

DETERMINATION OF AEROSOL METAL COMPOSITION AND CONCENTRATION DURING THE 2001/2002 HARMATTAN SEASON AT UTURU, NIGERIA.

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ABSTRACT

Atomic Absorption Spectroscopy (AAS) was used to determine the aerosol concentration for seven elements in air at Uturu during the harmattan season November 2001 to February 2002. The dust samples were collected by direct deposition method on a whatman filter paper daily throughout the period. In all, four samples were collected. The mean of the mass and mass concentration of the aerosols collected are 0.02235g and 1.35g/Cm² respectively while the mean thickness of the deposited aerosol is 1.2 x 10⁻⁵m. The mean of the elemental concentrations obtained for the period of deposition is 16.470 mg/kg for potassium (K), 9.098 mg/kg for magnesium, (mg), 331.995 mg/kg for calcium (Ca), 47.673 mg/kg for Iron (Fe), 81.598 mg/kg for Zinc (Zn), and 12.791 mg/kg for manganese (Mn) and 1.161 mg/kg for lead (Pb). A comparison of reported result from Jos Plateau State Nigeria (09.9°N, 08.9°E) and that obtained at Uturu, Nigeria (05.33°N and 07.29°E) indicates some differences in the elemental concentrations and this is explained in terms of the relative locations of the stations with respect to the aerosol source.

KEYWORD: Aerosol composition; Concentration; Atomic Absorption spectroscopy (AAS)

INTRODUCTION

ATMOSPHERIC AEROSOLS

According to McCormack (2001), aerosols are small solid or liquid particles that are suspended in a gaseous medium. Aerosols by definition are particles that have very small settling velocities and so they do not readily fall out of the "background gas". Cloud droplets, rain drops and ice particles are not included in the general definition of aerosols since they possess relatively large settling velocities (fall speeds). Aerosol particles range in size from 10⁻⁴µm to 100µm in diameter and as a result of this large variation in size, it is useful to introduce the following categories.

Table 1: Aerosol classification and size (McCormack, 2001)

Classification	Size
Aitken particles	r < 0.1µm
Large particles	0.1 ≤ r ≤ 1µm
Giant particles	r > 1.0µm

Where r is the radius of the aerosol particle

According to Utah (1995), in most parts of West Africa, during the months of November to the subsequent year's February, the atmosphere is loaded with a dry dusty air having a high concentration of fine dust particle whose origin is the Sahara Desert and blown to this part of the world (Uturu) by the cold North East Trade Winds locally called harmattan. The characteristics of the latter include low relative humidity, degradation of visibility, depletion of solar radiation, attenuation of radio signals and discomfort to the respiratory system and associated ailments.

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.

Utah (1995) observed that as a result of the intense heating over the Sahara Desert, sand and dust particles are uplifted into the atmosphere by convective forces to great heights estimated to reach 6.0km above the surface. Schultz (1976) showed that large particles, 0.1-1mm in radius, are transported over a distance of 6,000km before being deposited on the surface. William and Barbara (2001) noted that in cities throughout the world some of the oldest and most glorious buildings and works of art are being destroyed by air pollution. This of course will apply to Uturu. Noone et al (2004) noted that aerosols directly influence climate by scattering or absorbing incoming solar radiation, and indirectly influence climate by acting as nuclei on which clouds can form. Jointly these effects represent the largest uncertainty in our current understanding of the earth's energy balance. Due to the impact of aerosols on life, research interest has been directed to analyzing aerosols from major sources, the Sahara Desert having been identified as an important source of natural aerosol pollution in the Northern Hemisphere. Consequently, Prospero and Carlson (1972) estimated that 23-27 millions of dust particles are conveyed through the longitude of Barbados each year. Furthermore, Prospero and Nees (1977) noted a marked increase in the Sahara dust concentration in the atmosphere over a decade in Barbados.

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. Aerosol brings about great cooling effect on Earth surface temperatures.

Bierly and Gilman (1997) observed that the rationale for measuring pollutants includes the following: (i) for developing scientific hypotheses (ii) monitoring for trends (iii) to ascertain the level of human health effects, and ecosystem damage as input to environmental decision-making.

John et al (2003) carried out a research work in the United States of America (USA) so as to assess the toxicity of fine particulate matter (particulate matter with a mass median

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aerodynamic diameter less than $2.5\mu\text{m}$ [$\text{PM}_{2.5}$] released into the atmosphere which may adversely affect the health of workers and residents in the area, as a result of the destruction of the World Trade Centre (WTC) on 11th September, 2001. From the analysis of the collected dust samples, the concentrations of the determined elements K, Mg, Ca, Fe, Zn, Mn, in microgram/gram ($\mu\text{g/g}$) are reported as 2890, 2900, 287000, 2730, 813, and 107 respectively.

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 August to 2 September 2002 at the Pittsburgh Aerosol supersite. Weekly average concentrations for the measured elements in nanogram/cubic metre (ngm^{-3}) are reported as 304, 716, 225, 32, 30, 29, and 37 respectively.

According to Chiemeka (2000) the determination of the elemental composition of air was carried out at the Bauchi Road Campus of the University of Jos. 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 whole period of impaction starting from 13th October, 1989 to 31st January, 1990 are reported as 14.823 ± 0.016 , 9.330 ± 0.009 , 22.923 ± 0.052 , 5.627 ± 0.024 , 0.0608 ± 0.007 , 0.558 ± 0.019 for K, Mg, Ca, Fe, Zn and Mn respectively in milligram/litre (mg/L).

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. The chemical composition of atmospheric aerosols influences the visibility and human health.

THEORETICAL BACKGROUND

The concentration σ_i of an element in the particulate phase at a given point 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, i , in M_j is obtained using the relation:

$$\sigma_i = \frac{\sum_j C_{ij} M_j}{\sum_j M_j} \quad (1)$$

such that mass fraction, C_{ij} , now becomes:

$$C_{ij} = \frac{\sigma_i}{\sum_j M_j} \quad (2)$$

The intensity of light that is scattered by a particle is directly proportional to the concentration of the particle in air. According to Raleigh scattering, the intensity of light, I_{sc} , that is

scattered by a particle is inversely proportional to the fourth power of the wavelength, λ .

Thus:

$$I_{sc} \propto \frac{1}{\lambda^4} \quad (3)$$

This accounts for the blue colour of the clear sky in daylight since blue light of wavelength 4500\AA is scattered more intensely than red light of wavelength 6500\AA because of the inverse relationship existing between scattered intensity and wavelength. Raleigh scattering is applicable to those particles whose sizes are small when compared with the wavelength of the incident light.

1.2 MATERIALS AND METHODS

Dust sample was collected by means of whatman filter paper of uniform area by direct deposition method. The filter paper was placed inside a plastic jug and placed at the top base of an iron stand. The height of the iron stand is 2.47m.

The effective thickness of the deposited dust was determined using micrometer screw gauge.

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. For the dust samples to be in solution form which can be aspirated using AAS, then the collected dust samples were digested to dissociate and dissolve the elemental components.

The collected dust sample was digested by wet ash method for $1\frac{1}{2}$ hour over low heat at 60°C using 6ml conc. H_2SO_4 + 6ml conc. HCL. The digested sample was diluted to a volume of 20cm^3 with deionized water and then filtered to remove silicate and other insoluble materials that could clog the atomizer.

The analysis was carried out with AAS. As a control, no harmattan dust samples was deposited or collected on a control filter paper, which was placed outside during the rainy seasons July to August 2002. This in effect confirms the fact that dust particles are majorly air borne during the dry seasons. However, because of local effects small quantities of local dust may still be air borne within the rainy seasons.

1.3 RESULTS AND DISCUSSION

The elemental compositions and concentrations in mg/L of the collected and digested dust samples as revealed by analysis using AAS are as shown in Table 2.

Table 2. Elemental compositions and concentrations as revealed by AAS.

	K	Mg	Ca	Fe	Zn	Mn	Pb
Sample 1	0.018	0.010	0.362	0.052	0.089	0.014	< 0.001
Sample 2	0.020	0.012	0.396	0.057	0.097	0.015	0.002
Sample 3	0.017	0.009	0.344	0.049	0.085	0.013	< 0.001
Sample 4	0.012	0.006	0.249	0.036	0.061	0.010	< 0.001

Error = ± 0.001 mg/L

The mean value of the elemental concentrations obtained for the whole period of deposition is as shown in table 3. The choice of these metals was based on their prevalence in the atmosphere, ability of AAS to detect them and location. The concentration of each element that is determined in the wet

ash using AAS is normally converted to solid form in milligram/kilogram (mg/kg) of the sample so as to determine the exact quantity of each element in milligram that is contained per kilogram of the sample in solid form as shown in Table 3.

Table 3: Mean concentration for the harmattan season in mg/L and mg/kg

Element	mg/L	mg/kg
K	0.017 ± 0.002	16.47000 ± 0.00001
Mg	0.009 ± 0.002	9.09800 ± 0.00001
Ca	0.338 ± 0.040	331.99500 ± 0.00001
Fe	0.049 ± 0.005	47.67300 ± 0.00001
Zn	0.083 ± 0.009	81.59800 ± 0.00001
Mn	0.013 ± 0.001	12.79100 ± 0.00001
Pb	0.001 ± 0.000	1.16100 ± 0.00001

The concentration of an element, *i*, in the particulate phase (aerosol) at a given point is given by mass fraction c_i 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 *i* in M_j is obtained using equation 2. Four Samples of mass 0.01315g, 0.02627g, 0.02542g were collected over a period of

30 days (11th Nov. – 12th Dec. 2001), 30 days (12th Dec – 11th Jan. 2002). The samples were collected for another 30 days (11th Jan. – 10th Feb. 2002) and for a further 61 days (11th Nov. 2001 – 10th Feb. 2002). The period of collection for the last sample during the harmattan season lasted for 61 days instead of 30 days because of interference by rain during the period of collection.

Table 4: Mass fraction c_i of element, *i*, in M_j for the harmattan season.

Element	Sample 1 mass	Sample 2 mass	Sample 3 mass	Sample 4 mass
	0.01315g	0.02627g	0.02457g	0.02542g
Element	Mass Fraction C_{ij}			
K	0.033	0.033	0.033	0.032
Mg	0.018	0.020	0.017	0.016
Ca	0.663	0.661	0.664	0.664
Fe	0.095	0.095	0.095	0.096
Zn	0.163	0.162	0.164	0.163
Mn	0.026	0.025	0.025	0.027
Pb	0.002	0.003	0.002	0.003

The significance of the mass fraction is that the concentration of each element in air is directly proportional to the source contributions.

Relationship between element concentrations obtained at Uturu and that obtained by Chiemeka (2000) at Jos Plateau State were determined by calculating the Pearson Correlation coefficient (*R*) such that $R = 0.703$ which showed moderate correlation for all the samples.

Also from the analysis of the test of mean (using *t*-test), it was discovered that there is no significant difference between the mean concentrations of the elements obtained in 2001/2002 at Uturu and that obtained at Jos in 1989/1990 harmattan season. This is as a result of the fact that by *t*-test t_{cal} (1.977) lies between -2.776 and 2.776 of t_{tab} at 5% level of significance for the comparison between 2001/2002 with

respect to 1989/1990. Figure 1.0: shows relationship between concentration and elemental composition for 2001/2002 and 1989/1990.

The concentration of the elements in air obtained at Jos, Plateau State is in general higher than that obtained at Uturu. The aerosols at these stations are of non local origin and so the main source being harmattan haze that is blown from the Sahara Desert and transported by the North-East trade winds. However, small quantities of dust particles may also be air borne due to local effects. For us to describe adequately the mechanism of transportation of Saharan dust, then we must have a comprehensive knowledge of the aerosol characteristics, size, and shape, and concentration, true elemental and compound composition.

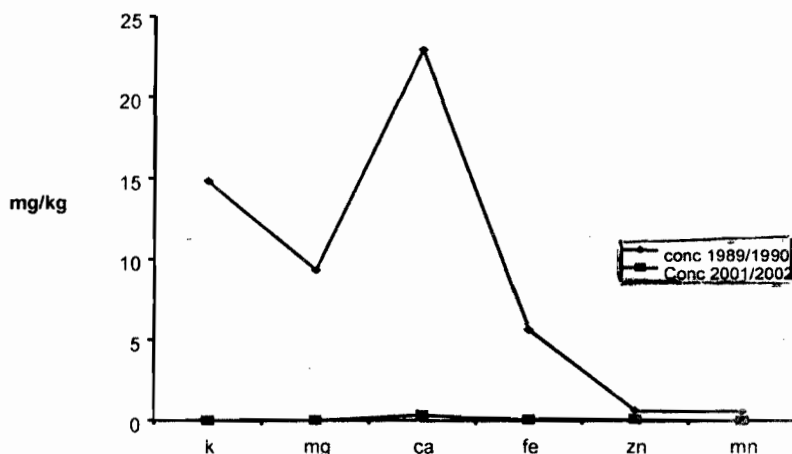


Fig. 1.0 Comparison between Uturu and Jos for 1989/1990 and 2001/2002

CONCLUSION

This work has illustrated the usefulness of AAS in determining the presence of multiple elements in air. 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, relatively low 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 latitudinal locations of the stations with respect to the aerosol source.

The mean values of the elemental concentrations obtained in mg/kg are 16.470 for potassium, 9.098 for magnesium, 331.995 for calcium, 47.673 for iron, 81.598 for zinc, 12.791 for manganese, and 1.161 for lead.

A comparison with the Arizona Ambient Air Quality (1999) acceptable level showed that the quality of air at Uturu is clean since the concentration of these elements in air is significantly below the deleterious level. This shows that air quality is cleaner over Uturu, at least when compared to over Jos.

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