

## Determination of Aerosol Metal Composition and Concentration During the 2004/2005 Harmattan Season at Uturu, Nigeria

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### Abstract

Atomic Absorption Spectroscopy (AAS) was used to determine the atmospheric aerosol metal composition and concentration for seven elements in the air at Uturu Abia State, Nigeria during the harmattan season of October 2004 to February 2005. Dust samples were collected by direct deposition method on a whatman filter paper for 24 hours each day for an average of 11 days in a month. In all, two samples were collected. The mean mass, mass concentration and mean thickness of the deposited aerosol are 0.06095g,  $3.67 \times 10^{-3} \text{g/cm}^2$  and  $2.2 \times 10^{-5} \text{m}$  respectively. The mean of the elemental concentrations is 5.071 mg/kg for potassium (K), 2.600 mg/kg for magnesium, (mg), 102.765 mg/kg for calcium (Ca), 14.859 mg/kg for Iron (Fe), 25.130 mg/kg for Zinc (Zn), 4.012 mg/kg for manganese (Mn) and 1.023 mg/kg for lead (Pb). A comparison of reported results from Jos Plateau State Nigeria (09.9°N, 08.9°E) and that determined at Uturu, Nigeria (05.33°N and 07.29°E) indicates some differences in the concentrations and this is explained in terms of the latitudinal locations of the stations with respect to the aerosol source.

Keywords: Aerosol composition; Concentration; Atomic Absorption spectroscopy (AAS).

### 1.0 Introduction

The term aerosol refers to a colloidal dispersion of solid or liquid in a gas (John, 2003). The compositions and elemental concentrations of aerosol particles within the atmosphere are of interest from environmental impacts and potential health hazards stand points.

Gobbi (1999) had observed that the scientific interest in the study of atmospheric aerosols is due to their role in controlling the earth's climate. In fact, one of the global effects of aerosols is to cool the planet by reflecting back to space part of the incoming solar radiation. It is estimated that the cooling effect of aerosols is approximately 1/30<sup>th</sup> of the cloud – induced cooling effect. Aerosols can also heat-up the climate if they are absorbing in nature such as black carbon. Charlson (1995) noted that aerosols scatter and absorb radiation and provide cloud condensation sites. The model-simulated effects of aerosols on climate tend to counter-balance green house warming.

Utah and Nggada (1994) reported that aerosols (dry dusty air) are characterized by low relative humidity and degradation of visibility. Oluwafemi (1981) reported depletion of solar radiation by aerosols. As a result of the impact of aerosols on life, research interest have been directed to analyzing aerosols from several sources, for their chemical composition. Aerosols can also affect plants. Prindla (1979) noted that the damage of aerosols to vegetation has been recognized for at least a century. Nrc Canada (1939), Seigworth (1943), Turc and Wittes (1978) observed that aerosols greatly damage fruits, vegetables, trees and ornamental flowers.

We note that polluted air is a threat to both living things and metal structures. For example, some of the oldest and most glorious buildings of the world are being degraded by air pollution (see Obodo 1995; William and Barbara 2001). Dockery and Pope (1994) have suggested that particulate matter (PM) may

cause discomfort to the human respiratory system. Aerosols could also affect health. Recent epidemiological studies have indicated association between ambient particulate matter and increased mortality and morbidity (Reyes, 1997). Aerosols may also be linked to the increasing incidence of Asthma. Attenuation of radio signals by aerosols has been reported by Owolabi (1987).

Bergametti et al (1998) noted that mineral dust aerosols are notably drawn earth ward by gravity along their transport paths and so are deposited to lands and oceans where they provide iron and other micro-nutrients to terrestrial and marine ecosystem. Crutzen (1998) observed that the chemistry of the atmosphere has major impacts on several important environmental factors: climate, the hydrological cycle, acid precipitation, stratospheric and tropospheric ozone, and local regional air quality.

## 2.0 Instrumentation and Theoretical Considerations

The working of AAS is based on the principle that the amount of energy absorbed in flame is proportional to the concentration of the element in the sample, since each element has its own characteristic absorption wavelength. The AAS apparatus is warmed for 15 to 20 minutes before analysis. Atomic-absorption spectroscopy uses the absorption of light to measure the concentration of gas phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration. Highly concentrated samples are diluted with distilled water to known volume. The schematic diagram is as shown in figure 1.

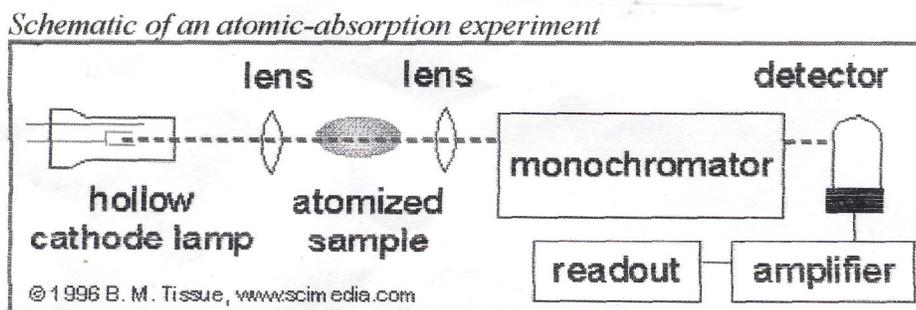


Figure 1.0 AAS Schematic Diagram.

According to King and Gilman (1971), the monochromatic radiation absorption by atmospheric aerosols can be described by the Lambert's law, which can be expressed in the form:

$$I = I_0 e^{-ad} \quad \dots 1$$

where  $a$  is the absorption coefficient and  $d$  is the thickness of the sample,  $I_0$  is the first direct measured intensity of monochromatic beam of radiation (from a monochromator) when no absorber was placed in between the source and detector while  $I$  is the measured intensity of a monochromatic radiation when an absorber was placed between the source and the detector.

Spectroscopists often use Lambert's Law in the form

$$I = I_0 10^{-md} \quad \dots 2$$

and ( $m = 0.434a$ )

where  $m$  is the linear extinction coefficient. When dealing with substances in solution it is found that the measured extinction coefficient is proportional to the concentration,  $c$ , of the absorbing substance (Beer's Law).

Thus

$$m = k\sigma_i \quad \dots 3$$

where  $k$  is the extinction coefficient per unit concentration.

Lithgow et al (2004) reported that Laser-induced breakdown spectroscopy (LIBS) was used to measure the distribution of seven species Ca, Na, Mg, Cu, Al, Mn, and Cr in individual ambient aerosol particles during an 8 day period from 26<sup>th</sup> August to 2<sup>nd</sup> September 2002 at the Pittsburgh Aerosol supersite. Weekly average concentrations for the measured elements in nanogram/cubic metre ( $\text{ngm}^{-3}$ ) are reported as 304, 716, 225, 32, 30, 29, and 37 respectively.

The determination of the elemental composition of air has been carried out at the Bauchi Road Campus of the University of Jos (Chiemeka, 2000). The mean of the elemental concentrations in ppm (parts per million) or milligram/litre (mg/L) of the impacted dust samples as revealed by atomic absorption spectroscopy (AAS) for the entire period of impaction starting from 13th October, 1989 to 31st January, 1990 were reported as  $14.823 \pm 0.016$ ,  $9.330 \pm 0.009$ ,  $22.923 \pm 0.052$ ,  $5.627 \pm 0.024$ ,  $0.0608 \pm 0.007$ ,  $0.558 \pm 0.019$  for K, Mg, Ca, Fe, Zn and Mn respectively.

The concentration  $\sigma_i$  of an element in the particulate phase at Uturu is given by mass fraction  $C_{ij}$  and is related to the source contributions  $M_j$ ; which is the mass of material from source  $j$  per unit volume of air at the point of measurement. The mass fraction  $C_{ij}$  of element is obtained using the relation (Hobbs, 1998).

$$\sigma_i = \sum_j C_{ij} M_j \quad \dots 4$$

such that mass fraction,  $C_{ij}$ , now becomes.

$$C_{ij} = \frac{\sigma_i}{\sum M_j} \quad \dots 5$$

In this paper, we report the concentrations of seven metals (K, Mg, Ca, Fe, Zn, Mn, Pb) determined using Atomic Absorption Spectroscopy (AAS) during an average of 11 days sampling period during the harmattan season at Uturu, Abia State Nigeria. The choice of the metals was based on their prevalence in the atmosphere, ability of AAS to detect them and location. The chemical composition of atmospheric aerosols influences visibility and human health.

The aim of the study is to determine the aerosol chemical composition and concentration as well as the mass and mass concentration in the atmosphere within Abia State University, Uturu using the Atomic Absorption spectroscopy (AAS)

### 3.0 Materials and Measurement Procedure

Uturu is one of the communities that make up settlements in Isukwuato Local Government Area of Abia State, Nigeria. It is Located within Latitudes  $05.33^\circ\text{N}$  and  $06.03^\circ\text{N}$ , and longitudes  $07.10^\circ\text{E}$  and  $07.29^\circ\text{E}$ , and is bounded on the West and South by a hilly escarpment as high as 240 meters above sea level. Allowing for slight variations in weather conditions which might occur as a result of differences in Location, climate data for Uturu Community is based on weather conditions at National Horticultural Research Institute (N.H.R.I.) meteorological station at Mbato Okigwe. The climate of Uturu is seasonal. The wet season in the community generally commences in March, with rainfall peak in July and September and a mean annual rainfall of about 1,367 – 1,672.4mm, and a total of not less than 97 rain days per year. The mean annual temperature in Uturu ranges from  $25.23^\circ\text{C}$  –  $27.20^\circ\text{C}$ . The map of the study area is as shown in Figure 2.0.

Dust samples were collected by means of whatman filter paper of uniform area by direct deposition method under the influence of gravity. The filter paper was placed inside a plastic jug and placed at the top base of an iron stand of height 2.47m. The mass of the deposited dust sample was weighed by electronic balance. The collected dust sample was stored in a desiccator to remove water molecules and prevents impurities.

The collected dust sample was digested by wet ash method. This consisted of using 6ml conc.  $H_2SO_4$  + 6ml conc. HCL to digest the sample for 1½ hour over a low heat at 60° C. The digested sample was diluted to a volume of 20cm<sup>3</sup> with deionized water and then filtered to remove silicate and other insoluble materials that could clog the atomizer. The analysis was then carried out with A.A.S. As a control, no dust samples were deposited or collected on a control filter paper, which was placed outside during the rainy seasons (July to August 2005). This in effect confirms the fact that dust particles are (mainly) air borne during the dry seasons.

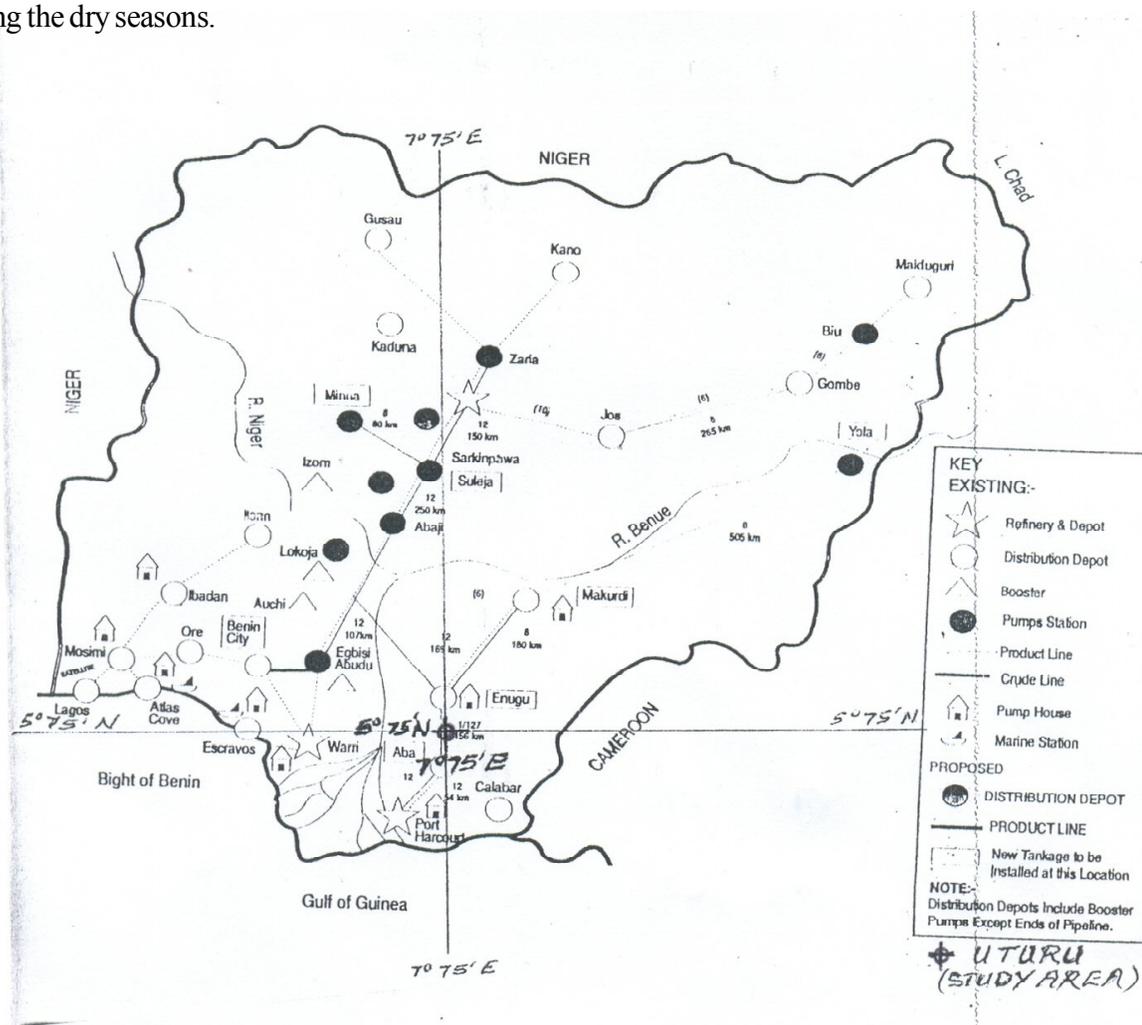


Figure 2: Map of the study area.

#### 4.0 Results and Discussion

The elemental compositions and concentrations in mg/L of the collected and digested dust samples as revealed by analysis using AAS, the mean value of the elemental concentrations obtained for the whole period of deposition and the mean of the mass fraction obtained are shown in Tables 1, 2 and 3 respectively.

The significance of the mass fraction is that the concentration of each element in air is directly proportional to the source contributions and it represents the concentration of each of the elements at a point in space.

Table 1: Elemental compositions and concentrations as revealed by AAS.

	K	Mg	Ca	Fe	Zn	Mn	Pb
Sample 1	0.015	0.008	0.307	0.044	0.075	0.012	<0.001
Sample 2	0.014	0.007	0.282	0.041	0.069	0.011	0.004

Table 2: Mean concentrations for the harmattan season in mg/L and mg/kg

Element	mg/L	mg/kg
K	0.015 ± 0.001	5.0710 ± 0.0001
Mg	0.008 ± 0.001	2.6000 ± 0.0001
Ca	0.295 ± 0.010	102.7650 ± 0.0001
Fe	0.065 ± 0.002	14.8590 ± 0.0001
Zn	0.072 ± 0.003	25.1300 ± 0.0001
Mn	0.012 ± 0.001	4.0120 ± 0.0001
Pb	0.003 ± 0.002	1.0230 ± 0.0001

Table 3: Mass fraction  $c_{ij}$  of element,  $i$ , in  $M_j$  for the harmattan season.

	Sample 1 mass 0.07710g	Sample 2 mass 04.04480g
Element	Mass fraction $c_{ij}$	
K	0.032	0.033
Mg	0.017	0.016
Ca	0.665	0.657
Fe	0.095	0.096
Zn	0.162	0.161
Mn	0.026	0.026
Pb	0.002	0.009

Comparison between elemental concentrations obtained at Uturu and that of Jos, Plateau State (Chiemeka 2000) was made by determining the Pearson Correlation coefficient (R) for which  $R \sim 0.684$ , which showed moderate correlation.

Also from the analysis of the test of mean (using t-test), it was found that there was significant difference between the mean concentrations of the elements obtained in 2004/2005 at Uturu and that obtained at Jos in 1989/1990 harmattan season. This is from the fact that by t-test,  $t_{\text{calculated}}$  (1.8748) lies between  $-2.776$  and  $2.776$  of  $t_{\text{tabulated}}$  at 5% level of significance for the comparison between 2004/2005 with respect to 1989/1990. Figure 3.0: shows relationship between concentration and elemental composition for 2004/2005 and 1989/1990.

The elemental concentration in air obtained at Jos, Plateau State was in general higher than that obtained at Uturu. The aerosols at these stations are partly of local origin, the main source being harmattan haze that is blown from the Sahara Desert and transported by the North-East trade winds. Toby and Richard (1977) noted that the great deserts, and semi-arid parts of the world such as the Sahara contribute vast quantities of these elements to the atmosphere.

However, it is also possible that these elements are enriched in the atmosphere as a consequence of man made pollutant emissions from industries.

According to Brian (1977), the major source(s) of these elements in the atmosphere is as a result of the

weathering of the igneous rocks in this environment. Weathering is the total process of physical disintegration and chemical decomposition of rock at or near the earth's surface.

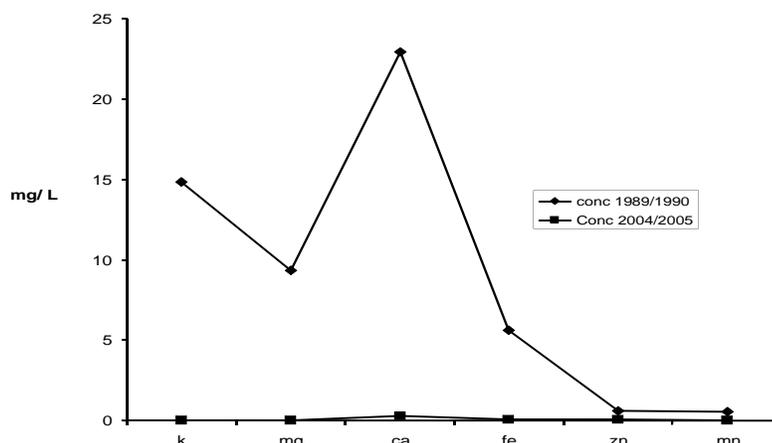


Fig. 3: Concentration and Elemental Composition for 1989/1990 and for 2004/2005.

## 5.0 Conclusion

The determination of aerosol composition and elemental concentration during the 2004/2005 harmattan season at Uturu was carried out in this work. The mean of the mass and mass concentration obtained for the period are 0.06095g and  $3.67 \times 10^{-3} \text{g/cm}^2$  respectively. The mean of the mass concentration of the collected aerosols per unit surface area of the filter paper was determined by calculation. The mean values of the elemental concentrations obtained using AAS in mg/kg are 5.0710 for potassium, 2.6000 for magnesium, 102.7650 for calcium, 14.8590 for iron, 25.1300 for zinc, 4.0100 for manganese, and 1.0230 for lead (Table 2). The concentration of each of the element in the aerosol phase at a point in space is represented by mass fraction as shown in table 3.

The extent to which these elements can be a health hazard is dependent on the ability of these elements to penetrate the respiratory system. These elements can affect light as it passes through the atmosphere by the mechanisms of scattering and absorption. The most obvious radiative consequence of airborne particles is the appearance of haze and the degradation of visibility. Less obvious, but more important, are the possible effects of these elements on the heat balance of the earth. These elements can cause a decrease in the amount of radiation reaching the ground, can increase or decrease the albedo, and if the elements absorb radiation, can cause atmospheric heating.

This method is equally applicable to other situations or studies where trace amount of the elements in air, liquids, soil, etc. are of interest. The elemental concentrations determined at Uturu is less than that obtained at Jos Plateau State. This is attributed to particles of non local origin, a less concentration of fine dust particles are blown to this part of the world (Uturu) by the Cold North East Trade Winds. This difference may also be attributed to the relative locations of the stations with respect to the aerosol source.

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