ANALYSIS OF TRACE ELEMENTS IN HARMATTAN DUST

A THESIS PRESENTED IN PARTIAL FULFILLMENT FOR
THE DEGREE OF MASTER OF SCIENCE
(ANALYTICAL CHEMISTRY) OF AHMADU BELLO UNIVERSITY

BY

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MARCH, 1981

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Dedication

Dedicated to my late mother and to my two sisters.

A C K N O W L E D G E M E N T S

I am indepted to my Supervisors Dr. K. Singh and Dr. E.U. Essiet for their guidance. I am grateful to Prof. B.J. Salter Duke, Head of Chemistry Department, Bayero University Kano for initiating this project and for suggestions.

I wish to thank the Head of Chemistry Department, Ahmadu Bello University, Zaria, for providing the facilities for this work.

D E C L A R A T I O N

This is to certify that this work has been carried out by Wahab Larin Olagoke Jimoh in the Department of Chemistry, Ahmadu Bello University, Zaria.

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A B S T R A C T

The concentrations of twelve trace and major elements were determined in dry and wet collections of Harmattan dust in Kano and Zaria Station.

Various methods of extraction were tried, however, hydrofluoric acid - hydrochloric acid - nitric acid digestion; a modified hydrofluoric acid - hydrochloric acid digestion; and Hydrofluoric acid - Sodium Carbonate fusion hydrochloric acid digestion were found to be the most suitable.

Determination of cobalt, chromium, copper, nickel, magnesium, manganese, Sodium, potassium, zinc, calcium Bead and iron in Harmattan dust samples were carried out by atomic absorption spectroscopy.

Two parameters were calculated: "enrichment factor" (E_f) which is the ratio of anelement to Fe in the media analysed relative to the ration of the same elements in soil (Crust), and the wet and drt deposition (WD and DD respectively) rates of the Harmattan dust.

Attempts were made to charaterise the minerals in the Harmattan dust using X - ray diffraction technique, to determine the particle size ranges using sedimentation method, and to find the percentage of benzene soluble organic compounds in the sample.

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CHAPTER I

1. INTRODUCTION

1.1 AIM OF THE PROJECT

There appears to be no reliable data, collected systematically over an adequate number of years, on the quantity, periodicity and chemical composition of dust received by soils of natural and agricultural ecosystems in oases, desert fringes and more distant peripheral vegetation. Studies are needed on the nutrient regimes of such soils and the dynamics of nutrient inputs via dust in order to determine whether air - borne deposition represents a significant percentage of the "total", "plant available" and "supplying power" for nutrients in different soil types.

Such studies are of particular importance with respect to the macro - nutrients (Magnesium, Calcium, Potassium and Sodium) and with micro - nutrients (Cobalt, Manganese, Copper, Zinc and Nickel)

1.2 AEROSOLS

An aerosol in the atmosphere is defined as being a dispersion of solid or liquid matter in air. When the natural

aerosol is supplemented by pollutant aerosol in the form of smoke, ash, acid mist, and soluble salts, the properties of the atmosphere may be adversely affected.

The physical properties of the atmospheric aerosol affect human health, either by allowing penetration of the lung and causing irritation to the internal membranes, or by transporting adsorbed toxic gases and vapours deeper into the lungs than they would normally travel. The respiratory air passages begin at the nasal cavity, pass through the trachea, bronchi and bronchioles, and end at the alveoli. The diameter of these passages and the velocity of air flow through them also decrease in this order. Larger particulates are therefore unable to penetrate into the narrow branches of passages, but smaller ones can easily reach the alveoli.[2]

A wide range of organic compounds has been found in the atmospheric aerosl. These include all the straight chain alkanes[1,2], from C18 to C34, at least thirty polycyclic hydrocarbons, and many heterocylic compounds. The best known aromatic polycyclic hydrocarbons are the benzpyrenes.

Harmattan:

Apparently a native name in West Africa, from haramata, the name in the Fanti or Twi language of West Africa (1671).

According to Norris (1780) "a corruption of Aherramantah, compounded of Aherraman to blow and tah tallow, grease, with which the natives rub their skin to prevent their growing dry and rough. A desiccating wind in Africa, blows from the north east between November and April in the north and for a decreasing period in the south. It has a hurtful effect on vegetation and on the human body, drying up the eyes, nostrils and mouth.

1.3 Mobilisation of Saharan Dust:

Desert dust originates[3] from wind erosion of alluvial deposits in desert mountain valleys.

Thus fine dust material would be ultimately produced by chemical weathering of primary minerals in mountains.

On the other hand, some of the desert dust may be produced by crystalline breakage of saltating grains (4), (5)

The production of dust is related to variables of surface soil texture, wind speed, vegetation, vegetative residue, surface roughness, soil aggregate, size distribution and soil moisture.[6]

There are different kinds of disturbances affecting parts of the Saharan area during different seasons.[7,8].

The impact of human action can considerably increase wind erosion through: Cultivation (for subsistence and market economy), improper grazing, cutting wood for fuel or other use, etc.

There are several well documented cases where an atmospheric transport of Saharan dust over distances of up to several thousand kilometers has been evident.[3,9].

These transports have been documented by measurements of turbidity and of dust concentration in the air, and have also been confirmed by statellite images.

There is also no doubt that a considerable transport of dust takes place from an area southwest of Tibesti region of the central Saharan into the countries along the northern coast of the Gulf of Guinea.[8] Occasional intrusion of Saharan dust into Europe as far north as Scandinavia have also been documented.

It has been estimated that the contribution of Saharan dust to the total burden of tropospheric aerosols is about 60 - 2000 million tons per year.[4] It is clear that the Saharan is a very important source and that appreciable variations in its strength could have significant implications on the regional and global burdens of mineral dust. This implies that changes in the dust output from the Saharan (be they natural or man-made) is of potential significance for the regional and global climate.

1.4 Deposition of Saharan Dust

Saharan dust is said to be the source for deposits in places such as Israel, the Nile Valley and the Cape Verde Islands.

It has been suggested that it also may be the origin of some soils on Islands in the Western Atlantic such as Bermuda, the Bahamas and the West Indies.[11]

The deposition of nutrients associated with Saharan dust into ocean water may under certain conditions contribute significantly to the productivity of the surface waters, for example, off the coast of West Africa.[12,13]

Saharan dust most likely also gives significant contributions to the sediments in the Mediterranean and in the Western parts of the equatorial Atlantic.

1 . 5 Production of Eolian Dust in the Sahel Zone and in the Sahara:

The aridity of the Sahara, the high temperatures reached by its soil and the strong diurnal thermic turbulence resulting from these, are all factors which favour the production of dust and its suspension in the atmosphere. The directions of the prevailing winds account for the transport of this dust towards the Sudan and towards the Atlantic off Mauretania and Senegal, but do not explain its movement towards the continent of Europe.

The Sahara, with its axis along the tropic of Cancer, is a hot desert, perhaps a typical example of a hot desert, It is a region where rain is extremely rare.

Drought is therefore a normal phenomenon. To this lack of rain is added the great evaporating power of the Saharan atmosphere. The lack of rain and the strong potential evaporation result in a thinning out and, later disappearance

of the Vegetation cover, which in its turn facilitates an eolian soil drift.

In winter and at ground level all the Sudaness regions are under the influence of the Saharan desert climate swept by the harmattan, drought sets in every where, ponds disappear and their alluvial surfaces become the prey of wind erosion. Thermic turbulence, due to high near-ground temperatures, is considerable in the day-time and keeps in suspension the dust torn away from the soil of the Southern Sahara and the Sudanese Sahel during dust storms.

This constitutes what has been aptly named the "harmattan haze" or "dry haze" or again "dust - haze". This haze is a striking phenomenon for aeroplane passengers as it entirely conceals the country side, in the same way as low clounds.

Indeed, it is difficult to distinguish between haze due to dust in suspension and that caused by humidity in the air, when the two are not combined. Their effect upon the soil is, however not the same.

The harmattan dust particles are very fine opalescent particles which are so minute that they can remain air-borne for a considerable length of time.

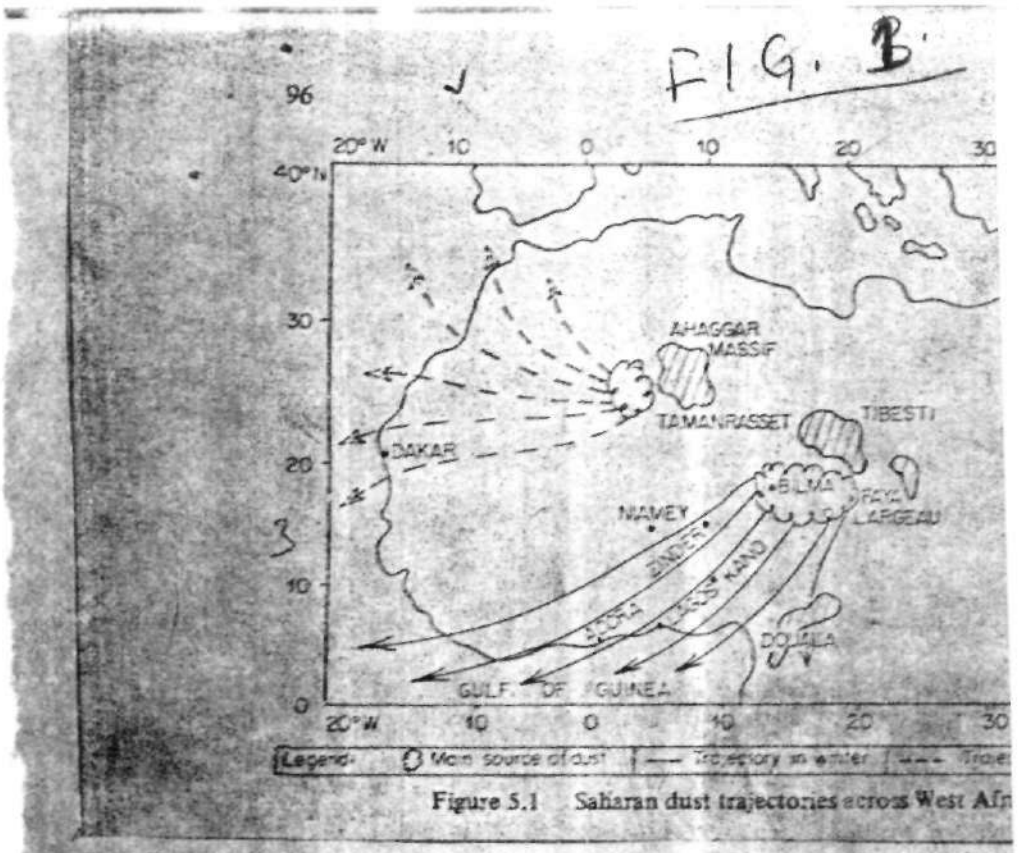
The presence of these harmattan dust particles constitutes a dusty atmosphere and a dusty atmosphere is defined as an atmosphere in which obstruction to vision is brought about by the presence of extremely dry and minute dust particles in the air with visibility reduced to less than 1 kilometre by natural dust.

It is known that the dust which affect a greater part of West A Africa in winter, particularly the Nigerian Zone, comes mainly from the north eastern Sahara usually along the alluvian plain of Bilma and Faya Largeau.[14,15]

This is illustrated in Figure 1. There are several source areas for the Saharan dust, but the one which is responsible for the existence of the dusty atmosphere over Nigeria and adjoining West Africa countries is the Bilma-Faya Largeau area.

The dust particles are then transported down wind from the source region in a "Plume" form towards the Gulf of Guinea by the strong north-easterly winds taken a south-westernly trajectory over Nigeria.

On the average it takes about 24 hours for the dust to reach the northern border of Nigeria with the dust front moving at 15 knots.[16] (1 knot = 1,853 metres per hour).



the transport of the Saharan dust.

The moisture content of the atmosphere or humidity is perhaps one of the most important factors controlling dust

transport in the atmosphere. Characteristically the tiny dust particles behave as condensation nuclei which have a great affinity for water and by absorbing water they grow becoming heavier and Sediment out of the atmosphere. Thus if the Sahara dust comes over to a section of the atmosphere where the moisture content is high, the immediate result will be that a large amount of it would Sediment out giving rise to improved visibility.

1 . 6 Present Studies

Analytical study of Harmattan dust samples collected from Zaria and Kano over the period October '79 - May' 80 by dry and wet methods of collection have been carried out to:

(i) determine the requisite condition to bring samples into Solution,

(ii) determine Ca, Mg,Mn, Co, Ni, Pb, Fe, Zn, Cu, and Cr Using A 3400 Atomic Absorption mode, and K and Na by the Emission mode of the same spectrophotometer.

(iii) investigate the organic materials by suitable extration methods and

(iv) determine the particle size ranges of the Harmattan dust.

CHAPTER II

SAMPLE COLLECTION AND ANALYSIS

2 . 1 Collection of The Harmattan Dust.

The dust collection technique was designed to measure the amount of Harmattan dust falling onto the ground from suspension in the atmosphere. Dust traps were set up 9 metres above ground level on the roof of a building on the campuses of Ahmadu Bello University, Zaria, and Bayero University Kano, isolated from local soil dust movement. Buckets exposed in the air stream to collect dry particles was used to estimate dry deposition.

Particles can blow both in and out of a container in varying degrees depending on the wind speed, and the particle size. Wet deposition method was then designed by placing distilled water in the buckets to avoid loss of dust already collected.

Experimental

Materials:

Enamel cooking bowl with a top diameter of about 60cm and 20cm deep;

Polyethylene buckets, each 30 cm diameter and 30cm deep;

Plastic and glass beakers;

Mosquito mesh built into a wooden frame;

Brush.

Procedure for Wet Deposition Method (W D):

The dust trap for wet deposition method was either an enamel cooking bowl or Polyethylene buckets filled to a depth of about 8cm with de-ionised water. To deter birds from drinking the water and polluting the Sample, a similar bowl was placed on the same roof filled to the top with tap water. Here, the birds find it easier to drink since they can stand on the tip of the bowl. They therefore avoid the collecting bowl.

Water level was maintained daily. The dust Samples were collected weekly, The dust laden water was carefully transferred to large plastic beakers and the bowl carefully washed out with de-ionised water. The beakers were then placed in large oven to evaporate off the de-ionised water. When the volume has been substantially reduced the sample was washed with de-ionised water into small pre-weighed

glass beakers and evaporated to dryness. The dust sample was then weighed and transferred to a sample bottle for subsequent analysis.

Procedure For Dry Deposition Method (DD):

This consists of enamel bowl covered with a mosquito mesh built into a wooden frame. This requires no attention and was collected weekly. The mesh was first brushed and then removed. Dust material was dissolved/rinsed out of the dry enamel bowl with de-ionised water.

The dust and de-ionised water were carefully transfered to large plastic beakers and the bowl carefully washed out with de-ionised water. The water was evaporated in laboratory ovens weekly and the residue weighed.

The rate of deposition of the harmattan dust for the period of collection (October - May) both in Kano and Zaria is shown in table 1.

Weekly Deposition Rates of Harmattan Dust (1979/80) In Kano and Zaria Stations

WEEK	PERIOD	KWD I g/m^2	KWD II g/m^2	KWD III g/m^2	KDD_2 g/m^2
1	Oct. 5th-Oct. 12th	-	2.3207	-	1.6509
2	Oct. 12th-Oct. 19th	-	3.9903	-	1.4674
3	Oct. 19th-Oct. 26th	-	3.5694	-	1.0896
4	Oct. 26th-Nov. 2nd	2.1659	2.3017	2.9560	1.57.90
5	Nov. 2nd-Nov. 9th	3.1064	3.3016	3.6758	1.4782
6	Nov. 9th-Nov. 16th	2,1739	2,6528	2.2715	1.2536
7	Nov. 16th-Nov. 23rd	3.1371	3.2767	3.1499	2.9789
8	Nov. 23rd-Nov. 30th	6.2180	5.4608	5.9550	2.7350
9	Nov. 30th-Dec. 7th	4.3712	4.5535	5.6017	2.3817
10	Dec. 7th-Dec. 14th	2.9631	2.6079	2.5837	1.3574
11	Dec. 14th-Dec. 21st	3.2878	3.5002	3.7269	2.0361
12.	Dec. 21st-Dec. 28th	2.3593	2.9928	2.6443	1.1658
13	Dec. 28th-Jan. 4th	4.9233	3.9070	3.2911	1.9517
14	Jan. 4th-Jan. 11th	4.1955	4.56.97	4.1513	2.2679
15	Jan. 11th-Jan. 18th	3.4850.	3.2848	3.5197	1.6152
16	Jan. 18th-Jan. 25th	7.9660	6.1715	6.4228	2.0557
17	Jan. 25th-Feb. 1st	2.6020	2.8887	2.6203	1.4992
18	Feb. 1st-Feb. 8th	8.2788	7.4396	7.9735	3.9279
19	Feb. 8th-Feb. 15th	5.8185	4.1482	5.2671	3.6342
20	Feb. 15th-Feb. 22nd	6.0938	5.9305	5.1370	2.4532
21	Feb. 22nd-Feb. 29th	4.9569	4.1571	5.0292	2.8758
22	Feb. 29th-Mar. 7th	8.2964	8.8838	8.4691	4.7356
23	Mar. 7th-Mar. 14th	4.7356	4.1482	4.9823	2.3127
24	Mar. 14th-Mar. 21st	7.9294	7.2788	7.9470	3.1937
25	Mar. 21st-Mar. 28th	6.8571	6.5855	6.0135	2.5927

Table 1 cont'd

WEEK	PERIOD	KWD$_2$I g/m^2	KWD II g/m^2	KWD III g/m^2	KDD$_2$ g/m^2
26	Mar. 28th-Apr. 4th	5.1477	5.2117	5.5524	3.6488
27	Apr. 4th-Apr. 11th	5.6368	3.6874	5.4023	2.5025
28	Apr. 11th-Apr. 18th	6.1319	6.7863	6.2998	2.5025
29	Apr. 18th-Apr. 25th	6.6440	6.9136	6.8650	2.3416
30	Apr. 25th-May 2nd	12.89.80	13.6275	11.6092	7.5166
31	May 2nd-May 9th	11.9189	10.5473	11.8595	7.2684
32	May 9th-May 16th	-	-	-	-
33	May 16th-May 23rd	-	-	-	-
34	May 23rd-May 30th	13.4289	14.3584	12.5075	-
	TOTAL	167.7272	173.0542	163.4844	82.1597

KWD I Kano Wet Deposition method I
KWD II Kano Wet Deposition method II
KWD III Kano " " method III
KDD Kano Dry Deposition
KESA Kano Dry Deposition Ecological Station
ZDD I Zaria Dry Deposition method I
ZDD II Zaria Dry Deposition method II
ZWD I Zaria Wet Deposition method I
ZWD II Zaria Wet Deposition

Table 1 cont'd

Weekly Deposition Rates of Harmattan Dust (1979/80) In Kano and Zaria Stations

WEEK	PERIOD	K ESA g/m^2	ZDD I g/m^2	ZDD II g/m^2	ZWD I g/m^2	ZWD II g/m^2
1	Oct. 5th-Oct. 12th	0.9912	1.1006	1.1372	2.8630	-
2	Oct. 12th-Oct. 19th	2.0875	0.6761	0.7073	0.956	-
3	Oct. 19th-Oct. 26th	3.1522	0.5136	0.4879	2.1586	-
4.	Oct. 26th-Nov. 2nd	3.4716	1.0270	1.6292	2.5923	2.0955
5.	Nov. 2nd-Nov. 9th	3.4437	1.0243	1.0518	2.5603	2.9965
6	Nov. 9th-Nov. 16th	2.3290	2.2067	1.9829	2.9149	2.0704
7	Nov. 16th-Nov. 23rd	2.7542	2.0964	2.7247	3.0100	3.5772
8	Nov. 23rd-Nov. 30th	3.2940	2.3824	1.7173	5.6396	5.6935
9	Nov. 30th-Dec. 7th	3.2048	1.7407	1.1328	4.8955	4.2183
10	Dec. 7th-Dec. 14th	3.1608	1.0852	1.2594	2.7170	2.7703
11	Dec. 14th-Dec. 21st	3.0420	1.3001	1.4509	2.2471	2.8434
12	Dec. 21st-Dec. 28th	3.9369	1.9796	1.5749	2.9028	2.4738
13	Dec. 28th-Jan. 4th	3.0575	1.5291	1.9014	3.3867	3.2503
14	Jan. 4th-Jan. 11th	3.1679	1.8735	1.3321	3.1208	3.3833
15	Jan. 11th-Jan. 18th	2.6608	1.2822	1.4924	3.9454	3.1708
16	Jan. 18th-Jan. 25th	3.1676	2.5583	2.3828	6.2759	6.1703
17	Jan. 25th-Feb. 1st	2.3090	1.9038	1.5712	2.4683	2.0553
18	Feb. 1st-Feb. 8th	4.0381	3.0628	3.1938	6.3039	6.5936
19	Feb. 8th-Feb. 15th	3.7077	2.7591	2.3479	5.4976	5.1199
20	Feb. 15th-Feb. 22nd	3.2305	1.0278	1.4684	3.8545	3.8966
21	Feb. 22nd-Feb. 29th	3.9569	2.9177	2.4595	4.6356	4.0633
22	Feb. 29th-Mar. 7th	4.7532	3.2059	3.0469	7.1305	7.9203
23	Mar. 7th-Mar. 14th	2.4962	1.5785	1.5329	4.7811	4.8966
24	Mar. 14th-Mar. 21st	3.3610	1.7621	1.7557	7.9001	7.7379
25	Mar. 21st-Mar. 28th	3.6801	2.3541	2.8175	6.5537	5.6345

Table 1 cont'd

WEEK	PERIOD	K ESA g/m^2	ZDD 1 g/m^2	ZDD II g/m^2	ZWD 1 g/m^2	ZWD II g/m^2
26	Mar. 28th-Apr. 4th	3.2631	2.5418	2.6982	5.9470	4.9315
27	Apr. 4th-Apr. 11th	3.5367	2.3406	2.2708	4.7001	4.9315
28	Apr. 11th-Apr. 18th	2.1570	2.0352	2.0090	6.4411	6.4345
29	Apr. 18th-Apr. 25th	3.5932	2.2818	2.3120	6.4011	6.3825
30	Apr. 25th-May 2nd	10.9575	11.7436	7.3088	10.4400	11.8345
31	May 2nd-May 9th	16.2867	-	-	12.0096	9.1868
32	May 9th-May 16th	-	-	-	11.5589	-
33	May 16th-May 23rd	-	-	-	-	-
34	May 23rd-May 30th	-	-	-	-	-
	TOTAL	118.2742	65.8906	60.7488	158.8094	137.3513

KWD I Kano Wet Deposition method I
KWD II Kano " " method II
KWD III Kano " " method III
KDD Kano Dry Deposition
KESA Kano Dry Deposition Ecological Station
ZDD I Zaria Dry Deposition method I
ZDD II Zaria Dry Deposition method II
ZWD I Zaria Wet Deposition method I
ZWD II Zaria Wet Deposition method II

2.2 Particle Size Analysis

This is done by the Sedimentation method, two types of which are known the pipette and the hydrometer methods.

The pipette method is the most accurate,[26] albeit a very laborious and time-consuming method of the particle size analysis. It involves the pipette sampling of the finer soil fractions, clay and silt, at a standard depth in a 1,000ml cylinder and at specified times according to the temperature of the suspension, and sieving mechanically to separate the different size grades of sand particles.

Experimental

Materials:

Analytical - reagent grade chemicals were used throughout

Acetate buffer solution (PH 4.8).

28.6ml of glacial acetic acid.

68.04g of sodium acetate trihydrate were made up to 500ml with de-ionised water

Hydrogen Peroxide 30% volume

Calgon 0.1% (m/v) (sodium hexa - meta phosphate)

Procedure: 2.0g of harmattan dust was weighed and soaked over night in acetate buffer solution to dissolve all the Carbonates. The suspension was centrifuged to allow the Soil Particles to settle. The supernatant liquid was thrown away with the dissolved Carbonates. Distilled water was added to the sample in the centrifuge bottle to wash the soil clean of the acid and the dissolved soluble salts. It was then centrifuge again.

The sample was transfered into a 1,000-ml beaker and 30% hydrogen peroxide was added. The beaker was place on a hot plate.

The dried sample was transfered into a 200-ml centrifuge bottle. Distilled water was added to wash away the hydrogen peroxide and the oxidised organic matter.

It was then centrifuge again.

Calgon (0.1%) (Sodium hexa - metaphosphate) was added. It was shaken overnight on a reciprocal shaker to disperse the soil particles. The solution was transfered into a 1000-ml graduated measuring cylinder and made up to mark with distilled water. The suspension was stirred vigorously.

It was allowed to settle for 4 minutes 15 seconds. The pipette was lowered into the solution to a depth of 10cm and 25-ml sample was withdrawn. The sample was transfered into a weighed evaporating dish and oven-dry at a constant temperature of 105°C. After drying, the soil and the dish was weighed.

The difference in weight (wt. of soil + dish minus wt. of dish) is 1/40 of the weight of coarse and fine silt and clay in the original sample of soil.

Immediately after taking the sample at 4 minutes 15 seconds, the suspension was stirred again vigorously and allow to settle for 47 minutes 20 seconds. 25ml sample at a depth of 10cm was pipetted into a weighed evaporating dish, and treated as the above. The difference in weight (wt. of soil + dish minus wt of dish) is 1/40 of the weight of fine silt and clay in the original sample of soil. The weight of coarse silt was then found.

The suspension was again siphoned off to about 10cm above the bottom of the cylinder. The residue was transfered into a 400-ml conical beaker, calibrated at 10cm.

It was made up to mark with distilled water, stirred vigorously and allow to settle for 4 minutes 15 seconds. The supernatant liquid was siphoned off. This process was repeated until the supernatant liquid was clear. The sand residue was then oven - dried at a temperature of 105°C after which it was put in a nest of sieves to obtain the different size grades.

Calculations:

The weights of all the different size - grades from clay to Coarse sand are added.

Each Weight is then expressed as a percentage of the total weight of the fractions. The following is a step by step description of calculations done in the sedimentation analysis using an ordinary pipette of capacity 25ml.

(1) Coarse Silt + Fine Silt + Clay:

Weight of dish + Oven dried 25ml sample	= 30.4663g
Weight of dish	= 30.4240g
Weight of Oven dried 25ml sample	= 0.0423g

∴ Weight of Coarse Silt + Fine Silt, + Clay in original sample = 0.0423 x 40g

= 1.694g.

(2) Fine Silt + Clay:

Weight of dish + Oven-dried 25ml sample = 28.347g.
Weight of Oven-dried 25ml sample = 0.0154g.
∴ Weight of Fine Silt + Clay in the Original Sample.

= 0.0154 x 40g
= 0.616g.

(3) Clay

Weight if dish + Oven-dried 25ml sample = 29.1625g
Weight of dish = 29.1584g
Weight of Oven-dried 25-ml sample = 0.0041g
∴ Weight of clay in the original sample = 0.164g.

Hence Coarse Silt = 1.694 - 0.616g
= 1.078g
Weight of Fine Silt= 0.6161 - 0.164
= 0.452g.

The sand residue is then oven-dried at a temperature of 105°C after which it is put in a nest of sieves (106um; 212um; 2000um) to obtain the different size grades.

The result of the particle size analysis is shown in Table 2 below:

TABLE 2 :

Particle Size Ranges of Harmattan Dust Samples

Sample	CLAY (~) (1-2) um	FINE SILT (2-20) um	COARSE (SILT) (20-63) um	FINE SAND (63-106) um	MEDIUM SAND (106-212) um	COARSE SAND (212-2000 um
K2042 (10g)	0.853g	0.3579g	4.056g	2.184g	1.505g	0.2202g
K2042 (2g)	0.1668g	0.0725g	0.8015g	0.3935g	0.3318g	0.0471g
K2185 (10)	0.6012g	0.1757g	2.932g	3.986g	0.888g	0.666g
K2185 (2G)	0.1181g	0.0636g	0.5472	0.7926g	0.1908g	0.1054g
Harmattan Dust						
ZDD	0.177g	0.521g	1.101g	0.092g	0.038g	0
KDD	0.164g	0.452g	1.078g	0.091g	0.036g	0

2.3 Dissolution of Harmattan Dust Sample:

When large quantities of silicates[2,17,18] are present in ash, these become conjugated with Al, Fe, Mn, etc; and the resulting compounds tend to be insoluble.
This situation becomes more conspicous at higher temperatures, but at ashing temperatures below 500°C, the problem[2] does not arise with Fe, Cu or Al.

Carbon also frequently remains at ashing temperature below 500°C due to insufficient ashing[18, 17, 2].

Samples are generally ashed at 500-550°C. However, within this temperature range, there are certain substances for which a risk of Volatile lost exists during the ashing process. A compromise exists, between the dry and wet ashing methods, in which a small quantity of concentrated sulphuric acid or concentrated nitric acid is added to the sample before heating. The ashing time is effectively shortened and some suppression of Carbon adsorption results.

Various methods have been reported to bring similar samples into solution.

Among these, the important ones are:

(i) Wet Oxidative decomposition

This is a method by which samples are thermally decomposed in some strong oxidising agent such as Sulphuric acid, hydrogen peroxide, perchloric acid etc.

Since decomposition is conducted at low temperature, evaporative loss of inorganic compounds is lower than in high temperature decomposition.

Many combinations of oxidizing agent are commonly used, including sulphuric acid + nitric acid; nitric acid + hydrogen peroxide; nitric acid + Perchloric acid; Sulphuric acid + nitric acid + hydrogen peroxide etc.[2, 17, 18]

(ii) Fusion decomposition:

Certain elements like Cr are insoluble in acids and must be treated by a fusion process for their dissolution.[17]

In this method, sample of compounds which are essentially insoluble in acid are placed in a platinium crucible and subjected to a dissolution procedure using a fusion reagent.[2,18]

This converts them to water or acid soluble compounds. The fusion reagents include compounds which are alkaline (Na_2CO_3 or K_2CO_3 $CaCO_3 + NH_4Cl$, etc) acidic ($K_2S_2O_7$),

oxidqtive (Na_2Co_3 + Na_2O_2; Na_2Co_3 + KNO_3; etc) and reducing (NaoH + KCN).

Organic Solvent Extraction

The objects of organic solvent extraction are: elimination of anions and interfering elements; enhancement of sensitivity by the organic solvent effect, and concentration of the sample.

Among the many extracting reagents, DDTC -Na (Sodium diethyl dithiocarbamate) and APDC (ammonium pyrrolidine dithio carbamate) are the most commonly used.

Dithizon (DZ) is also used in the analysis of lead and cadmium. These extracting reagents form indissoluble chelated compounds, and the chelated compounds are extracted to MIBK (methyl isobutyl Ketone) or n-butyl acetate.

2.4 Preparation of Sample Solution

Pretreatment of Sample

Wet ashing method, in which a small quantity of concentrated Sulphuric acid was added to a porcelain boat containing the sample before heating in a muffle furnace was conducted.

About 15g of the harmattan dust was used for the wet ashing.

The aim of the wet ashing was

(i) to suppress or prevent losses due to volatilization during ashing.

(ii) to make the combined samples homogeneous for subsequent analysis.

Before ashing, the combined samples were mixed thoroughly, followed by the addition of concentrated Sulphuric acid. The ashing was done at 425^{o}C until the fumes of the concentrated Sulphuric acid ceases.

The ashed sample was then mixed Sufficiently enough, for it to become homogeneous.

1.0g each of the ashed sample was used in different methods to dissolve the samples.

Experimental

Reagents:

All solutions were prepared with de-ionised water and analytical reagent grade materials, unless stated otherwise.

Hydrofluoric acid - (40%);

Nitric acid, Sp. gr. 1.42;

Hydrochloric acid Sp.gr. 1.16

Nitric acid, 10M. Prepared by diluting 443.7ml of HNO_3 of Sp.gr. 1.42 to 1 litre with distilled water;

1000ppm of Cs and La, in 1.5M HNO_3. Prepared by adding 66.55ml of nitric acid, Sp.gr. 1.42 to 3.1g of La $(NO3)_3.6H_2O$ and 1.60g of CsBr and diluting to 1 litre with distilled water.

Hydrochloric acid, 6M

Sodium Carbonate

Hydrochloric acid (1+1)

Hydrogen peroxide - 30% (m/v)

Nitric acid (2+98)

Methods:

(1) Hydrofluoric acid - hydrochloric acid - nitric acid digestion method:

Procedure: 1.0g of the dust sample was wet ashed at 425°C. Residue was dissolved in hydrofluoric acid (3ml), nitric acid (6ml) and hydrochloric acid (1.5ml) on a hot plate. The mixture was evaporated to dryness on a hot plate at 70°C. Residue was dissolved in 10ml, 10M nitric acid, and then evapor ated to dryness. Residue was again dissolved in 10ml, 10M nitric acid and then evaporated to dryness. The resulting residue was diluted to 25ml, using 1000ppm of Cs and La in 1.5M HNO_3.

(2) Hydrochloric acid - hydrofluoric acid digestion method:

Procedure: After ashing, the sample was tranfered to a 50ml egg-shaped flask and 6M, hydrochloric acid was added. After heating for 2 hours on a water bath with a reflux condenser, the sample was filtered through a whatman No. 41 filter paper. The residue on the filter was transfered to a crucible, ashed after drying in a drier and transfered to a platinium Crucible.

A small quantity of hydrochloric acid and subsequently the same quantity of hydrofluoric acid were added.

The mixture was heated to a solid residue which was dissolved in 6M hydrochloric acid for filtering. The filtrate obtained was combined with the previously prepared filtrate to serve as the test solution.

(3) Hydrofluoric acid - nitric acid digestion method:

Procedure:

The dissolution of the dust sample was initiated by the dropwise addition of 1ml of concentrated hydrofluoric acid. The contents of the beaker were gently warmed at low heat, until the hydrofluoric acid was almost completely evaporated.

At this points, 1 - 2ml of nitric acid was added and the heating continued gently until a few drop of nitric acid were left.

10ml of distilled water was added. The resulting solution was boiled and filtered through a whatman 41 filter paper into a glass beaker.

The solution was transfered to a 25ml volumetric flask. The beaker was rinsed down with another 10ml quantity of distilled water, warmed and filtered into the same beaker. This was again transfered to the 25ml volumetric flask and the test sample was made up to the mark at 25°C. The contents of the volumetric flask were mixed thouroughly after adjustment to volume. This was finally transfered to polyethylene storage bottle (screw cap, for storage of test samples 30ml capacity).

(4) Sodium Carbonate fusion method:

Procedure: Residual ashed substances were transfered to a platinum crucible and after adding 1-2g of Sodium Carbonate, this was sealed.

The Crucible was placed directly into the fire with occasional shaking. On conclusion of the fusion procedure, the crucible while still hot was placed on an iron or polished rock plate and rapidly cooled to loosen the "melt" from the crucible. Upon cooling, a small amount of water was added and when this has been absorbed between the melt and the crucible, the crucible was reheated using a small flame from a burner. The crucible and cover were transfered

to a 200ml beaker and the melt dissolved in a small quantity of warm water.

Both the crucible and its cover were removed and rinsed with a small quantity of warm water and the rinse was transfered to the beaker.

Later, the solution and residue were separated by a filtering operation.

The washing/rinsing operation was repeated several times to ensure high recovery of the element to be analysed.

(5) Sodium Carbonate fusion - hydrochloric acid digestion method:

Procedure:

Residual ashed substances were transfered to a platinium crucible and after adding 1-2g of Sodium Carbonate, this was sealed. The crucible was placed directly into the fire with occational shaking.

On conclusion of the fusion procedure, the crucible while still hot was placed on an iron or polished rock plate and rapidly cooled to loosen the "melt" from the crucible.

Upon cooling, a small amount of water was added and when this has been absorbed between the melt and the crucible, the crucible was reheated using a small flame from a burner. The crucible and filter were transfered to a 200ml beaker after cooling, and the melt was dissolved in a small quantity of warm water.

The crucible and cover were removed and washed thoroughly in a small portion of warm water. The washings were transfered to the former beaker.

8ml of HCl (1+1) and 1 drop of hydrogen peroxide (30%^{m}/v) were added to the beaker. The contents were then boiled, the Carbondioxide gas expelled, and the melt simultaneously dissolved.

(6) Hydrochloric acid - hydrogen peroxide digestion method:

Procedure: After ashing , 1.0g of the sample was transfered to a platinium crucible. Hydrochloric acid and hydrogen peroxide were added.

The mixture was heated on a boiling water bath. The resulting solution was filtered, and the filtrate evaporated to drymess.

Nitric acid (2+98) was added and the solution was transfered to a 25ml volumetric flask. The contents were mixed thoroughly after adjustment to volume. The contents of the volumetric flask were transfered to polyethylene storage bottle.

(7) Nitric acid - hydrogenperoxide digestion method:

Procedure: After ashing, 1g of the sample was transfered to a platinium crucible. Nitric acid and hydrogen peroxide were added. The mixture was heated on a boiling water bath. The resulting solution was filtered, and the filterate evaporated to dryness.

Nitric acid (2+98) was added and the solution was transfered to a 25ml volumetric flask. The contents were mixed thoroughly after adjustment to volume. The contents of the volumetric flask were transfered to polyethylene storage bottle.

(

(8) Hydrofluoric acid - digestion sodium carbonate fusion - hydrochloric acid digestion method:

Procedure: The residual ashed substances were transfered to a platinium crucible.

The dissolution of the ashed dust sample was initiated by the dropwise addition of 3ml of hydrofluoric acid . The contens of the crucible were gently warmed at low heat, untill the hydrofluoric acid was almost completely evaporated.

1 - 2.0g of sodium carbonate was added, and the crucible was placed directly into the fire with occational shaking. On conclusion of the fusion procedure, the crucible while still hot was placed on an iron or polished rock plate and rapidly cooled to lossen the "melt" from the crucible .

Upon cooling, the residue was dissolved in hydrochloric acid and the mixture was evaporated to dryness.

At this point 10ml mitric adid (2+98) was added, and the resulting solution was transfered to a 25ml volumetric flask.

The crucible was rinsed down with another 10ml nitric acid (2+98).

This was again transfered to the 25ml volumetric flask and the test sample was made up to the mark.

The contents of the volumetric flask were mixed thoroughly after adjustment to volume. This was finally transfered to polyethylene storage bottle.

Organic Solvent Extration:

Reagent:

Ammonium citrate (II)solution - 10 ^{m}/v%.

Prepared by dissolving 5g of the citrate in 50ml of de - ionised water;

m - cresol purple solution 0.1^{m}/v%;

Prepared by dissolving 0.1g in 100ml de - ionised water;

Ammonia water (1 : 1)

DDTC solution. 10^{m}/v%. Prepared by dissolving 10g in 100ml de - ionised water.

Nitric acid (1 + 11).

Nitric acid (2 + 98)

n - butyl acetate.

Procedure:

The sample solution was placed into a separating funnel. 10ml of ammonium citrate (II) solution and a few drops of m - cresol purple solution as indicator was added.

Ammonia water (1 . 1) was added until the solution was slightly purple (PH 7.4 - 9.0).

5ml of DDTC solution was added with shaking. 10ml of n-butyl acetate was then added and mixed thoroughly for one minute. It was then allowed to settle. The n - butyl acetate was then separated and evaporated to dryness with heat.

10ml of nitric acid (1 + 11) was then added and also evaporated to dryness by heating. The content was then cooled, and 10ml of nitric acid (2 + 98) was added. The whole solution was placed in a measuring flask (25ml) and nitric acid (2 + 98) was added to the mark line.

(9) Hydrochloric acid -hydrofluoric acid digestion followed by organic solvent extraction method:

1 1.0g of the dust sample was unashed and extracted with hydrochloric acid - hydrofluoric acid digestion. This was then following by organic solvent extraction.

10(0): Hydrochloric acid - hydrofluoric acid - digestion followed by organic solvent extraction:

1.0g of the dust sample was ashed withput adding Sulphuric acid followed by extraction with hydrochloric acid hydrofluoric acid digestion. Organic solvent extraction was then performed.

2A and 2A(0)

Duplicate extractions were done on 1.0g ashed sample each using hydrochloric aicd - hydrofluoric acid digestion. The combined extracts were divided into two equal portions.

Organic Solvent extraction was performed using one of the portions.

2.5 Elemental Analysis of Harmattan Dust Sample:

Flame methods of Analysis:

The quantitative aspect of spectral analysis relies on the fact that these characteristic spectral lines differ in their intensity.

The intensity of a spectrum line or band is proportional to the number of luminous atoms or molecules in the emitted light.

The number of luminous atoms or molecules is proportional to the aggregate number of the atoms or molecules of that kind. Some flame emission and absorption measurements[19] are performed with oxyhydrogen and quite a large number by air - acetylene flames the latter is a relatively hot flame.

Introduction of metals ions such as sodium, potassium, and calcium[20] into flames of relatively high temperatures produces intense radiations, and the intensities of these radiations are proportional to the concentrations of the salts introduced into the flame.[21]

Non - metals for example Sulphur, phosphorus and the halogens,[22,25] have their principal resonance lines in the vacuum ultra-violet region of the spectrum, where the background absorption of the oxygen in the atmosphere, and also of the burning flame gases is excessively high.

It is only recently that molecular emission in cool flames has been proposed as a technique to overcome the difficulties encountered in the determination of non-metals by flame spectroscopic methods, by using the emission of simple molecular species such as S2,[22] HPO[23] and InCl.[24]

Atomic Absorption spectroscopy:

Atomic absorption spectroscopy has now become a common analytical tool in many laboratories, due to its high sensitivity, accuracy and reproducibility, the ease of sample preparation and handling (incorporating less human error), and the comparatively low cost.

The principle of atomic absorption spectroscopy is first to vaporise atomically the metal-containing material by some appropriate method. The ground state atom absorbs a specific wavelength of light transmitted through this atomic vapour layer. The absorption is analyzed quantitatively using a photomultiplier apparatus.

The traditionaly type of atomic absorption spectroscopy incorporates a furnace apparatus. This consists of a nebulizer, disperser and burner head.

The sample is introduced into the sample atomizing apparatus (burner) into the flame. Here, the expected element is atomised to yield free atoms.

The excitation energy has no effect at all in contrast to emission spectro-chemical analysis.

The accuracy of analysis is very good since the ground state, which has a steady electron configuration, is measured. However, there is variability in accuracy between different instruments and different elements. That of the single beam type depends on the stability of light emission from the lamp the noise level is higher and the accuracy lower than in the double beam type.

The criteria governing the accuracy are: stability of light source (hollow cathode lamp), which depends on an appropriate current; smooth nebulization, and cleanliness of the burner.

The factors affecting sensitivity are: the state of the flame; selection of burning gas; efficiency of the nebulizer; working condition of the light source; optical system and dispersion ability of the diffraction grating.

The temperature of the flame used in atomic absorption spectroscopy should be sufficiently high as to dissociate the object element and produce free atoms.

If the flame temperature is higher than usual, ground state atoms decrease, and excited state atoms increase,

and the over all sensitivity then remains below that with a low temperature flame.

Of 68 elements now detectable by atomic absorption spectroscopy, 38 can be detected with an air-acetylene flame. The defects of this flame are: that the temperature is too low for the detection of oxides which do not dissociate easily in the flame, and that flame absorption is quite strong at far U.V. frequencies, rendering the signal of elements under 230nm too weak.

The nitrous oxide - acetylene flame is characterized by its high temeprature and strong reductive atmosphere, which permit the detection of very low concentrations of non-dissociable compounds that remain undetected with the air-acetylene flame. The elements which can be detected only by the nitrous oxide - acetylene flame are Al, Be, B, Si, Ti, V, W, Er, Eu, Gd, Hf, Ho, Ir, La, Lu, Nb, Nd, Pr, Re, Sc, Ta, Tb, Tm, U, Y, Yb and Zr.

These elements can form oxides (e.g.) Al_2O_3, VO, TiO, ZrO etc.) which require a large energy for dissociation, for which the temperature of the air - acetylene flame is too low but the temperature of the nitrous oxide acetylene flame

is sufficient.

More over in the nitrous oxide - acetyleme flame, these oxides cannot form readily due to the strong reductive atmosphere.

EXPERIMENTAL:

Instrument:

The A 3400 Atomic Absorption, Emission or fluorescence spectro--photometer was ued. The atomic Absorption mode of operation was used for the determination of Ca, Cu, Cr, Pb, Mg, Mn, Ni, Zn, and Fe. The Emission mode of operation was used for the determination of Na, and K.

The instrument consist of the energy source, the burner system, open sample presentation area, a monochromator, detector (photomultiplier) an associated power supply and amplifier.

An energy source (hollow cathode lamp) for each element to be analysed is required for the Atomic Absorption mode only. A Boiling burner using acetylene - air as the fuel is recommended for aqueous solutions.

The specific operating instructions supplied by the manufacturer of the instrument was followed. The general procedure includes : Choice of proper lamp, adjustment of lamp current, selection of proper monochromator wavelength and slit width, adjusting the fuel and oxidant for the flame to proper values, adjusting the burner and balancing the phototube- amplifier recorder system. Working standards were then introduced and calibration Curves constructed. With the working curve prepared, the samples were run.

A set of standards must be run each time a series of samples is run.

Preparation of Standard solutions[2]

All solutions were prepared from analytical reagent grade materials using de-ionised water.

Lead Stock Solution, 1mg/ml:

1.598g of lead nitrate was dissolved in dilute HNO3 (1 : 100) and made up to 1 litre with de-ionised water.

CopperStock Solution, 1mg/ml:

1.00g of copper flaskes was dissolved in 25ml of HNO_3, boiled and after removal of nitrogen oxides, the remainder was diluted with de-ionised water to make 1 litre.

Manganese Stock Solution, 1mg/ml:

1.00g of metallic manganese was dissolved in 10ml HNO3 and made up to 1 litre with de-ionised water.

Nickel Stock Solution, 1mg/ml:

1.000g of metallic nickel was dissolved in dilute HNO3, and then made up to 1 litre with de-ionised water.

Chromium Stock Solution, 1mg/ml:

5.124g of chromium chloride was dissolved in 2M Hcl and made up to 1 litre with de-ionised water.

Calcium Stock Solution, 1mg/ml:

2.497g of CaCO3 was dissolved in an excess of diluted Hcl and made up to 1 litre with de-ionised water.

Cobalt Stock Solution, 1mg/ml:

4.940g of cobalt nitrate was dissolved in 2M Hcl and made up to 1 litre with de-ionised water.

Zinc Stock Solution, 1mg/ml:

1.000g of metallic Zinc was dissolved in a slight excess of dilute Hcl and made up to 1 litre with de-ionised water.

Potassium Stock Solution, 1mg/ml:

1.907g of KCl was dissolved in de-ionised water to make up 1 litre.

Sodium Stock Solution, 1mg/ml:

Potassium Stock Solution, 1mg/ml:

1.907g of Kcl was dissolved in de-ionised water to make up 1 litre.

Sodium Stock Solution, 1mg/ml:

2.541g of Nacl was dissolved in de-ionised water to make up 1 litre.

Magnesium Stock Solution, 1mg/ml:

1.000g of metallic magnesium ribon was dissolved in 100ml of dilute Hcl (1:100) and deionised water was added to make 1 litre.

Iron Stock Solution, 1mg/ml:

1.000g of iron wire was dissolved in 25ml of HNO3 and after nitrogen oxides have been expelled, was diluted in de-inised water to make 1 litre.

Experimental Conditions For the Determination Of The Elements Using Atomic Absorption Spectrophotometer A 3400:

Zinc

Wavelength of most sensitive absorption line is 2138.6Å. A range of standards from 0 to 0.6ppm are prepared from the stock solution. Soil extractants are included to match the sample solutions.

Magnesium

Wavelength of most sensitive absorption is 2852.1Å. A range of standard from 0 to 0.8ppm are prepared from the stock solution. Sufficient $LaCl_3$ solution (BDH chemicals) are added to bring the concentration of La to 800ppm both in the sample and standards. Soil extractants are included to match the sample solutions.

Calcium

Wavelength of most sensitive absorption line is 4226.7Å

A range of standards from 0 to 2.0ppm are prepared from the stock solution. Sufficient stock $LaCl_3$ (BDH chemicals) solution are added to bring the concentration of La to 800ppm.

both in the sample and standards. Soil extractants are included to match the sample solution.

Manganese:

Wavelength of most sensitive absorption line is 2794.8 Å. A range of standards from 0 to 3ppm are prepared from the stock solution. Soil extractants are included to match the sample solutions.

Copper:

Wavelength of most sensitive absorption line is 3247.5 Å. A range of standards from 0 to 2ppm are prepared. Soil extractants are included to match the sample solution.

Chromium:

Wavelength of most sensitive absorption line is 3578.7 Å. A range of standards from 0 to 2ppm are prepared. Soil extractants are included to match the sample solution.

Lead:

Wavelength of most sensitive absorption line is 2170.0 Å. A range of standards from 0 to 5ppm are prepared. Soil extractants are included to match the sample solution.

Cobalt:

Wavelength of most sensitive absorption line is 2407.3Å. A range of standards from 0 to 2ppm are prepared. Soil extractants are included to match the sample solution.

Nickel:

Wavelength of most sensitive absorption line is 2320Å. A range of standards from 0 to 5ppm are prepared. Soil extractants are included to match the sample solution.

Iron:

Wavelength of most sensitive absorption line is 2483.0Å. A range of standards from 0 to 2.5ppm are prepared. Soil extractants are included to match the sample solution.

Sodium:

The determination of Sodium is carried out using flame emission spectroscopic technique. The wavelength used is 5890Å. A range of standards from 0 to 2.0ppm are prepared. Excess Cs and sufficient soil extractants are included to match the sample solution.

Potassium:

The determination of potassium is also carried out using flame emission spectroscopy technique. The wavelength used is 7664.9 Å. A range of standards from 0 to 2.0ppm are prepared. Excess Cs and sufficient soil extractants are included to match the sample solution.

The result of the preliminary analysis of six elements is shown in Table 3.

3 :

[illegible] chemical analysis of six [illegible] carried [illegible]

TABLE 3

Result of chemical analysis of six elements carried out on 15g bulk sample (mixture of Samples) of harmatta dust from 1979/80 collection using various digestion techniques:

Concentration In $\mu g\ g^{-1}$.

Sample	Pb	Cu	Mn	Ni	Cr	Co
1	145	60	232.5	85	150	137.5
2	90	45	332.5	500	140	140
2A	90	30	180.0	500	140	87.5
2A(0)	145	55	85.0	580	75	25.0
3	90	47.5	240	107.5	115	-
4	20	12.5	-	65	25	-
5	50	25	125	85	90	112.5
6.	62.5	48.75	235.5	75	-	95
7	20	45	195	75	90	105
8	117.5	20	195	500	195	192.5
9(0)	145	-	85	-	75	-
10(0)	117.5	50	125	412.5	75	105

Hydrofluoric acid - hydrochloric acid - nitric acid digestion, and Hydrochloric acid - hydrofluoric acid digestion give the highest values for Pb, Cu, Ni, and Mn.

Ashing of the residue on the filter paper is involved during the extraction procedure for hydrochloric acid - hydrofluoric acid - digestion. It is probable that contamination may arise from the ashed filter paper giving rise to higher concentration values observed in some cases e.g/ Nickel.

The organic solvent extraction performed; 2A(o), 9(0) and 10(0) using hydrochloric acid- hydrofluoric acid digestion is only suitable for Pb.

Hydrofluoric acid digestion sodium carbonate fusion- hydrochloric acid digestion is the most suitable extaction procedure for the determination of Cr and Co.

In view of the result of the preliminary analysis the properties of hydrofluoric acid is summarised below: Hydrofluoric acid attacks nearly all metals except gold and Platinium. Silica is dissolved and converted partly into Silicon tetrafluoride, and partly into hydrofluosilicic acid, $H_2 SiF_6$ - According to the reaction:

$SiO_2 + 4HF ____ 2H_2O + SiF_4$

$SiO_2 + 6HF ____ 2H_2O + H_2SiF_6$

Most metal oxides are attacked by the acid. Most of the oxides are transformed into fluorides and in many cases dissolved.

In the analysis of the Harmattan dust, hydrofluoric acid - hydrochloric acid - nitric acid digestion method is used for the extraction of some weekly samples. The result of the analysis is shown in Table 4, 5, 6 and 7.

A slight modification is made to the hydrofluoric acid hydrochloric acid digestion. This modified extraction technique given below is used for the monthly samples of the Harmattan dust.

Modified hydrofluoric acid - hydrochloric acid digestion method.

Reagents:

All solution were prepared with de-ionised water and analytical reagent grade materials, unless stated otherwise.

Sulphuric acid

Hydrofluoric acid - 40%

Hydrochloric acid, 6M prepared by diluting 200ml of HCl of

specific gravity 1.16 to 1 litre with de-ionised water.

Procedure: 0.5g of sample was placed in porcelain crucible and heated overnight to 400 - 450°C in a muffle furnace Gallen Kamp - o.PL. 500 KF. (0° - 1100°C).

The sample was cooled to room temperature and transfered with de-ionised, distilled water into Platinium crucibles. Excess of distilled water was evaporated in an oven and a few drops of distilled water, 5 drops of concentrated Sulphuric acid and 20ml of hydrofluoric acid were added.

The sample was heated on a water bath to dryness again.

After cooling, 10ml of 6M, Hcl was added and again heated until all salt have been dissolved.

The solution was transfered to 100ml flask and made up to the mark, after which was tranfeeed to polythylene storage bottles.

This method was used for the monthly samples of the harmattan dust. The result of this analysis is shown in tables 8 and 9.

The mean and the standard deviations of the readings are calculated. As shown in the table:

$\bar{X}$ = Mean value of the readings

N = No. of samples

S = Standard deviation

$\bar{X}$ is calculated from the formular:

$$\bar{X} = \frac{\sum_{i=1}^{n} Xi}{n}$$

and similarly S is calculated from the formular:

$$S = \sqrt{\frac{\sum_{i=1}^{n} (Xi - \bar{X})^2}{n - 1}}$$

TABLE 4

Elemental Concentration ($\mu g\ g^{-1}$) of some Harmattan dust samples collected*

Sample	Ni	Co	Cr	Mn	Na	K
ZDD1 14/12/79	140	22.5	61.25	320	3750	17625
ZDD1 1/2/80	300	57.5	125	495	4375	19250
ZDD1 8/2/80	202.5	37.5	81.5	362.5	4460	17325
ZDDII 15/2/80	240	66.25	95	487.5	3750	15665
ZDD1 22/2/80	280	62.50	120	510	3540	16380
ZDD1 29/2/80	205	56.60	45	272.5	2500	13690
ZDDII 14/3/80	390	57.5	121.25	257.5	2750	16625
ZDD1 2/5/80	168	72.50	151.25	268.75	4600	15500
n	8	8	8	8	8	8
$\bar{X}$	240.68	54.10	100.03	371.71	3715.62	16507.5
S	80.63	16.30	35.85	109.53	775.92	1653.20

*Zaria Dry Deposition method

Table 4 Cont'd .../2

TABLE 4 Continued - 2 -

Sample	Pb	Cu	Fe	Zn	Ca	Mg
ZDD1 14/12/79	142.5	31.25	4350	805	1625	4375
ZDD1 1/2/80	150.6	56.25	4750	990	3625	4125
ZDD1 8/2/80	205	70.0	7875	915	3305	4105
ZDDII 15/2/80	140	35.25	4435	875	2480	5205
ZDD1 22/2/80	165.0	67.0	3750	730	4630	4635
ZDD1 29/2/80	120.	35.0	3585	680	4845	3675
ZDDII 14/3/80	140	80.0	6135	780	3850	5790
ZDD1 2/5/80	117.5	37.50	3560	1000	4625	5875
n	8	8	8	8	8	8
$\bar{x}$	147.5	51.63	4805	846.87	3623.12	4723.12
s	27.80	19.12	1497.24	117.77	1131.52	816.31

TABLE 5

Elemental concentration ($\mu g\ g^{-1}$) of some Harmattan dust samples collected*

Sample	Ni	Co	Cr	Mn	Na	K	pb	Cu	Fe
KWD1 23/11/79	77.5	50	86.25	300	3750	16750	150	37.5	4125
KWD1 7/12/79	97	130	125	297.5	6750	14750	145	77.5	6135
KWD1 18/1/80	275	100	70	125	9875	18360	195	79.0	5985
KWDIII 26/1/80	132.5	41.25	92.5	257.5	8875	16125	150	60.0	5375
KWDIII 1/2/80	120	120	110	365	4750	16835	145	37.50	4540
KWDIII 16/2/80	257.5	110	130	437.5	6875	19500	185	52.50	4750
KWDII 22/2/80	310	61.25	120	397.5	6970	15890	138	55.0	4625
KWDIII 7/3/80	335	50	115	410	4375	16025	132	37.50	3750
KWD1 14/3/80	400	71.25	135	460	6890	13125	175	77.5	6375
KWDII 28/3/80	257.5	80	110	285	4775	17380	142.5	27.5	3890
KWD1 11/4/80	250	75.0	121.25	300	7125	12125	175	71.25	7875
KWDIII 9/5/80	185.0	41.5	123.75	312.5	3750	15285	142.5	75.0	6450
KWD1 30/5/80	310	97.5	137.5	467.5	9125	19400	210	85.0	5370
n	13	13	13	13	13	13	13	13	13
$\bar{X}$	231.30	79.05	113.55	339.6	6452.69	16273.07	160.38	59.44	5326.53
S	87.91	30.18	19.90	69.09	2052.19	2178.63	24.71	19.58	1203.58

*Kano Wet Deposition Method

Table 5 Cont'd/... 2

TABLE 5 Continued

Sample	Zn	Ca	Mg
KWD1 23/11/79	625	2375	3250
KWD1 7/12/79	865	5000	4375
KWD1 18/1/80	835	5100	3905
KWDIII 26/1/80	1037.5	5750	5625
KWDIII 1/2/80	735	3780	6125
KWDIII 16/2/80	937.5	4000	5500
KWDII 22/2/80	890	3240	5430
KWDIII 7/3/80	690	3655	4645
KWD1 14/3/80	587.5	4625	5125
KWDII 28/3/80	790	3950	4880
KWD1 11/4/80	745	4000	6125
KWDIII 9/5/80	685	4285	4275
KWD1 30/5/80	815	3935	4890
n	13	13	13
$\bar{x}$	787.5	4130.38	4934.6
s	127.64	861.96	848.82

TABLE 6

Elemental concentration ($\mu g\ g^{-1}$) of some Harmattan dust samples collected.*

Sample	Ni	Co	Cr	Mn	Na	K
K/ESA 19/10/79	235	80	95	522.5	3500	15650
K/ESA 26/10/79	195	67.5	92.5	375.0	2125	15625
KDD 30/11/79	88.0	75	59.0	320	4260	17535
KDD 11/1/80	190	37.5	71.25	332.5	3750	16850
K/ESA 8/2/80	95	75	95	545	5755	16050
KDD 8/2/80	115	66.25	85	375	4000	15835
K/ESA 29/2/80	240	57.5	80	350	2750	12300
KDD 18/4/80	362	105	157.5	460	8125	15375
KDD 2/5/80	240	77.5	96.25	382.5	4375	19875
FAO Standard	20.5	10.15	22.5	330	-	-
n	9	9	9	9	9	9
$\bar{X}$	195.55	71.25	92.38	406.94	4293.3	16121.66
S	87.6	18.2	27.47	82.31	1764.93	2010.42

* Kano Wet Deposition method

TABLE 6 cont'd

Elemental concentration ($\mu g\ g^{-1}$) of some Harmattan dust samples collected.*

Sample		Pb	Cu	Fe	Zn	Ca	Mg
K/ESA	19/10/79	142	69	4120	695	4905	5470
K/ESA	26/10/79	160	77.5	7500	812.5	2250	3625
KDD	30/11/79	148	52.0	4460	680	3670	4000
KDD	11/1/80	130	52.5	4750	740	4200	5080
K/ESA	8/2/80	152	48.50	5490	910	3455	3800
KDD	8/2/80	148	45.25	4875	640	5100	4670
K/ESA	29/2/80	148	31.25	4760	630	5125	3375
KDD	18/4/80	135	52.5	4895	635	4655	4735
KDD	2/5/80	160	42.5	3250	1062	3600	4250
FAO Standard		48.50	26.5	13065	94.0	-	-
	n	9	9	9	9	9	9
	$\bar{X}$	147	52.33	4900	756.0	4106.66	4333.8
	S	10.14	13.77	1155.17	147.59	954.57	702.39

* Kano Wet Deposition method

Elemental concentration ($\mu g\ g^{-1}$) of some Harmattan dust samples collected.*

Sample		Ni	Co	Cr	Mn	Na	K
ZWD 1	12/10/79	380	75.0	120.	167.5	8750	14000
ZWD 1	2/11/79	237.5	78,75	95	537.5	8875	18125
ZWD II	9/11/79	157.5	45	86.25	268.7	7875	19655
ZWD 1	16/11/79	212.5	28.75	92.5	265	5375	176 30
ZWD II	7/12/79	180	37.5	33.75	327.5	4750	16560
ZWD 1	25/1/80	257.5	75	95	487.5	4500	19250
ZWD 1	7/3/80	237.5	45	87.5	240	3000	17035
ZWD II	21/3/80	195	25	123.75	312.5	2750	16360
ZWD 1	28/3/80	132.5	28.75	105.0	247.5	2750	14875
ZWD 1	4/4/80	128	37.50	98.0	258.0	2750	16740
ZWD 1	11/4/80	150	83.75	62.5	267.5	3200	17380
ZWD 1	18/4/80	345	45	48.75	247.5	4750	17125
ZWD 1	25/4/80	132.5	66.25	87.5	230	3125	12500
	n	13	13	13	13	13	13
	$\bar{X}$	211.19	51.63	87.34	296.66	4803.8	16710
	S	80.15	21.13	25.75	103.65	2296.77	1984.97

* Zaria Wet Deposition

TABLE 7 cont'd

Elemental concentration ($\mu g\ g^{-1}$) of some Harmattan dust samples collected.*

Sample	Pb	Cu	Fe	Zn	Ca	Mg
ZWD 1 12/10/79	150	81.25	6250	9.5	4875	6625
ZWD 1 2/11/79	200	75	7430	830	2750	4625
ZWD II 9/11/79	185	77.5	5820	875	4590	3895
ZWD 1 16/11/79	165	27.5	3995	750	4950	4400
ZWD II 7/12/79	136	45.50	4630	625	4355	6335
ZWD 1 25/1/80	142.5	31.25	4255	755	3375	3375
ZWD 1 7/3/80	160	60	5395	710	2950	4360
ZWD II 21/3/80	155	30	3255	810	4675	3845
ZWD 1 28/3/80	132.5	31.25	4455	735	5280	3750
ZWD 1 4/4/80	136.0	59.0	4960	740	4675	4030
ZWD 1 11/4/80	142.5	81.25	5580	730	3890	5300
ZWD 1 18/4/80	217.5	71.25	7500	1095	2125	3000
ZWD 1 25/4/80	100	31.25	4275	1185	5270	4290
n n	13	13	13	13	13	13
	$\bar{X}$	157.07	54	5215.38	827.30	4135.38	4448.46
	S	31.74	21.87	1286.15	158.47	1026.72	1067.38

* Zaria Wet Deposition Method

TABLE 8

Elemental Concentration ($\mu g\ g^{-1}$) of some Harmattan dust samples collected*

Sample	Ni	Co	Cr	Mn	Na	K
K/10/79	215	66.0	92	482	7325	18636
K/11/79	195	140	118	476	6875	17985
K/12/79	235	126.0	138	500	6920	18125
K/1/80	180	168	132	460	5260	17380
K/2/80	130	134	114	452	5650	17560
K/3/80	200	148	162	512	8675	19653
K/4/80	245	120	114	492	7875	19360
K/5/80	295	86	108	292	3750	14825
FAO Standard	20.5	10.15	22.5	330	-	-
n	8	8	8	8	8	8
$\bar{X}$	211.87	123.5	122.25	458.25	6541.25	17940.5
S	48.83	33.15	21.36	70.03	1577.87	1494.44

*Kano monthly samples of the Harmattan dust.

Table 8 Continued ../2

Sample	Pb	Cu	Fe	Zu	Ca	Mg
K/10/79	143	49.0	5988	925	4805	4280
K/11/79	139	56.5	5100	835	3905	5120
K/12/79	170	69.0	6335	775	4190	3375
K/1/80	163	70.0	5415	1095	5320	4825
K/2/80	147	34.0	4315	1105	5636	3890
K/3/80	168	53.0	4485	1005	5025	5365
K/4/80	172	70.0	3750	695	3640	4630
K/5/80	136	39.0	4585	730	3430	4480
FAO Standard	48.50	26.5	13065	94.0	-	-
n	8	8	8	8	8	8
$\bar{x}$	154.75	55.06	4996.62	895.62	4493.12	4495.6
s	14.98	14.06	879.09	161.38	815.22	648.24

TABLE 9

Elemental Concentragion ($\mu g\ g^{-1}$) of some Harmattan dust samples collected.*

Sample	Ni	Co	Cr	Mn	Na	K
Z/10/79	270	140	78	516	6340	18935
Z/11/79	185	86	98	636	8875	15960
Z/12/79	205	126	112	428	7560	17785
Z/1/80	140	72	94	368	5860	17595
Z/2/80	115	32	100	344	4375	15865
Z/3/80	290	100	124	394	4750	14875
Z/4/80	330	60	92	379	7125	18890
Z/5/80	315	86	122	586	8875	19350
FAO Standard	20.5	10.15	22.5	330	-	-
n	8	8	8	8	8	8
$\bar{x}$	231.25	87.75	102.5	456.37	6720	17406.87
S	81.40	34.79	15.77	109.37	1708.03	1663.47

*Zaria monthly samples of the Harmattan dust

Table 9 Continued/... 2

Table 9 Continued - 2 -

Sample	Pb	Cu	Fe	Zn	Ca	Mg
Z/10/79	148	48.0	4630	880	2740	5605
Z/11/79	128	57.0	4825	895	5830	4285
Z/12/79	155	75.0	6385	675	3905	4355
Z/1/80	155	58	4230	790	3980	5295
Z/2/80	132	37.5	3250	920	1610	4630
Z/3/80	134	56.25	5450	690	3955	3000
Z/4/80	169	78	7680	825	1940	3860
Z/5/80	185	58	5580	940	4235	6705
FAO Standard	48.50	26.5	13065	94.0	-	-
	8	8	8	8	8	8
$\bar{X}$	150.75	58.46	5253.75	826.87	3524.37	4716.87
S	19.63	13.15	1360.007	101.48	1370.56	1139.08

2.6 Estimation of the Organic Components in Harmattan Dust

0.5g of the Harmattan dust is taken and extracted with benzene using a soxlet extraction apparatus and the result is given as the total amount of benzene soluble organic substances.

The percentages of the organic content of the Harmattan dust is found to vary between 4.04% to 13.62%.

TABLE 10

Percentages of the Organic Content

Sample	% of Organic Content
K/10/79	6.82
K/11/79	9.34
K/12/79	8.45
K/1/80	13.62
K/2/80	10.14
K/3/80	10.98
K/4/80	4.04
K/5/80	7.20
Z/10/79	11.85
Z/11/79	9.30
Z/12/79	8.86
Z/1/80	5.96
K/2/80	6.38
Z/3/80	4.18
Z/4/80	11.12
Z/5/80	9.44

2.7 X-Ray Diffraction Analysis

Procedure: Harmattan dust samples were used for the X-ray diffraction analysis. The oriented aggregates were analysed and diffractograms obtained from the philips X-ray instrument model PW1390 of the Department of Geology.

A typical X-ray diffractograms of the harmattan dust is shown in Figure 2.

The analysis of the spectra show that the major components of the dust is α - Quartz - SiO_2

Kaolinite - $Al_2 SiO_2O_5 (OH)_4$

Traces amount of Felspar, chlorite $(Mg_{10}Al_2 (Si_6Al_2)O_{20}(OH)_{16}$

Calcite $CaCO_3$;

FIGURE: 2
X-RAY DIFFRACTO GRAM
OF HAR MATTAN DUST

46°
45°
42.5°
40.5°
40°
39.8°
36.7°
35°
34°
28°
27°
25°
20°
15°
10°
5°

0 2 3 4 5 6 7

0 2 3 4 5 6 7 8

(1) (2) (3) (4) (5) (6)

PLAGIOCLASE FELDSPAR (ALBITE)

(3) ALKALI FELDSPAR.

— KAOLINITE

— MICA (?)

CHAPTER 3 :

DISCUSSION OF RESULTS.

3,1 Deposition Rates of the Harmatt an Dust Sample.

Matter is transfered from the atmosphere to the surface of the Earth by a number of processes during both wet and dry periods.[43,47]. During wet periods, transfer occurs mainly by scavenging (in - cloud and below cloud) and gravitational sedimentation of the precipitation elements.

During dry periods, matter in both gaseous and particulate phases is transfered by several processes including gravitational sedimentation, turbulent diffusion and molecular diffusion.

Buckets and bowl exposed in the airstream to collect dry particles have been used to investigate dry deposition. These techniques, while simple, are self - defeating in that all of them disturb the natural air flow.

Further particles can blow both in and out of a container in varying degrees depending on the design of the collector, the wind speed and the particle size.

Liquid is placed in the bucket to avoid loss of matter already collected.

Dry and wet deposition methods are used for the collection of the harmattan dust both in Kano and Zaria stations,between October and May (1979/80).

Table 1 shows the weekly variation of the deposition rates of the various methods.

The last three wet collections for Kano and Zaria stations have high deposition rates which signifies the commencement of the rain - 1st rain in Kano - 1st May 1980, and 1st rain in Zaria 28th April, 1980.

Table 11 below shows the total deposition rates for the various methods.

Wet deposition method show higher deposition rate compared to dry deposition method.

The deposition rate for the K/ESA (Ecological station) stands out clear.

Although this is a dry deposition, the result (118.27g/m^2) showed variation from the KDD (also dry deposition - 82.15g/m^2).

This can be attributed to the location of the KESA (Ecological station) and KDD (top of a building).

The later is set up 9m above ground level on the roof of a building on the campus of Bayero University, Kano, isolated from local soil dust movements.

The trap is a basin of 20cm deep and a surface area of $0.27m^2$ for collecting dust. The former is placed on the ground in the ecological study area of Bayero University which is surrounded by trees and shrubs. Dust particles freely settled on the leaves of these trees and shrubs.

Under windly condition, settled dust particles are easily blown over the surrounding giving the KESA a higher value than expected.

It is observed that the deposition rate for Kano station is higher than Zaria station. This is expected since the quantity of the deposited dust decreases with distance from the desert.

TABLE 11

Total deposition rates of various methods from 1979/80 collection:

Sample	Total deposition rate (g/m^2)
KWD1	167.72
KWDII	173.05
KWDIII	163.48
KDD	82.15
KESA	118.27
ZDDI	65.89
ZDDII	60.74
ZWDI	158.80
ZWDII	137.35

The start of the harmattan season coincides with the end of the wet season so that during (October to January) all grases abound and relative humidity levels are high thus minimising dust remobilisation. As the grasses die off relative humidity decreases and the total amount of deposited dust increases,[38] conditions become conducive to remobilization and secondary deposition. This process might be accetuated by grass burning during the latter part of the dry season adding coarser particles to the measured deposition.

Table 12 shows the breakdown of the monthly deposition rates. The histograms of the monthly deposition rates for the various methods are shown in figure 3 to 11.

Deposition rates generally increases from December to March (highest deposition rate in March). In April there is a general decrease in deposition rates.

This trend suggest the possibility of secondary deposition mentioned above.

The histogram of the KESA is more interesting. There is a gradual increase in the deposition rate from November to February and it gradually decreases again from February to April.

TABLE 12

Monthly Deposition rates of the harmattan dust in Kano and Zaria stations for the period October to April (1979/80)

Month	KWD 1	KWD II	KWD III	KDD	ZDD 1	ZDD II	KESA	ZWD 1	ZWD II
OCT.	2.1659	12.1823	2.9560	5.7869	3.3173	3.9616	9.7025	8.5703	2.0955
NOV.	14.6354	14.6919	15.0522	8.4457	7.7098	7.4767	11.8209	14.1248	14.3376
DEC.	12.9814	13.6544	14.5566	6.941	6.1056	5.418	13.3445	12.7624	12.3058
JAN.	23.1718	20.8217	20.0052	9.3897	9.1469	8.6799	14.3628	19.1971	18.03
FEB.	25.148	21.6754	23.4068	12.8911	9.7674	9.4696	14.9332	20.2916	19.6734
MAR.	27.8185	26.8963	27.4119	12.8347	8.9006	9.153	14.2905	26.3654	26.5085
APR.	23.5604	24.599	24.1195	11.0856	9.1994	9.29	12.58	23.4893	23.383
TOTAL	129.4814	134.521	127.5082	67.3747	54.147	53.44	91.03	124.8009	116.33

Figure 3

Monthly Deposition Rate for Kano Wet Deposition method 1.

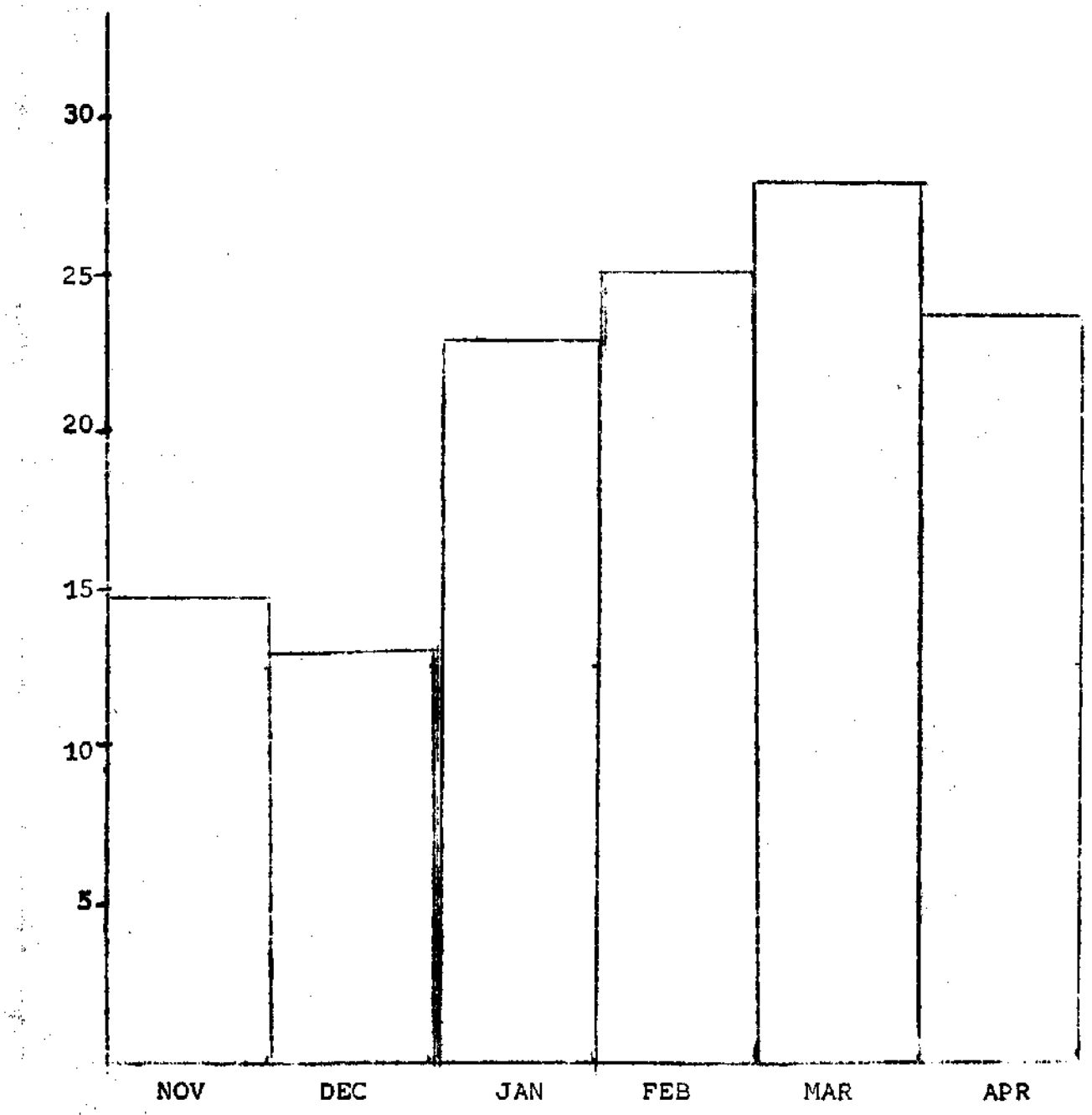


Figure 4

Monthly Deposition Rate for ^{K}ano Wet Deposition method II.

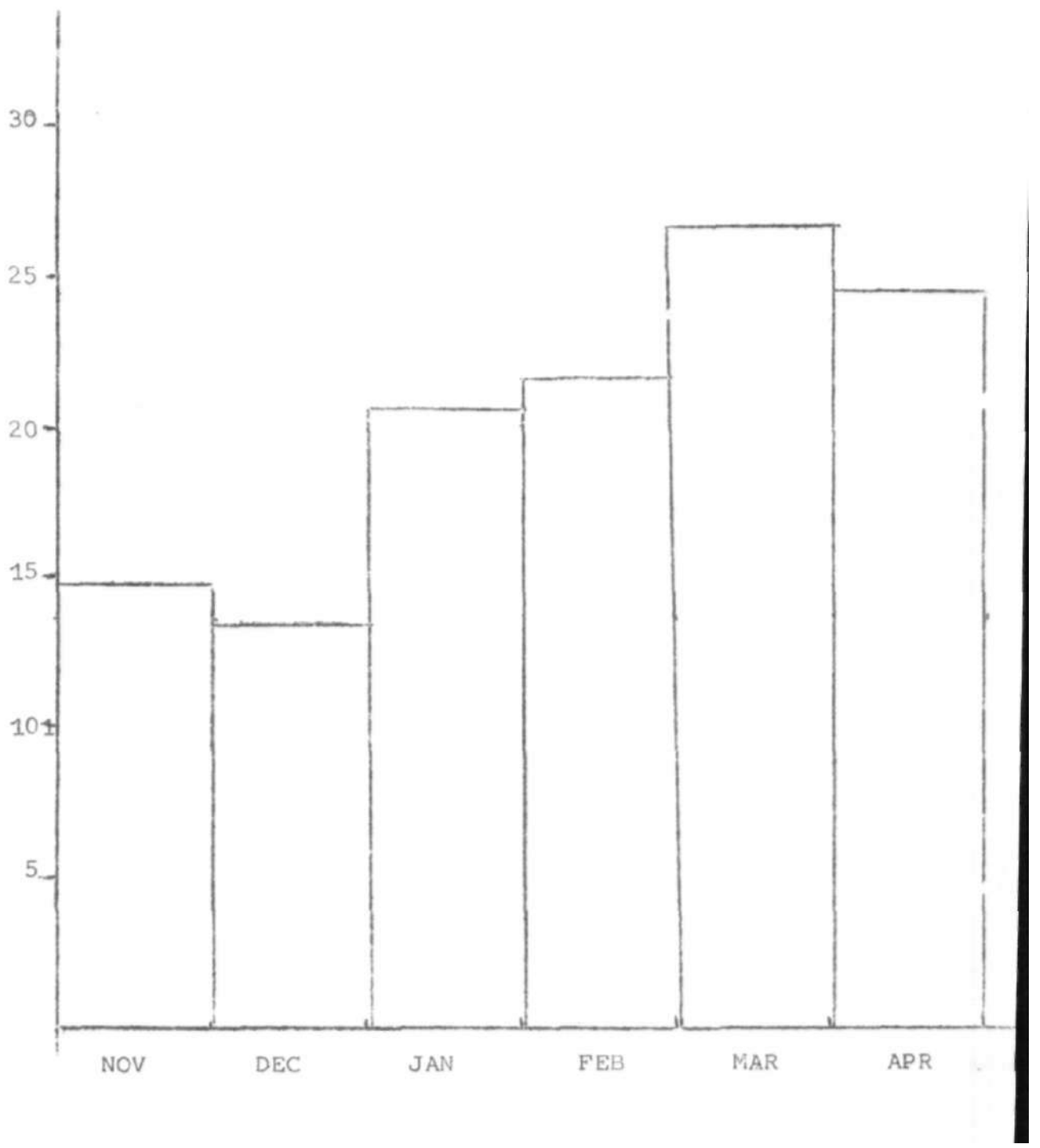


Figure 5

Monthly Deposition Rate for Kano Wet Deposition method III.

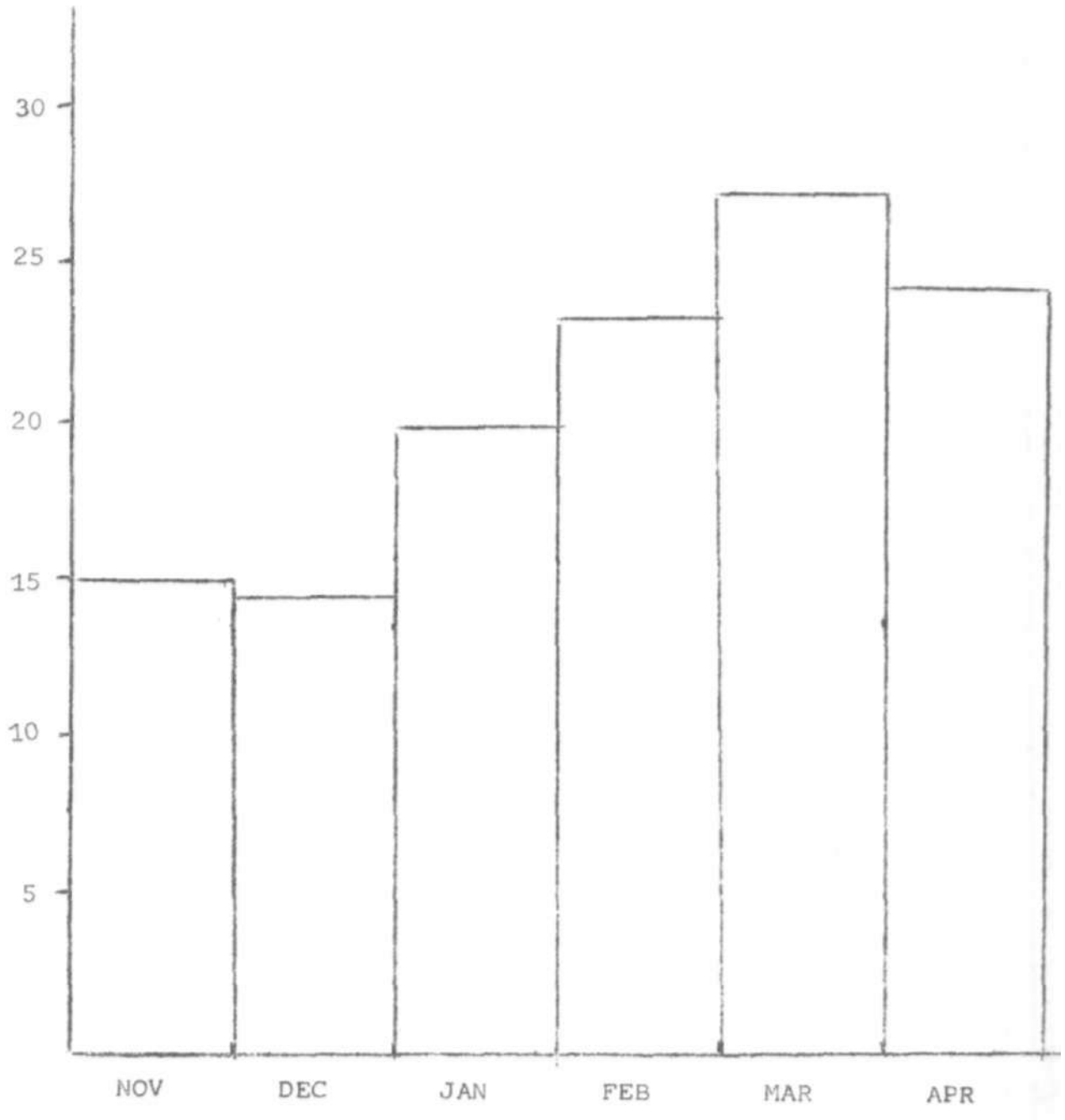


Figure 6

Monthly Deposition Rate for Zaria Wet Deposition method II.

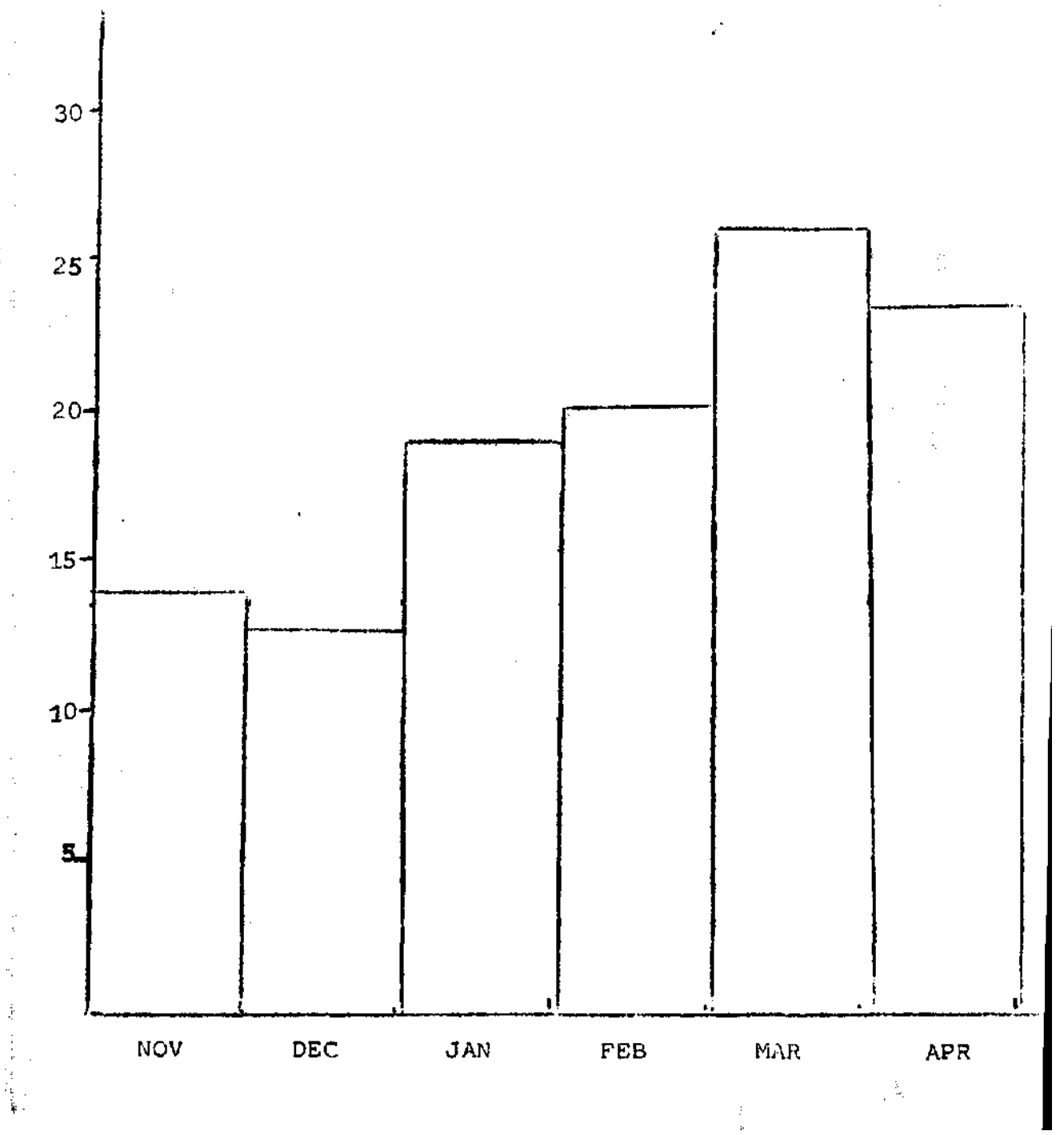


Figure 7

Monthly Deposition Rate for Zaria Wet Deposition method II.

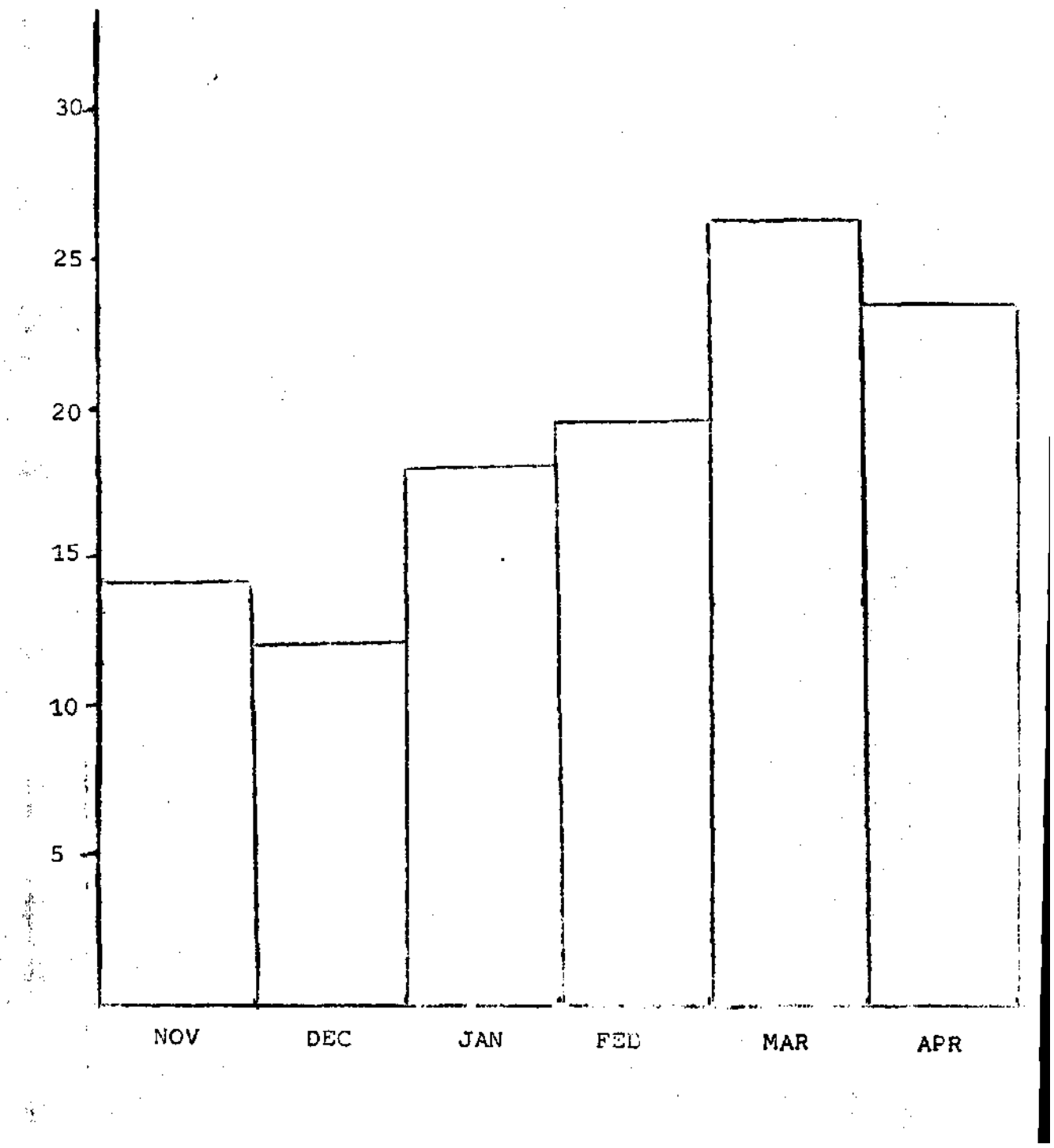


Figure 8

Monthly Deposition Rate for Kano Dry Deposition Method.

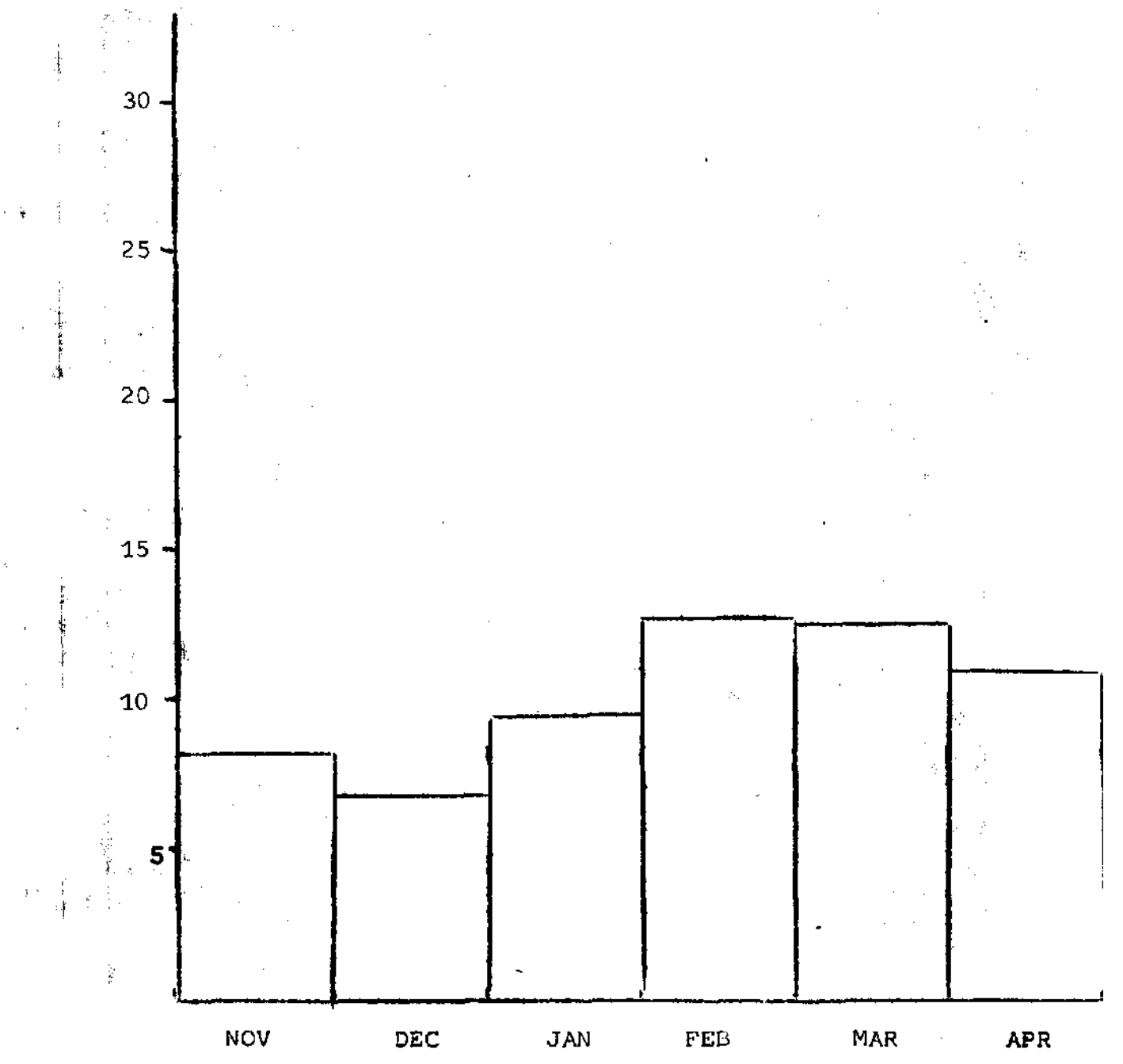


Figure 9

Monthly Deposition Rate for Zaria Dry Deposition method II.

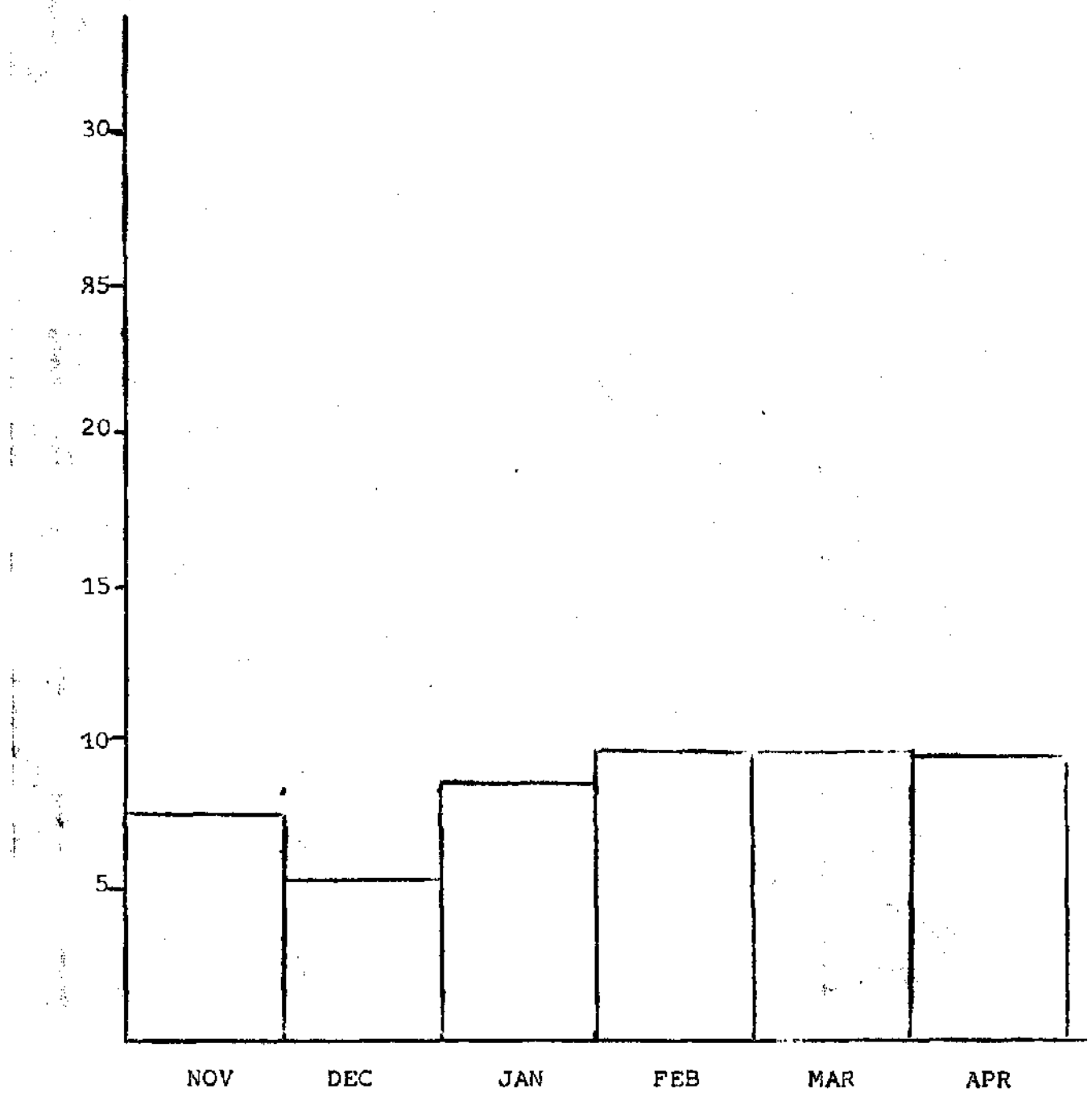


Figure 10

Monthly Deposition Rate for Zaria Dry Deposition method I.

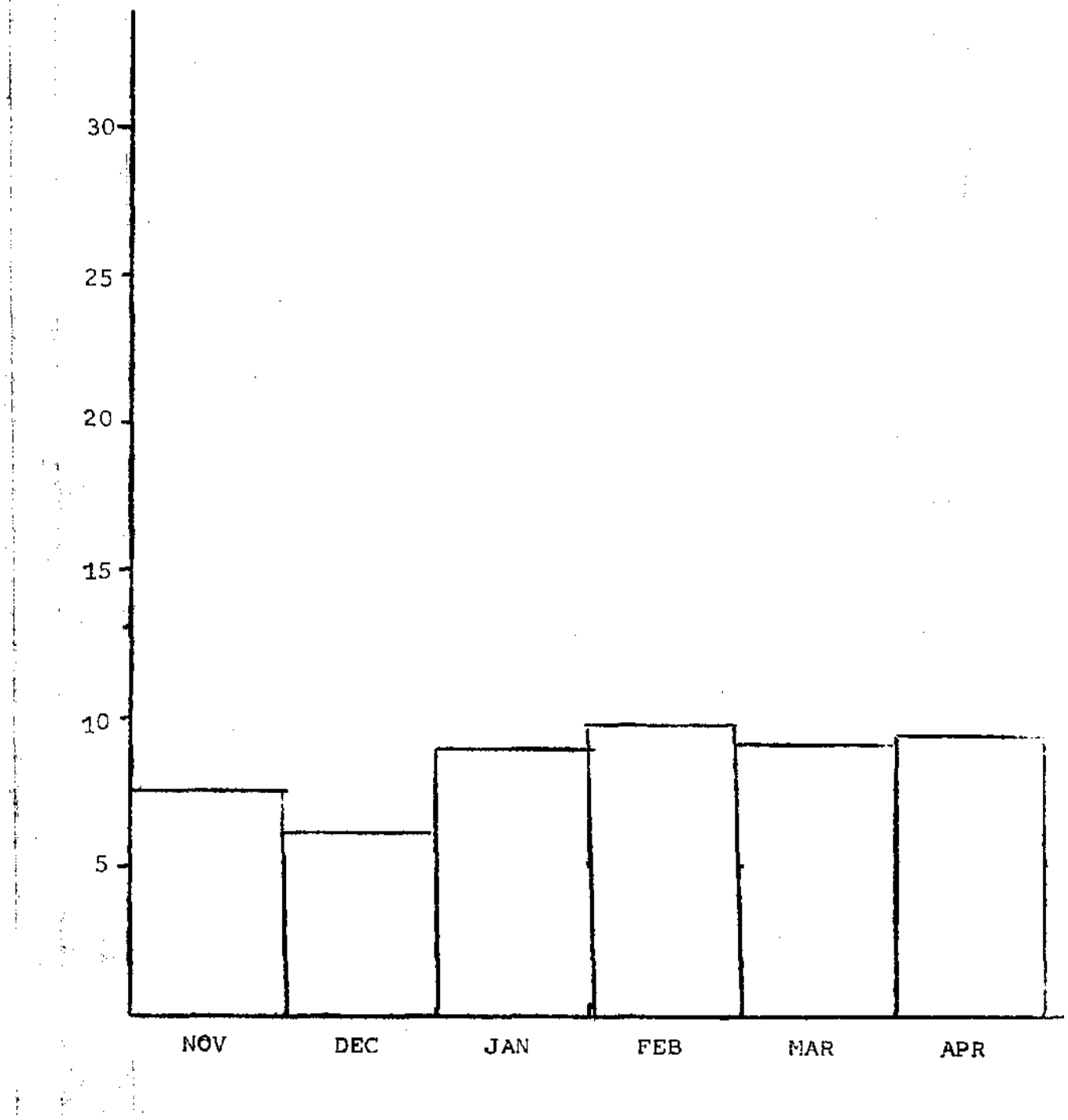
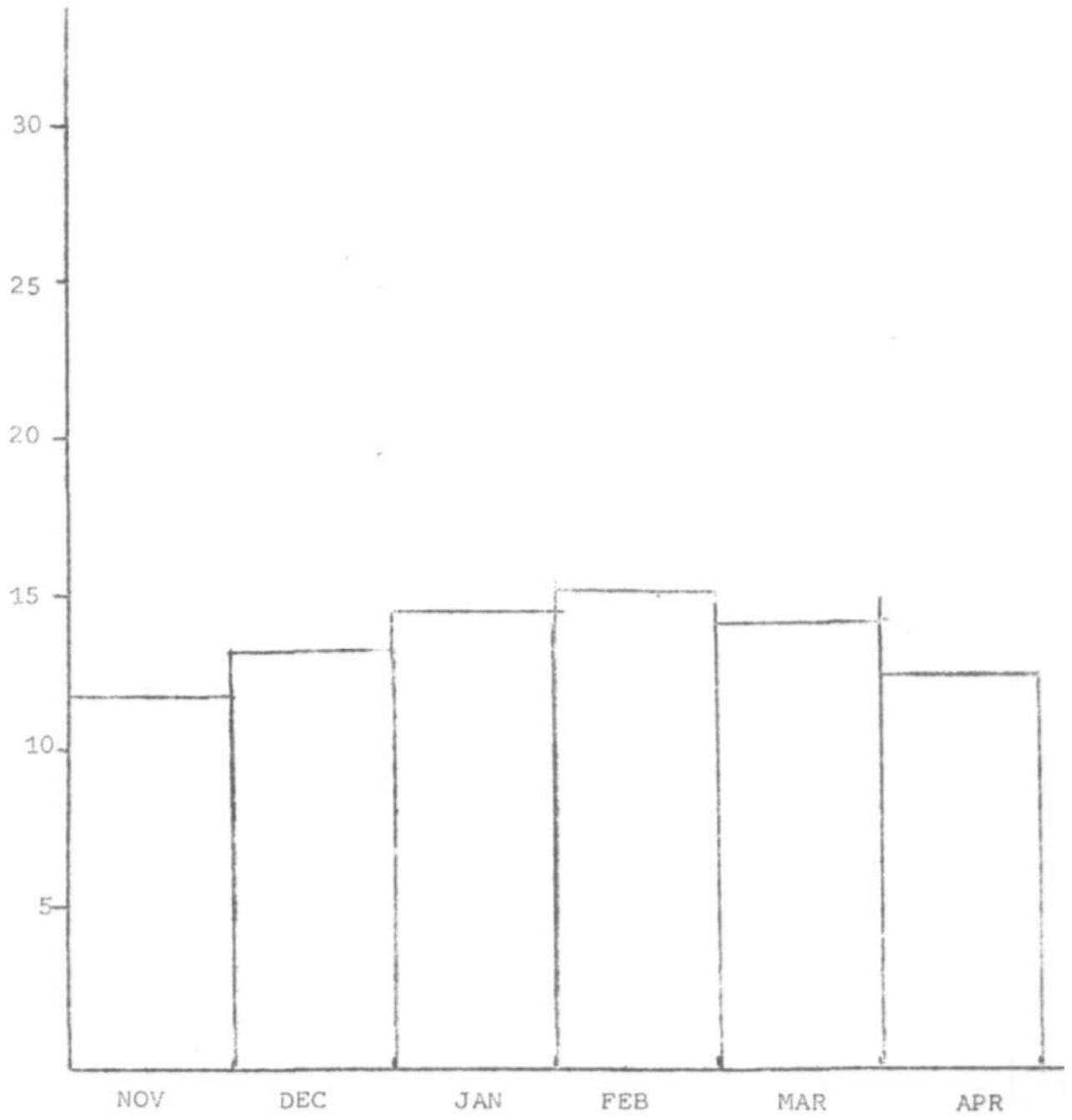


Figure 11

Monthly Deposition Rate for Kano Dry Deposition

(Ecological Station)



The harmattan dust particles may have relatively little influence on visibility.

Therefore, measured dust deposition rates during January-April overestimate the harmattan dust influx.

The relation between dust deposition and visibility can be used to predict expected deposition for each week.[37]

The difference between expected and measured deposition is assumed to be secondary deposition.

When the corrected data are derived (from the Visibility deposition regression line)[37], total Harmattan dust deposition at Kano during 1978-79 is $99.1 gm^{-2}$.

This figure represents a reduction in total measured deposition of 41.7% which is the amount of Secondary deposition.

Based on this assumption, the corrected total deposition rate is summarised in the table below.

Sample	Corrected deposition rate (g/m^2)
KWDI	97.78
KWDII	100.88
KWDIII	95.30
KDD	47.89
KESA	68.95
ZDDI	38.41
ZDDII	35.41
ZWDI	92.58
ZWDII	80.07

Harmattan dust deposition measurements made by Bromfield[38] in the same area during 1969-72 amount to 22.6gm^{-2} which is far lower than rates given here, and surprising during a time of drought.

Bromfield collected dust in a dry deposition gauge which can seriously underestimate deposition.[38]

Long-term total dust deposition monitoring 1979[29]

Period of study Jan. 5th-March 26th (82 days):

Station	Deposition g/m^2
Kano (B.U.K.)	39.1
Zaria (A.B.U.)	10.8
Jos (Uni)	2.1
Maiduguri (Uni.)	32.9

Clearly the amount deposited falls off rapidly as one moves south.

This is in line with satellite photography of dust plume spreeding.[48]

Comparison of day and night deposition rates are also made.

During the heavy harmattan of the period of Jan 20th- Jan 26th.

Samples are collected 8 a.m. and 8 p.m. giving a 12 hour collection with the following result:

The results show clearly that the dust is deposited more during the day than the night.

	Deposition g/m^2	
Day 8 a.m.-8 p.m.	Day Period	Night period
	0.802	0.435
	0.768	0.439
	0.674	0.276
	0.931	0.329
	1.079	0.182
	1.173	0.212

A 6-hourly collection[29] on March 10th/11th gives more detail.

		Deposition (g/m^2)
12.30 a.m.	7.00 a.m.	1.760
7.00 a.m.	12.30 a.m.	0.821
12.30 a.m.	6.30 p.m.	0.840
6.30 p.m.	12.30 p.m.	0.579
12.30 p.m.	6.30 p.m.	0.284

The cause of this daily variation is not clear. Convection currents during the heat of the day might be expected to keep dust in suspension but the reverse result is obtained.

More data is needed but these studies can only be done during heavy dust periods and they are very demanding on time and resources.

3.2 Particle Size Analysis.

Results of particle Size analysis carried out on two soil samples using the pipecte method and cal gon 0.1%^{m}/v as a dispersing agent showed that one can use 10g as well as 2g. This experiement is carried out because the amount of Harmattan dust is too small.

For fraction 63um to 2000um the sieveing technique is used.

Results obtained from Harmattan dust show that it is mainly composed of silty material.

According to results of particle size analysis of some Soils in Kano, there is no indication for Harmattan dust throughout the soils. The upper horizon are composed of loomy to sandy material.

Results shown in table 13 indicate the sand fraction to be major particle size in these soils. Due to this finding one could assume that there is not any Harmattan dust in these soils.

TABLE 13

Result showing percentages of particle size analysis carried out:

Sample	CLAY (1-2) um	FINE SILT (2-20) um	COARSE SILT (20-63) um	FINE SAND (63-106) um	MEDIUM SAND (106-212) um	COARSE SAND (212-2000) um
K2042 (10g)	9.3	3.9	44.2	23.8	16.4	2.4
K2042 (2g)	9.2	4.0	44.2	21.7	18.3	2.6
K2185 (10g)	6.5	1.9	31.7	43.1	9.6	7.2
K2185 (2g)	6.5	3.5	30.1	43.6	10.5	5.8
Harmattan Dust						
KDD (2g)	9	25	59	5	2	0
ZDD (2g)	9.2	27	57	4.8	2	0
Other Soil in Kano area A - horizon						
1	8	3	14	46	20	9
2	7	3	15	54	13	8
3	7	8	18	37	17	13

3.3 Extraction Methods :

Eight different methods of extraction are investigated. The objects of the organic solvent extraction in the preliminary analysis are :

(i) eliminary of anions and interfering element. ... t,

(ii) Enhancement of sensitivity by the organic solvent effect, and

(iii) concentration of the sample.

The effect of organic solvent extraction does not show a marked enhancement in the readings obtained in the preliminary analysis. The use of muffler furnace alone in the ashing process is not sufficient, but when it is used in conjunction with the sulphuric acid treatment, it becomes a very important piece of equipment in the preparation of sample solutions.

Three methods are used for the extraction of the Harmattan dust.

Hydrofluoric acid - hydrochloric acid - nitric acid digestion method is used for the extraction of some weekly samples; a modified hydrofluoric acid - hydrochloric acid digestion method is used for the monthly samples of the harmattan dust, and hydrofluoric acid digestion - Sodium Carbonate

fusion - hydrochloric acid digestion method is found to be the most suitable extraction procedure for the determination of Cr and Co.

3.4 Elemental Concentration in Harmattan Dust Samples:

There seems to be no uniformity in the elemental concentration of the Harmattan dust both in Kano and Zaria stations to allow for meaningful discussion.

However the variation in concentration of the twelve elements determined is summarised in Table 14

TABLE 14

Variation in concentration of the Twelve Elements Determined:

Element	Concentrations ($\mu g g^{-1}$)		
Ni	77.5	-	400
Co	22.5	-	168
Cr	33.75	-	162
Mn	125	-	636
Na	2125	-	9875
K	12125	-	19875
Pb7	100	-	217.5
Cu	26.5	-	85.0
Fe	3250	-	7875
Zn	625	-	1185
Ca	1610	-	5830
Mg	3000	-	6705

From this table the elements: Ni, Co, Cr, Pb and Cu can be grouped as trace elements ($<500\mu gg^{-1}$) and Ca, Fe, Zn, K, Mg, Na, and Mn as major elements ($>500\mu gg^{-1}$).

The calculated mean values ($\bar{X}$) and the standard deviations (S) of the elemental concentration of the Harmattan dust sample for the Kano and Zaria wet and dry collections are summarised in Table 15.

A discussion of the elemental concentration in terms of "enrichment factor" Ef, is discussed in 3.5

TABLE 15

Mean Valves and Standard Deviation of the Elemental Concentration in Harmattan Dust

	ZDD Weekly analysis		ZWD Weekly analysis		Zaria Monthly analysis	
Element	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Ni	240.68	80.63	211.19	80.15	231.25	81.40
Co	54.10	16.30	51.63	21.13	87.75	34.49
Cr	100.03	35.85	87.34	25.72	102.5	15.77
Mn	371.71	109.53	296.66	103.65	456.37	109.37
Na	3715.62	775.92	4803.8	2296.77	6720	1708.03
K	16507.5	1653.20	16710.38	1984.97	17406.87	1663.48
Pb	147.5	27.80	157.07	31.74	150.75	19.63
Cu	51.63	19.12	54	21.87	58.46	13.15
Fe	4805	1497.24	5215.38	1286.15	5253.75	1360.007
Zn	846.87	117.77	827.30	158.47	826.87	101.48
Ca	3623.12	1131.52	4135.38	1026.72	3524.37	1370.56
Mg	4723.12	816.31	4448.46	1067.38	4716.87	1139.08

Mean Valves and Standard Deviation of the Elemental Concentration in Harmattan Dust

	KDD Weekly analysis		KWD Weekly analysis		Kano Monthly analysis	
Element	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Ni	195.55	87.6	231.30	87.91	211.87	48.83
Co	71.25	18.2	79.05	30.18	123.5	33.15
Cr	92.38	27.47	113.55	19.90	122.25	21.36
Mn	406.94	82.31	339.6	96.09	458.25	70.03
Na	4293.3	1764.93	6452.69	2052.19	6541.25	1577.87
K	16121.66	2010.42	16273.07	2178.63	17940.5	1494.40
Pb	147	10.14	160.38	24.71	154.75	14.98
Cu	52.33	13.77	59.44	19.58	55.06	14.06
Fe	4900	1155.17	5326.53	1203.58	4996.62	879.09
Zn	756.0	147.59	787.5	127.64	895.62	161.38
Ca	4106.66	954.57	4130.38	861.96	4493.12	815.22
Mg	4333.8	702.39	4934.6	848.87	4495.6	648.24

3.5 Enrichment Factors in Air.

The abundances of many elements in the atmospheric aerosol are controlled by the crustal aerosol. This can be seen most easily by enrichment factor analysis, that is by calculating the enrichment factor of each element in the aerosol relative to the crust and some reference element. This is usually done for an element by using the following formula:

$$\text{Aerosol Crust Enrichment Factor} = \left(\frac{\text{Concentration of element X}}{\text{Concentration of reference element}}\right)_{\text{aerosol}} \Big/ \left(\frac{\text{Concentration of element X}}{\text{Concentration of reference element}}\right)_{\text{crust}}.$$

Innprinciple any of several elements (Si, Al, Fe, Ti, Sc.....) could be used for the crustal reference element, but Al is the most common choice. Because it is relatively easily determined and lacks major pollution sourses.

Fe is the next most common choice.

The crust reference material "crust" ought to be soil, probably desert soil, but it is usually taken to be average crust (i.e rock) because so much better data are available for rock than for soil. The composition of crust is taken from average calculation by Mason[27] (1966)

Iron is chosen as the reference element because it is the only one determined out of the other reference elements.

The enrichment factor E_{fe} is then defined as

$$E_{fe} = \frac{(X_{/fe}) \text{ aerosol}}{(X_{/fe}) \text{ crust}}.$$

The monthly and weekly arithmetic mean of the concentration of the 12 elements determined are used in the calculation of E_{fe}.

The arithmetic mean of the various elements are shown in Table 16 and 17

TABLE 16

Arithmetic Mean of the Concentrations ($\mu g\ g^{-1}$) of the Elements Determined for Zaria station

Element	Monthly Analysis	Weekly Analysis
Ni	231.25	222.40
Co	87.75	52.57
Cr	102.50	92.17
Mn	456.37	341.45
Na	6720.00	4390.71
K	17406.87	16633.09
Pb	150.75	153.42
Cu	58.46	53.05
Fe	5253.75	5059.04
Zn	826.87	834.79
Ca	3524.37	3940.23
Mg	4716.87	4553.09

TABLE 17

Arithmetic Mean of the Concentrations ($\mu g\ g^{-1}$) of the Elements Determined for Kano Station.

Element	Monthly analysis	Weekly analysis
Ni	211.87	216.68
Co	123.50	75.86
Cr	122.25	104.89
Mn	458.25	367.16
Na	6541.25	5569.31
K	17940.50	16211.27
Pb	154.75	154.90
Cu	55.06	56.53
Fe	4996.62	5152.04
Zn	895.62	774.60
Ca	4493.12	4120.68
Mg	4495.60	4688.86

The enrichment factors of the elements determined in Kano and Zaria stations (calculation based on average amounts of the elements in crustal rocks[27]) are tabulated in Table 18.

Six elements : Ca, Fe, Mg, Mn, Na, and K, have enrichment factors between 0.5 and 7. Four elements Cu, Cr, Coand Ni have enrichment factors between 8 and 50, while Zn and Pb have enrichment factors between 100 and 120.

Low enrichments close to unity imply a predominantly direct terrestrial origin.

The enrichment factors of the elements, basing the calculation on average amounts of elements in some soil sample around Zaria is shown in Table 19.

The high enrichment factors for some elements suggest that the harmattan dust though to originate from the Faya Largeau area in the Chad Basin (Fig. 1) are richer in these elements.

This calculated enrichment factors show that the harmattan dust is richer in Zn, Mg, Ca, Na and K.

Table 20 show the comparison of enrichment factors of Zaria aerosol particulates with other measurements.[28] This comparison is particularly valuable.

TABLE 19

Enrichment Factors (E_{fe}) of the elements in the Harmattan dust of Zaria station (calculation based on average amounts of elements in some soils sample[40] around Zaria)

Element	Enrichment Factors(E_{fe})
Pb	1.42
Cu	0.91
Fe	0.99
Mn	4.41
Zn	30.59
Mg	21.89
Ca	18.72
Na	19.91
K	49.89
Cr	1.11

TABLE 20

Comparison of the enrichment factors of Zaria aerosol particulates with other measurements

Element	Zaria	N. Sudan	S.Sudan	Harwel	Liege	Chicago
Co	27.21	0.71	0.50	2.20	2.00	1.70
Cr	1.11	0.92	2.70	7.10	5.20	3.50
Mn	4.41	0.62	0.21	3.20	1.70	9.00
Na	19.91	0.28	0.37	4.30	0.44	0.23
Zn	30.58	7.90	12.00	379.00	784.00	182.00

because ofthe difference in the method of collection of the samples.

Giant size particles which freely settled are collected in Zaria but a high volume sampler constructed by Rothroe and Mitchell[28] is used for the other determinations.

The higher values of Zn, enrichments at Harwell[28], Chicago, and Liege compared to Kano and Zaria can be explained by the fact that these cities are more urbanised than Zaria and there is the tendency of industrial processes in these areas.

The enrichment of Co and Na is higher in Kano and Zaria compared to N. Sudan, S. Sudan, Harwell, Liege and Chicago. This can be attributed to the differences in the particle size ranges of the aerosol particulate. The particle size ranges of the harmattan dust vary between 1-212um. High volume sampler is used for the collection of dust whose elemental concentration is determined at Harwell, Chicago and Liege compared to Kano and Zaria, where the dust is allowed to settle freely. There is the possibility of adsorption of metals by the giant particles giving rise to high enrichment factors for Co and Na.

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Mn and Cr show slight variation in the enrichments of the places compared.

No data is available for the comparison of enrichments for other elements.

3.6 Physiological Effects of Harmattan Dust

It is very difficult to demonstrate chronic effects caused by continued exposure to air pollution.

However, air pollution episodes with extremely high concentrations have been found to cause acute sickness and death.[54,55]

Gaseous and particulate irritants are intercepted by the cilia, which are hairlike cells that protect the air tracts.

When the insult is too large, this protective mechanism breaks downand the pollutants penetrate deeply into the bronchioles and alveoli, the tiny air sacs deep in the lung.[53]

If the insult continues year after year in large enough concentrations then any one of the following major chronic diseases may develop.

Asthma:

An asthmatic attack consists of the narrowing of the bronchioles, which is caused by a muscle spasm, an enrichment of the mucuous membrane, and by abundant mucuous secretions.

Bronchiotis and Emphysema:

The diagnosis of bronchiotis is justified, when the sufferer has a chronic cough with sputum lasting for at least four weeks.

In emphysema the patients air sacs or alveoli become over extended and eventually break down.

Both Bronchitis and emphysema induce shortness of breath in patients.

In advanced stages they are unable to blow out a lighted match only a few inches away from their mouths.

Lung Cancer:

Cancer is produced by uncontrolled cell growth. Lung cancer is the abnormal and uncontrolled growth of cells which usually originates in the bronchial mucuous membrane.[55] A large number of carcinogenic (Cancer producing) substances are known. The best known is perhaps the 3,4, benzopyrene (Ba P), a polycyclic hydrocarbon.

They are present in the air of cities and industrial areas.

They result from incomplete combustion and are present in large quantities in automobile exhausts, cigarette smoke, and industrial combustion processes. However large urban areas as compared with smaller urban areas have a higher rate of lung.cancer.

In general, irritation of the respiratory epithelium causes reflex broncho-constriction.[53,54] Irritants in the nose change breathing, increase blood pressure and slow the heart,[31] and possibly change pulmonary vascular resistance, which may complicate any primary reflex on the air ways.

3 . 7 The Functions of Trace Elements in Plants:

At the present time the following trace elements are known to be essential for the growth of plants:
Fe, Cu, Zn, Mn, Co and Na. Not all of these elements are universally required by plants but all of them have been shown to be required by some plant.

The classification of essential mineral element into :
(i) major or macro element and
(ii) minor element, trace element reflects a large or a small requirement of these by plants.

Although this may be aconvenient subdivision, it is arbitrary and has obvious limitations. Thus, for example, Ca, is essential in large amounts for higher plants, whereas for micro organisms it is required at mush smaller levels and could therefore be regarded as trace elements. A number of the essential trace elements for the growth of micro organisms and plants are transition metals, Viz. Fe, Zn, Cu, Mn, Co and V, which have electronic structures with distinct physical and chemical properties. These include variable oxidation states, complex formation, metallic nature and catalytic activity.

Proteins that possess Fe - S clusters as active sites have been isolated from a wide variety of bacteria, plant and animal sources and are usually known as ferredoxins. These non-haem Fe =S proteins, which have small molecular weights, are involved in key metabolic events such as N_2 Fixation , photosynthesis, electron transfer enzymes and hormone biosynthesis.[32]

In green plants, components of the respiratory chain located in the mitochondria are similar to those found in the animal system.

Various-haem- iron compounds are important respiratory electron carriers but these differ in detail from those in animal mitochondria.

Special cytochromes are present in chloroplasts.

Cobalt is essential for N_2 fixation by free-living bacteria, blue- green algae and symbiotic systems.

In root nodules the metal requirement is usually associated with the production of cobamide compounds by the rhizobia.

Cobamide coenzymes are required for metabolic processes of the bacteroids, especially for the enzymes methyl malonyl CoA isomerase.[34]

Knowledge of the functional role of Zn as a component of an enzyme is incomplete. It differs in many respects from Fe. Thus Zn enzymes are colourless, and the atom has no unpaired electrons at ambient temperature so that it has one stable state insolution.

The metal is usually tightly bound to the apoenzyme and can be removed only with severe chemical treatment.

It forms strong complexes with radicals of polar groups containing oxygen, nitrogen and Sulphur.

The oxidases catalysing reactions that reduce both atoms of molecular oxygen to water, namely cytochrome C oxidase, as-corbate oxidase and laccase, all contain Cu.[35]

The catalytic unit of cytochrome C oxidase is thought to contain two distinct forms of Cu in addition to cytochrome a.

There are various forms[36] of Cu present in laccase, i.e two Cu^{2+} types as well as a diamagnetic form consisting of a strongly coupled $Cu^{2+} - Cu^{2+}$ pair.

Arginase and phospho transferase are two Mn - dependent enzymes. It is also known that this element substitutes for Mg in many of the ATP - dependent enzymes of glycolysis.

In addition, Mn appears to participate in the O_2 - evolving system of photosynthesis and there are reports that the elements is required for glycollate formation in green algae.[37]

The functions of Na in plants metabolism are not known with any certainty.

Experiments with radioactive ^{24}Na indicate that the element is present in various combined forms in plants; one form is readily exchangeable; with all cations, whereas the other type exchanges with Na but only with difficulty with Ca, K amd Mg.

3.8 Conclusion

It is clear that the mobilization of Harmattan dust in the Sahara and its subsequent transport through the atmosphere well beyond the Sahara is a natural process that has been going on for a long period of time.

Wet deposition method show higher deposition rate compared to drv deposition method. The deposition rate of harmattan dust for Kano station is greater than that for Zaria station. The particle size analysis show that Harmattan dust is mainly composed of silty material.

Ni, Ci, Co, Cr, Pb and Cu occur in trace amount in the Harmattan dust and Ca, Fe, Zn, k, Mg, Na and Mn as major elements.

Six elements Ca, Fe, Mg, Na, Mn and K have enrichment factors between 0.5 and 7.

Cu, Cr, Co and Ni have enrichment factors between 8 and 50, while Pb and Zn have enrichment factors between 100 and 120.

Approximately one-half of the elements determined in the harmattan dust occur in near-crustal proportions, and are probably soil derived. Deserts are likely to be the main contributors.

3 . 9 Scope For Further Work

The following further studies are proposed:

(i) Studies on the methods for dust deposition, including comparisons between different methods.

(ii) Analysis of other elements not determined in the present studies.

(iii) Regular observations by high volume samplers of suspended particulate matters at all regional stations and at a selection of climatological stations in Nigeria.

(iv) Wind observations at suitably distributed stations over Nigeria for establishment of the relationship with air borne dust frequency.

(v) Investigation of the chemical and mineralogical composition of the Harmattan dust as a function of particle size.

3 . 10 *Suggestions*

It is essential that in all cases sufficient reserve samples should be stored for future research and follow up studies. It is most essential that the sampling be done by scientifically trained personel and that it should be supplemented by mapping expeditions carried out by a team of soil Scientists, geologists and mineralogists.

Again, this programme should be organised in such a way as to obtain maximum support from the appropriate international organisations.

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