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Elemental Concentrations of Total Suspended Particulate Matter in Relation to Air Pollution in the Niger Delta of Nigeria: A Case Study of Warri

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Abstract: Air particulate matter collected by gravimetric method at five locations where industrial activities are concentrated in Warri, Nigeria, was analyzed for 14 elements by Atomic Absorption Spectrophotometric method (AAS). The particulate matter range of 922-2333 μg m^{-3} was obtained. The highest elemental concentrations measured in the samples were for As, Se, V, Na and Ca. The results show that As, Cd, Se V and Pb are derived from combustion and industrial activities and are highly enriched while the elements Na, Ca and Al which are soil derived are moderately enriched. Data analysis show that steel/metal works, sea salts, residual oil combustion, motor vehicle and re-entrained soil dust are the major sources of the elements in the atmospheric environment. The chemical mass balance analysis revealed an anthropogenic contribution of 37-75%. The precision of measurement is 4-5.5%.

Key words: Air pollution, elemental concentration, Enrichment factor, TSPM

Introduction

Atmospheric environmental problems which had hither to receive 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 has become more concerned about the effects of environmental pollution.

Dust particles which are potential sources of trace elements in air, are generated in large quantities in the Nigerian environment by wind, motor vehicles, demolition and construction works. The operations of a number of petroleum producing companies such as Nigerian National Petroleum Corporation (NNPC), Nigerian Liquefied Natural Gas (NLPG), Shell Petroleum Development Corporation (SPDC), Chevron Nigerian PLC, Mobil Nigeria PLC, and others are concentrated in this area of study. Each of these companies produces its characteristic wastes, which are exhausted into the surrounding atmospheric environment. National gas flare sites are also located not far from this oil industrial city of Warri.

The most conspicuous form of air pollution in the country is atmospheric dust which 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). Because of the risk posed by elements in suspended particulate matter to human health and ecosystem, it is important to develop effective control measures for air particulate emission. However, an important step in air control program is the identification of

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pollutants, the contributing sources and the relative contribution of each source. Receptor modeling techniques applied to elemental concentration data have been shown to be quite useful in identifying sources and apportioning contributions of the sources to air particulate matter at specific sites (Cooper and Gordon, 1980; Chow, 1995; Cheng *et al*., 1980).

There have been reports of total suspended particulates, their elemental concentrations within and around industrial complexes, road side dust and its effect on soil, vegetation and crops in other parts of the country (Adejumo *et al.,* 1994; Ajayi and Kamso, 1983; Ndiokwere, 1985). However, similar reports have been very scanty in this part of the Niger Delta, Nigeria. Therefore, the present study focused at attempting to provide much needed baseline information on air quality in Warri and quantify the contribution of the industrial activities to the pollution of this Nigerian City using receptor modeling techniques.

Materials and Methods

This study was conducted in Warri, Nigeria. Samples were collected from the following locations: NNPC refinery, Petroleum training institute, Airport, Enerhen and Cemetery Road Junction areas. In these areas, small-scale businesses such as scrap metal dealers' yard, clusters of mechanics, welders, spray painters, vulcanizers and saw millers operate. In the NNPC complex, loading of various products of crude oil was at its peak during sampling period. Samples were collected for a period of 15–18 months to ensure that both wet and dry seasons were covered.

Particulate matter samples were collected using SKC side kick sampling pump 224-50 by filtration through what man membrane filters of 25 mm with a pore size of 3.0 μm for 8 h (Ogunsola *et al.,* 1994). The high volume air sampler (obtained from SKC limited, Bland ford Forum UK.) operates at a nominal flow rate of 0-10.0 L min^{-1}. A total of 1200 L 8 h^{-1} air was collected on each occasion. Each sample of the particulate matter was obtained by equilibrating the filter and the cassette in charged desiccators for 24 h and weighed before and after sampling. The amount of the total suspended particulate matter collected per volume of air is the difference between the two weights.

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 sites in the heart of the city were residential and public buildings.

For AAS 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% $HCl0_4$ was added, and then heating was continued at 120°C until the solution became 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.

The levels of the elements were measured 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.

Results and Discussion

The average load of total suspended particulates measured in Warri is 1332.75 μg m^{-3}. This is about five times the FEPA recommended allowable/permissible level and eleven times the WHO standard (Wedepohl, 1971). It is likely that both natural and anthropogenic sources contribute to this measured high level. There has been a tremendous increase in the volume of motor vehicle traffic in Warri and its environs. There are also a major steel plant and refinery located in Warri. The effluent gases and particulates from these factories are exhausted into the air. The level of industrialization has also been on the increase in recent times. The open burning of waste and poor management of few incinerators may also enhance the level of total suspended particulates. The high level of total suspended particulate matter can also be interpreted to be due to road dust re-suspension and vehicular movement. Fly ash from power plants, burning of wood in houses and other commercial activities contributed to the increased level of total suspended particulates.

The levels of total suspended particulates from other world cities and the studied area are shown in Table 1. The levels of these elements are quite high in V, Ni and As, which are contained in crude oil, are highly enriched in this part of the Niger Delta where the exploration of crude oil is prevalent (Table 2).

Enrichment Factor (EF) is a better indication of environmental contamination than gross elemental concentration (Table 2). The EF was calculated using Wedepohl's value (Wedepohl, 1971). The crustal type elements have enrichment factor less than one, except Na and K that are moderately enriched. The anthropogenic elements As, Cd, Se, V, Pb and Ni and highly enriched.

Results of Table 3 showed that V is strongly correlated with As, Mn, and Se and moderately with Pb. This is certainly not unconnected with anthropogenic sources because these elements are not crustal in origin. Ca is strongly correlated with Ni, Cd, Fe, Cu, Al and Cr. This could be as a result of sea spray, refuse incineration and bush burning and metal works that are common in this area.

Table 1: Total suspended particulate matter ($\mu g\ m^{-3}$) of the studied area and some other industrial world cities

Cities	TSPM ($\mu g\ m^{-3}$)	Source
Tokyo, Japan	28	Tanaka *et al.* (2000)
Brisbane, Australia	26.6	Chan *et al.* (1997)
London, England	28	Harrison *et al.* (1997)
Leeds, England	25	Ditto
Warri, Nigeria	1332.8	This study
Lagos, Nigeria	520-800	Baum Bach *et al.* (1995)
Quindoa, China	154	Davis and Jinxing (2000)
Beijing, China	766	Ditto
Khartoum, Sudan	114	Eltayeb *et al.* (1993)
Nairobi, Kenya	69.893-254.369	Karue *et al.* (1992)

Table 2: Elemental concentration of total suspended particulate matter ($\mu g\ m^{-3}$) in Warri

Elements	Range	Mean	Enrichment factor
As	3.01-5.21	3.97±1.00	3288.97
Mn	0.02-0.05	0.01±0.02	0.66
Ni	1.05-2.03	1.17±0.01	44.84
Cd	0.02-0.23	0.12±0.01	3395.82
Se	4.03-6.01	4.65±0.95	39,424.56
V	1.45-2.68	2.09±0.05	153.37
Fe	1.13-1.38	1.18±0.03	1
Pb	1.01-1.04	1.02±0.12	113.42
Cu	0.01-0.09	0.04±0.03	8.48
Al	0.01-0.68	0.19±0.03	0.16
Cr	0.03-0.06	0.02±0.01	1.35
Na	5.06-7.77	6.16±1.14	32.96
K	1.38-2.66	2.00±0.39	15.88
Ca	1.67-3.46	2.23±0.25	0.57

Table 3: Inter elemental correlation matrix for TSPM

Correlation	As	Mn	Ni	Cd	Se	V	Fe	Pb	Cu	Al	Cr	Na	K	Ca
As	1.00	0.71			0.986	0.844	0.825							
Mn	0.761	1.00			0.827	0.984								
Ni			1.00	0.918			0.677		0.934	0.998	0.938			0.913
Cd			0.918	1.00			0.906		0.751	0.923	0.927			0.999
Se	0.986	0.827			1.00	0.883		0.721						
V	0.844	0.984			0.883	1.00		0.544						
Fe			0.977	0.906			1.00		0.856	0.965	0.984			0.910
Pb	0.825				0.721	0.544		1.00				0.515		
Cu			0.934	0.751			0.856		1.00	0.940	0.758			0.734
Al			0.998	0.923			0.965		0.940	1.00	0.923			0.917
Cr			0.938	0.927			0.984		0.758	0.923	1.00			0.937
Na									0.515			1.00		0.605
K												0.605	1.00	
Ca			0.913	0.999			0.910		0.734	0.917	0.37			1.00

Table 4. Rotated Factor Loading for TSPM in Warri

Variables	Factors 1	Factors 2	Communality
As		0.844	0.949
Mn		0.690	0.923
Ni	0.979	0.255	0.988
Cd	0.925		0.918
Se	0.423	0.328	0.941
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		0.902
Variance	8.929	4.293	
% Variance	64.133	30.700	
Possible Sources	steel, metal works/sea Salts	Residual oil combustion Vehicle exhaust/Soil dust	

The ratio of vanadium to nickel in crude oil is about 2. This ratio can be use to identify residual oil as contributing to ambient fall out particles. In this study we obtained a value of 1.79. This value compares well with crude oil ratio. Potassium and iron are generally crustal in origin with a ratio of 4.5 (WHO, 1995). If this ratio is exceeded, it suggests that potassium has other sources besides earth crust. In this work a value of 1.69 was obtained.

The mean elemental concentrations of the total suspended particulates were subjected to Factor Analysis (FA) using SAS statistical package. To determine the number of factors to retain in our results, the values of variances after rotation were examined, and only factors with variances ≥ 1 after rotation were considered significant (Barr, 1984).

Two major factors were identified: (i) 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. (ii) has high loadings in Mn, V and Pb which can be interpreted as contribution from combination of residual oil combustion, vehicle exhaust and soil dust.

The result of the cluster analysis is in agreement with that of factor analysis. Four clusters were observed. There was a significant clustering of Cu, Cr, Mn, Cd, Al and Fe, Pb, Ni, V. Other clusters also observed are K, Ca and As, Se, Na (Table 4).

Chemical mass balance was used in source apportionment (Roscoe *et al.,* 1982; Watson *et al.,* 1998). This revealed a contribution of 26-42% from steel metal works and sea spray and 14-18% from soil dust and petroleum activities.

Conclusions

The recorded value of total suspended particulates exceeded both FEPA and WHO standards. Enrichment factors were computed for measured elements; Al, Mn, Ca (mainly lithophilic) have EF < 4. As, Ni, Cd, Se, V, Pb, and Cu, have high enrichment factors, an indicative of the fact that they are all anthropogenic in origin.

Measure elemental concentrations were subjected to factor and cluster analysis to identify major sources contributing to the atmospheric load of particulates in Warri. The major sources identified are petroleum, sea spray, soil dust and steel/metal works. Chemicals Mass Balance (CMB) was used for the apportionment of chemical species to determine the relative contribution of each source. The CMB analysis of the pollutant revealed an anthropogenic contribution of about 37-75%.

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