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Chemical Characterisation of Suspended Particulates along Air Corridors of Motorways in Two Nigerian Cities

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Abstract: Total Reflection X-ray Fluorescence (TXRF) technique was used to analyze Suspended Particulate Matter (SPM) collected by gravimetric sampling along air corridors of motorways in Lagos and Ile-Ife, Nigeria. Up to 16 elements were identified and quantified. The Toxicity Potentials (TP) for SPM were high for all sampling sites in the two cities, except for a residential site in Ile-Ife whose TP value is 0.43. For lead (Pb), the TP values were high for all the sites in Lagos and low for all sites in Ile-Ife, except for one bus stop site in the latter city. Because of the health implication of high lead burden in the atmosphere there is need for improved management of the transport sector, possibly through the introduction of integrated transport system to reduce the current over-dependence on road transport as well as the need for gradual phase-out of leaded gasoline in Nigeria.

Key words: Gravimetric sampling, TXRF technique, toxicity potential, traffic related air pollution

INTRODUCTION

Automotive pollution has been established to account for elevated levels of lead (Pb) and other heavy metals in ambient air along motorways and at urban sites[1,2]. Tail pipe emissions arising from gasoline combustion by motor vehicles result in increased air quality deterioration with respect to heavy metals and other air toxics. In Nigeria, problem of pollution from vehicular emission is worsened by limited street space, traffic jam delays, poorly maintained vehicles and roads, and lack of emission control and management programmes. Among the most serious consequences of the traffic induced urban pollution problems is the acute and chronic exposure of large fraction of the society to different doses of air pollution of different composition on daily basis. A large number of the populace intercept and inhale heavy metals and other air toxics as a result of direct exposure to pollution as part of their daily business and official activities which keep them within roadside environments. These include roadside shop operators, school children, street hawkers and police and traffic wardens. Many homes and offices are also built so close to major high traffic areas (especially in Lagos) that the occupants live their daily lives in traffic induced pollution conditions. For particulate matter pollutants, those of small aerodynamic diameter are able to penetrate the respiratory system either resulting in lung function deteriorations, or are introduced into the blood streams, with transport to major organs at which they pose a more serious risk by disrupting the normal functioning of these various organelles.

There is an extensive literature on the effects of particulate air pollution, most especially the respirable fractions ($PM_{2.5}$) on health. Acute effects include increased allergy, asthma, hospital admissions for exacerbated cardiopulmonary and cardiovascular diseases. The long-term effects include increased rate of cancer, mortality, respiratory morbidity and reduced life expectancy[2-4]. There is no known ambient air quality threshold for any atmospheric trace gas or particulate, below which no impact on human health or ecosystem is expected for both short-term and long-term cases. Some studies suggested that long-term exposure to SPM results in a reduction of life expectancy in the order of 2-3 years[3]. Other recent studies showed that the prevalence of bronchitis symptoms in children and reduced lung function in both children and adults are associated with SPM exposures[4]. Most of the studies on which WHO based its conclusion were conducted in the developed countries, where the particulate pollution loads are low[5]. It is expected that the situation in many urban centres in Nigeria will be worse, being a developing country, where the greater fraction of the roads is unpaved, the particulate loading will be much higher. This is made worse by unplanned road transport system and high tailpipe emission, especially for soot and other SPM.

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In recent years, Nigeria has witnessed increase in the importation of used motor vehicles which no longer meet environmental standards, especially tail pipe emission in Europe and other blocks of developed nations. There is a need to investigate the potential and actual impacts which this class of low technology vehicle may have on air quality and human health as a means to evaluating the long term cost on the economy. In Nigeria, apart from a few studies on air quality deterioration induced by transport undertaken in the early to mid 1990s by Ogunsola *et al.*[6], very little is known about the impact of the increase of these old vehicles on the air quality along the traffic corridors.

The study was carried out at different locations in Lagos, which is a fast growing city having a population of over 5 million people. The study was also carried out in Ile-Ife, a medium population non-industrial city, whose urban growth rate is low but which has a relatively high traffic density at certain periods of the day.

The assessment comprises sampling ambient air for airborne particulate matter at locations along motorways with varying traffic densities. This is followed by the application of a non-destructive nuclear analytical technique to identify and quantify the different elements present in the particles collected in the study areas. In an earlier work, the concentration of Pb and other heavy metals of TSPM in ambient air collected by gravimetric means along motorways in Nigeria, were determined using a combination of Proton Induced X-ray Emission (PIXE) and Energy Dispersive X-ray Fluorescence (EDXRF) techniques[6]. In this study however, the concentrations of different metals in the inhalable and respirable fractions of the SPM (PM_{10} and $PM_{2.5}$) as well as the Total Suspended Particulate Matter (TSPM) were determined using TXRF technique.

MATERIALS AND METHODS

The ambient air along motorways in an urban setting, Lagos and a semi-urban city, Ile-Ife, both in southwest Nigeria was sampled for SPM using portable Nigretti 1000 air sampler for TSPM and a stacked Gent PM_{10} sampler to determine the PM_{10} and $PM_{2.5}$ fractions. Sampling was done in June, 2002. At each location, sampling sites were chosen to reflect variations in traffic volume and human activities. Whatman 41 cellulose filters used for the TSPM and Nuclepore filters used for the PM_{10} sampler were humidity conditioned in a charged desiccator for 24 h prior to weighing before and after sampling. Filters were weighed using a micro-balance of 1 µg sensitivity. The basic principles for quantifying particulate matter loading in the atmosphere using the PM_{10} sampler have been reported elsewhere[7].

The sampling sites in Lagos include highways, marine, medium density residential areas, bus stops and motorways; while the sampling sites in Ile-Ife were bus stops, highways, motorways and low density residential areas. Highways are dual-carriage ways linking major cities and on which vehicles are at top speeds, while motorways are tarred roads within the city on which vehicular speeds are low. Bus stops are where vehicles stop to pick or drop passengers and are characterized by activities from petty traders, fuel and waste burning. The samples were collected at heights of about 1.6 m above ground level. The samplers were positioned on downwind pedestrian side of motorways at locations where free air circulation was not hindered. After each sampling, the loaded filters were stored in polyethylene bags and taken to the laboratory for sample preparation and analysis. The concentration of each Suspended Particulate Matter (SPM) fraction in µg m^{-3} collected per the volume of ambient air sampled is obtained by dividing the difference between the filter weight after and before sampling, W_A and W_B, respectively, by the total volume of air sampled, V_{air}.

$$SPM = \frac{\Delta W}{V_{air}} = \frac{W_A - W_B}{V_{air}}.$$

Each of the exposed filters was digested using ultra-pure acids. One unloaded filter of each type was digested in the same manner to serve as control. A 5 µL aliquot of each of the digested samples was pipetted unto a sample carrier and dried using infra-red lamp and at such distance where rapid evaporation was avoided. The sample on the carrier was then irradiated with x-ray beam from a secondary Mo-target x-ray tube. The x-ray tube was operated at a tube voltage of 40 keV and current of 20 mA. Ga was used as internal standard and irradiation and spectra acquisition time was 1000 sec.

Fluorescence x-rays from each sample were analysed using a spectrometer comprising of a Si (Li) detector with a resolution of 175 eV at 5.9 keV, a GENIE2K inspector and a computer. The energy calibration of the spectrometer was carried out using the known energies of x-rays of elements in a multi-element standard. The sensitivity of the spectrometer to each element under the operating condition was determined by using peak counts for concentrations ranging from 0.1 to 100 ppm. For quality control and assurance purposes, the IAEA reference material IAEA-Soil-7 was digested and analysed and its result compared with the certified/recommended values. The quantitative analysis of the spectra obtained was carried out using the QXAS software analysis package[8].

For a quantitative estimate of the possible impact of the airborne particulates on the health of those exposed, the Toxicity Potential (TP) of SPM was calculated by dividing its concentration for each sampling site with the daily average USEPA National Ambient Air Quality Standard level concentration of 150 and 65 μg m^{-3} for PM_{10} and $PM_{2.5}$, respectively. The toxicity potential of lead was calculated by dividing the concentrations of Pb measured by USEPA National Ambient Air Quality Standard of 1.5 μg m^{-3}.

RESULTS AND DISCUSSION

In Lagos, TD values was least for the residential areas (298 vehicles/h) and highest for the motorways (4832 vehicles/h) (Table 1). In between these, TD values were approximately 2400-4100 at bus stops, 1500 at highways and along the coastal marine areas. In all locations, cars/buses dominated the vehicle fleet. The SPM concentration in Lagos varied from 146 to 238 μg m^{-3} for $PM_{2.5}$, 371 to 599 μg m^{-3} for PM_{10} and 903 to 1413 μg m^{-3} for the Total Suspended Particulate (TSP) (Table 1).

The TD values for Ile-Ife ranged from 10 vehicles/h to 1500 vehicles/h. The SPM values ranged from 11 to 261 μg m^{-3} in respect of $PM_{2.5}$ particles, 18 to 531 μg m^{-3} in respect of PM_{10} particles and 107 to 1185 μg m^{-3} in respect of TSP (Table 1).

The range of concentrations of some heavy metals in suspended air particulate in Lagos and Ile-Ife are shown in Table 2. Lead (Pb) concentration in air is of primary importance in this study because of its high toxicity, inducing human health impacts even at lower concentrations. The concentrations of Pb in Lagos ranged between 1.84 and 9.58 μg m^{-3} and these values are generally higher than those obtained in Ile-Ife with a range of 0 to 8.09 μg m^{-3}. Similarly, most other elements such as Zn, Br, Fe, Ca and K showed the same pattern of higher values in Lagos like Pb.

For both Ile-Ife and Lagos, the PM_{10} concentrations were higher than the 150 μg m^{-3} for the United States National Ambient Air Quality Standards (NAAQS)[9] by factors of 2 to 4 except for the residential-2 site in Ile-Ife

Table 1: Concentration of suspended particulate matter and traffic density for the different site classes in Lagos and Ile-Ife

	SPM concentration (μg m^{-3})			Traffic density (Vehicle/h)			
Site category	$PM_{2.5}$	PM_{10}	TSP	Cars/Buses	Lorries	Motor cycles	Total
Lagos:							
Highway	196	421	1120	1270	228	02	1500
Motorway	198	411	903	4449	331	41	4832
Bus stop-1	191	423	992	1724	93	542	2359
Bus stop-2	222	599	935	3637	424	52	4113
Residential	238	569	1413	116	01	181	298
Marine	146	371	1355	1396	07	147	1550
Ile-Ife:							
Highway	172	353	794	335	18	13	366
Bus stop-1	178	391	946	806	15	170	991
Bus stop-2	185	431	946	964	15	550	1529
Motorway-1	166	367	1185	654	25	330	1009
Motorway-2	261	531	790	473	07	939	1419
Residential-1	174	380	860	24	01	40	65
Residential-2	11	18	107	09	00	01	10

Table 2: Elemental concentration (μg m^{-3}) $PM_{2.5}$, PM_{10} and total suspended particulate matter in Lagos and Ile-Ife

		Lagos								Ile-Ife							
Site class	Particulate class	V	Cr	Cu	Zn	Se	Br	Sr	Pb	V	Cr	Cu	Zn	Se	Br	Sr	Pb
Highway	$PM_{2.5}$	0.77	1.11	1.32	2.66	ND	ND	ND	3.11	ND	0.05	ND	0.15	ND	ND	ND	ND
	PM_{10}	ND	1.20	ND	1.77	0.23	0.21	0.40	4.65	ND	0.04	ND	ND	0.02	0.03	0.05	0.90
	TSP	1.40	2.34	2.11	4.67	0.53	0.27	0.06	8.84	0.67	0.11	ND	0.19	0.04	0.11	0.06	1.49
Marine	$PM_{2.5}$	0.57	0.50	0.83	1.28	ND	0.05	ND	1.84	-	-	-	-	-	-	-	-
	PM_{10}	0.11	0.12	0.35	0.40	0.32	0.22	0.29	3.59	-	-	-	-	-	-	-	-
	TSP	1.84	2.10	3.21	5.52	1.11	1.26	1.07	6.54	-	-	-	-	-	-	-	-
Residential	$PM_{2.5}$	0.83	1.55	1.05	1.49	0.10	0.23	0.29	3.20	0.25	ND	ND	ND	ND	ND	ND	0.04
	PM_{10}	ND	0.20	ND	0.43	0.08	0.11	0.19	3.06	ND	ND	ND	ND	0.01	0.04	0.03	1.42
	TSP	2.01	1.82	1.74	2.43	0.19	1.19	0.64	8.36	0.62	0.16	ND	ND	0.12	0.07	0.04	1.43
B/Stop-1	$PM_{2.5}$	ND	0.68	1.01	0.62	0.28	0.53	0.08	3.03	0.63	0.10	ND	0.42	ND	ND	ND	0.44
	PM_{10}	ND	0.88	0.32	ND	0.17	0.37	0.57	6.35	0.44	0.03	0.04	ND	0.01	0.05	0.04	0.56
	TSP	ND	1.87	1.37	1.11	0.62	1.18	1.88	9.58	1.12	0.25	0.22	0.47	0.11	0.16	0.06	1.08
M/Way	$PM_{2.5}$	0.83	1.12	0.35	0.37	0.14	0.61	1.52	2.40	0.59	0.07	ND	0.66	ND	ND	ND	6.12
	PM_{10}	ND	1.33	0.22	0.15	0.36	0.54	1.59	4.43	0.92	ND	0.18	0.11	0.07	0.22	0.08	1.66
	TSP	1.29	2.96	0.66	0.63	0.57	1.70	1.84	7.63	2.03	0.77	0.35	1.30	0.45	0.34	0.22	8.09
B/Stop-2	$PM_{2.5}$	0.89	0.57	0.57	0.25	0.38	0.48	0.24	2.84	0.43	0.06	ND	ND	ND	ND	ND	0.35
	PM_{10}	1.11	0.30	0.22	ND	0.41	0.14	5.69	6.59	0.43	0.12	0.46	1.83	ND	ND	0.11	0.61
	TSP	1.16	0.86	0.99	0.92	0.89	1.49	5.95	8.72	1.22	0.17	0.65	1.90	0.06	0.20	0.21	2.21

B/Stop = Bus stop, M/Way = Motorway, ND: Not detected

Table 3: Toxicity potential recorded for different site classes in Lagos and Ile-Ife

Site category	$PM_{2.5}$	PM_{10}	Pb (PM_{10})
Lagos:			
Highway	3.02	2.81	5.17
Motor way	3.05	2.74	4.55
Bus stop-1	2.94	2.82	6.25
Bus stop-2	3.42	3.99	6.29
Residential	3.66	3.79	4.17
Marine	2.25	2.47	3.62
Ile-Ife:			
Highway	2.65	2.35	0.60
Bus stop-1	2.74	2.61	0.67
Bus stop-2	2.86	2.88	0.64
Motorway-1	2.55	2.45	0.33
Motorway-2	4.02	3.54	5.19
Residential-1	2.68	2.53	0.97
Residential-2	0.17	0.12	0.03

with a value of 0.12 (Table 3). Also the respirable SPM fractions (Table 1 and 3) were higher than the 65 $\mu g\ m^{-3}$ of NAAQS by factors of between 2 and 4, except for the residential-2 site in Ile-Ife for which it is lower with a value of 0.17. The TSP values compare well with the values of an earlier work conducted in the areas[6]. For Lagos, the lead concentrations are higher than the 1.5 $\mu g\ m^{-3}$ of NAAQS[9] by factors of 3 to 6. This is however different for Ile-Ife as TP for Pb is below unity except at the motorway-2 site with a value of 5.19 $\mu g\ m^{-3}$.

There is very little correlation between traffic density and suspended particulate matter in the two cities. This may be due to soil entrainment by wind in the two cities and contributions from industrial sources in the case of Lagos since Ile-Ife is a non-industrial town. The correlation between traffic density and Cu, Zn and Pb in Lagos were observed to be weak. This may be as a result of other possible sources of these elements, like industries. However, in Ile-ife the observed correlation between Traffic Density (TD) and Cu and Zn were high while that of the TD and Pb was low. The higher correlation observed in Ile-Ife confirms the contribution from industrial sources in Lagos, as Ile-Ife is a non-industrial town.

Pb concentrations measured in this work compare well with the results earlier reported in major urban centers of the world where traffic pollution and ambient lead level reduction is of serious concern[3,5,10]. When compared with international standards for Pb such as WHO (1.5 $\mu g\ m^{-3}$) and European Union (2.0 $\mu g\ m^{-3}$), most Pb values exceeded the standards for Lagos locations but well below the standards for Ile-Ife locations.

The values of TP for $PM_{2.5}$, PM_{10} and TSP as well as those of major heavy metals such as Pb were significant. For PM_{10}, the TP values were in the range 2 to 4 in both cities except for the residential-2 site in Ile-Ife with a value of 0.12. For $PM_{2.5}$, the TP values were also in the same range except for the residential-2 site in Ile-Ife for which it is lower with a value of 0.17. For Lagos, the TP values for Pb were higher in the range 3 to 6, but below unit for all sites in Ile-Ife, except at the motorway-2 site with a value of 5.19. The results suggest the need for improved management of the transport sector, possibly through the introduction of integrated transport system to reduce the current over-dependence on road transport. The results for heavy metal pollution also suggests the need for gradual phase-out of leaded gasoline in Nigeria.

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