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Elemental and Some Anion Concentration of Total Suspended Particulate Matter in Relation to Air Pollution in Maiduguri, Borno State, Nigeria

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Abstract: Total suspended particulate matter was collected using SKC side kick sampling pump method from Shukwari Ward of Maiduguri Metropolis, Nigeria between the periods of January to December, 2004 and was analyzed for 13 elements by Atomic Absorption Spectrophotometric (AAS) method. The concentrations of the elements in the entire quarter range from 0.02-5.12 μg m^{-3}. The highest elemental concentrations were observed in the order second quarter (April-June) >first quarter (January-March) >forth quarter (October-December) >third quarter (July-September). The results showed that the concentration of Na, Zn and Ni were highest in the suspended particulate matter, while Cr, Mn and Mg were low. Significant positive linear correlation coefficients among elements in the suspended particulate matter were established, indicating common sources of heavy metal pollution. The concentration of SO_4^{2-} ranged from 250 to 312.50 μg m^{-3} while NO_3^- ranged from 9900.00 to 15033.33 μg m^{-3}. The concentrations of the elements, SO_4^{2-} and NO_3^- in the suspended particulate matter exceeded the limits set by WHO and FEPA.

Key words: Air pollution, elemental, anion concentration, total suspended particulate matter, Borno, Nigeria

INTRODUCTION

Atmospheric environmental problems which had received little attention in Nigeria have become a subject of increasing national interest and importance over the last few years. An Environmental Protection Agency of Nigeria (FEPA) was established a few years ago to set environmental protection guidelines and enforce compliance. The public have become more concerned about the effects of environmental pollution.

Dust particle which are potential sources of trace element, nitrate and sulphate in air, are generated in large quantities in the Nigeria environment by wind, vehicle, construction works. Maiduguri capital of Borno State is known for its high commercial activities with its few scattered industries located in the state capital (Maiduguri). The state share borders with Chad, Cameroon and Niger Republic and records a lot of transportation activities within and to the neighboring countries by heavy trucks. Consequently, toxic waste from exhaust of cars, motorcycles and trucks are emitted into the atmosphere. Welding and construction of metal doors and windows is commonly seen by the major roads in Maiduguri. These welding activities release a lot of metal particles into the environment. Lack of steady power supply in Maiduguri and elsewhere in the state, compelled business activities to rely on generator sets as alternative power source which in turn emit some pollutants into the atmosphere.

The most conspicuous form of air pollution in the country is atmospheric dust with levels as high as 40,000 μg m^{-3}, have been reported in some industrial sites and up to 1033 μg m^{-3} in ambient air (Akeredolu, 1989; Asubiojo *et al*., 1992). Elemental concentrations in air born particulate have been

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reported in some European cities and United State (Hamilton, 1974; Dams, 1975; Finkelman, 1994; Benson *et al*., 1988), from India (Sinha and Bandhopadhyay, 1998) and Japan (Kato, 1996). However, most of these studies were concentrated mainly on an industrial areas and measurement were taken from 5-50 m above the ground.

There have been reports of total suspended particulate matter, their element, nitrate and sulphate concentrations within and around industrial complexes, road side dust and its effect on soil, vegetable and crops in other parts of the country (Adejumo *et al*., 1994; Ajayi and Kamson, 1983; Ndiokwere, 1985). However, similar reports have been very scanty in this part of Borno state, Nigeria.

Maiduguri (Lat. 11° 50'N, Long 13° 10'E) is located in Borno State, occupies North east position of Northern Nigeria. It is underline by the sediments of the Chad basin. The temperature ranges from 22-28°C, with means of the daily maximum exceeding 40°C before the onset of the rain during March, April and May. It has a minimum temperature drop as low as 12°C in December-February.

The aim of this study is to determine elemental, sulphate (SO_4^{2-}) and nitrate (NO_3^-) ions concentrations in Total Suspended Particulate (TSP) matter. And it is hoped that the results would be helpful in defining future air quality in Maiduguri.

MATERIALS AND METHODS

Sample and Sampling

This study was conducted in Maiduguri; samples were collected from Shukwari Ward of Maiduguri metropolis. Suspended particulate were collected daily for the periods of January-December 2004. Pulled samples were analyzed quarterly.

Suspended particulate matter samples was collected using SKC side kick sampling pump 244-50 by filtration through Whatman membrane filter paper of 25 m with a pore size of 3.0 μm for 24 h (Ogunsola *et al*., 1994) The high volume of air sampler (obtained from SKC limited, Bland ford Forum UK) operates at a normal flow rate of 0-10 L min^{-1}. A total of 1000 L 24 h airs was collected at each occasion. The amount of the total suspended particulate matter collected per volume of air is the difference between the two weights of the filter paper before and after sampling.

The sampler was placed on the roof top of storey buildings with a protective slab base to avoid being blown away by wind, to prevent obstruction from nearby buildings and to minimize collection of dust from the underlying surface. The selected sampling site is in the heart of the city were there is residential and public building.

Determination of Heavy Metals in Suspended Particulate Matter

For elemental analysis, the loaded filter paper was carefully treated with 7.5 cm^3 boiling concentrated 65% HNO_3 inside a Teflon beaker 5.0 cm^3 of 70% $HC1O_4$ was added and then the heating was continued at 120°C until the solution become clear. The excess acid was boiled off and the residue was dissolved in 2.0 cm^3 of concentrated HNO_3 and 10.0 cm^3 of distilled water by gentle heating. The solution was cooled and diluted with distilled water to 50.0 cm^3 in a volumetric flask.

Levels of heavy metals (copper, cobalt chromium, iron, zinc, manganese, lead, nickel, cadmium, Aluminium, sodium, potassium and calcium) were determined using perkin-Elmer atomic absorption spectrophotometer (Buck scientific Model-200A/210) with double beam background corrector. Air-acetylene flame and graphite furnace (perkin-Elmer HGA 500) and a hallow cathode lamp were used. All chemicals and reagents used for the analysis were of analar grade.

Determination of Nitrate and Sulphate Concentration in Suspended Particulate Matter

The concentration of sulphate and nitrate were determined using a DR/2010 HACH Portable Data Logging Spectrophotometer. The spectrophotometers (HACH DR2010) were checked for malfunctioning by passing standard solutions of all the parameters to be measured; Blank samples (deionized water) were passed between every three measurements of samples to check for any eventual contamination or abnormal response of equipment.

Nitrate as N was determined by the cadmium reduction metal method 8036 (Standard Methods, 1976; DWAF, 1992). The cadmium metal in the added reagent reduced all nitrate in the sample to nitrite; while sulphate was determined by using Sulfa Ver methods 8051 (Standard Methods, 1976; DWAF, 1992).

RESULTS AND DISCUSSION

The mean elemental concentration of total suspended particulate matter in the first quarter (January- March, 2004) are 0.58 μg m^{-3} for Cu; 1.81 μg m^{-3} for Pb; 4.32 μg m^{-3} for Zn; 1.24 μg m^{-3} for Fe; 0.12 μg m^{-3} for Cd; 1.03 μg m^{-3} for Mg; 4.31 μg m^{-3} for Na; 1.14 μg m^{-3} for K; 0.05 μg m^{-3} for Mn; 0.20 μg m^{-3} for Ca; 0.03 μg m^{-3} for Cr; 0.29 μg m^{-3} for Al; and 2.09 μg m^{-3} for Ni. The concentrations of the element decrease in the order Zn>Na>Ni>Pb>Fe>K>Mg> Cu> Al> Cu> Mn>Cr in Table 1. Zn recorded the highest mean concentration while Cr indicate the lowest mean concentration.

The mean concentrations of the element in the suspended particulate matter are 0.63 μg m^{-3} for Cu; 1.87 μg m^{-3} for Pb; 4.91 μg m^{-3} for Zn; 1.46 μg m^{-3} for Fe; 0.16 μg m^{-3} for Cd; 0.05 μg m^{-3} for Mg; 5.12 μg m^{-3} for Na; 1.65 μg m^{-3} for K; 0.08 μg m^{-3} for Mn; 0.25 μg m^{-3} for Ca; 0.09 μg m^{-3} for Cr; 0.36 μg m^{-3} for Al and 2.50 μg m^{-3} for Ni. The concentrations of the element decrease in the order

Table 1: Elemental concentration of total suspended particulate matter (μg m^{-3}) between the periods of January-March 2004 (First Quarter) in Maiduguri Metropolis

Elements	Range	Mean	Standard deviation
Cu	0.59-0.62	0.58	0.03
Pb	1.80-1.83	1.81	0.02
Zn	4.30-4.34	4.32	0.02
Fe	1.14-1.41	1.24	0.15
Cd	0.11-0.13	0.12	0.01
Mg	1.01-0.05	1.03	0.02
Na	4.11-4.62	4.31	0.27
K	1.12-1.16	1.14	0.02
Mn	0.04-0.06	0.05	0.01
Ca	0.19-0.21	0.20	0.01
Cr	0.02-0.05	0.03	0.02
Al	0.04-0.58	0.29	0.27
Ni	1.92-2.23	2.09	0.16

Table 2: Elemental concentration of total suspended particulate matter (μg m^{-3}) between the periods of April-June 2004 (Second Quarter) in Maiduguri Metropolis

Elements	Range	Mean	Standard deviation
Cu	0.60-0.69	0.63	0.05
Pb	1.86-1.89	1.87	0.02
Zn	4.83-5.02	4.91	0.10
Fe	1.43-1.49	1.46	0.03
Cd	0.14-0.18	0.16	0.02
Mg	0.03-0.08	0.05	0.03
Na	5.01-5.26	5.12	0.13
K	1.46-2.01	1.65	0.02
Mn	0.06-0.10	0.08	0.04
Ca	0.21-0.28	0.25	0.03
Cr	0.06-0.11	0.09	0.03
Al	0.08-0.64	0.38	0.28
Ni	2.11-2.96	2.50	0.43

Table 3: Elemental concentration of total suspended particulate matter (μg m^{-3}) between the periods of July-September 2004 (Third Quarter) in Maiduguri Metropolis

Elements	Range	Mean	Standard deviation
Cu	0.41-0.60	0.50	0.10
Pb	0.51-0.70	0.61	0.11
Zn	3.42-4.11	3.67	0.38
Fe	1.11-1.40	1.21	0.17
Cd	0.09-0.14	0.11	0.03
Mg	0.02-0.03	0.02	0.01
Na	3.63-4.31	3.90	0.36
K	1.01-1.14	1.07	0.07
Mn	0.02-0.07	0.04	0.03
Ca	0.16-1.22	0.52	0.60
Cr	0.01-0.03	0.02	0.01
Al	0.02-0.47	0.28	0.23
Ni	1.24-2.01	1.54	0.41

Table 4: Elemental concentration of total suspended particulate matter (μg m^{-3}) between the periods of October-December 2004 (Forth Quarter) in Maiduguri Metropolis

Elements	Range	Mean	Standard deviation
Cu	0.56-0.61	0.60	0.01
Pb	1.76-1.82	1.79	0.03
Zn	4.29-4.14	4.20	0.08
Fe	1.13-1.40	1.25	0.14
Cd	0.10-0.12	1.11	0.01
Mg	1.00-0.04	0.38	0.55
Na	4.01-4.52	4.28	0.26
K	1.10-1.14	1.12	0.02
Mn	0.03-0.05	0.04	0.01
Ca	0.17-0.20	0.18	0.02
Cr	0.02-0.03	0.02	0.01
Al	0.02-0.57	0.30	0.28
Ni	1.95-2.21	2.05	0.14

Na>Zn> Ni>Pb>Fe>K>Mg> Cu> Al> Cu> Mn>Cr. The mean elemental concentrations are in the order of Na>Zn>Ni>Pb>K>Fe>Al>Cu>Ca>Cd>Cr>Mn>Mg, with Na showing the highest mean concentration while Mg indicate the lowest mean concentration (Table 2).

Table 3 present mean concentrations of elements in suspended particulate matter in the third quarter with values of 0.501 μg m^{-3} for Cu; 0.61 μg m^{-3} for Pb; 3.67 μg m^{-3} for Zn; 1.21 μg m^{-3} for Fe; 0.11 μg m^{-3} for Cd; 0.02 μg m^{-3} for Mg; 3.90 μg m^{-3} for Na; 1.07 μg m^{-3} for K; 0.04 μg m^{-3} for Mn; 0.52 μg m^{-3} for Ca; 0.02 μg m^{-3} for Cr; 0.28 μg m^{-3} for Al; and 1.54 μg m^{-3} for Ni. The mean elemental concentrations are in the order of Na>Zn>Ni>Fe>K>Pb>Ca>Cu>Al>Cd>Mn>Mg> Cr, with Na showing the highest concentration while Cr indicate the lowest concentration.

Table 4 present the mean concentrations of elements in suspended particulate matter in the forth quarter, with values of 0.60 μg m^{-3} for Cu; 1.79 μg m^{-3} for Pb; 4.20 μg m^{-3} for Zn; 1.25 μg m^{-3} for Fe; 1.11 μg m^{-3} for Cd; 0.38 μg m^{-3} for Mg; 4.28 μg m^{-3} for Na; 1.12 μg m^{-3} for K; 0.04 μg m^{-3} for Mn; 0.18 μg m^{-3} for Ca; 0.02 μg m^{-3} for Cr; 0.30 μg m^{-3} for Al; and 2.05 μg m^{-3} for Ni. The mean concentration are in the order of Na>Zn>Ni>Pb>Fe>K>Cd>Cu>Mg>Al>Ca> Mn> Cr, with Na showing the highest concentration while Cr indicate the lowest concentration.

The concentrations of sulphate and nitrate between the first to forth quarter with values of SO_4^{2-} ranged from 250 to 312.50 μg m^{-3} while NO_3^- ranged from 9900.00 to 15033.33 μg m^{-3} (Fig. 1).

The concentrations of the elements were comparatively higher in the second quarter (April to June, Table 2) than those of first third and forth, quarter. Zn, Na, Ni and Pb exhibited high concentrations in all the quarters, while Cr, Mn and Mg showed very low concentration in the

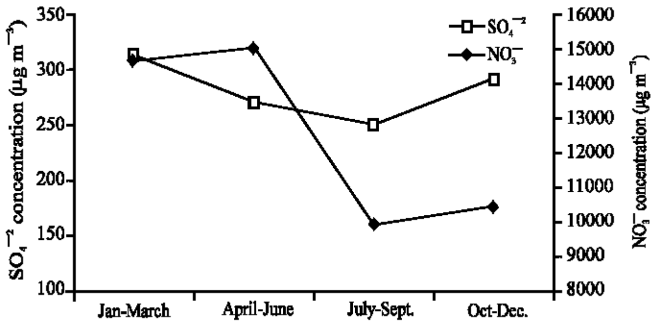

Fig. 1: SO_4^{2-} and NO_3^- concentration in SPM samples of Maiduguri

entire quarter. In general, the trend in the entire quarter decrease in the order second quarter (April-June, Table 2) >first quarter (January-March, Table 1) >forth quarter (October-December, Table 4) >third quarter (July-September, Table 3) as the season moved from dry to wet, there were decrease in concentrations of this element up to the third quarter as a result of washout and rainout within the area which finally result in the decrease of the element.

Sodium concentration was generally high in the entire samples analyzed (Table 1-4). Although sodium is essential for proper functioning of mammalian tissues, it is an important component of extra cellular fluid and function of potassium in normal irritability of muscles and permeability of cells. The deficiency of sodium has been reported to cause cardiac arrest and kidney failure; occasional case of diffuse cerebral disease including poliomyelitis, malignancy and tuberculosis, meningitis may exhibit sodium deficit (Mbadugha, 2005). The concentrations of Na and k were higher than the other elements determined in all the quarter. From the result of analysis, the concentrations of Na and K in the suspended particulate matter samples in all the entire quarter were higher than the safe limit set by WHO and FEPA for clean air. The high levels of Na, Ni and K was expected, because these elements are mostly associated with the natural background and in addition wind picks up particles enriched with Na and K from agricultural fields as a result of application of fertilizers containing these elements, though these elements are not environmentally hazardous. The result of Na, Ni and K in this study area was less than 28.00-254.34 µg m^{-3} obtained by Tanaka *et al*. (2000) and Karue *et al*. (1992).

Zinc is equally an essential element in the human diet. Zn deficiency in the diet may be more detrimental to human health than too much of it in the diet. Although Zn is not a human carcinogenic, ingestion of large doses can cause death (ATSDR, 1994). The concentration of zinc in the suspended particulate matter samples from Maiduguri exceeded the WHO guideline values for clean air.

Iron concentration was generally very high in all the sample analyzed (Table 1-4). Although, iron is one of the essential elements in human nutrition, however, when present at elevated concentration in aquatic ecosystems, serious pollution and health problems could result, Toxicity of iron in human beings has been found to bring about vomiting, cardiovascular collapse and diarrhoea. While iron deficiency may lead to failure of blood clothing to replenish (Turnland, 1988). The concentrations of Fe in the entire quarter were higher than safe limits set by WHO.

The concentration of lead in aquatic environment is risky to life since aquatic organisms used as food are particularly very sensitive to Pb and often retain about a percent of ingested lead which could be taken up by man through food chain (Young and Belvins, 1981). Lead can cause damage to the nervous system and the kidneys and it is a suspected carcinogenic (Radojevic and Bashkin, 1999). Copper is an essential substance to human life, however, in high concentrations, it can cause anaemia, liver and kidney damage, stomach and intestinal irritation (Turnland, 1988). Children exposed to high lead levels are particularly at risk. Exposure to high concentration of Cd damages the vasculature of the testicles. However, according to toxicological studies, excess Zn prevents many toxic effects of Cd (Haas, 2004). The levels of Pb, Cu, Cd, Ca and Mn in the analyzed suspended particulate matter (Table 1-4) showed that the limiting values of WHO were exceeded. The present of Pb, Cu, Cd, Ca and Mn in the suspended particulate may be attributed to metal mechanic, welding operations and vehicular emissions (Stern ***et al***., 1973). Concentration of Cr in the suspended particulate matter (Table 3, 4) were lowest in all the samples studied and does not give cause for concern presently, bio-magnification of it in the suspended particulate matter with time may lead to serious condition as chromium is extremely toxic.

Nitrate toxicity increases the risk of anaemia in infants and pregnant women and formation of carcinogenic nitrosamines (Bush and Meyer, 1982). A nitrate content of more than 100 mg L^{-1} impact bitter taste to water and may cause physiological problem. Both SO_4^{2-} and NO_3^- contribute to the acid deposition. According to epidemiological studies, atmospheric sulphates can contribute to the aggravation of asthma, heart and lung disease. Both sulphates and nitrates are responsible for the radiative cooling of the atmosphere as a result of scattering of solar radiation (Dorland ***et al***., 1997); Penner ***et al***. (1978) and Adams ***et al***. (2001). The presence of these ions (SO_4^{2-} and NO_3^-) were as a result of atmospheric processes of SO_2 and NO_2 (Pierson ***et al***., 1980; Appel ***et al***., 1981; Kalnay, 1996). From the result of analysis the concentration of SO_4^{2-} and NO_3^- in the suspended particulate matter samples exceeded the limits set by WHO for clean air. It could be observed that SO_4^{2-} and NO_3^- peaked at first (January-March) and second (April-June) quarter of the period of analysis, respectively. As the season moved from dry to wet, there were decrease in concentrations of both ions up to the third quarter as a result of washout and rainout (Ogugbuaja and Barsisa, 2001) and peaked finally at the forth quarter (October-December) (Fig. 1). The presence of these ions (SO_4^{2-} and NO_3^-) in the first and second quarter was as a result of atmospheric processes of SO_2 and NO_2 (Pierson ***et al***., 1980; Appel ***et al***., 1981; Kalnay, 1996), while the decrease of these ions in the third quarter might be attributed to washout of SO_2 and NO_2 by rain which reduces the concentration of SO_4^{2-} and NO_3^- (Ogugbuaja and Barsisa, 2001).

The correlations among elements in the suspended particulate matter (Table 5) indicate that coefficients between Cu, Pb, Zn, Fe, Na, K, Cr, Al and Ni; Pb, Zn, Fe and Ni; Zn, Fe, Na, K, Cr and Ni; Fe, Na, K, Cr Al and Ni; Na, K, Cr and Ni; K, Cr and Ni; Cr, Al and Ni; Al and Ni indicated positively significant ($p = 0.05$) correlations. Moreover, the correlations between Zn and Na, Cu and Ni, K and Cr were very significant ($R = 0.91$-0.94, $p = 0.05$), indicating the co-accumulation relation of both metals in suspended particulate matters. These results indicate that these element were bound to the suspended particulate matter within the same period and could be said to have a common anthropogenic pollution origin (Haas, 2004), from agricultural fields as a result of application of fertilizers containing Na and K, metal mechanic, welding operations and vehicular emissions

Table 5: Persons correlation matrix for pair of the analyzed elements

Elements	Cu	Pb	Zn	Fe	Cd	Mg	Na	K	Mn	Ca	Cr	Al	Ni
Cu													
Pb	0.75												
Zn	0.86	0.80											
Fe	0.73	0.73	0.76										
Cd	0.20	0.32	-0.05	-0.10									
Mg	0.17	0.42	0.08	-0.04	0.00								
Na	0.82	0.65	0.94	0.90	-0.09	-0.03							
K	0.65	0.42	0.80	0.69	-0.22	-0.26	0.84						
Mn	0.21	0.25	0.21	-0.12	-0.25	0.41	0.02	0.05					
Ca	0.16	-0.42	-0.02	0.32	-0.20	-0.23	0.04	-0.01	-0.03				
Cr	0.67	0.46	0.84	0.79	-0.29	-0.17	0.91	0.94	-0.01	0.00			
Al	0.56	0.15	0.35	0.71	0.01	0.17	0.54	0.43	-0.22	0.29	0.54		
Ni	0.93	0.74	0.92	0.77	0.07	0.16	0.89	0.80	0.11	0.07	0.83	0.60	

(Stern *et al*., 1973). Pb and Ca; Zn and Cd Ca; Fe, Cd Mg and Mn; Cd, K Mn Ca Cr and Al; Mg, Na K Ca Mn Cr and Al; Na, Mn and Ca; K, Ca and Al; Mn, Ca Cr Al and Ni showed no significant relation but were positively and negatively related (Table 5). This however does not mean that the elemental concentrations may not have come from the above sources. Their week relations could be attributed to physical disturbance or diagenesis, thus causing them to be released into the lower layer of the surrounding environment. However, this creates possibilities for further studies on the distribution and speciation of these metals in the suspended particulate matter so as to generate more information on the degree of pollution as well as the actual environmental impact of the discharges on metal availability.

CONCLUSIONS

In general, average elemental concentrations values in the entire quarter decrease in the order second quarter (April-June, Table 2) >forth quarter (October-December, Table 4) >first quarter (January-March, Table 1) >third quarter (July-September, Table 3), while the concentration of SO_4^{2-} and NO_3^- peaked at first (January-June) and second (April-June) quarter of the period of analysis, respectively as the season moved from dry to wet, there were decrease in concentrations of this element up to the third quarter as a result of washout and rainout of these elements from the atmospheric. Significant positive linear correlation coefficients among elements in the suspended particulate matter were established, indicating common sources of heavy metal pollution. Hence, based on the results obtained it can be concluded that the air was polluted at the time of this study.

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