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Elemental Characterization and Source Apportionment of Air Particulate Matter in Two Contrastive Industrial Areas in Nigeria

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Abstract: Total Suspended Particulate Matter collected at different sites located in Warri (WRR) and Ewu were analyzed for 14 elements by Atomic Absorption Spectroscopy (AAS). Multivariate statistical methods such as Factor Analysis (FA) and Enrichment Factor (EF) were used for the identification of sources. The results obtained showed that Total Suspended Particulate (TSP) concentration in the sampling locations were 922-2333 μg m^{-3} for WRR and 816-2600 μg m^{-3} for Ewu. The major sources of these elements were due to re-entrained soil, auto-mobile exhaust, residual oil combustion, petroleum activities, sea salt, steel/metal works and refuse/biomass incineration. Element such as Cd, Se, V and Pb were highly enriched while elements such as Ni, Cr, Na and K were moderately enriched in some of the sampling sites. Source apportionment by Chemical Mass Balance (CMB) and Factor Analysis of the pollutant revealed anthropogenic contribution of about 35-70% in the two locations.

Key words: Airborne particulate, characterization, multivariate statistical methods, anthropogenic, industrial areas

INTRODUCTION

Atmospheric pollution, which had received little attention in the past, has become a subject of national interest in the last few years. There are numerous human activities, which result in the environmental release of potential toxic substances in the atmosphere. The identity of these sources has been established in most cases but their quantitative importance is only rarely determined.

The air borne dust may have variety of sources. The chemical composition of all the emission sources varies strongly. In order to trace down the pollution sources and to determine the extent of the anthropogenic contribution, a fundamental study of the chemical composition is necessary. Also for studies of health effects, source characteristics, atmospheric transport processes and removal rates, the knowledge of the chemical composition is necessary.

The greatest air pollution in the Nigeria environment is atmospheric dust[1]. Several authors have determined the elemental constituents of air borne particulate in Nigerian cities[2-4]. Levels of TSP as high as 40,000 μg m^{-3} have been recorded in some industrial sites while up to 1033 μg m^{-3} were reported for ambient air[5]. Elemental concentrations in air borne particulate have been reported in some European cities and United States[6-9] from India[10,11] and Japan[12]. Trace elements have also been reported in South Pole[13] and in ocean air[14]. However, most of these studies were concentrated mainly on an industrial areas and measurement were taken from 5-50 m above the ground. Conscious of the more serious health implication we have carried out studies on the elemental constituents of TSP collected from 100 m above the ground in two Nigeria locations with a sharp contrast in industrial development. The two sites/locations are about 220 km apart.

MATERIALS AND METHODS

Sample locations: Airborne particulate samples were collected at two locations in Jan-Dec 2002. Sampling was done for both wet and dry seasons. Warri represents an urban and industrial area where a number of oil companies such as the Nigeria National Petroleum Cooperation, (NNPC), Shell Development Company, Texaco and Chevron etc., operate. Also prominent in this area are small-scale businesses, clusters of mechanics, filling stations, saw millers, spray painter etc. Ewu is rural but an industry, bendel feed and flour mills is located in this place. Ewu is also a transitory town and experiences a daily heavy traffic flow from western and eastern parts to the northern part of the country. Activities such as road construction and different artisans were common in this area.

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TSP was collected using SKC sidekick sampling pump 224-50. In Warri sample were collected from the following locations: NNPC refinery complex, Petroleum Training Institute (PTI), Aladja steel complex and Enerhen junction area. At Ewu samples were collected from Illeh, Bendel Feed and Flour Mill Spot, Idunwele village and Uromi/Agbor Road junction area. The sampling was carried out by filtration on whatman membrane filter of 25 mm with a pore size of 3.0 μm for 8 h[2,15], using a High Volume Air Sampler (HVAS), which operated at a nominal flow rate of 0.00 to 10.00 L min^{-1}. A total of 1200 L per 8 h air was sampled for each occasion.

Sample preparation and measurement: For the AAS analysis, the loaded filter paper was carefully treated with 7.5 cm^3 of boiling concentrated 65% HNO_3 inside a Teflon beaker. 5.00 cm^3 of 70% $HClO_4$ was added and heating continued at 120^{0}C until the solution become clear. The solution was further evaporated to dryness and the residue was re-dissolved in 2.0 cm^3 of distilled water, cooled and diluted with distilled water to 50.0 cm^3 in volumetric flack. The trace element analysis was carried out using Perkin-Elmer Atomic Absorption Spectrophotometer (Buck Scientific Model 200/210A) with double beam and background corrector. Air-acetylene flame and Graphite furnace (Perkin-Elmer HGA 500) and a hollow cathode lamp were used.

RESULTS AND DISCUSSION

The mean concentration of TSP obtained for the two locations are 1332.7 and 1327.3 μg m^{-3} for WRR and Ewu, respectively. These values are about 5-fold the 250 μg m^{-3} annual average stipulated by the National Regulating Agency[16]. The infringement being more if the World Health Organization, standard of 40-120 μg m^{-3} were used as basis for comparison. It is likely that both natural and anthropogenic sources contribute to the high levels of TSP in air. A natural source such as transatlantic transport of dust over West Africa during the dry season is suspected to contribute to the high levels of TSP particularly in Ewu which is in the northern part of the region. The high level of TSP concentration can also be interpreted to be largely due to road dust re-suspension and vehicular movement. Fly ash from power plants, burning of wood in houses and other commercial activities may also contribute to the increased level of TSP.

Compared to the industrialized world, the values obtained for the two locations were quite high, e.g., Tokyo, Japan had a mean TSP concentration of 38 μg m^{-3}[17], Brisbane, Australia recorded 26.6 μg m^{-3}[18,19] and London had 28 μg m^{-3} while Leeds, England had 25 μg m^{-3}[20].

Table 1: Elemental concentrations of TSP (μg g^{-1}) in WRR

Elements	Minimum	Maximum	Mean	Standard deviation
AS	3.000	5.21	3.97	0.99
Mn	0.02	0.05	0.04	0.02
Ni	1.00	2.03	1.17	0.012
Cd	0.02	0.23	0.12	0.01
Se	4.02	6.01	4.65	0.95
V	1.45	2.68	2.08	0.02
Fe	1.13	1.38	1.18	0.03
Pb	1.01	1.04	1.03	0.02
Cu	0.01	0.09	0.04	0.03
Al	0.12	0.68	0.19	0.03
Cr	0.03	0.06	0.04	0.01
Na	5.06	7.77	6.16	1.14
K	1.38	2.66	2.00	0.39
Ca	1.68	3.48	2.23	0.25

Table 2: Elemental concentration of TSP μg g^{-1} in Ewu

Elements	Minimum	Maximum	Mean	Standard deviation
As	NDL	NDL	NDL	-
Mn	0.01	0.03	0.02	0.003
Ni	0.02	0.13	0.12	0.003
Cd	0.03	0.14	0.05	0.004
Se	0.11	0.42	0.26	0.12
V	0.13	0.46	0.35	0.04
Fe	0.01	0.40	0.25	0.14
Pb	0.03	0.75	0.12	0.04
Cu	0.04	0.07	0.05	0.03
Al	0.12	1.55	0.45	0.01
Cr	0.01	0.06	0.04	0.05
Na	0.40	3.67	1.55	0.87
K	2.05	3.47	2.05	1.12
Ca	3.47	4.81	3.47	1.08

NDL - Not within Detection Limit

The concentrations obtained for Ewu sample are lower in comparison with that of WRR (Table 1 and 2). For example the concentration of Pb in WRR sample is about 9 times that of Ewu. Similarly the concentration of V in WRR sample is about 6 times that obtained in Ewu. This is in line with the pattern of vehicular distribution in the locations and V which is a major constituent of crude oil and also part of the major component of soot is expected to be at higher level in this part of the Niger Delta, where prospecting and exploration of crude oil is at its peak.

The concentrations of all the elements are quite close with exception of As (Table 3). This might be attributed to the geological locations of the two sites, vehicular movements, oil exploration and commercial activities. Apart from Cr, Na, K, Ca in WRR, levels of the other elements determined are within the same range.

To obtain better information on the particle loading, enrichment factors of the elements were calculated using Wedepohl's values for the composition of crustal rock and Fe as the normalizing elements as follows[23]:

Mn, Al and Ca have E.F less than 4 in WRR. Similarly the E.F of Mn and Al is < 4. In contrast the E.F of Ca is > 4 in Ewu (Table 4). This is consistent with the presence of flour mill in the area because of the use of $Ca_3(PO_4)_2$ in the production of flour.

Table 3: Comparison of mean elemental concentration with other cities (μg g^{-1})

Elements	WRR	Ewu	Rubidoux	Tokyo	Khart-trum	Antwerp
As	3.97	NDL	NAF	NAF	NAF	NAF
Mn	0.04	0.02	0.067	0.0401	0.091	0.0096
Ni	1.17	0.12	0.0077	0.00563	0.061	NAF
Cd	0.12	0.05	NAF	NAF	NAF	NAF
Se	4.65	0.26	NAF	NAF	NAF	NAF
V	2.08	0.35	0.016	0.0089	0.014	0.013
Fe	1.18	0.25	2.53	0.676	5.7	0.33
Pb	1.03	0.12	0.071	0.124	0.047	011
Cu	0.04	0.05	0.086	0.03	0.0069	NAF
Al	0.19	0.45	4.21	0.429	4.9	NAF
Cr	0.04	0.04	0.014	0.00609	0.014	0.021
Na	6.16	1.55	NAF	0.637	NAF	0.446
K	2.00	2.05	1.36	NAF	1.26	0.17
Ca	2.23	3.00	5.72	0.468	4.2	0.3

NAF = Not Analyzed For, Sources: Eltayeb[21] and Chow[22]

Table 4: Elemental concentration in typical crustal rock and calculated Enrichment Factor (EF)

Elements	Typical crustal rock	EF (WRR)	EF (Ewu)
As	40	3288.91	-
Mn	850	0.66	0.481
Ni	5750	44.84	4.205
Cd	2	3395.82	227.640
Se	4	508.62	340.502
V	500	163.86	49.032
Fe	2800	1.0	1.0
Pb	10-300	229.89	27.15
Cu	20	10.89	11.860
Al	7100	0.48	0.417
Cr	1500	21.15	0.133
Na	6,300	29.07	2.731
K	400	29.23	62.508
Ca	137000	0.52	8.728

Table 5: Rotated factor loading for TSP in Warri

Variables	Factor 1	Factor 2	Communality
As		0.844	0.949
Mn		0.960	0.923
Ni	0.679	0.255	0.988
Cd	0.925		0.918
Se	0.423	0.328	0.951
V		0.948	0.941
Fe	0.999	0.421	0.998
Pb		0.721	0.977
Cu	0.850		0.832
Al	0.968		0.990
Cr	0.988		0.984
Na	0.843	0.458	0.937
K	0.612		0.982
Ca	0. 929		
Variance	0.979	4.293	
%Variance	64.133	30.700	
Possible Sources	Steel, metal works/sea salts	Residual combustion, Auto/soil dust	

Pb, V and As enrichment should be due largely to vehicular emission and residual oil combustion. The release of lead from vehicle exhaust has been attributed to the addition of lead alkyl as anti knock additive to gasoline to increase its octane number; bromine is also added in the form of ethylene dibromide along with chloride in the form ethylene dichloride to scavenge the Pb from engine cylinders during combustion[24]. In Nigeria, the mean content of lead in super grade gasoline is 0.74 g L^{-1}[25], one of the highest in the world.

The EF for Na is 29.07 and 2.73 for WRR and Ewu, respectively. The level obtained for WRR should be due to pronounced effect of sea breeze in the region. The high EF for Cr, Cu, Ni Cd and Se is likely due to brake pad and tyre wears, refuse incineration and other industrial processes[3].

The results of inter-elemental correlation matrix showed that V is strongly correlated with Ni, Cd, Se. Fe, Cu and As and Mn at Ewu and WRR. This is certainly not unconnected with anthropogenic sources because the elements are not crustal in origin. Values of 1.838 and 1.678 were obtained for V/NI ratio in WRR and Ewu, respectively. The values compare well with the crude oil ratio of 2.0. The values obtained for K/Fe ratio in the two locations are 1.670 (WRR) and 8.056 (Ewu). Iron and potassium are generally crustal in origin with a ratio of 0.45. When this ratio is exceeded, it suggests that K has other sources besides earth crust[26].

The mean elemental concentrations of TSP were subjected to Factor Analysis (FA) using SPSS statistical package. To determine the number of factors to retain in the results, the values of variance after rotation were examined and only factors with variance ≥ 1 after rotation were considered significant, as suggested by Roscoe *et al.*[27]

Two major factors were identified in WRR. Factor 1 with high loadings in Ni, Cd, Fe, Cu, Al, Cr, Na, K and Ca. This factor represents a combination of steel, metal works and sea salt earlier referred to. Factor 2 has high loadings in Mn, V and Pb, which can be interpreted as contribution from combination of residual oil combustion, auto and soil dust (Table 5).

Five factors were identified in Ewu. Factor 1 has high loadings in Mn, Cd and Pb. This is attributed to automobile exhaust. Factor 2 with high loadings in Mn, Al and Cr but moderately in V is due to combination of

Table 6: Rotated factor loading for TSP in EWU

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Mn	0.871	0.851	0.248			0.946
Ni		0.385	0.885			0.916
Cd	0.874	0.378		0.351		0.953
Se	0.434			0.439	0.685	0.860
V	0.774	0.599		0.360	0.783	0.828
Fe		0.445		0.397		0.979
Pb	0.939		0.139	0.359	0.524	0.994
Cu		0.205				0.933
Al	0.269	0.813				0.754
Cr		0.940	0.401			0.972
Na		0.128	0.216	0.617		0.894
K		0.459	0.728	0.690		0.961
Ca		0.396		0.796		0.980
Variance	4.792	2.936	1.926	1.251		1.065
%Variance	36.860	22.587	14.817	9.624		8.196
Possible Sources	Auto exhaust	Construction/ entrained soil factor	Refuse incineration and biomass burning	Emission from industrial processes	Emission from metal works/ other artisans	

construction works and entrained soil factor. Factor 3 with high loadings in Ni and K is also a combination of refuse incineration and biomass burning. Factor 4 and 5 have high loadings in Na, K and Se, V, Cr and moderately in Pb, respectively (Table 6). This is due to emission processes from industries, metal works and artisans.

The result of elemental characterization of TSP were also subjected to cluster analysis with the aid of cluster package using Euclidean distance and complete linkage farthest neighbors as a measure of correlation. The results showed a significant clustering of Fe, Pb Ni and V. Other clusters also observed are K, Ca and As, Se and Na in WRR. In Ewu the clustering observed are Mn, Cd, Se, Cu, Ni, V, Pb and Al and Cr.

The results of CMB showed contribution of 10-12% from construction works and entrained soil factor, 15% for emission from metal works and artisans, 18% each from refuse/biomass incineration and industrial processes in Ewu while in WRR the contribution of soil dust and petroleum ranged 14-18%, steel/metal works and sea spray ranged 26-42%.

CONCLUSIONS

The value of TSP for the two industrial locations are closed but exceeded both the Federal Environmental Protection Agency, (FEPA) and WHO standards.

The enrichment factor showed that anthropogenic elements are highly enriched while the soil-derived elements are weakly enriched. There is a sharp contrast in the elemental concentration obtained in the two locations and this suggests that WRR is more of an urban/industrialized area than Ewu.

REFERENCES

1. Akeredolu, F.A., 1989. Seasonal Variation in Deposition Rates. Concentrations and chemical composition of particulate matter in Ile-Ife, Nigeria. Atmos Environ., 23: 783.
2. Ogunsola, J.A., O.I. Asubiojo, O.A. Akanle and N.M. Spyrou, 1994. Analysis of suspended air particulate along some motor ways in Nigeria by PIXE and EDXRF. Phy.Res., 79: 404-407.
3. Ndiokwere, C.L. 1984. A study of heavy metal concentration from motor vehicle emission and its effect on road side soil, vegetation and crops in Nigeria. Environ. Poll. Series, 7: 35-42.
4. Akeredolu, F.A., H.B. Olaniyi, J.A. Adejumo, I.B.Obioh, O.J. Ogunsola, O.I. Asubiojo and A.F. Oluwale, 1994. Determination of elemental composition of TSP from cement industries in Nigeria using EDXRF technique. Nuc. Instru. Meth. Phy. Res., 353: 542-545.
5. Asubiojo, O.I., I.B. Obioh, E.A. Oluyemi, A.F. Oluwole, N.M. Spryou, A.S. Faroogi, W. Arshed and O.A. Akanle, 1992. Elemental characterization of airborne particulates at two Nigerian locations during the harmattan seasons. Radio. Anal. Nuc. Chem., 5: 213-219.
6. Hamilton, E.I., 1974. Heavy metals in the environment. Sci. Total Environ., 3: 8.
7. Dams, R., 1975. Elemental concentrations of airborne particulates. Atmos. Environ., 9: 1099.
8. Finkelman, R.B., 1994. Modes of occurrence of potentially hazardous elements in coal. Levels of confidence. Fuel Process Technol., pp: 101-120.

9. Benson, S.A., J.H. Pavlish and C.J. Zygarlicke, 1988. Trace elements in low-rank coals. Proceeding of 15th International Pittsburgh Coal Conf., pp: 98-110.
10. Sinha, S. and T.K. Bandhopadhyay, 1998. Review of trace elements in air environment and its health impact in some Indian Cities. IPHE, Ind., 1: 35-46.
11. Banerjee, S.P. and S. Sinha, 1997. Characterization of haul road dust in indian open cast iron ore mine. Atmos. Environ., 31: 17.
12. Kato, T., 1996. Effects of atmospheric pollutants. Talanta, 23: 517.
13. Maenhaut, W., 1993. Source and Composition of aerosol from Khartoum, Sudan, Atmos. Environ., 27: 67-76.
14. Bressan, D.J., 1974. Elemental constituents of airborne particulates. J. Radioanal. Chem., 19: 373.
15. Annonymous, 1996. Measurement of Suspended Particulate Matter in Ambient Air, WHO/EOS/94.3, UNEP/GEMS/94, A.4 UNEP, Nairobi. GEMS/AIR Methodology Review, 3: 242.
16. Annonymous, 1991. Guidelines and standards for environmental pollution control in Nigeria. Federal Environmental Protection Agency, Federal Republic of Nigeria, pp: 149-194.
17. Tenaka, S., F. Var and Y. Narita, 2000. The concentration, trend and seasonal variation of metal in the atmosphere of 16 Japanese cities shown by result of National Air Surveillance Network (NASN). Atmos. Environ., 34: 2755-2770.
18. Chan, Y.C., R. Simpson, G.H. Mctainsh and P.D. Vowels, 1997. Characteristics of chemical species in $PM_{2.5}$ and PM_{10} Aerosol in Brisbane, Australia. Atmos. Environ., 31: 3737-3785.
19. Chan, J.C., 1995. Measurement methods to determine compliance with ambient air quality standard for suspended particulate matter. Air and Waste Manage. Ass., 45: 320-382.
20. Harrison, R.M., A.R. Deacon, R.G. Derwant, D.R. Middleton and S. Moorcroft, 1997. Analysis and interpretation of measurement of suspended particulate matter at urban background sites in the United Kingdom. Sci. Total Environ., 203: 17-36.
21. Eltayeb, M.H.J., C.G. Xhofter, P.J. Vanesspen, R.E. Van Grieken and W. Meanhaut, 1993. Sources and composition of aerosol from Khartoun, Sudan. Atmos. Environ., 27: 67-76.
22. Chow, J.C., 1995. Measurement methods to determine compliance with ambient air quality standard for suspended particulate matter. J. Air Waste Manage. Assoc., 45: 320-380.
23. Wedepohl, K.H., 1971. Geochemistry. Holt Rinchart and Winston, New York, pp: 94.
24. Annonymous, 1991. Automotive air pollution: Issues and options for developing counties. World Bank Report, pp: 142.
25. Arah, A.R.O. and J.N. Nwankwo, 1987. Lead free gasoline in Nigeria. International seminar on the petroleum industry and the Nigeria environment. Owerri, Longmans, pp: 128.
26. Lewan, M.D. and J.B. Maynard, 1988. Factors controlling enrichment of vanadium and nickel in the butimen of organic sedimentary rocks. Geochim ET Cosmochim Acta, 46: 2547-2560.
27. Roscoe, B.A., P.K. Hopke, S.L.Dattner and J.M Jenks, 1982. The use of principal component factor analysis to interprete particulate compositional set air poll. Contr. Ass., 32: 637-647.