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Trace Metals and Mineral Composition of Harmattan Dust Haze in Ilorin City, Kwara State, Nigeria

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ABSTRACT: Trace metals and mineralogical composition of harmattan dust haze was carried out on samples collected at Ilorin (8^0 32'N, 4^0 34'E) a guinea Savanna African City located at the central state of Nigeria. These dusts were gathered at different locations using clean Petri-dishes and plastic bowls of 10cm in diameter. These were analyzed using X-ray Florescence (XRF) and Particle Induce X-ray Emission (PIXE) machine. The average concentration of the metals was (13351.75±45) mg/kg and minerals (7.22%).The mean soil content of the total size of particles for the harmattan season for the station was calculated to be1.79765 μg/m^3. In conclusion, it was observed that harmattan dusts that blow across Nigeria predominantly comprise quartz and high elements.

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During the period of this study (November to March), the West African region experiences the prevailing north-easterly wind regime known as Harmattan (Falaiye *et al*., 2003). Harmattan dust lifting, transportation and deposition, occurs naturally (Kalu, 1974, Falaiye *et al*., 2013).This could be as a result wind transportation that blows the dust from the source and deposition along the trajectory path (Falaiye *et al*., 2017).

It has been observed that harmattan season begins from November to March of the following year. This could be as result of dust that emanate from the Sahara desert which transports the dust by wind. Junge (1979) reported that on the average, it takes about twenty-four hours for the harmattan to reach the Northern part of Nigeria. As reported by Aweda *et al.,* (2017), elements present in the harmattan dust comprise light and heavy metals. Bertrand *et al*., (1979) account for the dust particles deposited over the region where dust plumes predominantly originated from the Bodele depression in the Chad Basin.

MATERIALS AND METHODS

Minerals and Trace Metals analysis was carried out on harmattan dust samples gathered over Ilorin, Nigeria. This process was done using clean Petri-dishes and plastic bowls of 10cm in diameter which were exposed on the ground level (half a metre above ground) and an elevated platform (five metres) above the ground level in twelve different locations around Ilorin metropolis including the University of Ilorin campus for five months (November to March). The samples were stored in clean desiccators prior to the analysis in order to avoid contamination. This followed what was reported by Falaiye *et al*., 2017and Falaiye *et al*., 2013.

The analysis was carried out using PIXE (Particle Induced X-ray Emission) and XRF (X-Ray Fluorescence) to determine the minerals and the trace metals present in the samples gathered across the selected locations. These were done at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria.

Site Location: As reported by Falaiye *et al*., 2013 Ilorin (8°32' N, 4°34' E), a guinea savanna African central state of Nigeria in West Africa, is in the transition zone between the deciduous forest of the south and the savannah of the north. Precisely, Ilorin is located at the upper tip of the guinea-savannah zone with a mean monthly average temperature of about 30.2º C and average annual rainfall of about 873 mm (Olaniran, 1991a,b) as shown in figure 1.

RESULTS AND DISCUSSION

Elemental analysis for Ilorin: Harmattan dust samples collected at Ilorin show that some elemental

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concentrations are present in the samples as shown in the table 2.

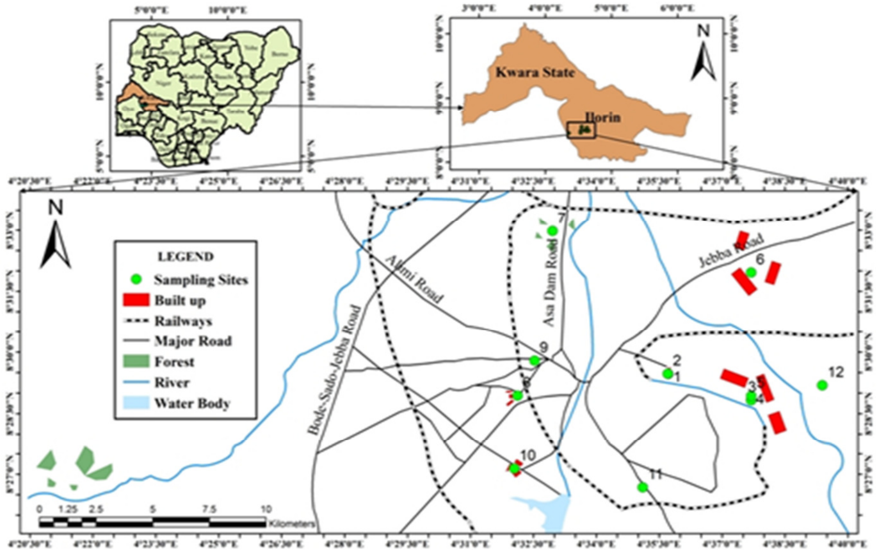

Fig. 1.0: Map of Ilorin showing the sampling site. Source: Falaiye, *et al*. (2017)

Table 1: Geographical Characteristics of the Ilorin

Location Number	Location	Latitude (^{0}N)	Longitude (^{0}E)	Altitude (m)	Average Annual Rainfall(mm)	Climatic classification	Vegetation
1	Block 4 Unilorin	8.4911	4.5952	303.89	1217	Tropical hinterland	Guinea Savanna
2	Works Department Unilorin	8.4912	4.5951	303.28			
3	Oke-Odo	8.4805	4.6282	284.53			
4	Tanke Tipper Garage	8.4804	4.6282	281.94			
5	GRA	8.4822	4.6283	285.92			
6	Zango	8.5327	4.6282	291.89			
7	Taiwo	8.5497	4.5493	303.89			
8	Saw mill	8.4823	4.5354	302.98			
9	Gari-Alimi	8.4965	4.5422	303.78			
10	Oja-Oba	8.4524	4.5341	252.98			
11	Olunlade	8.444698	4.585178	333.00			
12	Post Office	8.4865	4.6565	300.56			

Source: Falaiye et al., 2017

The elements present include Cu, Zn, Fe, Pb, Ca, Cr, Mn, Ni, As, K, Ti, Mo, V, Sr, Zr and Ce. They were observed in the samples collected at Ilorin using XRF machine at OAU Ile-Ife. It was observed that Fe has 113086mg/kg and 52.94% concentration value of the harmattan dust samples collected at Ilorin; it was followed by Ca with value of 42314mg/kg and 19.81% concentration value of the sample. K has 42030mg/kg concentration value with 19.67% value of the elemental concentration. Ti has 8719mg/kg with 4.08% concentration present in the sample. More so, Mn has 3479mg/kg with 1.63% concentration present in the sample. Zn has 875mg/kg with percentage concentration of 0.41% present in the sample collected. Ce has 688mg/kg with 0.32% concentration. Zrhas 673mg/kg with 0.32% of concentration value. V has 648mg/kg with 0.30% present in the sample collected. Pb has 260mg/kg with 0.12% of concentration present in the sample. Ni has 217mg/kg with 0.01% while Cu has 193 mg/kg with 0.09% of concentration. Sr has 69mg/kg with 0.03% of concentration. Mo has 59mg/kg with 0.03% of concentration in the sample collected. The element As is the last element found in the sample collected at Ilorin with the concentration value of 48mg/kg and 0.02%.

These elements followed the order Fe>Ca>K>Ti>Zn>Zr>Ce>V>Cr>Pb>Ni>Cu>Sr>Mo >As.According to Table 2.0 below as reported by Schwela *et al* 2002, it was observed that road transport emission sources include motor vehicle emission and this emission elements include Pb, Mn, Zn, V, Ni and As. Engine wear emission is Fe present in the sample. Catalytic converter emission elements were not detected in the sample collected at Ilorin.

Tyre wear emission elements were not also detected in the sample. Nonferrous metal smelters elements present in the sample are Cu, As, Zn and Pb. Iron and steel mills elements presents in the sample are Zn and Pb. Copper refinery elements present in the sample are Cu and Zn. Refuse incineration element present are Zn, Pb Cu and K. Mineral and material processing elements present in the sample collected are K, Fe and Mn. Sea spray element is K. Re-suspended soil elements include Ca, Fe, Ti, Sr and Mn. Road side dusts emission elements detected in the sample include Ca, Ti, Fe, Zn and K. industrial facilities emission elements that were present in the sample collected are oil fire power plants elements such as V and Ni. Coal combustion elements present in the sample include Ar, Cu and C. Oil refineries element present is V as shown in the table 3

Table 2. X-Ray Fluorescence (XRF) Laboratory Analysis Report for Ilorin

Elements	Conc. (mg/kg)
K	42030 ± 100
Ca	42314 ± 100
Ti	8719 ± 100
Cr	270 ± 21
Mn	3479 ± 68
Fe	113086 ± 100
Ni	217 ±15
Cu	193 ± 9
Zn	875 ± 25
Mo	59 ± 10
As	48 ± 5
Ce	688 ± 77
Zr	673 ± 27
Pb	260 ± 23
V	648 ± 38
Sr	69 ± 7

Soil Mass Concentrations: Zhang *et al.,* (2010) calculated the soil mass concentration of elements using the formula proposed by Malm *et al.,* (1994).Soil mass concentrations of aerosols can be estimated by summing the concentrations of several elements in soil, and oxygen assuming that the compounds involved are mostly common oxides. The formula recommended for the calculation of soil mass concentration by elemental concentrations is as follows:

$$Y_{soil} = 2.2Y_{Al} + 2.49Y_{Si} + 1.63Y_{Ca} + 2.42Y_{Fe} + 1.94Y_{Ti} \quad 1.0$$

Where Y_u represents concentration and the names of crustal elements are shown as subscripts as u.

Table 4 shows the calculation for the soil mass concentration using equation 1.0 above. The mean soil content of total size particle for the harmattan for Ilorin was calculated to be 1.79765 $\mu g/m^3$. This can be attributed to higher value of Calcium (Ca), Iron (Fe) and Titanium (Ti) collected during the period of the harmattan season. This could be as a result of much of human activities taking place during the period of sample collection.

PIXE (Particle Induced X-ray Emission) Method: The results of harmattan dust sample mineral collected across Ilorin for the period of study are presented in tables 1 and 5. These results show the lower and higher elements present in the sample collected and the oxides of harmattan. The heavy grouped minerals are having specific gravity greater than 2.88 (S.G > 2.88), the Quartz minerals have specific gravity less than 2.88 but are greater than 2.62Jimoh (2012). The feldspar minerals grouped have specific gravity less than 2.62Jimoh (2012). The minerals that have specific gravity greater than 2.59 but less than 2.62 are known as Fraction B (Jimoh 2012). The minerals that have specific gravity greater than 2.50 but less than 2.59 are Fraction D minerals (Jimoh 2012). Fraction E minerals are those with specific gravity greater than 2.0 but less than 2.50 (Jimoh 2012). Those minerals that have specific gravity less than 2.0 together with the organic material are known as Fraction F minerals (Jimoh 2012). The mineralogical study of harmattan dust sample collected at Ilorin was analyzed and it was observed that minerals such as Quartz [SiO_2] (77.07%) with specific gravity 2.65 predominantly dominate the sample. Some minerals present are lower or in small amount quantity of trace mineral. These minerals include, Corundum [Al_2O_3] (8.25%), Hematite [Fe_2O_3] (8.11%), Lime [CaO] (1.97%). Minerals such as Periclase [MgO](0.42%), Rutile [TiO_2](0.51%), Zincite [MnO](0.09%), Montroydite [HgO](0.001%), Cuprite [Cu_2O](0.004%), Zincite [ZnO](0.11%), Baddeleyite [ZrO_2](0.08%), Litharge [PbO](0.001%), Monazite [P_2O_5] (0.18%),while, minerals such as Petzite [Au_2O_3], Bunsenite [NiO] had zero or no percentage concentration.

Mineralogical analysis of Ilorin: Studies have shown that the harmattan dust mineralogies have major components such as; quartz, haematite, illite, micas feldspars, kaolinite, chlorite and other accessory minerals as reported by Jimoh (2013), Falaiye *et al*., (2013) and Adedokun *et al*., (1989). It was reported by Falaiye *et al*., (2013) that minerals such as quartz, gibbsite, rutile, goethite, halloysite and kaolinite were detected at Ilorin using X-ray Diffraction (XRD) machine. Quartz, Hallosite, microcline and mica were similarly identified in the harmattan dust sample collected at Ile-Ife. Minerals such as quartz, gibbsite, rutile, and goethite were major minerals detected at Ilorin using XRD machine as reported by Falaiye *et* *al*., 2013 while for Ile-Ife (Adedokun *et al*., 1989) minerals such as quartz were detected as compared with what was found at Ilorin using PIXE

Table 3. Elements emitted from particle sources

Emission Source	Characteristic Elements Emitted World Health Organization (WHO).	Elements Emitted Ilorin
Road transport		
Motor vehicle emissions	Br, Pb, Ba, Mn, Cl, Zn, V, Ni, Se, Sb, As	Pb, Mn, Zn, V, Ni, As
Engine wear	Fe, Al	Fe
Catalytic converters	Rare earths, Pt	ND
Tyre wear	ZnO, carbon black	ND
Road side dusts	EC, Al, Si, K, Ca, Ti, Fe, Zn	Ca, Ti, Fe, Zn, K
Industrial facilities		
Oil fire power plants	V, Ni	V, Ni
Coal combustion	Se, As, Cr, Co, Cu, Al, S, P, Ga	As, Cu
Oil Refineries	V	V
Nonferrous metal smelters	As, Sb, Cu, Zn, Pb, Cd, Hg	As, Cu, Zn, Pb
Iron and steel mills	Zn, Pb	Zn, Pb
Copper refinery	Cu, Zn	Cu, Zn
Refuse incineration	Zn, Pb, Cu, Cd, Hg, K	Zn, Pb, Cu, K
Mineral and material processing	Si, Al, Ca, Mg, K, Sc, Fe, Mn	Ca, K, Fe, Mn
Sea spray	Na, Cl, S, K	K
Re-suspended soil	Si, Al, Ca, Mg, Fe, Ti, Sr, Mn, Sc	Ca, Fe, Ti, Sr, Mn

Source: Adapted from Guidelines for concentration and exposure-response measurement of fine and ultra-fine particulate matter for use in epidemiological studies. Schwela, et al., 2002.World Health Organization (WHO). ND Means: Not Detected

Table 4. Soil Mass Concentration Elements

Location	$C_{Al}(\mu g/m^3)$	$C_{Si}(\mu g/m^3)$	$C_{Ca}(\mu g/m^3)$	$C_{Fe}(\mu g/m^3)$	$C_{Ti}(\mu g/m^3)$	$C_{soil}(\mu g/m^3)$
Ilorin	ND	ND	0.6897	2.7367	0.1691	3.5951

Table 5: Percentage Proportion of Minerals Present in Harmattan Dust at Ilorin Compared To that of Ile-Ife (Adedokun *et al*., 1989) and Ilorin using XRD Machine (Falaiye *et al*., 2013)

Mineral	Specific Gravity	Ilorin, (%)	Ile-Ife, (%)	Ilorin (PIXE) (%)
Quartz [SiO_2]	2.65	76.47	74.78	77.07
Gibbsite [$Al(OH)_3$]	2.35	7.09	-	7.42
Rutile [TiO_2]	4.2	5.78	-	0.51
Goethite [$Fe_2O_3.H_2O$]	4-4.2	4.59	-	2.65
Halloysite [$Al_4Si_4O_{10}(OH)_8 \cdot 8H O$]	2.6	3.93	1.45	-
Kaolinite [$Al_4 Si_4 O_{10} (OH)_8$]	2.6	2.09	10.29	-
Microcline [$KAlSi_3 O_8$]	2.56	-	17.63	-
Mica [$Si_4 O_{10}$ Sheet Structure]	2.7-3.1	-	2.54	-
Periclase [MgO]	3.56	-	-	0.42
Corundum [Al_2O_3]	4.0-4.2	-	-	8.25
Zincite [MnO]	5.66	-	-	0.11
Hematite [Fe_2O_3]	5.26	-	-	8.11
Cuprite [Cu_2O]	6.13-6.15	-	-	0.04
Baddeleyite [ZrO_2]	5.4-6.02	-	-	0.08
Litharge [PbO]	9.14	-	-	0.001
Monazite [P_2O_5]	4.6-5.4	-	-	0.18
Zincite [ZnO]	5.66	-	-	0.09
Montroydite [HgO]	11.23	-	-	0.01
Lime [CaO]	1.97	-	-	3.3

Source of Specific Gravity: Read, 1973

It was observed that minerals such as halloysite, kaolinite were observed at Ilorin and Ile-Ife as reported by Falaiye *et al*., 2013 and Adedokun *et al*., 1989, while minerals such as microcline and mica were observed at Ile-Ife which were not observed at Ilorin as reported by Falaiye *et al*., 2013.It was observed that minerals such as periclase, corundum, zincite, hematite, cuprite, baddeleyite, litharge, monazite, zincite, montroydite and lime were observed in the sample collected at Ilorin which could be as a result of PIXE machine used for this research work. As expected, it is observed that PIXE machine can detect many minerals as shown in the sample gathered. All these could be as a result of Ilorin being a central/middle state of Nigeria which could observe more minerals as compared with Ile-Ife as reported by Adedokun *et al*., 1989. The result shows that quartz is the dominant as its constituents have an average value of 77.07% as compared with Adedokun *et al*., 1989 and Falaiye, *et al*., 2013, which was also observed to be high percentage proportion. This shows that the harmattan that blows across Nigeria has much of quartz mineral which could be as a result of dust that emanated from the

Sahara desert. But other minerals are present either in small quantities or trace as shown in the table 5 above. These results are in line with what was observed at Ile-Ife (Adedokun *et al.*, 1989) and Ilorin (Falaiye *et al*., 2013), except that mica and microcline were not detected in Ilorin as reported by (Falaiye *et al*., 2013) and this study. It was observed that NaO (0.60%), Cl (0.18%), K_2O (2.34%), Cr_2O_3 (0.02%), Rb_2 (0.003%), Nb_2O_5 (0.009%) were oxide present in the sample without minerals, while oxides with zero percentage value include SO_3, Sc_2O_5, V_2O_3, As_2O_5 and BaO. The percentage oxides of the mineral present in the sample shows that Quartz is the major constituent of minerals collected at Ilorin. It was observed that if some oxides are combined they produce minerals such as Geikielite [$MgTiO_3$], Perovskite [$CaTiO_3$], Zinnmetatitanate [$ZnTiO_3$] and nickel titanium oxide [$NiTiO_3$]. This shows that the combination of TiO_2 produces some other minerals. The oxides gotten from the harmattan dust sample collected at Ilorin were as a result of PIXE machine.

Conclusion: Atmospheric aerosol and mineral dust production are as a result of desert dust that emanated from the Sahara. These amount to the largest dust production of the global aerosol loading and have strong impact on climate change and reduction in the visibility of both human and animal as the case may be. Therefore, it could be observed that the Sahara is the major contribution of the earth aerosol and minerals dust. This shows that the mineral composition of the harmattan dust at each location is as a result of source and distance from the harmattan dust sample.

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