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# Mineralogy of harmattan dust over Iwo, south western Nigeria

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## ABSTRACT

Harmattan period in Nigeria, characterized by dust laden atmosphere begins from the month of November and ends in the month of March of the following year. Samples of harmattan dust were collected using clean plastic bowls of diameter 10 cm which were exposed indoor and on elevated platforms at different locations at Iwo. The bowls were exposed so as to collect dust particles for a period of five months (November to March) of the following year. A total of five (5) samples were collected and stored in desiccators prior to the analysis in order to avoid contamination which could affect the results. Mineral and Elemental study carried out on harmattan dust samples gathered at Iwo ($7^0$37'N, $4^0$11'E), sub-sahara region of African city, shows the presence of elements such as **K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Mo, As, Ce, Zr, Pb, V**, and **Sr** in the dust samples collected. Minerals such as Quartz [$SiO_2$], Gibbsite [$Al(OH)_3$], Rutile [$TiO_2$], Goethite [$Fe_2O_3.H_20$] and Microcline [$KAlSi_30_8$] were also found to be present in different percentages at the station under consideration. The mean soil content of the total size of particles for the harmattan season for the station was found to be (). The Enrichment Factor for the station was also calculated and showed the dust samples to be rich in **Fe** and **K**.

***Keywords: Mineral, Element, Enrichment Factor, Harmattan and Dust.***

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## INTRODUCTION

The dry wind transports and deposits the Saharan dust plumes which predominantly originate from the Bodélé depression in the Chad basin over the entire region extending as far as to the Gulf of Guinea (*Bertrandet al., 1979*). It has been observed that harmattandust lifting, transportation and deposition begins from the month of November and ends in March of the following year due to the prevailing north easterly wind over the West Africa region. During this period, the wind blows the harmattan dust haze across the Nigerian cities and this usually has effects on indoor and outdoor activities in the country. The harmattan period is also usually associated with low and poor visibility of the atmosphere sometimes less than 1000 m *(Kalu, 1979,Falaiye, et al., 2003, Falaiye, et al., 2013, Adimula, et al., 2010,Falaiye, et al., 2017)* also reported that the more the harmattan dust mass in the air, the less the visibility of both human and animal. According to *Balogun, (1974)* two sources of dust plumes were identifiedviz; the dust originating from the region around Mauritania, Algeria and Morocco, which accounts for most dusts observed over the Atlantic extending as far west as the Barbados Island and dust originating from the Chad Basin which accounts for the dust observed over countries around the Gulf of Guinea and as far as South America *(Glaccum, and Prospero 1980, Shutz, et al., 1981, Prospero,et al., 1981, Muhhs,et al., 1990, Ott, et al 1991, Regnon, and Coude- Gaussen, 1996).*

To the best of our knowledge, there were no reports on the mineralogical, elemental and heavy metals in the harmattan dust across the Iwo to support the presence of mineral and element in harmattan dust. Hence, there is need to carry out analysis on the mineralogical and elemental analysis of harmattan dust haze across Iwo town in Nigeria.

## MATERIALS AND METHODS

Clean plastic bowls of diameter 10cm were exposed on an elevated platform and indoor of domestic buildings. Some of the bowls were exposed to collect dust particles for a period of one week, others for a period of one month, while some of the bowls were exposed to collect the dust samples for a period of five months *(November to March)* of the following year. A total of ten *(10)* samples were collected and stored in desiccators prior to the analysis in order to avoid contamination which could influence the results. This experiment follows what was done by *(Falaiye, et al., 2013, Falaiye, et al., 2017, Falaiye and Aweda, 2018)* where Petri dishes were exposed on elevated platform to collect harmattan dust sample for mineralogical and chemical analysis to be conducted. The particle mass of the dust samples was also determined. During the collection process as reported by *Falaiye, et al., (2013),* measures such as keeping the samples

containers away from public road and high ways were taken into consideration in order to minimize the input of the local dust.

***Sample Analysis***

Mineral and Elemental analysis was carried out on the harmattan dust gathered across Iwo, Nigeria using PIXE (Particle Induced X-ray Emission) to determine the mineral and the element present in the sample gathered across the station. XRF (X-Ray Fluorescence) analysis was also carried out on the samples gathered at Iwo.

***XRF and PIXE Machine Description***

Harmattan dust particulate matters collected from five different locations at Iwo, Nigeria were analyzed using Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry and PIXE (Particle Induced X-ray Emission) analyzers. The spectrometer of the XRF machine is a self-contained miniature X-ray tube system with a detection system Model XR-100CR which have a high performance X-ray Detector with preamplifier and a cooler system that uses a thermoelectrically cooled Si-PIN photodiode as an X-ray detector. The power to the XR-100CR is provided by a PX2CR power supply. The quantitative analyses of samples were carried out using the XRF-FP Quantitative Analysis Software package which converts elemental peak intensities to elemental concentrations and or film thickness. While, PIXE (Particle Induced X-ray Emission) analyzer of the National Electrostatics Corporation Model 5SDH pelletron of 1.7MV tandem electrostatic ion accelerator, which is designed to accelerate light ions for material science research using such techniques as Rutherford backscattering, PIXE, hydrogen profiling, implantation and nuclear physics experiment.

The detailed setup of the proton-induced X-ray emission technique (PIXE) setup used for this work has been reported *(Shutthanandan, et al. 2002; Ezeh and Obiajunwa, 2017)* which are briefly described by *(Ezeh, et al., 2018)*. According to *Ezeh, et al., (2018)*, the accelerator tank is linked with the charge exchange ion (beam) source which is equipped with hydrogen and helium. More so, the accelerator has provisions for five beam lines maintained by quadrupole magnets but presently only a beam line with multi-general end station has been installed as stated by *Ezeh, et al., (2018)*. The end station has a turbo pump and variable collimator to regulate beam size. It also has a target scattering chamber which contains the sample holder and linked with the detectors for PIXE and Rutherford Back Scattering (RBS) experiments. PIXE detectors were placed at a glancing angle of $135^0$ perpendicular to the normal beam windows for observing the beam lines at $0^0$. The detector used was liquid nitrogen cooled solid state Si-Li detector which was connected to the multi-channel analyser (MCA). All these were reported by *Ezeh, et al., (2018)*.

***Sample Preparation***

The dry Harmattan dust sample was pelletized before analysis. The pelletization of the samples is done with steel molds, pellets and a hydraulic press, by aluminum foil as the binder to hold the sample particles together after the removal from the molds. Then the sample was transferred into the accelerator.

***Enrichment Factor (EF) of Chemical Elements***

The Enrichment factor analysis was carried out on the sample

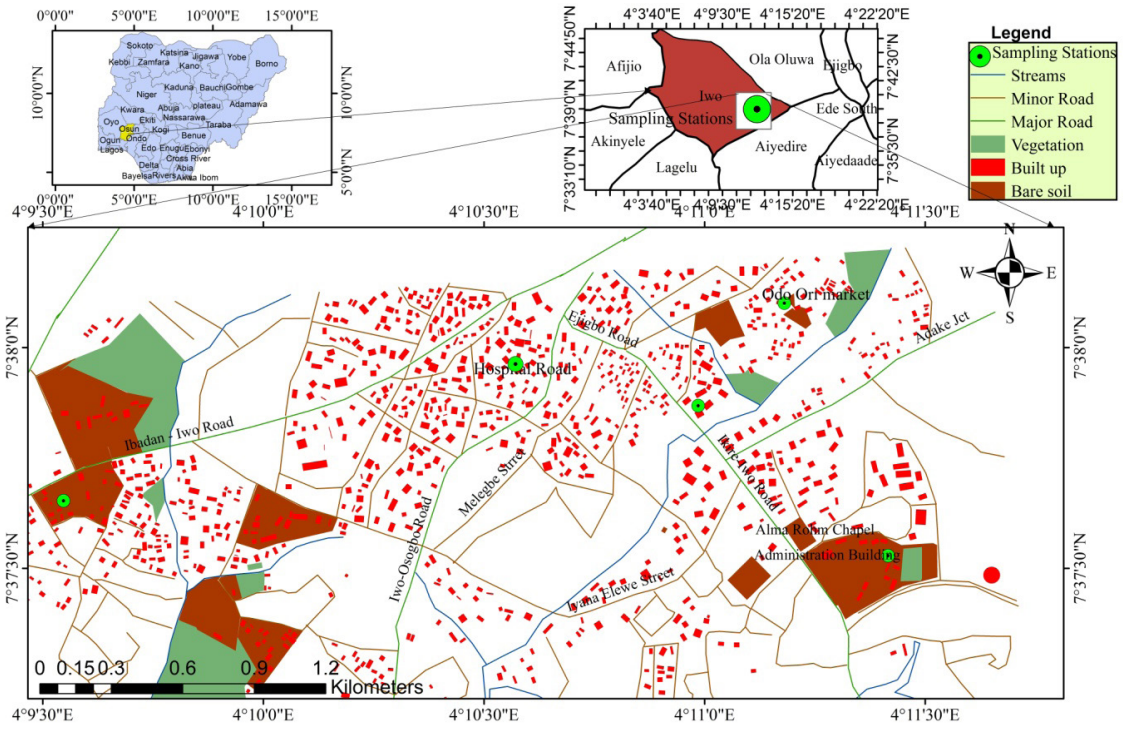


**Figure 1: Map of Iwo showing the sampling location**

collected at the study area to differentiate anthropogenic source from natural ones. This shows the degree of enrichment of a particular element compared to the relative abundance of those elements in Earth's crust *(Behera, and Sharma, 2010, Chakraborty, and Gupta, 2010)*. The reference element that was used is Ca which is assumed to be the crustal origin as reported byGhosh, *et al*., (2014). Enrichment factor is defined as follows:

$$EF_x = \frac{C_x / C_{Ca}}{C_x / C_{Ca}} \quad 1$$

Where $C_x$ and $C_{Ca}$ are concentrations of the element x and Ca in the samples, $C_x$ and $C_{Ca}$ are average concentration in the Earth's upper crust *Taylor, et al., (1981)*. By convention *Zhang, et al., (2010)*. If EF ≤ 10, it is considered that element in aerosol has a significant crustal contribution, and hence it is termed as the non-enriched element. EF > 10 indicates that element has an important proportion derived from non-crustal sources and hence it is termed as an enriched element as reported by *Ghosh, et al., (2014).*

**Soil Mass Concentrations**

*Zhang et al., (2010)* calculated the soil mass concentration of elements using the formula proposed by *Malmet 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:

$$W_{soil} = 2.2W_{Al} + 2.49W_{Si} + 1.63W_{Ca} + 2.42W_{Fe} + 1.94W_{Ti} \quad 2$$

where $w_v$ represents concentration and the names of crystal elements are shown as subscripts as v.

## RESULTS AND DISCUSSION

**Elemental analysis**

The locations are: Location A (Adekee area), Location B (Bowen University area), Location C (Odori area), Location D (Hospital road area), and Location E (Oja ale area).

It was observed that elements such as **Cu, Zn, Fe, Pb, Ca, Mn, Ni, As, K, Ti, V, Sr, Zr,** and **Mo** are the constituents of elements present in Iwo during the period of the study. The concentration values of the elements are in milligram per kilogram (mg/kg). The average results are presented as shown in table 1 above. However, for the average result it was observed that Ca has the highest concentration and percentage values with 76584 mg/kg and 35.82%. The element K has concentration and percentage value of 62976 mg/kg and 29.45%. Fe has 55210 mg/kg concentration and 25.82%, Ti with 11095 mg/kg and 5.19%, Mn with 3307 mg/kg and 1.54%, Zn 1354 mg/kg and 0.63% conc., V has 839 mg/kg and 0.39% concentration value present in the harmattan dust collected at Iwo. The presence of lead was not over rule with the value of Pb 791 mg/kg and 0.37%. Ni has 662 mg/kg and 0.31% concentration value of the sample. Zr 391 mg/kg concentration and 0.15% which were also present in the sample. Cu has 180 mg/kg concentration value and with 0.08%, while Sr has 122 mg/kg and 0.06%. Meanwhile, As and Mo have 74 and 54 mg/kg have a concentration percentage of 0.03% respectively to take the lowest elements present in sample collected at Iwo. However, Figure 1 above shows the sampling locations for the harmattan dust collected at Iwo which includes Adekee area, Bowen University area, Odori area, Hospital road area and Oja ale area. As shown in Figure 1 above, it was observed that some of these elements are in different concentrations at different locations; this may be due to the activities going on in the area. This activities include, refuse incineration, trampling the ground, road side kitchen and more so, road construction taking place in some of the area. These may affect the quality of air.

**Table: 1: X-Ray Fluorescence (XRF) Laboratory Analysis Report for the five locations around Iwo township**

| Element | Location A Conc. (mg/kg) | Location B Conc. (mg/kg) | Location C Conc. (mg/kg) | Location D Conc. (mg/kg) | Location E Conc. (mg/kg) | Average Conc. (mg/kg) |
|---|---|---|---|---|---|---|
| K | 6302 | 6290 | 6296 | 6301 | 6291 | 6296 |
| Ca | 76584 | 76580 | 76588 | 76500 | 76668 | 76584 |
| Ti | 11095 | 11000 | 11085 | 11190 | 11105 | 11095 |
| Mn | 2500 | 3307 | 4114 | 3000 | 3614 | 3307 |
| Fe | 55420 | 54000 | 55210 | 55000 | 56420 | 55210 |
| Ni | 662 | 423 | 213 | 901 | 1111 | 662 |
| Zn | 1408 | 1440 | 1354 | 1300 | 1268 | 1354 |
| Mo | 54 | 50 | 58 | 65 | 43 | 54 |
| As | 70 | 78 | 60 | 74 | 88 | 74 |
| Zr | 300 | 391 | 482 | 330 | 452 | 391 |
| Pb | 791 | 700 | 882 | 750 | 832 | 791 |
| V | 800 | 878 | 839 | 839 | 839 | 839 |
| Sr | 122 | 120 | 124 | 100 | 148 | 122 |

**Table 2: Soil Mass Concentration Elements as revealed by XRF**

| Location | () | () | () | () | () | |
|---|---|---|---|---|---|---|
| **Iwo** | ND | ND | 1.2483 | 1.3361 | 0.2152 | 2.7996 |

Table 2 above shows the calculation for the soil mass concentration using equation 1 above followed Zhang *et al*., (2014) which were proposed by Kang *et al*., (2011). The mean soil content of total size particle for the harmattan season for Iwo was 1.3998 . The soil mass concentration of the elements present in the samples collected across Iwo was observed to be 2.7996 . This could be attributed to lower value of Calcium (**Ca**), Iron **(Fe)** and Titanium (**Ti**) collected during the period of the harmattan season. This could be the result of less activities taking place during the period of sample collection. More so, the value of the sample could be as a result of dust drop during the transportation of the harmattan particle. Likewise this could be attributed to some activities going on in the area during the period of sample collection, such as vehicular movement, road construction and due congestion of the environment considered.

**Mineralogical analysis for the five stations and the specific gravity**

Table 3 showed the mineralogical analysis of the aerosol sample collected at Iwo. It was observed that quartz, gibbsite, rutile and goethite are the major constituent minerals present in the samples collected across the station. The results show that quartz has the highest value (80.50%). But other minerals are present in small quantity. This followed what was done by Falaiye, *et al*., (2013) and Adedokun, *et al*., (1989) in Ilorin and Ife Nigeria. Minerals such as gibbsite, rutile and goethite were recorded in Ilorin and Iwo which were not recorded in Ile-Ife. But minerals such as halloysite, Kaolinite, mica and Microcline were recorded in Ile-Ife which was not found at Iwo. More so, for Ilorin Halloysite and kaolinite were present which was also present in Ile-Ife, these were not present in Iwo. The results obtained from Ilorin, Ile-Ife and Iwo is compared in table 4.0 above. Mineral such as gibbsite was present in Iwo which is almost equal but a little lesser than what was observed in Ilorin. This could as a result of these stations in the north central and western part of the country. Minerals such as rutile were at lower proportion as compared with what was observed in Ilorin and Ile-Ife has no trace of such mineral. All these minerals may be at lower quantity or higher quantity due to some activities in the country and the distance of the source of dust from the Stations. Rutile being relatively heaver mineral as reported by *Adedokun, et al., (1989)* has lower percentage concentration as compared with what was recorded in this research.

However, microcline and mica have the specific gravity values that are in the range of that of quartz, halloysite and kaolinite as reported by *Adedokun, et al., (1989).* The results as compared with what was done in Ile-Ife and Ilorin indicated that the harmattan is quartz dominated. This could be as a result of the fact that quartz is associated with sandy sedimentary rock as also reported by *Adedokun, et al., (1989)*. More so, it could be as a result of the wind transportation that blows the dust from the source and deposition along the trajectory path as reported by *Falaiye, et al., (2017)*. As reported by *Falaiye, et al., (2017)*, the more the harmattan dust in air, the less the visibility of both human and animal. As reported by *Adedokun, et al., (1989)*, the constituents of harmattan dust at Ile-Ife, Nigeria, shows that quartz is the most abundant constituent of harmattan dust. This confirmed the results presented in the table 4.0 above. The mineralogical composition of the harmattan dust at a locality is most probably determined by the source and distance from the source of the harmattan dust. *(Adedokun, et al., (1989)*. 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 2.62 *(Jimoh, (2012)*. The

**Table 3: Percentage Proportion of Minerals Present in Harmattan Dust for the five stations Compared to that of Ilorin Falaiye, et al., (2013) and Ile-Ife Adedokunet al., (1989).**

| Mineral | Specific Gravity | Ilorin (%) | Ile-Ife (%) | Iwo (%) |
|---|---|---|---|---|
| Quartz [$SiO_2$] | 2.65 | 76.47 | 74.78 | 80.50 |
| Gibbsite [$Al(OH)_3$] | 2.35 | 7.09 | - | 6.94 |
| Rutile [$TiO_2$] | 4.2 | 5.78 | - | 0.50 |
| Goethite [$Fe_2O_3.H_2O$ ] | 4-4.2 | 4.59 | - | 3.84 |
| 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 | - |

***Source of Specific Gravity (Read, 1973)***

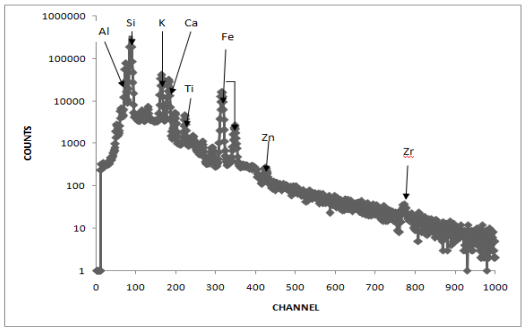


**Figure 2:** A PIXE Spectrum of Harmattan Dust Sample from Iwo Deposit

enrichment factor for the entire element present in the sample calculated. It was observed that Fe has the highest EF across the station. This shows that the dust that blows across Nigeria may have more of Fe as compared with other elements present in the sample. This was followed by the element **K** which has almost closed range with that of **Fe** while other elements have their EF in lower quantity as compared with that of **Fe** and **K**, which shows that the dust across Nigeria is rich in **Fe** and **K**. *(Aweda, et al., 2017)*. However, Figure 2 above revealed the PIXE results of the harmattan dust from Iwo.

## CONCLUSION

The study concluded that minerals such as quartz, gibbsite, and rutile are major constituents of harmattan dust gathered across Iwo. However, the abundance of quartz[$SiO_2$] shows that the harmattan dust that blows across Nigeria has more of the mineral quartz than Gibbsite [$Al(OH)_3$], Rutile [$TiO_2$], Goethite [$Fe_2O_3.H_20$] and Microcline [$KAlSi_30_8$]. The results showed that quartz percentage of Iwo is higher than what was observed at Ilorin and Ile-Ife. In another vein, the presence of elements in the sample gathered across Iwo station shows that the dusts, in Nigeria may have almost all the elements present in harmattan. Some of the elements are in lower quantity and some are in high quantity. However, these elements can affect light as it passes through the atmosphere by scattering and absorption.

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