



Ministry of Science, Research & Technology  
Iranian Research Organization  
for Science and Technology

## Assessment of an atmospheric heavy metal from a transport pool within the Ilorin Metropolis, Nigeria

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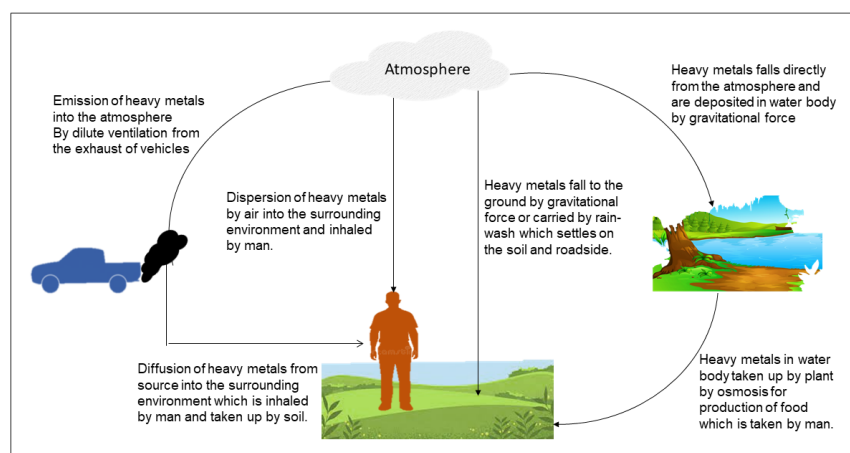
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### HIGHLIGHTS

- Vehicular emissions are the dominant source of air pollution in cities throughout the world especially in developing countries.
- Heavy metals are among main transport-related air pollutants.
- The suspended heavy metals particulates present in the polluted air in different forms are notable for their wide environmental diffusion, dispersion, and tendency to enter the human body.
- Heavy metals accumulate in tissues of the human/animal body and various parts of the ecosystem (soil, water) which may transfer to the food chain.
- This study suggested and recommended the need to shift from fossil fuel to hydrogen economy to mitigate heavy metal pollution.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 28 July 2021

Revised 27 August 2021

Accepted 28 August 2021

#### Keywords:

Particulate pollution  
EDXRF  
Hydrogen economy  
Diffusion  
Dispersion  
Vehicular emission

### ABSTRACT

Particulate emission from a high density of vehicles has become a subject of interest and great concern for the assessment of local air quality within the Ilorin metropolis, Nigeria. This study aims to determine possible heavy metal pollution from vehicular emission along the major transport pool within the Ilorin metropolis. Deposition gauges were placed on a pole above human breathing height at 1.5 m at selected major roundabouts within the Ilorin metropolis. Gauges were planted for one month (April 27<sup>th</sup> to May 30<sup>th</sup>, 2020) during the Covid-19 lockdown and one month (January 15<sup>th</sup> to February 14<sup>th</sup>, 2021) after the Covid-19 lockdown. The collected samples were rinsed with deionized water, filtered, and dried in a desiccator. The dried samples were characterized using Energy-dispersive X-ray fluorescence (EDXRF). Twenty-one heavy metals were detected from all sampling locations. The total sum concentrations of the heavy metals recorded during and after the Covid-19 lockdown were 1018.58785 and 1359.15479 mg.m<sup>-3</sup>, respectively. The averaged measured concentration of most of the heavy metals sampled along selected major roundabouts within the Ilorin metropolis during and after Covid-19 lockdown exceeded the permissible emission limit. The Deposition Flux (DF) of the measured heavy metals ranged from 4.53 to 8.91 g.m<sup>-2</sup>.month<sup>-1</sup> during the lockdown and from 6.23 to 29.55 g.m<sup>-2</sup>.month<sup>-1</sup> after the lockdown. The enrichment factor and concentration ratio were also determined. The results of both indicated that heavy metal pollutions originated from multiple similar anthropogenic sources, and photochemical degradation was active in all the sampling locations. This study suggested the need to shift from a fossil fuel economy to a hydrogen economy to mitigate heavy metal pollutions from vehicular emissions to the barest minimum.

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## 1. Introduction

Vehicular emissions have become an increasing and dominant source of air pollution in cities throughout the world, especially in developing countries. The increasing use of vehicles has left many streets in developing countries with high levels of congestion and an indiscriminate release of vehicular exhaust emissions polluting the air and exposing the population to severe health risks [1-3].

Traffic emission is of special concern both because of its global nature and because emission occurs at the ground level (troposphere) in urban streets where human activities are greatest [4]. The main transport-related air pollutants include Particulate matter, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), nitrogen oxides ( $\text{NO}_x$ ), sulfur oxides ( $\text{SO}_x$ ), carbon monoxide (CO), hydrocarbons, and heavy metals [5].

Heavy metals mainly arise from vehicular exhaust and include elements such as arsenic, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, and so on [6]. The suspended heavy metals present in different forms of polluted air are notable for their wide environmental diffusion, dispersion, and their tendency to enter the human body. They also accumulate in the body tissue of animals and various parts of the ecosystem (soil, water) and may transfer to the food chain, in addition to their overall potential to be toxic even at relatively minor levels of exposure [7]. After entering the body via inhalation, digestion, and/or absorption, heavy metals present in polluted air may act with macromolecules of cells directly or after biotransformation into reactive metabolites, which alters the chemical composition and structure of the cells and thus affects human health [8].

A recent emission inventory study in the USA indicated that 23.01 tons.km<sup>-2</sup> of heavy metals are contributed by 2.01 million vehicles in cities, which is a higher proportion of heavy metals emissions when compared to other vehicular pollutants [9].

The results of a study carried out in Rumuola, Artillery, Mile One, and Bodo Junctions in Port Harcourt, Nigeria, confirmed that the dwellers or pedestrians along Rumuola, Artillery and Mile One Junctions were being exposed to high levels of vehicular emissions due to the high vehicle volume passing those areas and high traffic congestion, while people at the Bodo Street in New GRA, away from high traffic density, were safer

and enjoyed a much healthier environment [1].

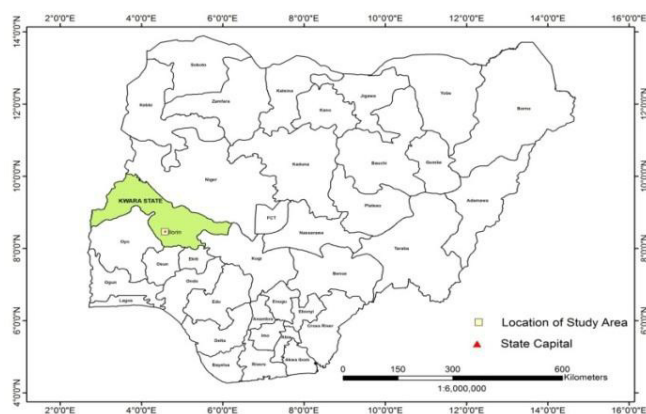
Being a major route linking the northern and southern regions of Nigeria, the Ilorin metropolis has witnessed an increased level of cars, buses, lorries, motorcycles, and heavy trucks traffic due to the current political and economic stability of the state. All these have given rise to high traffic emissions and dust generation in the metropolis. Although deposition of particulate emission in urban areas is widely recognized, only a few studies have been devoted to the Ilorin metropolis.

Therefore, keeping in mind the environmental significance of the potential influence of toxic heavy metals in the atmosphere and their continued high level increased contamination, this study aims to assess the atmospheric heavy metallic pollution composition of the airborne particulate within the Ilorin metropolis from vehicular emissions in a selected transport pool and suggest possible ways to mitigate or control the heavy metal pollution that has an adverse effect on human health.

## 2. Materials and methods

### 2.1. Description of Sampling Locations

Ilorin is the capital of Kwara State, Nigeria, with a population of about 777667, making it the 7<sup>th</sup> largest city by population in Nigeria according to NPC record [10]. The longitude and latitude of Ilorin city are 8.4799° N, 4.5418° E. Fig. 1 shows the Ilorin metropolis within Kwara State in Nigerian map [12]. The Ilorin metropolis consists of three Local Government Areas; Ilorin West, East, and South. It has an estimated land area of 105 km. Ilorin has a tropical climate and enjoys two seasons, a



**Fig. 1.** Map of Nigeria showing Ilorin metropolis within Kwara State [12].

dry and wet season. The wet season begins in April and lasts until October, while the dry season is between November and March. The annual rainfall varies from 1000 to 1500 mm, with the peak between September and early October. Also, the mean monthly temperature is generally high throughout the year, ranging from 23 to 28°C [11].

Four different busy roundabouts with a heavy traffic presence and a good number of pedestrians and commercial activities were identified and selected for sampling during and after the Covid-19 lockdown (Fig. 2). These areas include the General hospital roundabout (8°28'41.84" N, 4°32'04.50" E), Post office roundabout (8°29'16.82" N, 4°33'52.74" E), Geri-Alimi roundabout (8°27'12.93" N, 4°34'49.92" E), and Offa Garage roundabout (8°27'12.93" N, 4°34'49.03" E), respectively. These locations are characterized by a high transport pool (high rate of vehicle movement), traffic congestion, pedestrian movement, roadside traders, and petrol and gas filling stations. The populace within the Ilorin metropolis is continuously exposed to heavy metals pollution from these major roundabouts.

## 2.2. Sampling and extractive procedure

The dry Deposition method was employed for sampling using empty deposition gauges. The gauges were placed in a single open bucket sampler (0.25 m in depth and 0.20 m in diameter) that was attached at different sampling points on street light poles at a height 1.5 m above ground level to prevent any form of external intrusion (Fig. 3). Vehicular emission particles from the surrounding air were deposited in the deposition

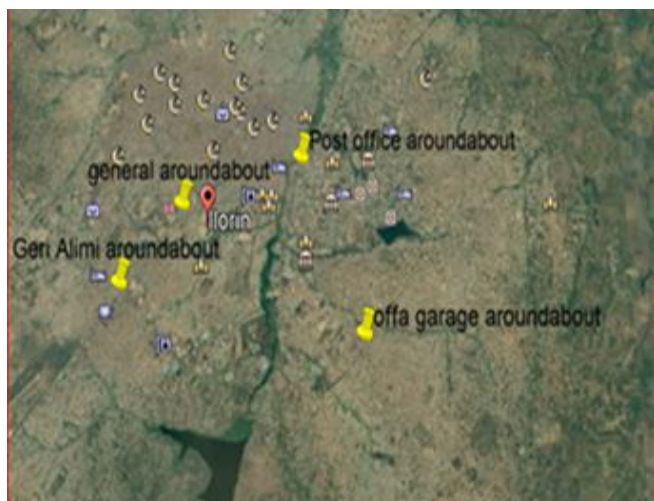


Fig. 2. Map of study area indicating sampling site [13].



Fig. 3. Air sampling system (deposition gauge) at sampling location.

gauges during a sampling period of two months in April 27<sup>th</sup> to May 30<sup>th</sup>, 2020, during the Covid-19 lockdown, and from January 15<sup>th</sup> to February 14<sup>th</sup>, 2021, after the lockdown to allow for sufficient deposition of particles. At the end of the successful sampling period, the collected air particles in the deposition gauges were washed using 300 ml of deionized water. The washed particles were then filtered through a pre-weighed Whatman filter paper (125 mm diameter, Cat. No. 1001 125) on a digital weighing balance (Model: PA2102). The air particles settled on the filter paper while the water passed through the paper. The filter paper containing the air particles was air-dried in a petri dish for two weeks and reweighed, after which it was taken for analysis.

The procedure was carried out separately for the air samples collected from all sampling locations, both during and after the Covid-19 lockdown.

The deposition flux was determined using Eq. (1) [14].

$$\text{Deposition Flux} = W_p / A.t \quad (1)$$



where  $W_p$  is the weight of the particulate matter (g),  $A$  is the area of the deposition gauge ( $m^2$ ), and  $t$  is the duration of exposure (month).

### 2.3. Characterization of heavy metals collected from selected major roundabouts

The concentration of heavy metals present in the air particles collected from the sampling points were analyzed at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Osun State using an Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF) (Model: Mesa-50). The elements detected at all the sampling locations during and after Covid-19 lockdown included Potassium (K), Calcium (Ca), Titanium (Ti), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Gallium (Ga), Arsenic (As), Selenium (Se), Bromine (Br), Rubidium (Rb), Strontium (Sr), Yttrium (Y), Niobium (Nb), Zirconium (Zr), Lead (Pb), and Cadmium (Cd).

The enrichment factors ( $EF$ ) of the heavy metals were calculated based on the abundance of elements in the earth's crust from the CRC Handbook [14]. The  $EF$  of each element was evaluated using Eq. (2).

$$EF = [C_x / C_{ref}]_{aerosol} / [C_x / C_{ref}]_{crust} \quad (2)$$

where  $C_x$  and  $C_{ref}$  are the concentrations of the element  $x$  and the reference element, and  $[C_x / C_{ref}]_{aerosol}$  and  $[C_x / C_{ref}]_{crust}$  are the ratios of mean concentrations of the target element in the particulate matter and the earth's crust, respectively. Fe was used as a reference element for the  $EF$  evaluation with respect to crustal abundance, assuming that the contribution of its anthropogenic source to the atmosphere is negligible [15-17].

## 3. Results and discussion

Table 1 shows the total sum of all the heavy metal concentrations from all sampling locations both during and after the Covid-19 lockdown, and Table 2 shows the corresponding average measured concentrations for each of the heavy metals. The total sum concentrations of heavy metals during and after Covid-19 were 1018.58785 and 1359.15479  $mg.m^{-3}$ , which amounts to about 42.84% and 57.16% of the cumulative heavy metals concentrations both during and after Covid-19

lockdown, respectively. Iron (Fe) was found to be the most abundant heavy metal emitted from vehicles and other anthropogenic sources, while Cadmium (Cd) was the least heavy metal measured for both during and after Covid-19 lockdown.

The total concentration of heavy metals recorded after the lockdown was higher than the total concentration of heavy metals recorded during the lockdown, which indicates the degree of heavy metals pollution caused by vehicular emission and other anthropogenic sources. Iron (Fe) concentrations were found to be the most abundant in all sampling locations with average mean values of 159.0092 and 499.9529  $mg.m^{-3}$  for during and after Covid-19 lockdown, respectively, which also depicts a higher transport pool after the lockdown compared to during the lockdown.

The total heavy metals concentration measured from the transport pool during the Covid-19 pandemic at the major roundabouts within the Ilorin metropolis were 212.84062, 190.90334, 419.30171, and 196.00739  $mg.m^{-3}$  for the Geri-Alimi, Offa-Garage, Post Office, and General roundabouts, respectively. The reasons the Post-Office roundabout has the highest concentration of heavy metals of the sampling locations along the highway may be due to the presence of a flyover (which allows for more vehicular mobility), the large market at the location, motor pack, and fillings station. The results implied that the Post-Office was more polluted than the other sampling locations during the pandemic. This could be a result of movement during the week only being allowed within a specific time frame with the consequences of overcrowding, heavy vehicular movement, and high traffic hold-ups generating lots of pollution from vehicular emission.

The heavy metals concentration measured from the transport pool after Covid-19 lockdown at the major roundabouts within the Ilorin metropolis were 719.66541 and 639.48938  $mg.m^{-3}$  for the Geri-Alimi and Offa-Garage roundabout, respectively. The lifting of the lockdown and the resumption of all human activities with free movement of people and vehicles throughout the week resulted in a significant increase in heavy metals pollution from vehicular emission. The presence of the flyover could be responsible for a high concentration of heavy metals at the Geri-Alimi roundabout, while the presence of a filling station very close to the Offa-Garage roundabout could also be responsible for its high heavy metals concentration.

**Table 1.** Average measured concentrations ( $\text{mg.m}^{-3}$ ) of heavy metal species within the Ilorin metropolis during COVID-19 lockdown.

Concentration of heavy metals from selected major roundabouts within the Ilorin metropolis ( $\text{mg.m}^{-3}$ )								
S/N	Heavy metal	Geri-Alimi Roundabout	Offa-Garage Roundabout	Post Office Roundabout	General Roundabout	Summation	Mean	Standard Deviation
1	Potassium	12.02411	7.7482	9.95647	7.50209	37.23087	9.30772	2.12070
2	Calcium	22.62687	21.6697	21.53257	18.89225	84.72139	21.18035	1.60118
3	Titanium	11.35818	8.61056	12.12405	12.97960	45.07239	11.26811	1.89143
4	Vanadium	0.65349	0.54545	171.30167	0.55944	173.06005	43.26501	85.35778
5	Chromium	0.14076	0.12831	1.66103	0.29537	2.22547	0.55637	0.74035
6	Manganese	4.48623	3.83438	7.49782	5.20152	21.01995	5.25499	1.59607
7	Iron	157.86784	144.10071	189.63247	144.43589	636.03691	159.0092	21.39885
8	Nickel	0.17886	0.17212	0.18621	0.18962	0.72681	0.18170	0.00781
9	Copper	0.39706	0.27472	0.22602	0.31071	1.20851	0.30213	0.07218
10	Zinc	1.34448	1.88392	3.3219	4.09394	10.64424	2.66106	1.26849
11	Gallium	0.02790	0.04890	0	0.04515	0.12195	0.03049	0.02229
12	Arsenic	0.05809	0.03893	0.04048	0.03964	0.17714	0.04429	0.00925
13	Selenium	0.03973	0.02739	0.03110	0.0236	0.12182	0.03046	0.00690
14	Bromine	0.03285	0.04740	0.03420	0.04202	0.15647	0.03912	0.00684
15	Rubidium	0.10725	0.06865	0.10477	0.05817	0.33854	0.08471	0.02499
16	Strontium	0.20130	0.14792	0.15281	0.06357	0.56560	0.14140	0.05721
17	Yttrium	0.13717	0.10119	0.12027	0.09016	0.44879	0.11220	0.02078
18	Zirconium	0.75801	0.98458	0.91459	0.37485	3.03213	0.75801	0.27244
19	Niobium	0.35980	0.3915	0.35192	0.21218	1.31540	0.32885	0.07964
20	Lead	0.02535	0.05352	0.07564	0.07994	0.23445	0.05861	0.02501
21	Cadmium	0.01529	0.02529	0.03572	0.05267	0.12897	0.03224	0.01597
TOTAL				1018.58785				

A comparative account of average measured concentration sampled at major roundabouts within the Ilorin metropolis with Ambient Air Quality Standards of the World Health Organization (WHO), National Environmental Standards and Regulations Enforcement Agency (NESREA), United States Environmental Protection Agency (USEPA), and National Institute for Occupational Safety and Health (NIOSH) are presented in Table 3. All the specified heavy metals concentrations were above the WHO, EPA, and NIOSH standard permissible emission limit except Nickel, Copper, Zinc, Arsenic, and Cadmium, which were less than the permissible emission limit set by NESREA. Continuous heavy metal emission can cause a significant increase in its concentration in the atmosphere, which will consequently increase its toxicity potential. In summary, it can be said that the environment and the general public are overly exposed to heavy metal pollution from

vehicular emission within the Ilorin metropolis.

### 3.1. Deposition flux

Table 4 shows the average deposition fluxes of particulate matter at selected major roundabouts within Ilorin metropolis. Deposition flux of particulates deposited in all the sample locations were determined to be 9.64 for Geri-Alimi roundabout and 12.79  $\text{g.m}^{-2}.\text{month}^{-1}$  for Offa-Garage roundabout after the Covid-19 lockdown. The highest deposition flux recorded during the Covid-19 lockdown was at the Post-Office roundabout (29.55  $\text{g.m}^{-2}.\text{month}^{-1}$ ), followed by Offa-Garage roundabout (8.91  $\text{g.m}^{-2}.\text{month}^{-1}$ ), General roundabout (6.23  $\text{g.m}^{-2}.\text{month}^{-1}$ ), with Geri-Alimi roundabout recording the least concentration of (4.53  $\text{g.m}^{-2}.\text{month}^{-1}$ ). As seen in Fig. 4, the deposition flux obtained for Offa-Garage and Geri-Alimi after COVID-19 lockdown

**Table 2.** Average measured concentrations ( $\text{mg.m}^{-3}$ ) of heavy metal species within the Ilorin metropolis after Covid-19 lockdown.

Concentration of heavy metals from selected major roundabouts within Ilorin metropolis ( $\text{mg.m}^{-3}$ )						
S/N	Heavy metal	Geri-Alimi Roundabout	Offa-Garage Roundabout	Post Office Roundabout	Mean	Standard Deviation
1	Potassium	23.02863	28.59367	51.6223	25.81115	3.93508
2	Calcium	97.46320	79.22968	176.69288	88.34644	12.89305
3	Titanium	36.63623	32.67769	69.31392	34.65696	2.79911
4	Vanadium	0.20452	2.18900	2.39352	1.19676	1.40324
5	Chromium	1.52829	0.87436	2.40265	1.20133	0.46240
6	Manganese	17.45983	14.70997	32.1698	16.0849	1.94444
7	Iron	530.0012	469.90452	999.90572	499.9529	42.49479
8	Nickel	0.54482	0.52081	1.06563	0.53282	0.01698
9	Copper	1.11243	1.14364	2.25607	1.12804	0.02207
10	Zinc	4.90577	4.62310	9.52887	4.76444	0.19987
11	Gallium	0.09563	0.13541	0.23104	0.11552	0.02813
12	Arsenic	0.14288	0.12028	0.26316	0.13158	0.01598
13	Selenium	0.11405	0.08291	0.19696	0.09848	0.02202
14	Bromine	0.16369	0.31273	0.47642	0.23821	0.10539
15	Rubidium	0.24152	0.31927	0.56079	0.28040	0.05498
16	Strontium	0.49144	0.62103	1.11247	0.55624	0.09163
17	Yttrium	0.32901	0.34702	0.67603	0.33802	0.01274
18	Zirconium	3.72598	1.91103	5.63701	2.81851	1.28336
19	Niobium	1.35437	0.93683	2.2912	1.1456	0.29525
20	Lead	0.07605	0.16056	0.23661	0.11831	0.05976
21	Cadmium	0.04587	0.07587	0.12174	0.06087	0.02121
TOTAL		1359.15479				

**Table 3.** Comparison of selected average heavy metal concentrations with ambient air quality standards.

S/N	Heavy metals	NESREA air emission guidelines for heavy metals ( $\text{mg.m}^{-3}$ )	WHO air emission guidelines for heavy metals ( $\text{mg.m}^{-3}$ )	US EPA air emission guidelines for heavy metals ( $\text{mg.m}^{-3}$ )	US EPA air emission guidelines for heavy metals ( $\text{mg.m}^{-3}$ )	Major roundabouts in ILORIN sampled during COVID-19 (av. meas. conc.) ( $\text{mg.m}^{-3}$ )	Major roundabouts in Ilorin sampled after COVID-19 (av. meas. conc.) ( $\text{mg.m}^{-3}$ )
1	Calcium	NA	NA	$6 \times 10^{-3}$	$6 \times 10^{-3}$	21.18035	88.34644
2	Chromium	NA	$10^{-3} \times 1$	$6 \times 10^{-3}$	$6 \times 10^{-3}$	0.55637	1.20133
3	Manganese	NA	$10^{-4} \times 1.5$	NA	NA	5.25499	16.08490
4	Iron	NA	NA	NA	NA	159.00920	499.95290
5	Nickel	20.0	$10^{-8} \times 3.8$	NA	NA	0.18170	0.53282
6	Copper	20.0	NA	NA	NA	0.30213	1.12804
7	Zinc	11.72	NA	$1.03 \times 10^{-4}$	$1.03 \times 10^{-4}$	2.66106	4.76444
8	Arsenic	6.0	$10^{-3} \times 1.5$	$4.3 \times 10^{-9}$	$4.3 \times 10^{-9}$	0.04429	0.13158
9	Selenium	NA	NA	NA	NA	0.03046	0.55624
10	Lead	0.0014	NA	$1.5 \times 10^{-4}$	$1.5 \times 10^{-4}$	0.05861	0.11831
11	Cadmium	5.0	$10^{-6} \times 5$	$1.8 \times 10^{-9}$	$1.8 \times 10^{-9}$	0.03224	0.06087

**WHO** – World Health Organization, **NESREA**- National Environmental Standards and Regulations Enforcement Agency, **US EPA**- United State Environmental Protection Agency, **NIOSH**- National Institute for Occupational Safety and Health. **NA**- Not Available.

Source: [18], [19], [20-22], [23], [24-27].

**Table 4.** Average deposition fluxes of particulate matter at selected major roundabouts within Ilorin metropolis.

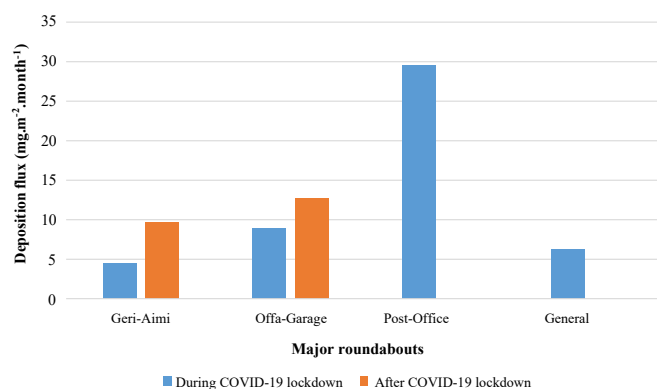
S/N	Geri-Alimi	Offa Garrage	Post Office	General
During Covid-19 lockdown	4.53	8.91	29.55	6.23
After Covid-19 lockdown	9.64	12.79	0.00	0.00

was higher than the deposition flux obtained for Offa-Garage and Geri-Alimi after COVID-19 lockdown at the same sampling point which indicates that there is an abundance of particulates containing heavy metals in the atmosphere after the lockdown.

### 3.2. Enrichment factor

The Enrichment factor (*EF*) makes it possible to differentiate an anthropogenic source from one of natural origin; therefore, it can also assist in determining the extent of the contamination [28-30]. Normally, an *EF* less than 10 indicates that a large fraction of the element can be attributed to crustal-derived heavy metal sources in the atmosphere; whereas, those higher than 10 are viewed as having a primarily non-crustal or anthropogenic source. Fe was used as a reference element for the *EF* evaluation with respect to crustal abundance, assuming that the contribution of its anthropogenic source to the atmosphere is negligible [17].

The *EF* values of several heavy metals are presented in Table 5. As can be seen, the *EFs* of K, Ca, Ti, Ni, Cr, Mn, Rb, Ga, Y, and Sr are less than 10 and are significantly low values, which suggests that these metals are mostly of crustal origin. On the other hand, the *EFs* of V, Zn, As, Se, Br, Nb, and Cd recorded higher *EFs*, which indicate that these originated from

**Fig. 4.** Average deposition fluxes at selected major roundabouts within Ilorin metropolis.

anthropogenic sources; automobile emissions, in particular, contribute more significantly to these metals. The high enrichment factors indicated for these metals suggest that their presence in atmospheric particulates was at levels too excessive to be due to expected crustal weathering processes. As such, they were mainly of anthropogenic origin [31]. Heavy metals, including V, Se, and Cd, displayed the maximum enrichment factors during COVID-19 lockdown, while Se, Br, and Cd revealed the highest *EFs* after the COVID-19 lockdown.

### 3.3. Concentration ratio

The concentration ratio specified for heavy metal determination within the Ilorin metropolis was the Iron (Fe) concentration ratios, which are represented in Table 6. Iron (Fe) had the highest mean concentration of all elements in the characterized samples for both during and after the covid-19 lockdown; hence, we needed to determine the concentration ratio of Iron (Fe) with the other heavy metals for all sample locations.

All ratio values below 1.00 suggest that the concentration of iron was high in those sampling locations, other heavy metals have been exposed to photochemical degradation, and their concentration decreases quickly in the ambient air basin. A small ratio is also a strong indication of photochemical reactions on heavy metals. The determined concentrations ratio of heavy metals suggests that photochemical degradation was active in all the sampling locations.

### 3.4. Correlation matrix of heavy metals concentration within Ilorin metropolis

The correlation coefficient is a measure of the linear relationship or correlation between two variables that gives an expected value between +1 and -1, where '1' is a total positive correlation, '0' is no correlation, and '-1' is a total negative correlation. This is extensively used in science as a measure of the degree of linear dependences between two variables. Therefore, the correlation analysis for various heavy metals was determined [32].

The determined correlation is presented in Table 7 and discussed in more detail below. The positive correlation 0.50-0.59 indicates a moderate correlation, 0.60-0.69 above shows a moderate correlation, 0.70-0.79 a strong correlation, and 0.8 and above a very strong correlation. The concentration of K was strongly correlated with Ca

**Table 5.** Enrichment factor of heavy metals at selected major roundabout within Ilorin metropolis.

Enrichment Factors for heavy metals in the selected major roundabouts during Covid-19 lockdown																					
Metal	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Ar	Se	Br	Rb	Sr	Y	Zr	Nb	Pb	Cd
Geri-Alimi	0.21	0.19	0.72	1.94	0.49	1.68	1.00	0.76	2.36	6.85	0.52	11.51	283.38	4.88	0.42	0.19	1.48	1.64	6.42	0.65	36.35
Offa-Garage	0.15	0.2	0.6	1.78	0.49	1.58	1.00	0.8	1.79	10.51	1.01	8.45	214.02	7.72	0.3	0.16	1.2	2.33	7.65	1.5	65.87
Post-Office	0.14	0.15	0.64	423.81	4.83	2.34	1.00	0.66	1.12	14.09	0	6.68	184.67	4.23	0.35	0.12	1.08	1.65	5.22	1.6	70.7
Enrichment Factors for heavy metals in the selected major roundabouts after Covid-19 lockdown																					
Geri-Alimi	0.12	0.25	0.69	0.18	1.59	1.95	1.00	0.69	1.97	7.44	0.53	8.43	242.30	7.25	0.29	0.14	1.06	2.40	7.19	0.58	32.48
Offa-Garage	0.16	0.23	0.69	2.19	1.03	1.86	1.00	0.74	2.28	7.91	0.85	8.01	198.67	15.61	0.43	0.20	1.26	1.39	5.61	1.37	60.60

**Table 6.** Characteristics/concentrations ratio of heavy metals at selected roundabouts within the Ilorin metropolis.

Iron elemental ratio for selected heavy metals concentration before Covid-19																
Metal	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Nb	Zr	Pb	Cd		
Geri-Alimi Underpass	0.076	0.076	0.072	0.004	0	0.028	1.00	0.001	0.003	0.009	0.002	0.005	0	0		
Offa-Garage Roundabout	0.054	0.15	0.06	0.004	0	0.03	1.00	0.001	0.002	0.013	0.003	0.006	0	0		
Post Office Roundabout	0.053	0.114	0.064	0.903	0	0.02	1.00	0	0	0.018	0.002	0.005	0	0		
General Hospital Roundabout	0.052	0.131	0.09	0.004	0	0.036	1.00	0	0	0.03	0	0.003	0	0		
Iron elemental ratio for selected heavy metals concentration after Covid-19																
Offa-Garage Roundabout	0.045	0.184	0.065	0	0.03	0.033	1.00	0.001	0.002	0.009	0.003	0.007	0	0		
Geri-Alimi Underpass	0.061	0.169	0.007	0.005	0.002	0.031	1.00	0.521	0.002	0.01	0.002	0.004	0	0		

( $r = 0.739$ ), it has a very strong correlation with Ar ( $r = 0.882$ ), Rb ( $r = 0.926$ ), Sr ( $r = 0.826$ ), Se ( $r = 0.974$ ), Y ( $r = 0.984$ ) and was moderately correlated with Cu ( $r = 0.513$ ). The Ca concentration has a very strong correlation with Se ( $r = 0.840$ ), Sr ( $r = 0.989$ ), Y ( $r = 0.842$ ), Nb ( $r = 0.916$ ) Cd ( $r = 0.957$ ), an above moderate correlation with Ar ( $r = 0.601$ ), and also a strong correlation with Rb ( $r = 0.771$ ) and Zr ( $r = 0.797$ ). The concentration of Ti has a very strong correlation with Ni ( $r = 0.962$ ), an above moderate correlation with Mn ( $r = 0.611$ ), Zn ( $r = 0.69$ ) and Cd ( $r = 0.606$ ), and a moderately correlated with Br ( $r = 0.562$ ). The concentration of V has a very strong correlation with Cr ( $r = 0.994$ ), Mn ( $r = 0.936$ ) and Fe ( $r = 0.954$ ). The concentration of Cr has very strong correlation with Mn ( $r = 0.965$ ) and Fe ( $r = 0.989$ ). The concentration of Mn has a very strong correlation with Fe ( $r = 0.893$ ), an above moderately correlated with Ni ( $r = 0.682$ ), and a moderately correlated with Zn ( $r = 0.580$ ). The concentration of Ni has a very strong correlation with Zn ( $r = 0.859$ ) and Cd ( $r = 0.781$ ) and an above moderately correlated with Pb

( $r = 0.664$ ). The concentration of Cu has a very strong correlation with Ar ( $r = 0.855$ ). The concentration of Zn has a very strong correlation with Pb ( $r = 0.941$ ) and Cd ( $r = 0.976$ ). Concentration of Ga has very strong correlation with Br ( $r = 0.789$ ). The concentration of Ar has a very strong correlation with Se ( $r = 0.910$ ), Se ( $r = 0.701$ ), Y ( $r = 0.827$ ) and moderately correlated with Rb ( $r = 0.642$ ). The concentration of Se has a very strong correlation with Rb ( $r = 0.876$ ), Sr ( $r = 0.909$ ) and Y ( $r = 0.849$ ). The concentration of Y has a moderate correlation with Nb ( $r = 0.572$ ). The concentration of Zr has a very strong correlation with Nb ( $r = 0.96$ ). The concentration of Cd has a very strong correlation with Pb ( $r = 0.913$ ). All the determined correlations suggested that these heavy metals could have originated from multiple similar sources along with the traffic.

### 3.5. Strategies to abate and control heavy metal pollutions from vehicular emission in transport pools

Heavy metals pollutions from vehicular emissions that



Table 7. Heavy metals correlation matrix for the selected major roundabouts within Ilorin metropolis.

	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Ar	Se	Br	Rb	Sr	Y	Zr	Nb	Pb	Cd		
<b>K</b>	1.000																						
<b>Ca</b>	<b>0.739</b>	1.000																					
<b>Ti</b>	0.154	-0.527	1.000																				
<b>V</b>	0.205	0.147	0.302	1.000																			
<b>Cr</b>	0.154	0.049	0.381	<b>0.994</b>	1.000																		
<b>Mn</b>	0.165	-0.117	0.611	<b>0.937</b>	<b>0.965</b>	1.000																	
<b>Fe</b>	0.487	0.342	0.336	<b>0.954</b>	<b>0.936</b>	<b>0.893</b>	1.000																
<b>Ni</b>	-0.084	-0.675	<b>0.962</b>	0.385	0.473	0.682	0.337	1.000															
<b>Cu</b>	0.513	0.223	<b>0.076</b>	-0.703	-0.711	-0.594	-0.465	-0.167	1.000														
<b>Zn</b>	-0.560	-0.875	0.690	0.347	0.439	0.580	0.153	<b>0.859</b>	-0.516	1.000													
<b>Ga</b>	-0.578	-0.365	-0.397	-0.912	-0.895	-0.875	-0.992	-0.365	0.351	-0.118	1.000												
<b>Ar</b>	<b>0.882</b>	0.601	0.082	-0.274	-0.314	-0.256	0.026	-0.194	<b>0.855</b>	-0.66	-0.140	1.000											
<b>Se</b>	<b>0.974</b>	<b>0.840</b>	-0.056	0.063	-0.003	-0.029	0.349	-0.299	0.573	-0.732	-0.435	<b>0.91</b>	1.000										
<b>Br</b>	-0.881	-0.407	0.562	-0.48	-0.469	-0.553	-0.704	-0.379	-0.285	0.105	<b>0.789</b>	-0.663	-0.752	1.000									
<b>Rb</b>	<b>0.926</b>	<b>0.771</b>	0.116	0.536	0.479	0.434	<b>0.757</b>	-0.051	0.153	-0.441	-0.811	0.642	<b>0.876</b>	-0.877	1.000								
<b>Sr</b>	<b>0.826</b>	<b>0.989</b>	-0.417	0.133	0.041	-0.093	0.359	-0.595	0.321	-0.863	-0.398	0.701	<b>0.909</b>	-0.514	<b>0.826</b>	1.000							
<b>Y</b>	<b>0.984</b>	<b>0.842</b>	0.006	0.260	0.195	0.158	0.528	-0.213	0.415	-0.639	-0.602	0.827	<b>0.980</b>	-0.824	<b>0.954</b>	<b>0.906</b>	1.000						
<b>Zr</b>	0.254	<b>0.797</b>	-0.727	0.383	0.291	0.038	0.400	-0.705	-0.363	-0.600	-0.341	-0.004	0.361	-0.001	0.474	<b>0.708</b>	0.425	1.000					
<b>Nb</b>	0.418	<b>0.916</b>	-0.76	0.193	0.092	-0.144	0.281	-0.808	-0.089	-0.796	-0.251	0.248	0.552	-0.078	0.545	<b>0.849</b>	0.572	<b>0.960</b>	1.000				
<b>Pb</b>	-0.69	-0.777	0.434	0.453	0.526	0.583	0.202	0.664	-0.763	<b>0.941</b>	-0.128	-0.861	-0.827	0.281	-0.48	-0.813	-0.71	-0.326	-0.576	1.000			
<b>Cd</b>	-0.687	<b>0.957</b>	0.606	0.144	0.241	0.387	-0.067	0.781	-0.436	<b>0.976</b>	0.102	-0.690	-0.828	0.277	-0.95	-0.953	-0.770	-0.679	-0.855	<b>0.913</b>	1.000		

result from the combustion of fuel have the potential to be significant from health, environmental, and economic perspectives. The daily increase in the use of vehicles and an over-dependence on fossil fuel signifies continuous emission of heavy metals from vehicular exhausts, which degrade the environment (alters air, water, and soil composition and pH). When heavy metals are emitted into the air and later settle in bodies of water and soil, they cause serious health problems through inhalation (air), oral consumption (water), and ingestion (soil and plant). Controlling heavy metal pollution is a major challenge and of serious concern. Researchers and scientists have developed devices such as the catalytic converter, catalytic incinerator, thermal incinerator, enclosed oxidizing flares, and others to meet these challenges. Unfortunately, these devices have been unable to control heavy metals pollution, and the environment continues to be exposed to heavy metals.

There is a need to move away from the fossil fuel economy and to adopt a more sustainable and renewable energy that will cause zero pollution. The Nigerian government and global community need to invest significantly in clean energy such as hydrogen gas energy technology, which involves the use of hydrogen gas to power vehicles, and any other fuel engines which have zero carbon emission and other related pollutions. Adopting a safer, cheap, and alternative source of fuel will greatly decrease the concentration of heavy metals and other related pollutants in the air making the environment a safe place to live and prolonging the life span of humanity.

#### 4. Conclusion

The concentration and distribution of heavy metals along selected major transport pools within the Ilorin metropolis in Kwara State, Nigeria, during and after Covid-19 lockdown have been reported using the dry deposition method and EDXRF. The total concentration of heavy metals recorded after the lockdown was significantly higher than the total concentration of heavy metals recorded during the lockdown, which indicates the degree of heavy metal pollution caused by vehicular emission and other anthropogenic sources. Iron (Fe) concentrations were found to be the most abundant in all sampling locations with average mean values of 159.0092 mg.m<sup>-3</sup> and 499.9529 mg.m<sup>-3</sup> for during and after the covid-19 lockdown, respectively,

which also depicts higher vehicular emission after the lockdown compared to during the lockdown.

The averaged measured concentration of most of the heavy metals sampled along selected major roundabouts within the Ilorin metropolis during and after Covid-19 lockdown exceeded the permissible emission limit set by the Nigerian environment by the National Environmental Standards and Regulations Enforcement Agency (NESREA) and the international standards of the United States Environmental Protection Agency (USEPA), World Health Organization (WHO), and the National Institute for Occupational Safety and Health (NIOSH). The correlation matrix, Enrichment factor, and Concentration ratio were also determined. They indicated that heavy metal pollution originated from multiple similar anthropogenic sources and that photochemical degradations were active in all the sampling locations.

There is a need for the adoption of sustainable clean energy of a hydrogen economy to replace the current fossil fuel economy. This will mitigate heavy metals emission and other related pollutants from vehicle exhaust into the environment.

#### Acknowledgment

The authors gratefully acknowledge the staff of the Centre for Energy Research and Development (CERD) at Obafemi Awolowo University, Ile Ife, Nigeria, for the analysis.

#### References

- [1] P.O. Fatoba, C.O. Ogunkunle, G.K. Olawepo, Assessment of atmospheric metal depositions in the industrial areas of the Southwest of Nigeria, *Ethiopian J. Environ. Stud. Manag.* 5 (2012) 260-267.
- [2] M. Ferenčik, L. Ebringer, Modulatory effects of selenium and zinc on the immune system, *Folia Microbiol.* 48 (2003) 417-426.
- [3] D.J. Ferner, Toxicity of heavy metals, *eMedicine J.* 2 (2001) 1.
- [4] P.L. Kinney, M. Aggarwal, M.E. Northridge, N.A. Janssen, P. Shepard, Airborne concentrations of PM (2.5) and diesel exhaust particles on Harlem sidewalks: a community-based pilot study, *Environ. Health Persp.* 108 (2000) 213-218.
- [5] D.M. DeMarini, Genotoxicity biomarkers associated

- with exposure to traffic and near-road atmospheres: A review, *Mutagenesis*, 28 (2013) 485-505.
- [6] Å. Danielsson, I. Cato, R. Carman, L. Rahm, Spatial clustering of metals in the sediments of the Skagerrak/Kattegat, *Appl. Geochem.* 14 (1999) 689-706.
- [7] A.K. Gupta, K. Karar, A. Srivastava, Chemical mass balance source apportionment of PM10 and TSP in residential and industrial sites of an urban region of Kolkata, India, *J. Hazard. Mater.* 142 (2007) 279-287.
- [8] J. Gromadzińska, W. Wąsowicz, Health risk in road transport workers part I. Occupational exposure to chemicals, biomarkers of effect, *Int. J. Occup. Med. Environ.* 32 (2019) 267-280.
- [9] T.V. Ramachandra, S. Kashyap, Emissions from India's transport sector: Statewise synthesis, *Atmos. Environ.* 43 (2009) 5510-5517.
- [10] National Population Commission, FEDERAL REPUBLIC OF NIGERIA: 2006 Population.
- [11] Y.A. Ahmed, Waste management in Ilorin metropolis; lesson for Nigerian cities, *Futy J. Environ.* 3 (2008) 49-58.
- [12] J.A. Olatunji, D.A. Olasehinde, P.I. Olasehinde, M.O. Awojobi, O.A.I. Akinrinmade, Preliminary Integrated assessment of hydrogeological conditions a case study of parts of Ilorin crystalline rocks southwestern Nigeria, *IOSR J. Appl. Geol. Geophys. (IOSR-JAGG)* 8 (2020) 01-06.
- [13] [www.googleearth.com](http://www.googleearth.com).
- [14] D.R. Lide, CRC Handbook of Chemistry and Physics, Geophysics, Astronomy, and Acoustics, Abundance of Elements in the Earth's Crust and in the Sea, Section 14, CRC Press, Boca Raton, FL, USA, 85<sup>th</sup> ed., 2005.
- [15] K.-M. Vuori, Direct and indirect effects of iron on river ecosystems, *Ann. Zool. Fenn.* (1995) 317-329.
- [16] S. Wang, X. Shi, Molecular mechanisms of metal toxicity and carcinogenesis, *Mol. Cell. Biochem.* 222 (2001) 3-9.
- [17] N.I. Ward, R.D. Reeves, R.R. Brooks, Lead from motor-vehicle exhausts in sweet-corn plants and soils along a highway in Hawke's Bay, New Zealand, *New Zeal. J. Sci.* 18 (1975) 261-267.
- [18] NESREA, National Environmental Standards and Regulations Enforcement Agency (Establishment) Act, Lagos: The Federal Government Printer, Lagos Nigeria, 2007.
- [19] US EPA, 2017 National Emissions Inventory (NEI) Data, *Air Emission Inventories*, Retrieved from EPA: <https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-data>, 2017.
- [20] The Risk Assessment Information System, Toxicity and Physical Properties of Chemicals 2009, Available online: [http://rais.ornl.gov/cgi-bin/tools/TOX\\_search?select=chem](http://rais.ornl.gov/cgi-bin/tools/TOX_search?select=chem) (Accessed on 16 March 2020).
- [21] US EPA, Toxicological review of benzene (non-cancer effects): In support of summary information on Integrated risk information system (IRIS), 2002, Available from [www.epa.gov/iris](http://www.epa.gov/iris) (Accessed October 2, 2021).
- [22] US EPA, Exposure Factors Handbook, National Center For Environmental Assessment Office of Research and Development, Office of Research and Development, Washington, DC, 1997.
- [23] ATSDR, Agency for Toxic Substances and Disease Registry, Minimal Risk Levels (MRLs), 2021.
- [24] World Health Organisation, Air quality guidelines for Europe, 2<sup>nd</sup> ed., WHO Regional Office for Europe: Copenhagen, Denmark, 2000.
- [25] World Health Organization (WHO) Guidelines for air quality, WHO, Geneva, (1984) pp. 99-102.
- [26] World Health Organization (WHO) Guidelines for air quality 3<sup>rd</sup> ed., WHO, Geneva, 2008.
- [27] World Health Organization (WHO) Guidelines for air quality, 3<sup>rd</sup> ed., WHO, Geneva, 2011.
- [28] A.J. Haagen-Smit, Chemistry and physiology of Los Angeles smog, *Ind. Eng. Chem.* 44 (1952) 1342-1346.
- [29] M. Haldimann, T.Y. Venner, B. Zimmerli, Determination of selenium in the serum of healthy Swiss adults and correlation to dietary intake, *J. Trace Elem. Med. Bio.* 10 (1996) 31-45.
- [30] M. Horsfall Jr, M.N. Horsfall, A.I. Spiff, Speciation of heavy metals in inter-tidal sediments of the Okrika river system, Rivers State Nigeria, *Bull. Chem. Soc. Ethiopia*, 13 (1999) 1-10.
- [31] B. Rani, U. Singh, A.K. Chuhan, D. Sharma, R. Maheshwari, Photochemical smog pollution and its mitigation measures, *J. Adv. Sci. Res.* 2 (2011) 28-33.
- [32] S.A. Adebajo, L.A. Jimoda, A.O. Alade, A.O. Alamu, Elemental composition of total dry particulate matter deposited in the selected industrial areas within Lagos state, *Environ. Qual. Manage.* 29 (2019) 63-76.