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Characterization of Traffic Heavy Metals at SelectedLocations Along Benin-Ore-SagamuExpressway in Southwestern, Nigeria.

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ABSTRACT
This study determined the concentration levels of heavy metals in aerosol associated with vehicular activities in four different sampling sites along Benin-Ore-Sagamu expressway inSouthwestern, Nigeria. Air samplerwas used for the collection of aerosols and was characterized using ThermoscientificNilton XL2, ahighly sensitive Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF). The results revealed that the concentrations of the twenty-one detectable metals were above the permissible limits recommended by the air quality standards.It is worthy to note that, despite the ban of leaded fuel, Lead (Pb), a toxic element and a known carcinogen wasfound in all the sampling locations with the concentrations ranged between 0.368x $10^3$and 2.611 x 10^3µg/m^{3}which is above the set values stipulated by WHO (0.01 µg/m^3), NAAQS (0.05 µg/m^3) and USEPA (0.15 µg/m^3).The metalconcentration levels followed a descending order of Ti>Rh > Fe >In>Cd> Sn >Cr>Ag>Pd>Mn > Ni > Ru>Cu > Pb >W> Co >Zn>Ga>Ge >Ir> Pt. The host communities aroundBenin-Ore-Sagamu expressway are at risk of health-related problemassociatedwith traffic heavy metals pollution.Hence, this study suggests strict regulationson vehicular-induced emissions for effective reduction of heavy metals pollution in the environment.

KEYWORDS: Heavy metals, Vehicular activities, Pollution,EDXRF, Leaded fuel

I. INTRODUCTION

Heavy metals are referred to as any metal or metalloid elementwith high specific density greater than 4 g/cm^{3}which are natural constituents found in the earth crust utilized for various industrial purposes [1].However, heavy metals are also released into the atmosphere through anthropogenic activities such as industrial processes, agricultural processes and combustion of fossil fuel [2]-[4]. Motor vehicles are a source of increasing heavy metals concentrations in the atmosphere through combustion of fuels, evaporation of fuels from the fuel system, wear of brake linings and tyres, road abrasion, corrosion of batteries and metallic parts such as radiators [5] -[6].

Vehicular emissions of heavy metals have been identified as a worldwide environmental concern due to its adverse effects on human health and the environment at concentrations above the permissible level[7]-[11]. Heavymetals bioaccumulates and displaces the functional groups of enzymes within the body,thereby, modifying physiological and biochemical processes,causing nervous function leading to mental disorder, damage of the lung, breast cancer, kidney and liver, blood constituents damage and other vital organs promotingdifferent disease[12]-[16].Heavy metals released from motor vehicles include Copper (Cu), Arsenic (As), Manganese (Mn), Zinc (Zn), Chromium (Cr), Cadmium (Cd), Nickel (Ni) and Lead (Pb) [17] -[22]. Some of these metals are essential nutrients needed by man for developmental purpose. For instance, Copper and Zinc are essential elements for foetal and infant growth, brain development and immune function [23] -[24] but, when found in high concentrations through ingestion and inhalation, can cause intestinal irritation, anaemia, liver and kidney damage [25] -[26].The ingestion of Nickel metal helps the body to absorb and use iron which is important for oxygen transport and red blood cell production, however, Nickel absorption above permissible limit can cause health-related problems such as lung embolisms, asthma, respiratoryfailure and increased possibilities of cancer mechanisms [27]. Chromium, is also an essential mineral that plays a vital role in keeping the blood sugar levels normal by improving the way the body uses insulin but on entering into the bloodstream at high concentrations through liver,spleen, bone marrow, lymph nodes and liver forms toxic complexes with vital macromolecules leading to carcinogenicity and DNA

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(Deoxyribonucleic acid) damagewhile Cadmium and Lead is taken up by the gastrointestinal tract and distributed throughout the body mostly to the bones, at extremely low concentrations may result in toxicity and lead to cancer[28] -[29]. To control and reduce the pollution of heavy metals from motor vehicles, accurate information on the characterization and its distribution is required.

Till date, there have been no studies evaluating the contribution of vehicle emissions to heavy metal concentrations in the study area. Hence, this research focused on characterizationand presentation of comprehensive and quantitative assessment ofheavy metals emitted by motor vehicles atBenin-Ore-Sagamu expressway.

II. METHODOLOGY

2.1 Study Area

The study area is located at the Benin-Ore-Sagamuexpressway inSouthwestern, Nigeria. Benin-Ore-Sagamuexpressway is one of the busiest routes in Nigeria due to the interstate linkage it provides which enables goods and services to be transported, hereby, resulting to increase in high vehicular movement on a daily basis [30]. Four sampling locations selected in the study area include Sagamu (6.8622^{o} N, 3.6219^{o} E), Ijebu-Ode(6.8132^{o} N, 3.8967^{o}E), Ore (6.7546^{o}N, 4.8746^{o} E) and Okada Junction (6.6332^{o} N, 5.3592^{o} E). These sampling locations happened to be a traffic populated areas wherein, different categories of vehicles such as motorcycles, cars, buses and trucks/trailers ply everyday as a result of various anthropogenic activities.The road traverses Ogun, Ondo and Edo States of Nigeria and passes through the towns such as Shagamu, Ijebu-Ode, Ore, Ofosu and Benin City

Figure 3.1illustrates the sampling locations of the study area at Benin-Ore-Sagamu expressway.

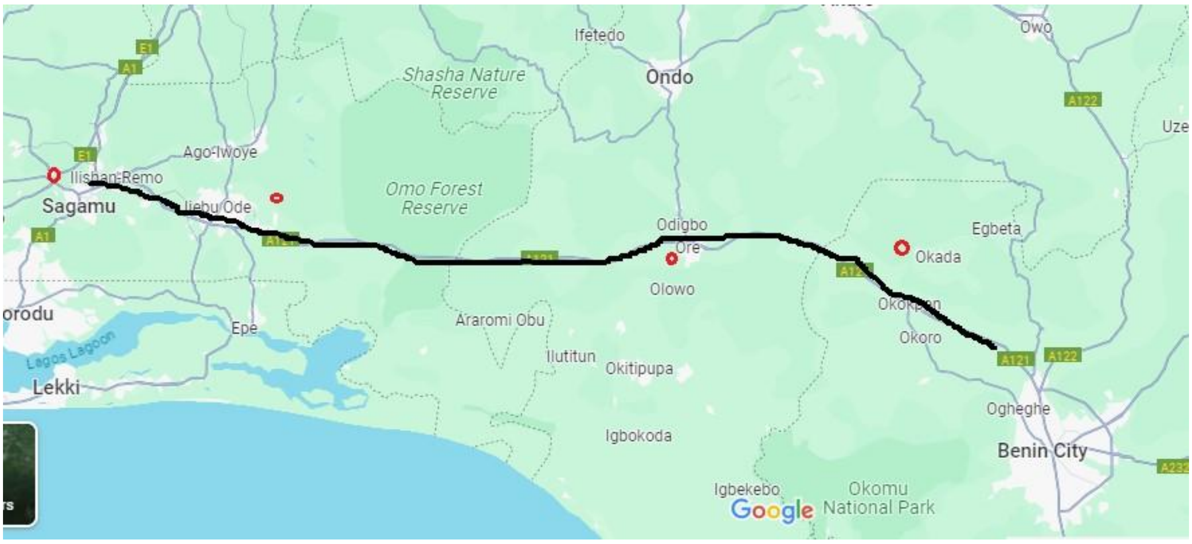

Figure 1: A Section of the Benin-Ore-Sagamu Expressway Showing the Study Area

2.2 Particulate Sample Collection and Analysis of Heavy Metals

An indigenous multi-fraction air sampler with three stage perforated stacked filter units arranged in parallel was used for collection of aerosols needed for analysis of heavy metal concentrations.Theair samplerwas connected to a 0.75 kilowatts suction pumpto enable active samplingand was placed at a height of 2 m from the ground and at a minimal distance of 10m away from the road in all study locations. Before sampling, theair sampler was pre-cleaned and tested with a zero filter to ensure that it is functioning properly. At each sampling process, pre-weighed nucleoporecellulosefilter papers of 47 mm quartz fibre with a pore size of 10 µm was used for the collection of particles.The particulate matter collected on nucleopore filter papers isshown in Figure 2, which was characterized usingThermoscientificNilton XL2, ahighly sensitive Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) at the Central Research Laboratory, Tanke, Ilorin, Nigeria.The World Health Organization(WHO), United State Environmental Protection Agency (USEPA), Occupational of Health Administration (OSHA), National Air Quality Standard (NAAQS) are air quality standards used to compare with the

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obtainable results from this study for health risk assessment and compliance purpose.

Figure 2: Loaded Filters Collected in allSampling Locations

III. RESULTS AND DISCUSION

The metals analysed in this work are metals that are regarded as toxic that can cause harm tohumanwhen found in values above permissible limits. Table 1 shows results of the characterized samples of each metal detected in the dry and wet season at the four sampling locations. The twenty-one metal analysed include, Lead (Pb), Titanium (Ti), Manganese (Mn), Copper (Cu), Tin (Sn), Zinc (Zn), Chromium (Cr), Cobalt (Co), Nickel (Ni), Cadmium (Cd), Rhodium (Rh), Tungsten (W), Ruthenium (Ru), Germanium (Ge), Gallium (Ga), Palladium (Pd), Platinum (Pt), Indium (In), Silver (Ag), Iron (Fe), Iridium (Ir).

Iron (Fe) is an essential element that is found naturally in the earth crust but anthropogenic activities influence its concentration in the environment. Iron (Fe) was found in all the sampling locations in this study as presented in Table 1 and its concentrations in the dry and wet season at location A, B, C, D were 6.494 x 10^3, 6.541 x 10^3, 6.215 x 10^3 and 8.318x 10^3; 4.969 x 10^3, 6.706 x 10^3, 7.164 x 10^3 and 7.362 x 10^3µg/m^3 respectively.The concentrations obtained in the dry and wet seasons in all the locations were higher than the stipulated values by WHO (35 µg/m^3) and USEPA (25 µg/m^3).Also, this study concentrations were marginally higher than 0.336 µg/m^3, 0.70068 µg/m^{3}and 1.34 x 10^{-3}µg/m^3 reported by [31] - [33], respectively. This implies that the study area is polluted with Fe, a toxic metal that can cause health issue such as respiratory irritation and DNA damage.

Cadmium (Cd) is known human carcinogen. Exposure to higher cadmium levels severely irritates the stomach, leading to diarrhoea. The concentrations of Cadmium obtained in all sampling locationsin this study ranges from 5.278 x 10^3 – 7.999 x 10^3 µg/m^3. The highest concentration (7.999 x 10^3 µg/m^3) was found at location D in the dry season while the lowest concentration (5.278 x 10^3 µg/m^3) was found at location B. These values were found to be far above the recommended value by OSHA (5 µg/m^3) and USEPA(0.1 µg/m^3). The results obtained was also compared with preceding studies of[31] - [32], who reportedthe concentrations of Cd to be 0.0839 µg/m^{3}and 0.0122µg/m^{3}respectively. The host environment is at risk of Cd poisoning.

Chromium (Cr) is one of metals released from motor vehicles and it highest concentration (7.995 x 10^3 µg/m^3) was found to be above the permissible limit stipulated by USEPA (0.5000 µg/m^3) and OSHA (1.000 µg/m^3). Cr concentrations obtained in this study were also compared with the preceding investigations and was found to be marginally higher than the values (32.69 x 10^{-3} µg/m^3 and 0.29 µg/m^3) reported by [34] - [35], respectively. Zinc (Zn) concentrations ranges from 0.361 – 0.692x10^3 µg/m^3. The concentrations in the dry and wet season at location A, B, C, D were 0.585 x10^3, 0.606 x10^3, 0.573 x10^3, 0.692 x10^3 and 0.361 x10^3; 0.681x10^3,0.623x10^3, 0.671x10^3 µg/m^3, respectively. The value of Zn obtained is found to be higher than 0.0667µg/m^{3}reported by [36] and were also higher than the recommended values by WHO (35 µg/m^3) and USEPA (25 µg/m^3).

The concentration levels of Copper (Cu) in location A, B, C D in the dry and wet season were 1.641 x 10^3 µg/m^3, 1.449 x 10^3, 1.549 x 10^3, 1.357 x 10^3 and 1.405 x 10^3; 1.592 x 10^3, 1.319 x 10^3, 2.215 x 10^3 µg/m^3, respectively.

Table 1:Dry and Wet Season Heavy Metal Concentrations from Sampling Locations (µg/m^3) x 10^3

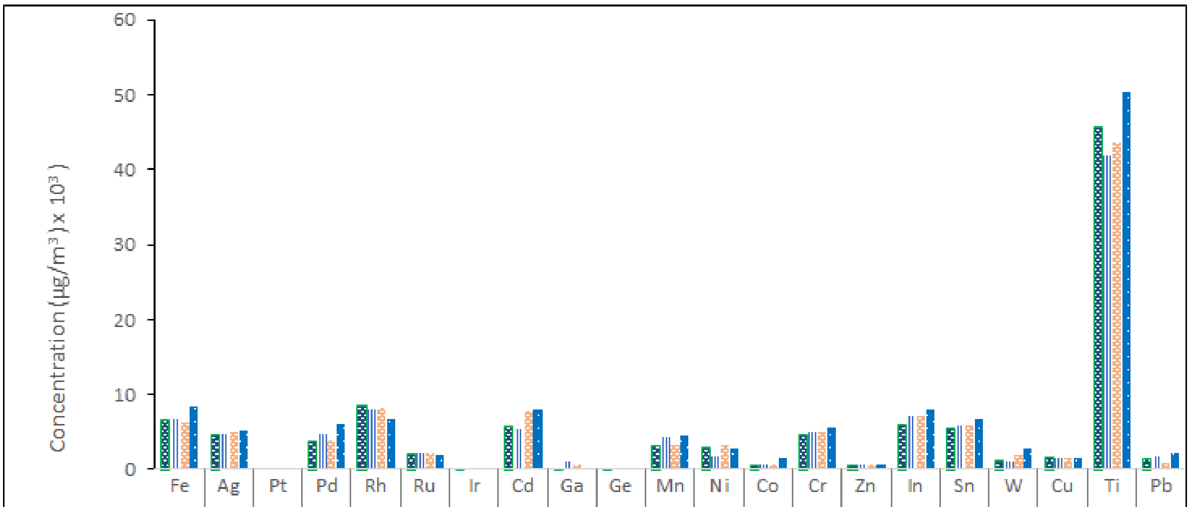
Elements	Location A		Location B		Location C		Location D	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Fe	6.494	4.969	6.541	6.706	6.215	7.164	8.318	7.362
Ag	4.608	5.921	4.736	4.214	5.019	4.511	5.166	4.892
Pt	-	-	-	-	-	0.106	0.123	0.423
Pd	3.775	3.222	4.613	3.451	3.883	3.968	5.894	4.282
Rh	8.376	7.126	8.047	9.647	8.132	8.358	6.577	7.243
Ru	2.005	2.47	2.105	1.965	2.075	2.064	1.994	1.978
Ir	0.0015	0.141	0.134	-	-	-	0.268	0.026
Cd	5.776	6.352	5.278	5.944	7.688	6.302	7.999	6.393
Ga	0.115	0.154	1.102	-	0.512	-	0.062	0.106
Ge	0.121	-	0.451	-	0.007	0.022	0.029	0.356
Mn	3.143	3.378	4.232	2.683	3.231	2.777	4.381	5.119
Ni	2.841	2.427	1.587	1.102	3.212	3.117	2.674	3.281
Co	0.573	0.472	0.541	0.294	0.563	0.893	1.358	1.025
Cr	4.619	5.125	4.909	4.226	4.909	4.441	5.564	7.995
Zn	0.585	0.361	0.606	0.681	0.573	0.623	0.692	0.671
In	5.821	6.59	6.993	5.572	6.988	5.967	7.885	6.605
Sn	5.451	4.264	5.678	5.257	5.843	5.919	6.721	6.825
W	1.098	0.063	1.113	0.274	1.906	0.074	2.801	1.513
Cu	1.641	1.405	1.449	1.592	1.549	1.319	1.357	2.215
Ti	45.672	44.543	41.837	47.424	43.624	44.845	50.329	52.685
Pb	1.396	0.835	1.589	0.665	0.915	0.368	2.017	2.611

**Location A (Okada Junction), Location B (Ore), Location C (Ijebu-Ode) and Location D (Sagamu)

In the wet season, location D had the highest concentration (2.215 x 10^3 µg/m^3) followed by location B (1.592 x 10^3 µg/m^3) while the lowest concentration (1.319 x 10^3 µg/m3) was found at location C. Whereas, in the dry season, location A had the highest concentration of 1.641 x 10^3 µg/m^3 followed by location C (1.549 x 10^{3}µg/m^3). These concentrations were higher than NAAQS set values of 0.29 µg/m^3 and the concentration (0.0593 µg/m^3) reported by [37].

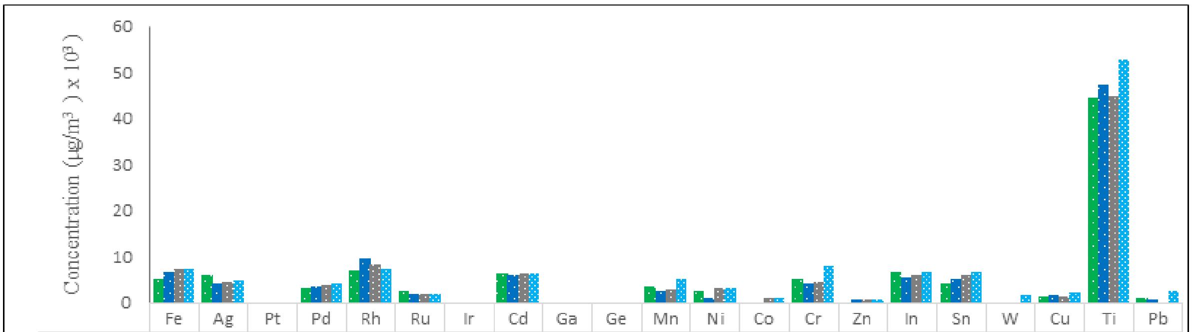
Lead (Pb), a toxic metal found in leaded-gasoline fuel was detected in all the characterized samples at each sampling location. The concentrations of Pb ranged 0.368-2.611 µg/m^{3}and was found to be higher than the permissible safe limits recommended by WHO (0.01 µg/m^3), NAAQS (0.05 µg/m^3) and USEPA (0.15 µg/m^3) standards.More so, Pb concentrations were equally higher than (0.129 µg/m^3), (0.019 µg/m^3) and (0.109 µg/m^3) reported by [32],[34] and[38] respectively. The fact that this study values are higher than the air quality standards and those published by other authors, is an expected result in view of the sub-standard fuel used in Nigeria.

Figure 3 and 4 shows the concentrations of all elements detected across the sampling locations during dry and wet season, respectively. Titanium (Ti) had the highest concentration across the sampling locations,although, Ti is known to be a naturally enriched metal. Whereas, Rh, Fe, In, Cd and Sn were the 2nd, 3rd ,4th, 5th and 6th largest pollutants in the study area while, Ga, Ge, Ir and Pt had the smallest concentrations. It could be deduced from the result that the elemental composition in the road dust along the Benin-Ore-Sagamu expressway is significantly variable from one sampling location to another as a result of intensive transportation and commercial activities at each sampling location.Although, similar pattern in elemental concentrations is shownin Figure 3 and Figure 4, however, the metallic concentrations in the wet season across sampling locations were mostly observed to be lower than the dry season due to the effect of rainfall that causes deposition of particulates.More so, out of the twenty-one metals detected, nineteen of the metals with the highest concentrations were recorded at location D, this may be attributed to the high vehicular influx observed at the location. It is also worthy to note that, the concentrations of all the metals obtained in this study were higher than values reported in the literatures and the set values stipulated by the air quality standards. One of the reasons for the high traffic heavy metals could be attributed to lack of stringent emission standards in Nigeria, use of sub-standard fuel and aged vehicles called "Tokunbo".



	Fe	Ag	Pt	Pd	Rh	Ru	Ir	Cd	Ga	Ge	Mn	Ni	Co	Cr	Zn	In	Sn	W	Cu	Ti	Pb
Location A	6.49	4.61	0.00	3.78	8.38	2.01	0	5.78	0.12	0.12	3.14	2.84	0.57	4.61	0.58	5.82	5.45	1.09	1.64	45.7	1.4
Location B	6.54	4.74	0.00	4.61	8.05	2.11	0.13	5.27	1.01	0.45	4.23	1.59	0.54	4.90	0.60	6.99	5.67	1.11	1.45	41.8	1.59
Location C	6.22	5.02	0.00	3.88	8.13	2.08	0.00	7.69	0.51	0.01	3.23	3.21	0.56	4.90	0.57	6.98	5.84	1.90	1.54	43.6	0.91
Location D	8.32	5.17	0.12	5.89	6.58	1.99	0.27	8	0.06	0.03	4.38	2.67	1.36	5.56	0.69	7.89	6.72	2.8	1.36	50.3	2.02

Figure 2: Dry Season Concentration of Heavy Metal in Characterized Samples across the Selected Sampling Locations



	Fe	Ag	Pt	Pd	Rh	Ru	Ir	Cd	Ga	Ge	Mn	Ni	Co	Cr	Zn	In	Sn	W	Cu	Ti	Pb
Location A	4.969	5.921	0.000	3.222	7.126	2.47	0.141	6.352	0.154	0.000	3.378	2.427	0.472	5.125	0.361	6.59	4.264	0.063	1.405	44.54	0.835
Location B	6.706	4.214	0.000	3.451	9.647	1.965	0.000	5.944	0.000	0.000	2.683	1.102	0.294	4.226	0.681	5.572	5.257	0.274	1.592	47.42	0.665
Location C	7.164	4.511	0.106	3.968	8.358	2.064	0.000	6.302	0.000	0.022	2.777	3.117	0.893	4.441	0.623	5.967	5.919	0.074	1.319	44.84	0.368
Location D	7.362	4.892	0.423	4.282	7.243	1.978	0.026	6.393	0.106	0.356	5.119	3.281	1.025	7.995	0.671	6.605	6.825	1.513	2.215	52.69	2.611

Figure 3: Wet Season Concentration of Heavy Metal in Characterized Samples across the Selected Sampling Locations

IV. CONCLUSION

The characterization of heavy metals was successfully carried out in this study in which, twenty-one elements were detected from the sample analysis and Titanium (Ti) was found to have the highest concentration across the sampling locations followed by Rhodium. The concentrations of heavy metals obtained in this study were above the permissible values stipulated by WHO, NAAQS and USEPA. The concentration levels of all the detected metal were in the order of Ti>Rh> Fe >In>Cd> Sn >Cr>Ag>Pd>Mn > Ni > Ru>Cu > Pb >W>Co >Zn > Ga > Ge >Ir> Pt. Among the atmospheric elements, Lead (Pb), a toxic primary element of interestand a known carcinogen that is detrimental to human body when exposed to at concentrations above the permissible limits was recorded in all the sampling locations with the highest concentration recorded at location D. This high concentration implies that, Nigeria fuel still contains appreciable amount of Pb despite the ban of leaded gasoline. It is therefore concluded that the communities in the host environment are at risk of heavy metal contamination.

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