# Determination of Heavy Metals in Soots from Petroleum Vehicles Exhaust Tailpipes

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Abstract— In recent times, the skyrocketing vehicular population has been accompanied by a decreasing level of vehicle maintenance, aging of vehicle, and increasing inclusion of metal-based additives in fuel. Heavy metals have deleterious health implications ascribed to their propensity to displace the functional groups of enzyme thereby modifying physiological and biochemical processes within the body. With the aid of a plastic spatula, accumulated soot particles were scrapped and collected from the inner surface of the tailpipe of vehicles located at Maraban Jos and Pantaker of Kaduna State. Samples were analyzed for the presence of Cd, Hg, Cu, Pb and Fe via atomic absorption spectrophotometer (AAS). The results showed that Fe emission was the most significant with 1153.560±0.361 mg/kg and 796.816±0.522 mg/kg being the mean concentration for gasoline engine vehicle (GEV) and diesel engine vehicle (DEV) respectively. Pb followed in the order of higher concentration having an average concentration of 14.097±0.644 mg/kg for (GEV) and 11.278±0.028 mg/kg for (DEV). Mercury average concentration was found to be 5.899±0.070 mg/kg for GEV while 2.044±0.054 mg/kg was obtained for DEV. 3.083±0.034 mg/kg for GEV and 1.453±0.051mg/kg for DEV was attributed to Cu. Cd had the least concentrations for both engines, with  $0.044\pm0.036$  mg/kg and 0.0403±0.037 mg/kg for GEV and DEV respectively. Hence, the result shows GEV to have higher heavy metals pollution as compared to DEV. There exists also a similar trend associated with the emitted metal concentrations of the two fuels (gasoline and diesel) engine which follow the order of Fe > Pb > Hg > Cu > Cd. All the results exceeded the maximum permissible limit for air control given at 0.5 mg/Nm<sup>3</sup> of an averaging period of 30 minutes to 8 hours according to (European commission 1991) with the exception of Cd from all the samples and lead from two sample of the diesel engine which recorded no detection. It is therefore inferred that soots from the exhaust tail pipes of petroleum vehicles are a major source of toxic heavy metals which are capable of altering physiological health states.

Keywords— Heavy Metals, Petroleum Soot, Physiology, Vehicle Exhaust, Diesel and Gasoline.

## I. INTRODUCTION

Transportation is an imperative component for comfortable human existence. The liberty to travel petite and stretched distances creates the prospect for individual progress and professional activities, increases the alternative for leisure and holidays, and allows better contact and understanding with people. The economic expansion of whole regions depends on the effortless contact to citizens and goods ensured by modern transport machinery. Due to its suppleness, road transport is a major transport means, and cars are substance of aspiration and pride in various societies. Sorry to say, these positive aspects are very much related with the hazards to the surroundings and human health caused by transport, chiefly road transport (Dora & Philips 2000).

This has resulted in the rising transport volume, associated risk of harm to air quality and health, and an increased threat to the guiding principles of many countries, as affirmed by the European Union (EU) in its 6th Environment Action Programme; to realize pollution levels that do not give rise to damaging effects on human health and the environment (European Commission, 2001)

Transportations by means of gasoline and diesel engine vehicles, have received growing consideration as a cause of air contamination at both local and international scales since 1970. Greater than 95% of mechanical transport relies on petroleum and accounts for nearly 50% of world use of petroleum (Woodcock *et al*, 2007). There is a substantial increase in the number of vehicle (Quari & Hassan, 2017). At the moment there are more than 700 million vehicles on roads, and this numeral figure is projected to double in 30 years to come (Iaych *et al*, 2009). This significant contribution led to (Guilherme *et al*, 2017; Lu Qi *et al*, 2016) findings of vehicular exhaust emission as a primary source apportionment of particulate matter which he performed using positive matrix factorization (PMF).

Heavy metals, such as Ni, Cd, Pb, Zn, Cu, Hg, Cr and others refer to metals with densities greater than 5 g/cm<sup>3</sup> (Li *et al*, 2014) Inappropriate disposal of engine oil, brake fluid, and petroleum exhaust transmission oil and leaded gasoline in the surrounding region of fuel contributes to the heavy metals load (Dauda & Odoh, 2012; Khorshid & Thiele-Bruhn 2016; Luo *et al*, 2012).

Heavy metals can be able to affect human health when exposed by means of ingestion, inhalation and dermal contact (Ling *et al*, 2008; McLaughlin *et al*, 2000). For instance, excessive exposure to Pb can damage the skeletal, nervous, endocrine, circulatory, immune and enzymatic systems (Zhang *et al*, 2012). Mean while, exposure to Cd can cause pulmonary adenocarcinomas, hypertension, kidney dysfunction, lung cancer, prostatic proliferative lesions and bone fractures, (Chen *et al*, 2015)

Different reasons leads to the addition of various compounds to liquid fuels (such as methyl tert-butyl ether (MTBE), tetraethyl lead (TEL) so as to get higher the octane number of the fuel and also to oxygenate the fuel in winter months to lessen urban smog (US EPA 2008). Several of these sources have been directly linked to adverse health effects. Instances shows that the major aerosol cause of human toxicity in Barcelona was credited to traffic activities which has to do with vehicle emissions, road dust and secondary nitrate), with fuel burning and industrial emissions also contributing to increased cancer risk (Reche *et al.*, 2012; Turoczi *et al.* 2012) reported higher toxicity from direct emissions (e.g. from traffic) than from aerosol processed photochemically.

It is imperative to comprehend the degree to which emission sources affect air quality, particularly in urban areas, where the worldwide population has increased from 34% (in 1960) to 56% (in 2014) and is projected to grow further (WHO 2014). Having access to cheaper road transport in developing countries is a deciding cause for percentage share of vehicle types. This has brought about exponential boost in their figures over the few years. Consequently, changes in the percentage share of vehicles plying on urban roads influence traffic and emission characteristics such as average traffic fleet speed, delay due to congestion and fuel consumption. Vehicles running with more than fixed capacity use more fuel leading to higher emissions (Virtanen et al, 2004). Too little maintenance of vehicles enhances emission from them: catalytic converters and filters make them even larger emitters of pollutants, especially soot particles (Frey et al, 2007; Lawson et al, 1990; Stedman et al, 1991 and Stedman et al, 1994).

This research aimed at determining some heavy metals concentration emitted by commercial vehicles making used of premium motor spirit otherwise known as gasoline and diesel fuel, see if there are statistically significant differences between these metals concentrations in the diesel and gasoline engine vehicles and their attendant's health effect.

# II. RESEARCH METHODOLOGY

## 2.1 Study area

This study was undertaken in Kaduna metropolis which lies at latitude 10°28N and at longitude 7°25E. It is situated in the central region of what is used to be called the Northern Region of Nigeria, Kaduna. Founded in 1917 as governmental head quarter of Northern Nigeria, it is currently one of the most significant cities in the country. The mean annual rainfall in the area ranges from 924.3 to 1,543.6mm. Annual temperature varies between 29 to 38.6°C. It occupies an area of approximately 48,473.2 square kilometers and falls into Guinea Savanna climate, which has distinct rainy and dry seasons. As at 1991 census it had a population of 993,600 but projected to be about 1.56 million people (www.kaduna-state.com., 2018) but by 2006 census it had a population of 6,066,563 which is 4.333% of the total country's population just behind Kano and Lagos (Nigerian muse, 2005)

## 2.2 Samples collection and pretreatment

Accumulated soot particles were collected from the inner surface of the tailpipe of the vehicles and were considered to have similar characteristics as that of those emitted into the atmosphere. Soot particles were collected by scraping using plastic spatula. Different soot samples were collected from various sources; the carbon soot from diesel vehicle was obtained from Maraban Jos, a town located about 4 km away from Kaduna metropolis along Kaduna – Zaria express road. While the carbon soot from gasoline vehicle were obtained from New Pantaker located along Nnamdi Azikwe Express by-pass, Kaduna which is an automobile based market. The soot samples were scratched from the exhausts and were stored in a pre-wash plastic sample bottle for further study.

## 2.3 Sample grouping

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GASOLINE ENGINE VEHICLES		
Sample site: New pantaker		
Sample	Sample identity	
Sample A	Golf	
Sample B	Honda	
Sample C	Mercedes Benz	

Table 1.b			
DIESEL ENGINE VEHICLES			
Sample site: Maraban Jos			
Sample	Sample identity		
Sample D	Iveco		
Sample E	DAF		
Sample F	Turbo		

## 2.4 Reagents

Analytical grades of 37% Hydrochloric acid, 70% nitric acid and deionised water were purchased from Sigma Aldrich.

## 2.5 Quality assurance

Quality assurance was adhered by observing all precautions and working guides from the points of sample collection to the analysis. Blanks were taken to ensure precision in the analysis.

## 2.6 Sample digestion

1.0g of each pretreated sample was weighed and placed in 100ml beaker, after which 25ml of freshly prepared aqua regia (HCl :  $HNO_3 = 3:2$ ) was added. The mixture was heated until the sample completely dissolves in the aqua regia). The mixture was then allowed to cool and filtered; the residue (unburnt carbon black) was washed with distilled water. The combined aqueous extract was then made up to 50ml volumetric flask with distilled water (Ang and Lee 2005)

# 2.7 Sample Analysis (AAS Analysis)

The digested samples were analyzed by the atomic absorption spectrometric method employing the use of the atomic absorption spectrometer, model: ICE 3000 C13300129 v1.30 a device of analytical grade whose operation is to determine the concentrations of unknown solutions by comparing the concentrations of known standard solutions to the unknown solutions which results in a calibration curve following the Beer's Lamberts law. The method measures the concentration of atoms of an element by passing light, emitted by a hollow cathode lamp of that element, through a cloud of atoms from a sample. Only those atoms that are the same as those in the lamp will absorb the light from the lamp.

A reduction in the amount of light reaching the detector is seen as a measure of the concentration of that element in the original sample.

The Beers Lambert law states that: A = Ecl

Where: A: is the absorbance at a fixed wavelength  $(\Lambda)$ 

E: is a constant called molar absorptivity C: is the solutions concentration

L: is the path length which the light travels usually (1cm)

# III. RESULT

The results of the analysis subjected to Atomic Absorption Spectrophotometer were as shown in the table below:

S	ONO METALS UN	NIT SAM	PLE A	SAMPLE B	SAMPLE C	AVERAGE
		(Gol	f)	(Honda)	(Benz)	
1	CADMIUM	(mg/kg)	0.054±0.057	0.042±0.021	0.035±0.031	0.044±0.036
2	MERCURY (mg/kg)	14.235±0	.093	1.906±0.090	1.557±0.027	5.899±0.070
3	CUPPER	(mg/kg)	3.680±0.047	3.730±0.016	$1.841 \pm 0.039$	3.083±0.034
4	LEAD	(mg/kg)	$0.444 \pm 0.022$	1.277±0.074	$40.571 {\pm} 1.837$	14.097±0.644
5	IRON	(mg/kg)	1047.867±0.35	51 1269.273±0.257	1143.542±0.	474 1153.560±0.361

TABLE 3: Result showing the concentration of the heavy metals from the tail pipes exhaust of a diesel engine vehicle SINO METALS UNIT SAMPLE A SAMPLE B SAMPLE C AVERAGE

0/14	U WILLIALS UNI	I SAN		SAMELL D	SAMELE C	AVLINAGL	
		(Iv	veco)	(DAF) (Tu	rbo)		
1	CADMIUM	(mg/kg)	$0.047 \pm 0.058$	0.034±0.039	$0.040 \pm 0.014$	$0.0403 \pm 0.037$	
2	MERCURY (mg/kg)	3.344±0	.027 2.095±0	.071 0.692	±0.063 2.044±0	.054	
3	CUPPER	(mg/kg)	0.923±0.062	1.329±0.047	2.108±0.043	$1.453 \pm 0.051$	
4	LEAD	(mg/kg)	ND	33.835±0.	085 1	ND	11.278±0.028
5	IRON	(mg/kg)	1263.749±0.8	19 221.156±0.1	32 905.542±0	0.615 79	96.816±0.522
ND	= Not detected						

TABLE 3: Recommended standard for air emissions (European Commission 1991).					
SUBSTANCE	EMISSION LIMIT	AVERAGING PERIOD			
Cadmium and its compound	0.05 mg/Nm <sup>3</sup> expressed as cadmin	am 30 mins to 8 hours			
Mercury and its compound	0.05 mg/Nm <sup>3</sup> expressed as mercur	ry 30 mins to 8 hours			
Cupper and its compound	0.05 mg/Nm <sup>3</sup> expressed as cupper	30 mins to 8 hours			
Lead and its compound	0.05 mg/Nm <sup>3</sup> expressed as lead	30 mins to 8 hours			
Iron and its compound		30 mins to 8 hours			

 $Mg/Nm^3 = milligram$  per normal cubic meter



Figure 1: Bar chart representation of the mean data of the whole metals



Figure 2: Bar chart representation showing clear distinction for Cd, Hg, Cu and Pb

## 3.1 Cadmium

Table 1 and 2 shows the Cd concentration in different samples, which were collected from heavy duty and passenger cars sources. The average data of Cd concentration for the gasoline engine vehicle, GEV, soots is  $0.044\pm0.036$  (mg/kg) which is 0.004 mg/kg higher than that of diesel engine vehicle, DEV, soots having a concentration of  $0.0403\pm0.037$  mg/kg the concentrations of  $0.054\pm0.057$ 

mg/kg to  $0.034\pm0.039$  mg/kg. It can be seen that the concentration of Cd in all sample of the two fuel engine were within the maximum acceptable limits for air which is  $0.05 \text{ mg/Nm}^3$  of an averaging period of 30 minutes to 8 hours.

# 3.2 Mercury

The two fuels show some considerable concentration of mercury with the GEV having the highest average concentration, 5.899±0.070 mg/kg, while DEV has the least concentrations of emitted mercury standing at 2.044±0.054 mg/kg. The entire samples exceeded the maximum permissible limit of exposure set at 0.05 mg/ Nm<sup>3</sup> for 30 minutes to 8 hours.

## 3.3 Cupper

The concentrations of Cu in the GEV are generally higher than those of the DEV and both were high enough to exceed the stipulated maximum acceptable limit for air of Cu, set at  $0.05 \text{ mg/Nm}^3$  for 30 minutes to 8 hours. This high concentration of Cu,  $3.083\pm0.034$  mg/kg and  $1.453\pm0.051$ mg/kg in the two fuels engine (GEV and DEV respectively) may be due to the use of certain Cu alloys in the internal combustion engine which sublimes due to high process temperature.

## 3.4 Lead

The increased Pb contamination in soot sample C,  $(40.571 \pm 1.837 \text{ mg/kg})$ , and sample E,  $(33.835 \pm 0.085)$ mg/kg), according to Docekal et al. (1992) can be credited to the use of metal lead-based additives that was used as an anti-knock or alkyl-lead contamination compounds. Whereas the lower concentration can be attributed to the use of low level of Pb based additives in Sample A and B of the GEV having the concentration of 0.444±0.022 mg/kg and 1.27680±0.074 mg/kg respectively as compared to sample C and E which can originate from various sources such as engine wear, lubrication oil, fuel, fuel additives or coatings from exhaust gas after-treatment systems (Docekal et al, 1992). In the DEV, there wasn't Pb detection in sample D (Iveco) and sample F (Turbo). This can only means the absence of the use of lead-based additives, fuel and as such, DEV fuel shows more tendency of not emitting Pb.

In contrast to the maximum acceptable limit, all the GEV results were higher than the recommended limit and can be harmful to humans. While from the DEV, only one sample was above the recommended permissible limit.

## 2.5 Iron

It can be seen from Table 1 and 2 that there is an extremely high concentration of iron being emitted by the two fuel engine of the various vehicle with the concentration as  $1269.273\pm0.257$  mg/kg >  $1263.749\pm0.819$  mg/kg >

221.156 $\pm$ 0.132 mg/kg > 1143.542 $\pm$ 0.474 mg/kg > 1047.867 $\pm$ 0.351 mg/kg > 905.5416 mg/kg > 221.156 $\pm$ 0.132 mg/kg. The same is true for Fe: that the average concentration of Fe in the GEV has closely double that of the DEV. The GEV and DEV average concentration is given as 1153.560 $\pm$ 0.361 mg/kg and 796.816 $\pm$ 0.522 mg/kg.

# IV. DISCUSSION

The research within this study paid attention to particle emissions of inorganic elements such as, Cd, Hg, Cu, Pb, and Fe from commercial vehicles. Gaseous emissions are not reported. Just as Yousaf reported the emission characteristics of heavy metal and the particulate matter from small incineration or ignition were influence by many factors such as operating conditions, fuel capacity etc. Nonetheless, the chief factor in the discharge of metal is the volatility, which increases with temperature as well as with hydrochloric acid production in the flue gases (Yousaf, 2012). But also, metal emissions in vehicle engines emissions happen from fuel additives, engine or exhaust system wear, and metals absorbed into the engine from resuspended soil, asphalt, or other airborne materials (Docekal *et al*, 1992; Lighty *et al*, 2000).

The result obtain from this research point to the fact that vehicle emissions add immensely to the metal concentrations in the urban and industrial settlement more than rural settlement in terms of increasing vehicular number which can be justify by previous observations such as (Lu *et al*, 2016; Pan *et al*, 2013; Zhou *et al*, 2014; Okorie *et al*, 2010) and tends to contradict what (Visser *et al*, 2015) reported; heavy-duty vehicles appeared to have a larger effect than passenger vehicles on the concentrations of all elements influenced by re-suspension and wearing processes.

Seeing that heavy metals occurred at different phases; as solids, gases or absorbed to particles of aerodynamic sizes (US EPA 1996; Wedepohl, 1991) (Ismal et al., 2018) was able to point out the order of the average concentration of total particulate matter and that of the heavy metals to be Residential < Urban < Industrial. From Ismal findings, it can be deduced that more heavy metals are absorbed by more particulate matter; in view of the fact that industrial areas has more particulate matter: Since therefore DEVs produces more soots than GEVs, more heavy metal can be accumulated from the released of DEVs soots as to GEVs soots which has an enhanced catalytic converters and efficient filters thereby producing lesser quantity of soots. This might be the possible reason on which (Visser *et al*, 2015) assertion was made on heavy duty vehicles appearing

to have a larger effect than passenger vehicles on the concentrations of all elements: But taking the same proportions of petroleum soots from both engine vehicles as this research highlight; gasoline engine has higher concentration of element. Another points to consider is a research by (Platt *et al*, 2017) in which gasoline cars was found to produce more carbonaceous particulate matter than modern filter-equipped diesel cars is; (Jeff, 2017) diesel is now better than gas. In share autos, average weight percentage of heavy metals was found to be higher than that in buses (Ravi *et al*, 2016).

#### 4.1 Cadmium

Atiku et al. (2011) suspected volatilization and escape of Cd in to the surrounding air as cadmium content in soot is 90% less than the values in the reference Diesel. But Lu shows concentration of Cd obtained to be less than 10 ng/m<sup>3</sup> below the permissible limit of 500 ng/m<sup>3</sup> in the ambience. Irrespective of the concentration of the liberated metals to the ambience, such concentrations are influence by atmospheric conditions as reported by (Lu et al, 2016) and also the wind current or wind speed (Abdullah 2015). The Cd concentration obtained from this research just as Lu were within the maximum permissible limit but this same concentration after liberated can be influenced by the factors highlighted by Lu et al and Abdullah. The lack of large variation we obtained might simply be due to the nature of the fuel used and dissimilar processing methods. In addition, the low quantity of Cd in all samples might be due to high volatility of Cd as compared to other metals and high temperature facilitating the fly ash generation (Atiku et al, 2011; Smith, 1990 and Nogawa et al, 1981)

Cd can cause sharp and chronic intoxications (Chakraborty *et al.*, 2013). Cd is highly lethal to the kidney and it accumulates in the proximal tubular cells in higher concentrations. Cd can result to bone mineralization by bone damage or by renal dysfunction. Studies on humans and animals have revealed that osteoporosis (skeletal damage) is a critical effect of cadmium exposure along with disturbances in calcium metabolism, formation of renal stones and hypercalciuria. Inhaling higher levels of cadmium can cause brutal harm to the lungs. Cd when ingested in higher amounts, it can lead to irritation of the stomach and result in vomiting and diarrhea. Overtime exposure at lower concentrations, can become deposited in the kidney and finally lead to kidney disease, fragile bones and lung damage (Bernard, 2008).

## 4.2 Mercury

The presence of Hg to the environment can be attributed to chlor-alkali production waste, plastics, batteries, electronics,

and throw away medical devices causing damage to the ecosystemand the human body in the appearance of various compounds (Yang et al., 2014).whereas, others traced the source of Hg to be from fluorescent lamps, hospital waste and fossil fuels and burning of these fuels has been acknowledged as the primary anthropogenic source of Hg in the atmosphere (Cooper and Alley, 2002; Manahan, 2005; Migliavacca, 2009; Moreira, 2010). (Habeebullah 2016) identified Hg alongside As to be the most abundant heavy metals in particulate matter of size 2.5 micron (PM<sub>2.5</sub>). Hg among all the investigated metals has the highest toxicity factor of 40 with Cu and Pb having 5 while Cd is 30 (Yang et al., 2014). Mercury has the ability to react with other elements to form organic or inorganic mercury. Exposure to elevated levels of metallic, organic and inorganic mercury can be able to harm the brain, kidneys and the developing fetus (Alina et al., 2012). Therefore, from the obtainable result with Hg being the second largest dangerous emitted metal among others but having the highest toxicity factor calls for concern toward safeguarding the lives of humanity. One of the probable reasons for the high quantity detected may be attributed to the re-suspended dust developed inside the tailpipes of the exhaust and lower height of the tailpipes in gasoline engine (Ravi et al, 2016).

# 4.3 Copper

Cu rank third in the order of most used metal in the world (VCI 2011). Atmospheric Cu can emanate from wearing of brake and employing copper parts in automotive vehicles (Manahan, 2005; Nogueira, 2006; Kabata-Pendias, 2011). Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. The high concentrations of Cu detected in this study may be ascribed to the activities of copper additives which decreases particulate matter emissions, lower the soot combustion temperature and facilitate filter generation as recorded in previous research (DieselNet Technology Guide 2000 and Mayer 1998). Cu is certainly vital, but in high amount it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. While Cu's interaction with the surroundings is intricate, research points that the majority of Cu introduced into the environment quickly becomes stable and results in a form which does not pose a threat to the environment. In actuality, Cu is not bioaccumulated in the body or in the food chain (Mart'inez and Motto 2000)

4.4 Lead

The result obtained from this research shows Pb coming first in the discharge as the most behind Fe which agrees with Gunawardena: the use of gasoline with Pb was hindered a decade ago; Pb was the second most commonly detected heavy metal. This is credited to the association of earlier generated Pb with roadside soil and re-suspension to the ambiance (Gunawardena et.al 2012). Pb is found as a trace element in diverse fuels, though is not allowed as additive constituent in petrol fuels (Paola et al, 2018). In addition to this, (Atiku et al, 2011) could not identify the source of Pb in a soot sample whose reference gasoline was absent. According to (Jozef M. Pacyna and Elisabeth G. Pacyna, 2001) combustion of all kinds of gasoline leads to emission of Pb to the ambiance. There are also other trace metals that can be emitted from this source but these emissions are negligible. In the US, more than 100 to 200,000 tons of lead per year is being released from vehicle exhausts. Some is taken up by plants, fixation to soil and flow into water bodies, hence human exposure of lead in the general population is either due to food or drinking water (Goyer, 1990; Marian, 2017). Lead toxicity also referred to as lead poisoning, can be either acute or chronic. Acute exposure leads to loss of appetite, headache, hypertension, abdominal pain, renal dysfunction, weariness, insomnia, arthritis, hallucinations and dizziness. Acute exposure is obtained at place of work and in some manufacturing industries which make use of lead. Chronic exposure of lead can result in mental retardation, birth defects, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, kidney damage and probably death (Martin & Griswold, 2009).

#### 4.5 Iron

The emission of metals found in this work correspond to that obtained by (Alves *et al*, 2015; Nkansah et al, 2017), with Fe having an outrageous concentration as compare to Cd, Hg, Cu and Pd. The levels of emission of Fe can be classified as a class 4 emission which is a very high emission (Klumpp *et al*, 2004). Thus, these emissions pose a great danger to human health if such levels of concentration should be ingested into the body: even though Fe is very vital to the body but then, they still have limit.

Fe happens to be the most abundant transition metal in the world. In nature it is the most imperative nutrient for most animals as a result of being a cofactor for many essential enzymes and proteins. Fe mediated reactions support the majority of the aerobic organisms in respiration processes. When Fe is not secured appropriately, it can catalyze the reactions involving the formation of radicals which can harm biomolecules, cells, tissues and the whole organism. Fe poisoning has for all time been a topic of concern primarily to pediatricians. Children are greatly at risk to Fe toxicity as they are exposed continually to a maximum of Fe containing products (Albretsen, 2006; Monisha *et al*, 2014)

Although the emission level of Fe is very high and as (Paola et al, 2018) will find Fe and Al to consist above 50% of the 13 metals concentration analyzed, thus confirming the report that the concentration level of Fe in the ambience is highly influenced by the industrial activities and traffic of vehicle (Sekhavatjou 2010), Fe plays a very vital role in the metabolism of the body. Hence, the National Academy of Sciences (NAS's) dietary reference intake (DRI) for children 1 to 3 years old is 7 mg/day. The median daily intake of dietary iron is roughly 11 to 13 mg/day for children 1 to 8 years old and 13 to 20 mg/day for adolescents 9 to 18 years old (Abdullah 2015; Nowak 2006). The vehicular activities is said to increase the level of Fe in the atmosphere. The high concentration of iron is a clear indication of the wearing out of the moving part of an internal combustion engine, as they are largely made up of iron. It might also be due to different types of fuel used and also due to different process temperature (Ulrich et al, 2012).

## V. CONCLUSION

In general, gasoline engine vehicle has proven to be more hazardous to health than diesel engine vehicle when exposure to the same quantity of the soot or its particulate matter in terms of metals concentrations. This study has however highlighted the various concentrations of these heavy metals in the environment. Concentrations of most of these metals are above the permissible maximum limit for air quality. These objectionable releases however increase the presence of these metals in air and water bodies. Therefore, the attendant health effect becomes harmful to persons living around the study area. The attendant risk factor of injecting these metals into the body that causes various associated illness has been discussed, varying from stroke, cardiovascular diseases, death, genetic disorder, skeletal damage (osteoporosis), sleep disorder, memory loss, and convulsion etcetera. There is need to identify strategies to limit vehicular emissions of these harmful metals in addition to seeking for alternative fuels that are safer for our health and ecosystem.

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#### AUTHORS CONTRIBUTIONS

The experiment was conceived, design and performed by Stephen Ezekiel Nyan and supervised by G.C. Nwaedozie; whereas, the manuscript was compiled by both authors.

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## STANDARD COMPLIANCE

Standard compliance was adhered to

#### COMPETING INTEREST

The authors declare no competing interest

#### REFERENCES

- Abdullah A. (2015). Sources of metal pollution in the urban atmosphere (A case study: Tuzla, Istabul). Aksu Journal of Environmental Health Science & Engineering 13:79
- [2] Albretsen J. (2006). The toxicity of iron, an essential element. Veterinary medicine 82–90.
- [3] Alina A. A., Mohd Yunus A.S., Mohd Zakiuddin S., Mohd Izuan E. H., & Muhammad R. R. (2012). Heavy metals (mercury, arsenic, cadmium, plumbum) in selected marine fi sh and shellfish along the Straits of Malacca. Int Food Res J 19(1): 135–140.
- [4] Ang H, Lee K.. (2005): Analysis of mercury in Malaysian herbal preparations: A peer review. Biomed., Sci; 4:31-6.
- [5] Atiku F. A., Ikeh P. O., Faruk U. ZItodo., A. U., Abdulhamid A. & Rikoto I. I. (2011). Comparative test analysis of petroleum (diesel and gasoline) soots As potential sources of toxic metals from exhausts of power plants; Arch. Appl. Sci. Res., 3 (4)147-156
- [6] Bernard A. (2008). Cadmium & its adverse eff ects on human health. Indian J Med Res 128(4): 557–64.
- [7] Chakraborty S., Dutta A.R., Sural S., Gupta D., & Sen S., (2013). Ailing bones and failing kidneys: A case of chronic cadmium toxicity. *Ann Clin Biochem* 50(5): 492–495
- [8] Chen, H., Teng, Y., Lu, S., Wang, Y., & Wang, J. (2015). Contamination features and health risk of soil heavy metals in China. Science of the Total Environment, 512, 143–153. https://doi.org/10.1016/j.scitotenv.2015.01.025
- [9] Cooper C.D. and Alley F.C., 2002: Air pollution control: a design approach. 3rd ed. Illinois: Waveland Press. 738 p.

- [10] Dauda, M., & Odoh, R. (2012). Heavy metals assessment of soil in the vicinity of fuel filling station in some selected local government areas of Benue State, Nigeria. Pelagia Research Library, Der Chemica Sinica, 3, 1329–1336.
- [11] DieselNet Technology Guide., (2000). Diesel Filter Systems, Traps with Fuel Additives. DieselNet.
- [12] Docekal B, Krivan V, Pelz N. (1992). Trace and minor element characterization of diesel soot. Fresenius' J. Anal. Chem., 343(12): 873-879.
- [13] Dora C., & Philips M., (2000). Transport, environment and health. Copenaen, WHO Regional Pulications, European Series, No. 89; (http://www.euro.who.int/document/e72015. pdf)
- [14] European Commission (2001). Communication from the Commission to the European Community -Environment 2010: Our future, our choice. Office for Official Publications Luxembourg, of the European Communities (http://europa.eu.int/eurlex/en/com/pdf/2001/en-501PC0031.pdf)
- [15] European Commission., (1991). Economic evaluation for air quality targets for heavy metals. Final Report, January 2001. Entec UK Limited Atlanta, GA., Centers for Disease Control and Prevention Preventing lead poisoning in young children: A statement by the, Centers for Disease Control and Prevention
- [16] Frey, H. C., Rouphail, N. M., Zhai, H., Farias, T. L. and Gonçalves, G. A., (2007): Modeling and comparing real world fuel consumption for current science, VOL. 111, NO. 564 3, 10 August, 2016 diesel- and hydrogen-fueled transit buses and implication for emissions. Transport. Res. D, 12, 28
- [17] Goyer R. A. (1990). Lead toxicity: From overt to subclinical to subtle health effects. *Environ Health Perspect* 86: 177–181.
- [18] Guilherme M. P., Kimmo T. D., Aldenor G. S., Huang X., Risto H., Célia A. A., Jailson B. de A., Gisele O. da R., Prashant K, Rajasekhar B., Maria de F. A., & Pérola de C. V. (2017). Particulate pollutants in the Brazilian city of São Paulo: 1-year investigation for the chemical composition and source apportionment. Atmos. Chem. Phys., 17, 11943–11969;; https://doi.org/10.5194/acp-17- 11943-2017
- [19] Gunawardena, Janaka, Egodawatta, Prasanna, Ayoko, Godwin A., & Goonetilleke, Ashantha (2012): Role of traffic in atmospheric accumulation of heavy metals

and polycyclic aromatic hydrocarbons. Atmospheric Environment, 54(July), pp. 502-510

- [20] Habeebullah M.A. (2016). Chemical Composition of Particulate Matters in Makkah – Focusing on Cations, Anions and Heavy Metals. Aerosol and Air Quality Research, 16: 336–347 doi: 10.4209/aaqr.2015.08.0486
- [21] Iaych, K., Alexeev, V., & Latipov, O. (2009). IRF world road statistics 2009. International Road Federation, Geneva. Webpage <u>http://www.irfnet.ch/files-upload/pdf-</u> files/wrs2009 sample.pdf
- [22] Ismal I. M., Basahi J. M., Hassan I. A., Summan A. S. & Hammam E. (2018). Source of Heavy Metals in Aerosol Particles in Atmosphere of Jeddah City, Saudi Arabia. J Pollut, 1:1
- [23] Jeff H., (2017.) Diesel is now better than gas, study says. Provided by University of Montreal, retrieved 11 October 2018 from <u>https://phys.org/news/2017-07diesel-gas.html</u>
- [24] Kabata-Pendias, A., 2011. Trace elements in soils and plants. 4th ed. Boca Ratón: Taylor and Francis Group. 534 p.
- [25] Khorshid, M. S. H., & Thiele-Bruhn, S. (2016). Contamination status and assessment of urban and non-urban soils in the region of Sulaimani City, Kurdistan, Iraq. Environmental Earth Sciences, 16, 1– 15.
- [26] Lawson, D. R., Groblicki, P. J., Stedman, D. H., Bishop, G. A. and Guenther, P. L., (1990). Emissions from in-use motor vehicles in Los Angeles: a pilot study of remote sensing and the inspection and maintenance program. J. Air Waste Manage. Assoc. 40, 1096–1105, 1–291.
- [27] Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z., & Huang, L. (2014). A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. Science of the Total Environment, 468, 843–853. <u>https://doi.org/10.1016/j.scitotenv.2013.08.090</u>
- [28] Lighty, J. S., Veranth, J. M., & Sarofim, A. F. (2000).
   Combustion Aerosols: Factors Governing Their Size and Composition and Implications to Human Health, J. Air & Waste Manage. Assoc. 50:1565–1618
- [29] Ling, W., Shen, Q., Gao, Y., Gu, X., & Yang, Z. (2008). Use of bentonite to control the release of copper from contaminated soils. Soil Research, 45, 618–623.

- [30] Lu Q., Mindong C., Xinlei G., Yafei Z., & Bingfang G. (2016). Seasonal Variations and Sources of 17 Aerosol Metal Elements in Suburban Nanjing, China. Atmosphere, 7, 153; doi:10.3390/atmos7120153
- [31] Luo, X.-S., Yu, S., & Zhu, Y.-G. (2012). Trace metal contamination in urban soils of China. Science of the Total Environment, 421–422, 17–30. <u>https://doi.org/10.1016/j. scitotenv.2011.04.020</u>
- [32] Manahan S.E., 2005. Environmental chemistry. 8th ed. Boca Raton: Lewis. 783 p.
- [33] Marian A. N., Godfred D., Matt D., Francis O., Thomas B. E. & Joshua A. B. (2017). Assessment of pollution levels, potential ecological risk and human health risk of heavy metals/ metalloids in dust around fuel filling stations from the Kumasi Metropolis, Ghana. Cogent Environmental Science; 3: 1412153 https://doi.org/10.1080/23311843.2017.1412153.
- [34] Martin S, Griswold W. (2009). Human health eff ects of heavy metals. Environmental Science and Technology Briefs for Citizens (15): 1–6
- [35] Mart'mez C. E. and Motto H. L.: "Solubility of lead, zinc and copper added to mineral soils," Environmental Pollution, vol. 107, no. 1, pp. 153–158, 2000.
- [36] Mayer A. (1998). Available Particulate trap systems for diesel engines, VERT: Suva, AUVA,TBG, BUWAL. Report TTM W04/4/98, version Nr. 5.
- [37] Migliavacca, D.M., 2009. Estudo dos processos de remoção de poluentes atmosféricos e utilização de bioindicadores na região metropolitana de Porto Alegre RS. Porto Alegre: Universidade Federal do Rio Grande do Sul, 182 p. Tese de Doutorado em Ecologia.
- [38] McLaughlin, M. J., Hamon, R., McLaren, R., Speir, T., & Rogers, S. (2000). Review: A bioavailabilitybased rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Australian Journal of Soil Research, 38, 1037–1086. <u>https://doi.org/10.1071/SR99128</u>
- [39] Mohr C., Xu, Ng N. L, Detournay A., Barlow J. F., Halios C. H., Fleming Z. L. Baltensperger U., and Prévôt A. S. H., Kerb., 2012. Urban increment of highly time- resolved trace Elements in pm10, pm2:5 and pm1:0 winter aerosol In london during clearflo Atmos. Chem. Phys., 15, 2367–2386, 2015 www.atmos-chem phys.net/15/2367/2015/S.
- [40] Monisha J., Tenzin T., Naresh A., Blessy B. M., Krishnamurthy N. B. (2014). Toxicity, mechanism

and health effects of some heavy metals., Interdiscip Toxicol.; Vol. 7(2): 60-72.

- [41] Nkansah M.A., Darko G., Matt Dodd M., Opoku F., Essuman T.B. & Boasiako J.A. (2017). Assessment of pollution levels, potential ecological risk and human health risk of heavy metals/ metalloids in dust around fuel filling stations from the Kumasi Metropolis, Ghana Cogent Environmental Science 3: 1412153. https://doi.org/10.1080/23311843.2017.1412153
- [42] Nogawa, K. and Nariagu, J. O. Weilly J. interscience Publication John weilly and Sons, Inc.
- [43] Nogueira, C.A., 2006. Avaliação da poluição atmosférica por metais na Região Metropolitana de São Paulo, Brasil, empregando Tillandsia usneoides L. como biomonitor. São Paulo: Universidade de São Paulo, 112 p. Tese de Doutorado em Ciências na Área de Tecnologia Nuclear Aplicações.
- [44] Okorie E., Olorunfemi C. & Sule H. (2010). Assessment of some selected heavy metals in soot from the exhaust of heavy duty trucks and power generating plants in Nigeria by flame atomic absorption spectrophotometer. Int. J. Biol. Chem. Sci. 4(4): 1146-1152.
- [45] Pacyna J.M. & Pacyna. E.G. (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Norwegian Institute for Air Research (NILU), Kjeller, Norway
- [46] Pan, Y., Wang, Y., Sun, Y., Tian, S. & Cheng, M.
  (2013). Size-resolved aerosol trace elements at a rural mountainous site in Northern China: Importance of regional transport. Sci. Total Environ.461–462, 761–771.
- [47] Pant, P., & Harrison, R. M., (2013). Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. Atmospheric Environment, 77, 78–97. <u>https://doi.org/10.1016/j.atmosenv.2013.04.028</u>
- [48] Paola D.V., Elisa M., Giuseppe C., Angela C., Ferdinando F., Francesco F., Irene S., Vincenzo S., Beatrice S., Giuseppe O., Giuseppina D'O. F., Cosimo M. & Elisa P. (2018). Heavy Metals Size Distribution in PM10 and Environmental-Sanitary Risk Analysis in Acerra (Italy). Atmosphere, 9, 58; doi:10.3390/atmos9020058.
- [49] Platt S. M., El Haddad I., Pieber S. M., Zardini A.
  A., Suarez-Bertoa R., Clairotte M., Daellenbach K.
  R., Huang R.-J., Slowik J. G., Hellebust S.,

Temime-Roussel B., Marchand N., de Gouw J., Jimenez J. L., Hayes P. L., Robinson A. L., Baltensperger U., Astorga C. & Prévôt A. S. H. (2017). Gasoline cars produce more carbonaceous particulate matter than modern filter-equipped diesel cars. Scientific Reports 7, Article number: 4926

- [50] Qari H. A., Hassan I. A. (2017). Bioaccumulation of PAHs in Padina boryana alga collected from a contaminated site at the Red sea, Saudi Arabia. Pol J Environ Stud 26: 435-439.
- [51] Ravi S., Prasenjit A. and Suresh P. E. (2016). Characterization of hazardous solid waste (soot) accumulated in tailpipe of typical Indian share autos. Current Science, Vol. 111, No. 560 3. doi: 10.18520/cs/v111/i3/553 - 560.
- [52] Reche, C., Moreno, T., Amato, F., Viana, M., van Drooge, B. L., Chuang, H.-C., Bérubé, K., Jones, T., Alastuey, A., & Querol, X., 2012: A multidisciplinary approach to characterise exposure risk and toxicological effects of PM10 and PM2:5 samples in urban environments, Ecotox. Environ. Safe., 78, 327–335.
- [53] Sekhavatjou M. S, Rostami A, Alhasemi A., (2010).
   Assessment of elemental concentrations in the urban air (case study: Tehran City). Environ Monit Assess. 163:467–76.
- [54] Smith K.A. (1990). Heavy metals in soils. Alloway, B.J (Ed). Blackie; New York : Halsted Press, Glasgow. https://trove.nla.gov.au/work/17304135
- [55] Stedman, D. H., Bishop, G. A., Beaton, S. P., Peterson, J. E., Guenther, P. L., McVey, I. F. and Zhang, Y., (1994). On-road remote sensing of CO and HC emissions in California, Final Report to California Air Resources Board, Contract No. A032-093, California Environmental Protection Agency, Air Resources Board, Research Division, Sacramento, CA, USA,
- [56] Stedman, D. H., Bishop, G. A., Peterson, J. E., Guenther, P. L., McVey, I. F. and Beaton, S. P., (1991). On-road carbon monoxide and hydrocarbon remote sensing in the Chicago area. Final Report to Illinois Department of Energy and Natural Resources, Report ILENR/RE-AQ 91/14, ENR Clearing House, Springfield, IL, USA,
- [57] Turóczi, B., Hoffer, A., Tóth, Á., Kováts, N., Ács, A., Ferincz, Á., Kovács, A., and Gelencsér, A., (2012). Comparative assessment of ecotoxicity of urban aerosol, Atmos. Chem. Phys., 12, 7365–7370.

- [58] Ulrich1 A., Wichser A., Hess A., Heeb N., Emmenegger L., Czerwinski J., Kasper M., Mooney J., Mayer A., (2012). Particle and metal emissions of diesel and gasoline engines - Are particle filters appropriate measures? Empa, Swiss Federal Laboratories for Material Testing and Research, 8600 Dübendorf, Überlandstrasse 129, Switzerland
- [59] US EPA (US Environmental Protection Agency),
   (2008). Fuel trends report Gasoline 1995-2005. January 2008. EPA420-R-08002. http://www.epa.gov/otaq/regs/fuels/rfg/properf/420r08 002.pdf
- [60] US EPA, (1996). Toxic heavy metals: sources and specific effects.. Retrieved on 30/10/2004 from http://www.extremehealth.com.
- [61] VCI, Copper history/Future, Van Commodities Inc., (2011).http://trademetalfutures.com/copperhistory.htm l.
- [62] Virtanen, A. K. K., Ristimaki, J. M., Vaaraslahti, K. M. and Keskinen, J., (2004). Effect of engine load on diesel soot particles. Environ. Sci. Technol., 38, 2551– 2556.
- [63] Visser S., Slowik J. G., Furger M, Zotter P., Bukowiecki N., Dressler R., Flechsig U., Appel K., Green D. C., Tremper A. H., Young D. E., Williams P. I., Allan J. D., Herndon S. C., Williams R., (2015). Kerb and urban increment of trace elements in aerosol in London. Atmos. Chem. Phys., 15, 2367–2386.
- [64] Wedepohl, K.H. (1991): The composition of the upper earth's crust and the natural cycles of selected metals. Metal in natural raw materials, natural resources. In: *Metals and Their Compounds in the Environment. Occurrence, Analysis and Biological Relevance* (ed. E. Merian), pp. 3–17. VCHWeinheim, New York.
- [65] WHO: World Health Statistics 2014, Report, World Health Organization, Geneva,
- [66] Woodcock, J., Banister, D., Edwards, P., Prentice, A.M., Roberts, L. (2007) Energy and transport. Energy and Health 3(this is the third in a Series of six papers about energy and health), Published Online. Lancet; 370:1078-88.www.kaduna-state.com, 2014
- [67] Yang G., Chaofeng S. and Meiting J., (2014). heavy metal contamination assessment and partition for industrial and mining gathering areas., Int. J. Environ. Res. Public Health, 11, 7286-7303;
- [68] Yousaf I., Syed M. S., Imtiaz A. and Khalid S., (2012). heavy metals In domestic,

commercial And industrial soot samples - Article in Tenside Surfactants Detergents

- [69] Zhang, X., Yang, L., Li, Y., Li, H., Wang, W., & Ye,
  B. (2012): Impacts of lead/zinc mining and smelting on the environment and human health in China. Environmental Monitoring and Assessment, 184, 2261–2273.
- [70] Zhou, S., Yuan, Q., Li, W., Lu, Y., Zhang, Y. & Wang, W. (2014).Trace metals in atmospheric fine particles in one industrial urban city: Spatial variations, sources, and health implications. J. Environ. Sci., 26, 205–213.