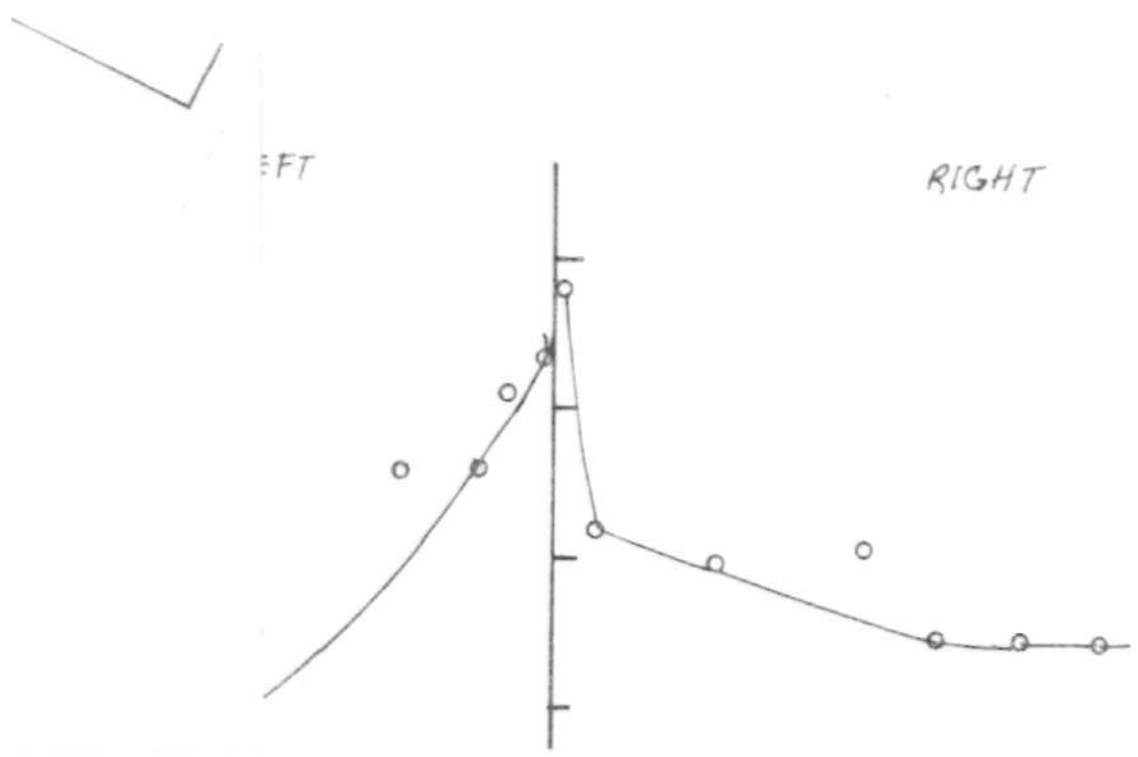
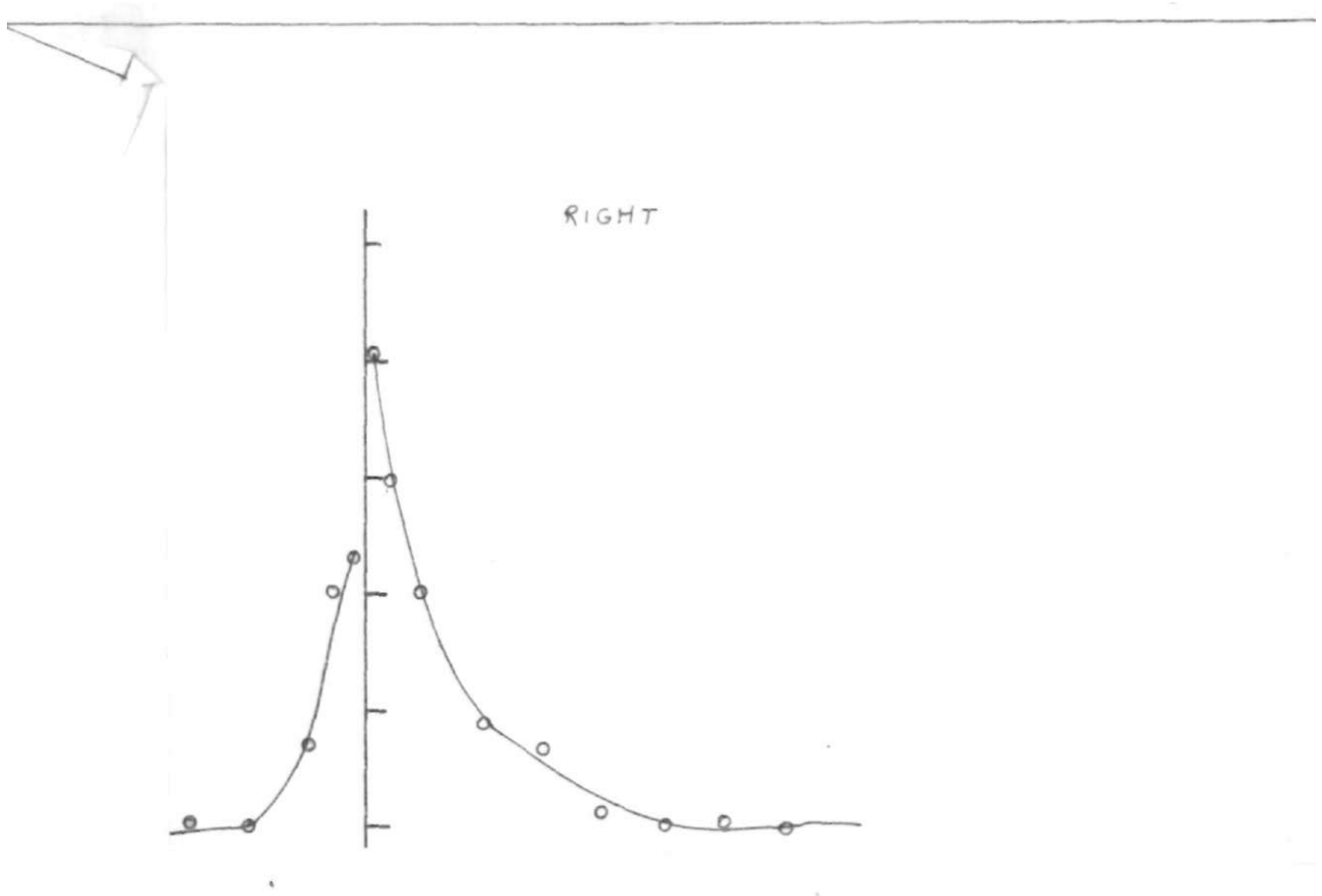


FIG 8. VARIATION OF LEAD CONCRATION IN LEAF SAMPLES WITH DISTANCE FROM ZARIA – KANO ROAD.


FT
RIGHT


RIGHT

From the result obtained for the heavy metals, it may be concluded that the heavy metals are mainly found at about 1 metre to 15 metres from the road and they become negligible at about 20 metres from the road.

TABLE 30 AMOUNTS OF HEAVY METALS ($\mu g g^{-1}$) IN SOIL SAMPLES WITH ESTIMATED DAILY TRAFFIC VOLUME OF SOME NIGERIAN STATE CAPITALS

State Capital	3 METRE FROM ROAD					9 METRE FROM ROAD				15 METRE FROM ROAD			
	Daily Traffic Volume	Pb	Ni	Cr	Cu	Pb	Ni	Cr	Cu	Pb	Ni	Cr	Cu
IBADAN	26088	252.0	67.0	14.0	8.7	173.0	60.3	11.1	4.4	37.3	66.3	10.8	4.0
LAGOS	33303	377.0	71.0	15.0	12.3	279.0	62.0	8.0	7.9	31.0	51.3	8.1	6.1
AKURE	20767	145.3	87.0	18.0	8.1	86.1	39.8	10.1	4.0	21.5	37.0	8.5	4.0
ABEOKUTA	19831	157.0	81.0	33.0	25.5	85.6	68.0	13.0	14.6	31.5	50.3	7.6	7.5
ILORIN	21267	147.6	73.3	9.0	15.0	89.2	52.0	8.1	7.8	41.0	63.6	1.1	4.9
KANO	34368	269.3	82.3	19.0	8.5	154.0	64.5	14.0	3.8	81.1	63.0	1.6	3.9
MAKURDI	16143	83.6	49.5	8.0	6.5	42.0	28.5	3.6	8.3	17.3	19.0	1.8	7.8
MAIDUGURI	16123	65.8	34.0	1.0	8.2	39.3	23.0	0.93	3.4	26.0	11.5	0.8	4.8
KADUNA	24468	273.0	91.3	19.5	10.6	157.3	93.0	13.3	6.2	35.0	66.5	7.0	3.5
JOS	24240	221.6	92.0	18.0	13.0	94.8	79.1	14.4	10.3	37.3	75.0	9.4	6.3
OWERRI	22776	140.0	86.0	18.9	15.0	92.0	73.3	14.0	13.6	31.6	51.0	7.0	7.8
SOKOTO	19032	132.1	51.4	14.4	9.4	86.1	34.2	10.4	8.0	24.2	42.0	5.4	5.4

TABLE 31

AMOUNTS OF HEAVY METALS (μgg^{-1}) IN LEAF SAMPLES WITH ESTIMATED DAILY TRAFFIC VOLUME OF SOME NIGERIAN STATE CAPITALS

State Capital	Estimated Daily Traffic Volume	2 METRE FROM ROAD				20 METRE FROM ROAD			
		Pb	Ni	Cr	Cu	Pb	Ni	Cr	Cu
IBADAN	26088	23.0	2.2	15.5	7.0	15.8	0.7	4.8	2.25
LAGOS	33033	47.2	1.3	10.4	12.4	25.5	0.52	7.0	1.4
AKURE	20767	44.6	0.60	8.9	13.9	17.3	0.60	4.5	7.4
ABEOKUTA	19831	24.6	0.94	5.1	18.6	14.4	0.37	2.0	15.1
ILORIN	21267	24.5	1.0	7.2	2.6	11.3	0.45	4.2	7.1
KANO	34368	48.0	1.5	4.6	7.46	29.5	0.53	3.8	0.44
MAKURDI	16143	27.0	0.53	2.7	0.88	18.4	0.23	1.8	1.3
MAIDUGURI	16123	20.9	1.3	4.5	1.7	3.9	0.51	2.3	6.2
KADUNA	24463	44.3	1.03	13.0	9.1	28.3	0.46	3.7	4.4
JOS	24240	26.3	0.9	6.7	10.1	11.1	0.31	4.9	2.5
OWERRI	22726	15.5	0.53	3.0	8.3	10.2	0.32	1.9	1.5
SOKOTO	19032	19.4	0.73	3.1	3.2	9.2	0.42	1.6	0.9

TABLE 32:

AMOUNTS OF HEAVY METALS ($\mu g L^{-1}$) IN WATER SAMPLES WITH ESTIMATED DAILY TRAFFIC VOLUME OF SOME STATE CAPITALS OF NIGERIA

State Capitals	Estimated Daily Traffic Volume	Pb	Ni	Cr	Cu
IBADAN	26088	3.0	263.0	0.00	43.6
LAGOS	33033	8.6	360.0	0.00	60.6
AKURE	20267	7.5	438.9	0.00	48.8
ABEOKUTA	19831	7.7	504.1	0.00	19.3
ILORIN	21267	4.5	454.0	0.00	34.9
KANO	34368	3.2	186.6	0.00	21.3
MAKURDI	16143	2.6	27.0	0.00	12.6
MAIDUGURI	16123	4.0	50.5	0.00	14.1
KADUNA	14463	6.1	348.4	0.00	15.5
JOS	24240	6.2	230.6	0.00	16.7
OWERRI	22726	7.4	276.0	0.00	19.4
SOKOTO	19632	3.8	132.6	0.00	25.3

Hence the result of these independent studies serve as a guide in determining the distance where the sample collections should be stopped.

4-2.1 AMOUNTS OF HEAVY METALS IN SOIL, VEGETATION AND WATER AND ESTIMATED DAILY TRAFFIC VOLUME

EDTV

A summary of the amounts of heavy metals in the soil, vegetation and water samples at 3, 9 and 15 metres from the road, with the estimated daily traffic volume (EDTV) is shown in tables 30, 31 and 32.

4-2.2 LEAD CONCENTRATION AND ESTIMATED DAILY TRAFFIC VOLUME

From the analysis, the highest amount of lead was found to be 377.6 μgg^{-1} for Lagos where the estimated daily traffic volume is 33303. Kaduna has the value of 273 μgg^{-1} with a EDTV of 24,463. Ibadan and Kano, with comparable EDTV values have 252 μgg^{-1} and 269 μgg^{-1} respectively. Makurdi and Maiduguri have the lead values 83.6 μgg^{-1} and 65.5 μgg^{-1} respectively, which follows their EDTV values. Other state capitals with EDTV of 14000 - 15000 have lead concentration between 120 and 160 μgg^{-1}. This suggests that much of the lead in the environment comes from the exhaust of the motor vehicles. Table 33 gives

some correlation coefficients of the various metal concentrations in soil samples with estimated daily traffic (EDTV) and the number of vehicles staying up to 10 - 15 minutes during hold-ups. This could explain why Kaduna with a lower EDTV than Kano has higher lead concentration in the soil samples

TABLE 33

Correlation of metal concentrations in soil samples with EDTV and number of vehicles at hold - up (N)

Metal	Correlation Coefficient		Significance	
	EDTV	N	EDTV	N
Pb	0.96	0.67	P 0.001	P 0.02
Ni	0.65	0.17	P 0.05	Not Significant
Cr	0.49	0.09	Not Significant	Not Significant
Cu	-0.16	-0.06	Not Significant	Not Significant

Kaduna with a higher number of vehicles staying at a particular point for 10 minutes has a higher Pb concentration than Kano with lower value of vehicles staying at a particular point despite the higher value

of EDTV for Kano.

Therefore it can safely be said that the lead concentrations in the soil samples show a very good correlation with the number of vehicles at hold-ups. These coefficients also suggest that the bulk of the lead along the highways are of vehicular origin.

4-2.3 Amounts of Nickel Chromium and Copper with EDTV

The amounts of these heavy metals as seen in the tables 19 - 25 do not suggest that they are mainly from the exhaust of the motor vehicles. Other sources tend to be more important than motor exhaust.

Lagos with EDTV of 33303 has nickel amounting to 71.3 μgg^{-1}, copper 12.3 μg^{-1} and chromium 15.0 μgg^{-1} at 3 metres from the road. Abeokuta with EDTV of 19831 has nickel amounting to 61.5 μgg^{-1}, copper 25.3 μgg^{-1} and chromium 33.0 μgg^{-1}.

The correlation coefficients as shown in table 33 suggests that Nickel shows a significant correlation with EDTV, while chromium is marginal and copper is apparently uncorrelated. Also the number of vehicles at hold-ups does not appear to have any significant influence on the latter metals. These observations are in agreement with the earlier suggestion

that contributions from other sources are probably important for the latter metals. Correlations of the concentrations in leaf and water samples were not significant.

4-3.1 VARIATION OF HEAVY METALS WITH DISTANCE

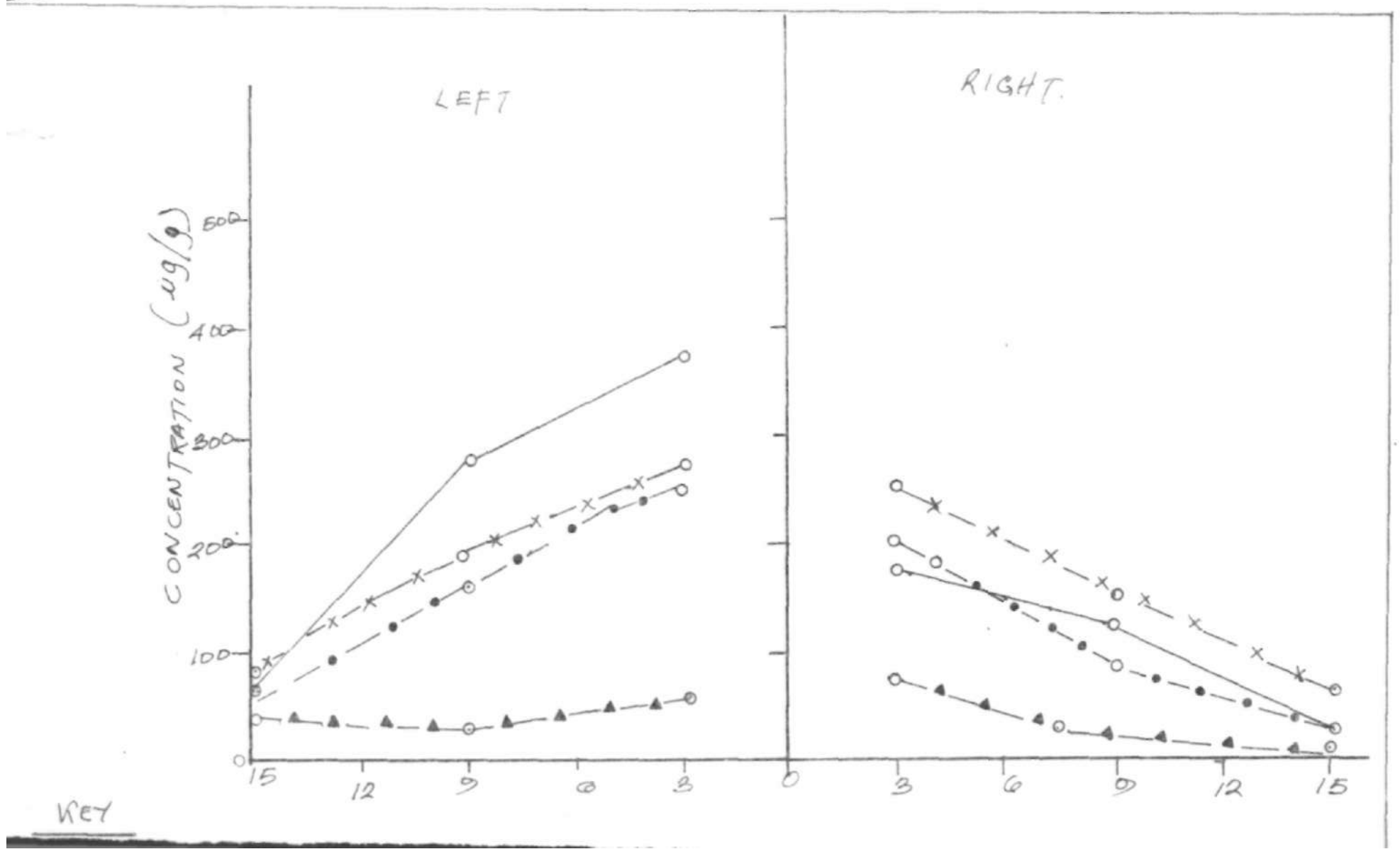
Lead:

The amount of lead in soil and vegetation samples was found to decrease rapidly with distance from the road in all the state capitals. As can be seen from tables 13, 14, 16 and figure 9, the lead concentrations for all the states covered were found to be highest at 3 metres from the road and reduced to background concentrations at about 15 metres away from the road. These results are in agreement with the observation that lead from combustion emissions, in general, is not actively transported to long distances, and levels are highest near the roads (Rulling & Tyler 1964)[22].

Local variation in natural concentrations of lead could also lead to slight irregularities. Generally the amount of lead on the right side of the highway is smaller than the amount on the left side. This holds for all the states except in Borno and Imo

state capitals. The differences in concentrations on the different sides of the road is probably due to the wind direction along the various road (Binis 1973)[23].

This would also tend to support the earlier observation that the lead comes mainly from motor exhausts. The lead concentrations in the vegetation samples (table 14) are generally much lower than the concentrations in the soil samples. The amount of lead estimated from the leaf samples may be derived from two sources namely, direct deposition from the atmosphere and absorption through the roots of the same plants. Concentrations from the former sources, may be depleted by fairly strong winds and by rain water. Also the leaf surface areas may affect the amount of lead deposited. Further more plants absorb metals only in its soluble form and there may be a limited traslocation to the shoots (Zimdahl and Arvk, 1973)[24]. These factors may possibly account for the low lead concentrations obtained from the leaf samples, but its amounts show a decrease with distance from the road as seen in figure 4.


LEFT
RIGHT
CONCENTRATION (µg/g)
EOP
400
300
200
100
0
15
12
9
6
3
0
3
6
9
12
15
KEY

4-3.2 Variation of Nickel Concentrations with Distance from Road

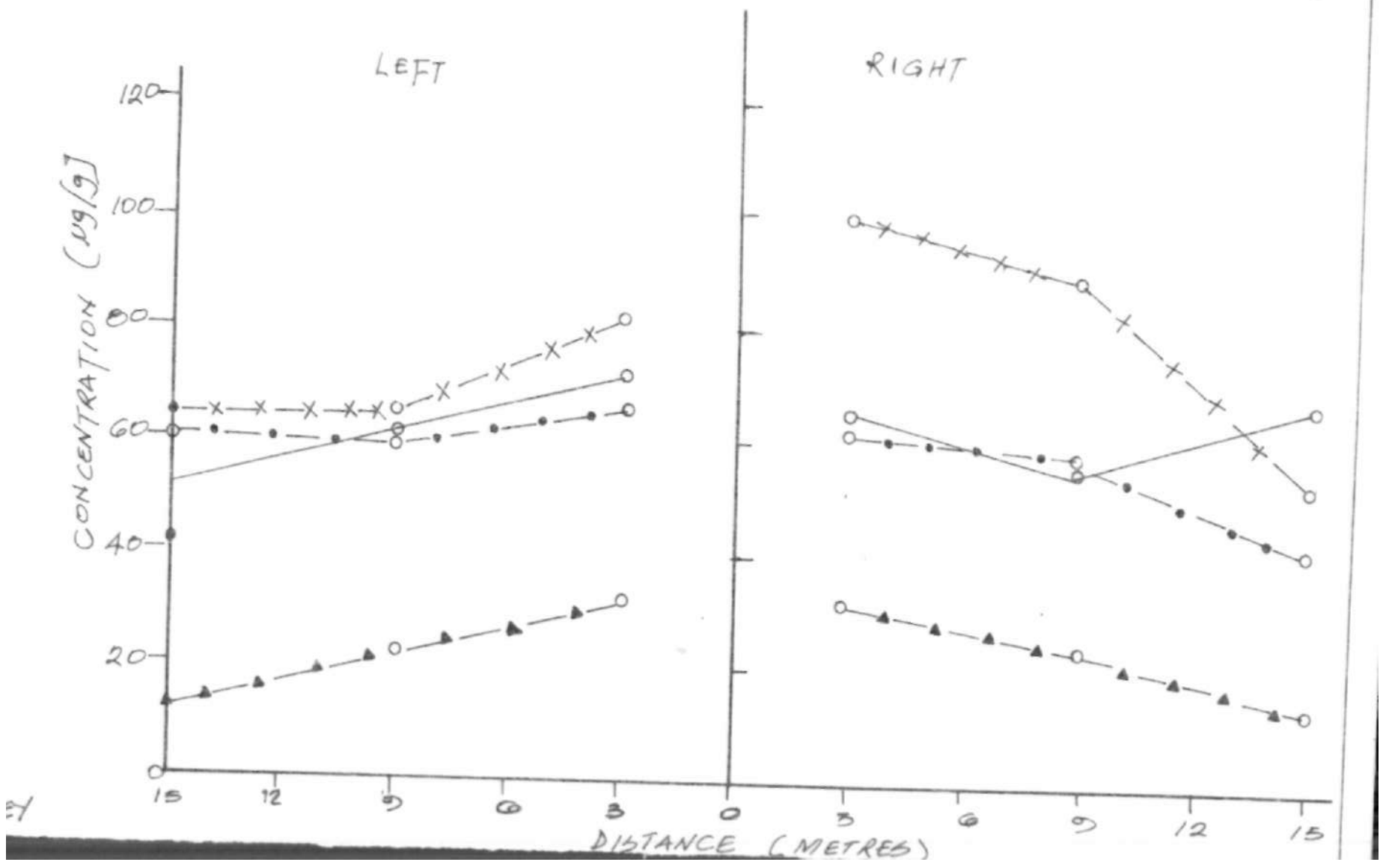
The variation of nickel with distance was found not to be as consistent as that of lead. For example, Ibadan has nickel concentration of 67 μgg^{-1} at 3 metres from the road. This decreased to 66.3 μgg^{-1} at 15 metres from the road. This may suggest that other sources of nickel to the environment are more important than motor exhaust. The independent studies of soil and vegetation samples show the same trend for nickel concentration as in those of the state capitals.

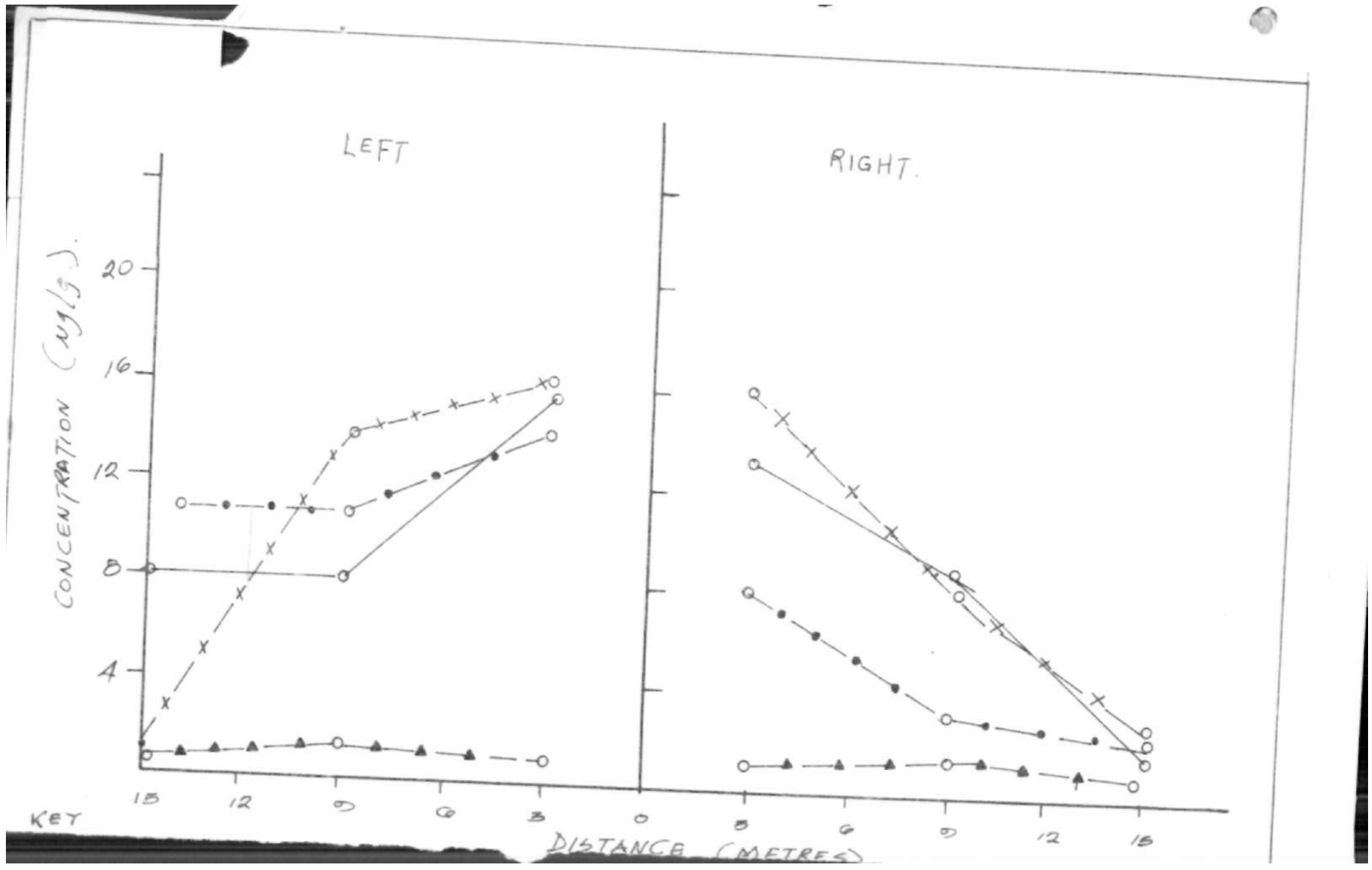
4-3.3 Variation of Amounts of Copper and Chromium with Distance from Road

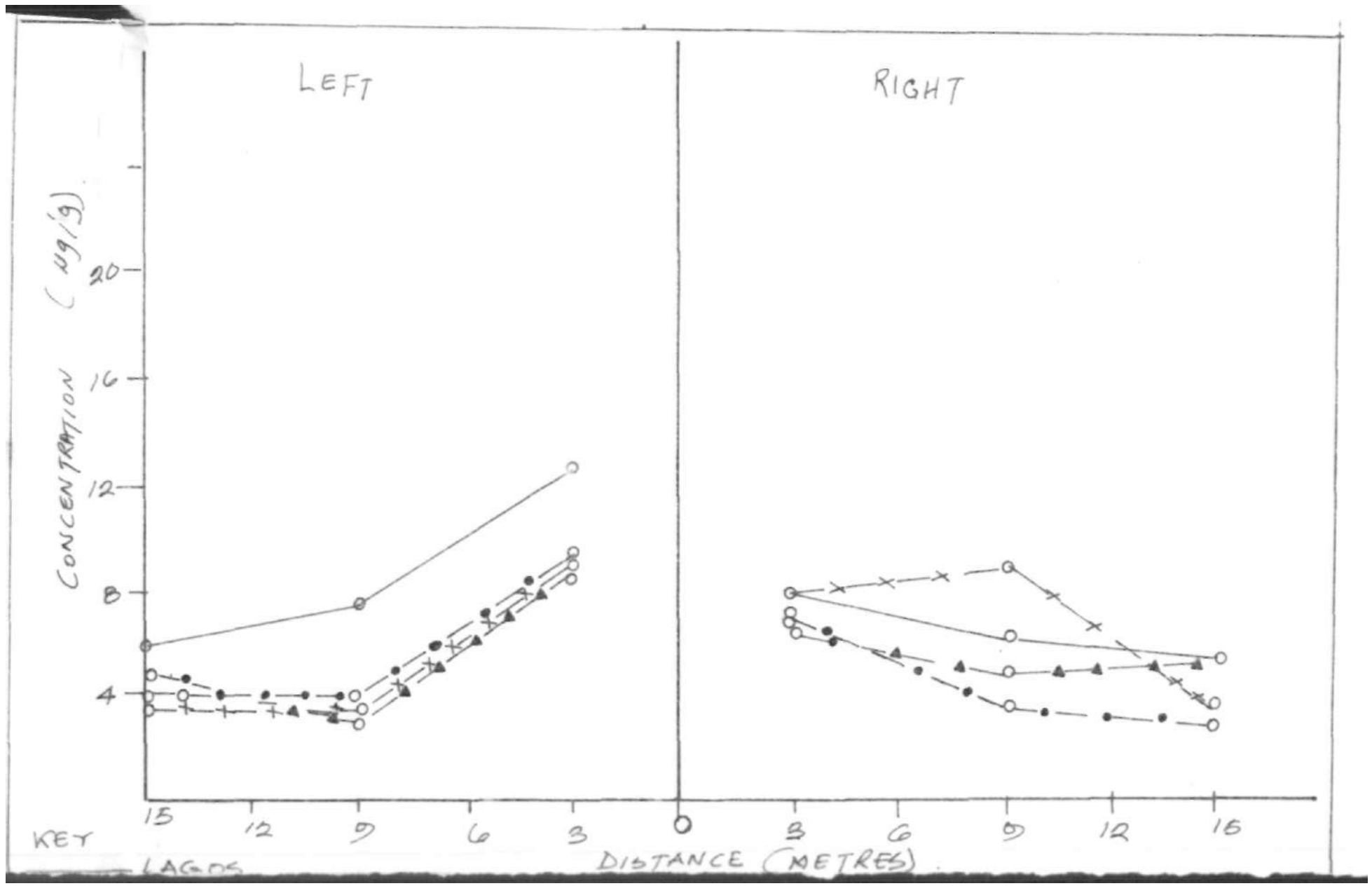
The amounts of copper in the soil samples at 3, 9, 15 metres away from road show similar trend as that of lead as seen in tables 22, 23 and 24. For soil samples, Ibadan has copper concentration of 8.7 μgg^{-1} at 3 metre which decreases to 4.0 μgg^{-1} at 15 metres away from road. The same is true for the amount of copper in soil and vegetation samples of Lagos, Kano and Maiduguri. This may suggest that copper in the environment decreases rapidly with distance from the highways as seen in figure 12.

The result for chromium show the same variation with distance from the road as those for copper, the highest value being obtained at 3 metres from the road for all the state capitals. Ibadan, Lagos, Kano and Maiduguri have 14.2 μgg^{-1}, 15 μgg^{-1}, 19.1 μgg^{-1} and 1.0 μgg^{-1} respectively for soil samples at 3 metres. These values decrease to 10.8 μgg^{-1}, 8.1 μgg^{-1}, 1.6 μgg^{-1} and 0.8 μgg^{-1} for the above mentioned state capitals respectively at 15 metres from the road. From the independent studies, the soil and vegetation along Samaru-Zaria and Kano - Zaria roads have the highest chromium concentration at 1 - 3 metres from the road being between 13.7 - 15 μgg^{-1}. This decreases to between 4.0 to 4.5 μgg^{-1} at about 20 metres from the road.

The concentrations of the various metals in the water samples are shown in tables 16 - 19. The amounts of nickel and copper are much higher in the water samples than in the soil samples, while lead shows a decrease. While stagnant surface waters may receive metals by direct deposition from atmosphere, additional source of metal input to stagnant surface waters would be running surface water which flows into


LEFT
RIGHT
120
100
80
60
40
20
CONCENTRATION (µg/g)
15
12
9
6
3
0
3
6
9
12
15
DISTANCE (METRES)


LEFT
RIGHT.
CONCENTRATION (ug/g).
20
16
12
8
4
15
12
9
6
3
0
3
6
9
12
15
KEY
DISTANCE (METRES)


LEFT
RIGHT
(ng/g)
20
16
12
8
4
CONCENTRATION
15
12
9
6
3
0
3
6
9
12
15
KEY
LAGDS
DISTANCE (METRES)

them, particularly during the rains. This would probably explain the enhanced metal concentrations in the water samples. While the heavier metal lead is most probably deposited at the bottom of the pools, the lighter metals, nickel and copper could be held as suspended particles. An analysis of the sediments from the sampled pools might be quite informative. The copper and chromium concentrations in water also show a decrease with distance from the road.

4-4 POSSIBLE ENVIRONMENTAL POLLUTION THAT MAY RESULT FROM HEAVY METALS

In order to assess whether the amounts of the heavy metals determined by this analysis are sufficiently high to cause environmental pollution, our results may be compared with some accepted thresholds shown in table 33. It can be seen that the amount of lead at any particular soil sample point is not high enough to cause environmental pollution, except for the soil samples from the Sokoto park.

Threshold limits of some heavy metals in the environment*

TABLE 34

Metal	Plants ($\mu g g^{-1}$)	Water ($\mu g L^{-1}$)	Soil ($\mu g h^{-1}$)
Pb	12 - 20	50	500**
Ni	-	30 - 40	-
Cr	10 - 12	150 - 200	-
Cu	10 - 15	100 - 200	-

* (WHO, 1971)

** (BINI, 1973)

Pb is probably present as a contaminant than as a pollutant. Copper and chromium are present in water in concentrations which are below the permissible thresholds. However, nickel concentrations in the water samples and lead in water sample from Lagos exceed the specified limits except for samples from Makurdi and Maiduguri.

The vegetation samples have lead concentrations that exceed the specified limits. It would appear that lead at the observed levels may be toxic to the vegetation at about 3 metres from the road. However, vegetation tolerance may prevail. The levels of the other metals as found in the vegetation samples are generally below the specified limits.

Sokoto and Kano Motor Park Soil Samples

The heavy metal concentrations in soil samples from Sokoto and Kano motor parks are summarized in tables 28 and 29 respectively. The average lead concentration for the soil samples of Sokoto park with estimated daily traffic volume of 3104$\frac{2}{}$ was found to be 774.6 $\mu g g^{-1}$. Kano motor park soil samples, with estimated daily traffic volume of 4231 was found to contain 277.9 $\mu g g^{-1}$ of lead. It is not certain why the levels of the metal are much higher in Sokoto park than in Kano park, but probably more prolonged stay of vehicles at the former park and subsequent starting of cold engines could play a significant role (Harrison and Laxen, 1980)[25].

4-5 Comparism of the Two Analytical Methods Used

In comparing the two analytical techniques used, t values were calculated for atomic absorption spectroscopy data and those of spectrophotometric method. A two-group-test (t = -0.08, 0.23, 1.85 respectively) shows that both A.A.S. and colorimetric methods are statistically equivalent at the 95% confidence limit. Hence one can be used as an alternative method to the other. The trend in the t-values is probably a reflection of the decreasing sensitivity of these methods

with decrease in metal concentrations in going from lead to chromium.

SUGGESTIONS TO MINIMISE ENVIRONMENTAL POLLUTION CAUSED BY HEAVY METALS

In order to minimise pollution due to lead, it is suggested

1. That addition of lead additives to gasoline be gradually abolished. Already some refineries in Nigeria especially Kaduna refinery have started using aromatic and branched alkanes as anti-knocking agents. This would reduce not only the environmental lead, but would presumably reduce lead content of food, water and street dust.

2. That exhust gas filters be used in vehicles which will reduce the lead content of the exhaust, without a reduction of the lead content of the fuel (Turner, 1980)[26].

Suggestions for Further Work

1. It is suggested that the "Behavioural abnormalities consistent with the long term effect of heavy metals on urban populace" be a topic for further work.

2. That environmental pollution caused by heavy metals in the rest of the 19 state capitals of Nigeria be studied.

CONCLUSION

Generally, the concentrations of the heavy metals as obtained from this work do not appear to pose very serious environmental problems at the moment. However significant increases in level may occur within the next decade as the level of industrialisation in the country is raised and the number of vehicles in our Urban centres increase. The results obtained showed that the amounts of heavy metals in soils and water along highways are related to estimated daily traffic volume, which agrees with findings of Daniel et al (1970)[27].

It was also found that the distribution of lead in soil and vegetation decreases with distance and become constant (background lead) at about 15 metres from the road).

It is therefore necessary that the amounts of heavy metals (particularly lead) produced into the environment as a result of human activity be regulated in order to have a relatively clean environment.

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