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BIOMONITORING OF ATMOSPHERIC HEAVY METALS IN AGBARA INDUSTRIAL AREA OF OGUN - STATE, SOUTH –WESTERN, NIGERIA USING *Sphagnum compactum*AS BIOMONITOR.

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ABSTRACT

The presence of heavy metals in the environment beyond the acceptable limits is a serious concern to the environmentalists.The present research reports the results of some heavy metal content (Zn, Pb, Ni, Cu and Cd) in Agbara Industrial area of Ogun - State using the moss plant Sphagnum compactum as bioindicator. The samples of the Moss plant were collected randomly from September to November, 2018 at ten different locations inAgbara Industrial Area between 2 to 2.5 metres high from unplastered buildings in Ogun - State and analysed for their heavy metal contents as at the time of sampling. The samples were properly cleaned from all the debris then weighed and digested with a mixture of $HNO_3$and H_2O_2 for 35 min. The concentrations of the five heavy metals were determined using Atomic Absorption Spectrophotometer (AAS) PG-990. Results of the analysis, show that the average concentration of the heavy metals at Agbara Industrial area is: Zn 69.71mg/l,68.89%; Pb 16.502mg/l,16.3%; Ni 7.78mg/l,7.7%; Cu 6.869mg/l, 6.8% and Cd 0.395mg/l,0.41%, with the most abundant pollutant heavy metal being Zn(69.71mg/l) in all the sites while the least abundant was Cd(0.395mg/l).The most polluted site is Eko Supreme Limited (29.871mg/l) while the least polluted is Elphitina (2.269mg/l). The sequence of bioaccumulation and distribution follows the pattern thus: Zn> Pb>Ni>Cu>Cd . There is a significant difference in the levels of each heavy metals in the atmosphere of Agbara Industrial area ($p_{value} < 0.05$). Moreover, the concentrations of heavy metals obtained exceeded the recommended limits of the Federal Ministry of Environment (FME), European Communities (EC) and United Nations Environmental Programme (UNEP) permissible level for heavy metals in the atmosphere, which suggests that the study area is polluted with heavy metals.

Keywords: ***A****nthropogenic, bioaccumulation, bioindicator, concentrations, pollution****, spectrophotometer****.*

INTRODUCTION

Air quality is rapidly deteriorating in major cities around the world especially in developing countries like Nigeria due to industrialization and urbanization. Atmospheric heavy metal contamination has

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been a major environmental problem in Ogun State, South - Western, Nigeria due to emissions from energy generation, vehicular traffic, combustion of fossil fuel and poor waste management strategies. Human activities such as industrial production, mining, agriculture and transportation release a high amount of heavy metals to the biosphere. Heavy metals are the stable metals or metalloids whose density is greater than 4.5 g/cm^3, namely Pb, Cu, Ni, Cd, Zn, Hg and Cr, etc.(Chopra et. al. (2009)). Evidently, some of these metals are essential for life at very low concentration levels but at high levels of concentration they may lead to harmful effects in humans, plants and animals(Cao et. al.(2009). These heavy metals can be found in the atmosphere in varying proportions in different areas or locations (residential areas, industrial areas) and these varying proportions can be determined by using moss plant as the indicator. Air quality can be monitored by measuring the pollutants directly in the air or in deposition, by constructing models depicting the spread of pollutants or by using biomonitors/bioindicators (Markert et al. (2003)). Biomonitors provide information on both the quantity of pollutants and their effect on the occurrence and condition of biomonitors. Although, the methods are fast and inexpensive, they only provide a relatively approximate picture of air quality and the deposition of pollutants (Poikolainen, 2004)). There is considerable variation in the use of the terms bioindicator and biomonitor but bioindicator generally refers to all organism that provide information on the environment or the quality of environmental changes and biomonitor to organisms that provide quantitative information on the quality of the environment (Markert et al. 2003).Monitoring of air pollution using biomonitors is emerging as a potentially effective and more economical alternative performing by direct ambient air measurement. Biomonitoring is defined generally as the use of bio-organisms to obtain information on certain characteristics of the biosphere (Sharmistha et al., 2006). Biomonitors have been considered as a complementary tool in order to monitor the environmental pollution and also could overcome some of the shortcomings to the conventional monitoring techniques which is normally done through direct measurement by using electronic devices(Poykio et al., 2005). The use of bioindicators is of considerable interest because it allows measurements on a large scale, relatively quickly at low cost. In particular, the use of mosses has gone increasingly spreading in monitoring high-risk areas for the environmental capacity to absorb atmospheric pollutants and provide integrated responses on the air quality.Although there are critical issues regarding different storage capacity of the species used and the influence of environmental factors (Micaela et al., 2013). Air pollution is a serious problem in urban and industrial areas. The advantages of biomonitoring are the opportunity of long term monitoring of pollution and easy sampling without the use of expensive equipment (Serbula et al., 2012). Mosses are living organisms of plantae kingdom and classified in the phylum bryophyte.They are cryptogams that thrive in humid climate. They grow in forests, on burnt bricks on abandoned automobiles, crack on concrete side walls, on rock, on bare soil, trees, and uncompleted buildings (Adie et al., 2014). Lower plants, especially mosses and lichens, due to their high capacity for metal accumulation, are probably the most frequently used in biomonitoring surveys (Kabata - pendias and Pendias, (2001)). Mosses are found in almost every habitat that supports life and their ecological role is significant (Saxena et al., 2008). They occur on every continent and in every location habitable by photosynthetic plants. These group of plants which many plant scientists refer to as the "amphibians" of the plant kingdom, live on land and in damp places but breed only in the presence of water (Saxena et al., 2008). Mosses are better than other higher plants in scanning heavy metal deposition because: i.They are perennial without deciduous periods. ii.They have a high cation exchange capacity that allows them to accumulate great amounts of heavy metals between apoplast and symplast compartments without damaging vital functions of the cells and one of the main factors influencing cation exchange capacity is the presence of polygalacturonic acids on the external part of cell wall and proteins in the plasma membrane. iii. Mosses do not possess thick and strong protective layers like cuticles. This is the reason why ions from the surface have direct access for cationic exchanges in the cell membranes. They have a great capacity for trace element retention (Marko et al., 2009). iv. Mosses have undeveloped rootsand therefore have to obtain minerals from rain and atmosphere particles.They depend entirely on the uptake of nutrients from atmosphere because of lack of roots, curticle and epidermis (Zechmeister et al., 2003; Chakrabortty et al., 2006; Ekpo et Al., 2012). There are several species of mosses available in Nigeria and earlier surveys have shown these local species to be suitable for biomonitoring atmospheric heavy metal pollution. Some of these surveys include among others (Ekpo et. al., 2012; Fatoba and Oduekun, 2004; Bako et al., 2008; Adebiyi and Oyedeji, 2012; Aniefiok et al., 2014; Sa'idu, 2015; Fatoba et al., 2012; Ojiodu et al.,2018a). The dense carpets that *Sphagnum compactum*and other pleurocarpous mosses form on the ground have turned out to be very effective traps of heavy metals in precipitation and airborne particles.*Sphagnum compactum*moss has a long history of diverse uses and is certainly the moss of greatest importance to humans. In its natural habitat, *Sphagnum compactum* selectively absorbs certain ions and secretes others. The bogs in which it grows become acidic and anaerobic over time, and the decomposition rate by bacteria is particularly slow in these bogs. Organisms buried in *Sphagnum compactum* bogs remain well-preserved for a very long time. Currently, the gardeners make most use of *Sphagnum compactum.*The objectives of this research are to assess and evaluate the levels of some heavy metals (Zn, Pb, Cu, Ni and Cd) content in the atmosphere of Agbara Industrial areas of Ogun - State, determine the baseline levels and bioaccumulation of heavy metals (Zn, Pb, Cu, Ni and Cd), determine the percentage contribution of each of the heavy metals to the atmosphere of Agbara Industrial area and finally to determine whether there is a significant difference in the levels of heavy metals from one location to another within the study area.

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Figure 1: *A Cross sectional view of the moss Sphagnum compactum used as biomonitor.*

MATERIALS AND METHODS

Study Area / Sampling Locations

This study was conducted in Agbara Industrial Area (N 6°.4332, E 3°.0726 - N 6°.5371, E 3°.4594) of Ogun - State namely: Diya Gate, Abbey microfinance bank, Agbara Hotels & Suites, Eko Supreme Ltd, Agbara Site Office, Opic Estate, Gas Station, Rock of Ages Hospital, Elphatina, Oke - Ira and GZ Industries (control). The sampling points were at least 300m from main roads and 100m from minor roads.

Figure 2: GIS Map of Agbara IndustrialArea Showing the Concentrations of Heavymetals in*Sphagnum compactum*.

KEY : A = Eko Supreme Limited ; **B =** Diya Gate ; **C =**Rock of Ages Hospital ; **D =** Gas Station ; **E=** Elphatina; **F =**Agbara Hotels & Suites ;**G =** Agbara Site Office; **H =** Abbey Microfinance Bank; **I** = Oke - Ira ; **J** = Opic Estate; **K** = GZ Industries (control).

Selection of sampling sites

The sites were carefully chosen based on the following criteria: accessibility to the Moss plant, availability of open spaces and of course areas with minimal influence from traffic as well as industrial activities. The sites were also chosen to reflect activities in the areas. The geo-referencing was carried out by using Garmin GPS MAP 76S.

Moss sampling

Samples of *Sphagnum compactum*were collected from Ten sites(10) within the studied area at least 10 metres apart, once in a month from September to November, 2018. The moss plant *Sphagnum compactum* was chosen because it is widespread across Agbara Industrial Area and can be found in all parts of the study area. Sampling below canopy of shrubs and large-leafed herbs was avoided. Moss species were collected randomly between 2 - 2.5 m high from unplastered perimeter fences within the sample area. The samples were collected using stainless steel trowel into polyethylene bags, labelled accordingly and transported to the laboratory for analysis.

Sample Preparation and Analysis

Sampling and samples handling of mosses,*Sphagnum compactum* were carried out using hand gloves and polyethylene bags. Eleven samples of mosses were cleaned from all debris (soil, leaves, and needles). Samples were handled by clean laboratory equipment. In order to remove the moisture content of mosses, the unwashed samples were dried at 45°C to a constant weight. After removal of moisture, samples were weighted again in order to calculate the real mass of sample (Blagnyte and Paliulis, 2000). Sample of the mosses (0.50g) were mixed with a mixture of 10ml nitric acid (65%) and 2ml of hydrogen peroxide (30%) HNO_3: H_2O_2 (4:1) and digestion was performed using hot plate for 35minutes. After mineralization, samples were left to cool toroom temperature for one hour, poured into 50ml flasks and finally make-up with distilled water (Baltrenaite et al., (2011). Mineralization conditions do not allow the total digestion of mineral particles and a filtration was necessary. Determination was performed for the most popular heavy metals that are spread in the atmosphere (Cr, Cu, Pb, Ni and Zn).The absorption metal contents Cr, Cu, Ni, Pb and Zn in the filtrate were determined by flame atomic absorption spectrophotometer (Perkin Elmer AA 200) using an air-acetylene flame. The analytical wavelengths used were 357.9 nm for Cr, 324.7 nm for Cu, 232.0 nm for Ni, 283.3 nm for Pb and 213.9 nm for Zn.

RESULTS

Statistical Analysis

The results of heavy metal accumulation *Sphagnum compactum*were evaluated by analysis of variance (ANOVA) together with mean, standard deviation of each metal. T-test (IBM SPSS 23) was also performed to check the significant variation between each metal and sites.

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Table 1: **Statistical analysis of the mean concentration of heavy metals(mg/l) in*Sphagnum compactum* in Agbara Industrial Area**.

S/N	Locations / Sites / Code		Lead (Pb) Mean ± std dev.	Zinc (Zn) Mean ± std dev.	Cadmium (Cd) Mean ± std dev.	Copper (Cu) Mean± std dev.	Nickel (Ni) Mean ± std dev.
A	Eko Supreme Limited	**ESL**	8.17 ± 0.61^{d}	20.21 ± 2.95^{d}	0.06 ± 0.002^{d}	0.98 ± 0.06^{e}	0.46 ± 0.06^{a}
B	Diya Gate	**DYG**	0.72 ± 0.13^{ab}	2.31 ± 0.51^{a}	0.02 ± 0.001^{abc}	0.45 ± 0.03^{ab}	0.29 ± 0.05^{a}
C	Rock of Ages Hospital	**RAH**	0.82 ± 0.29^{ab}	1.63 ± 0.58^{a}	0.02 ± 0.001^{ab}	0.42 ± 0.05^{ab}	0.28 ± 0.06^{a}
D	Gas Station	**GAS**	0.27 ± 0.12^{a}	12.20 ± 0.85^{c}	0.02 ± 0.001^{ab}	0.45 ± 0.11^{ab}	0.10 ± 0.001^{a}
E	Elphatina	**ELP**	0.40 ± 0.13^{a}	1.58 ± 0.26^{a}	0.02 ± 0.003^{ab}	0.25 ± 0.03^{a}	0.02 ± 0.001^{a}
F	Agbara Hotel and Suites	**AHS**	1.77 ± 0.11^{c}	14.9 ± 1.13^{c}	0.04 ± 0.003^{c}	1.33 ± 0.02^{f}	0.44 ± 0.05^{a}
G	Agbara Site Office	**ASO**	1.24 ± 0.29^{bc}	3.29 ± 0.34^{ab}	ND	0.72 ± 0.03^{cd}	0.24 ± 0.02^{a}
H	Abbey Microfinance Bank	**AMB**	0.64 ± 0.13^{ab}	2.38 ± 0.55^{a}	0.03 ± 0.001^{bc}	0.57 ± 0.21^{bc}	0.25 ± 0.03^{a}
I	Oke-Ira	**OKI**	1.07 ± 0.11^{abc}	5.94 ± 0.75^{b}	0.03 ± 0.006^{bc}	0.88 ± 0.08^{de}	5.37 ± 0.63^{b}
J	Opic Estate	**OPE**	0.88 ± 0.05^{ab}	3.94 ± 0.29^{ab}	0.14 ± 0.015^{e}	0.61 ± 0.003^{bc}	0.32 ± 0.02^{a}
K	GZ Industries (control).	**GZI**	0.52 ± 0.06^{ab}	1.33 ± 0.18^{a}	0.01 ± 0.00^{a}	0.21 ± 0.08^{a}	0.01 ± 0.001^{a}
	F- Statistics		$F_{10,22} = 87.490$; $p < 0.001$	$F_{10,22} = 36.713$; $p < 0.001$	$F_{10,22} = 51.228$; $p < 0.001$	$F_{10,22} = 16.748$; $p < 0.001$	$F_{10,22} = 65.256$; $p < 0.001$

ND= Not detected

Table 2: Concentrations of heavy metals (mg/l) in *Sphagnum compactum* at different Locations of Agbara Industrial Area.

KEY	Locations / Sites	Lead (Pb)	Zinc (Zn)	Cadmium(Cd)	Copper(Cu)	Nickel(Ni)
A	Eko Supreme Limited	8.165	20.207	0.060	0.981	0.458
B	Diya Gate	0.723	2.305	0.024	0.445	0.290
C	Rock of Ages Hospital	0.824	1.628	0.019	0.418	0.282
D	Gas Station	0.195	12.219	0.022	0.452	0.102
E	Elphatina	0.399	1.581	0.020	0.249	0.200
F	Agbara Hotels & Suites	1.771	14.897	0.040	1.334	0.439
G	Agbara Site Office	1.238	3.293	ND	0.706	0.240
H	Abbey Microfinance Bank	0.644	2.383	0.032	0.532	0.254
I	Oke - Ira	1.070	5.943	0.031	0.884	5.370
J	Opic Estate	0.860	3.943	0.016	0.605	0.321
K	GZ Industries (control)	0.516	1.131	0.010	0.214	0.011
Total Value		16.405	69.53	0.274	6.82	7.967
Mean Value		1.6405	6.953	0.0274	0.682	0.7967
UNEP, 2009		**≤0.50**	**≤ 1.00**	**≤ 0.50**	**≤ 1.00**	**≤ 1.00**

N.B: Values in italics in the columns indicates the mean of all the heavy metals in each location that in the rows indicates the mean of each heavy metal in all the locations.

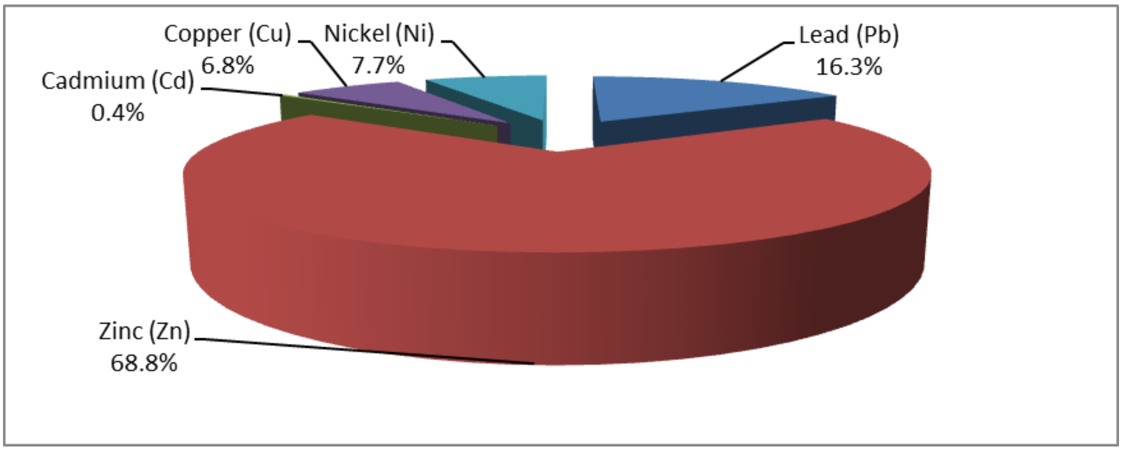

Figure 3: Distribution of heavy metals (mg/l) in *Sphagnum compactum* in the sampling sites in Agbara Industrial Area.

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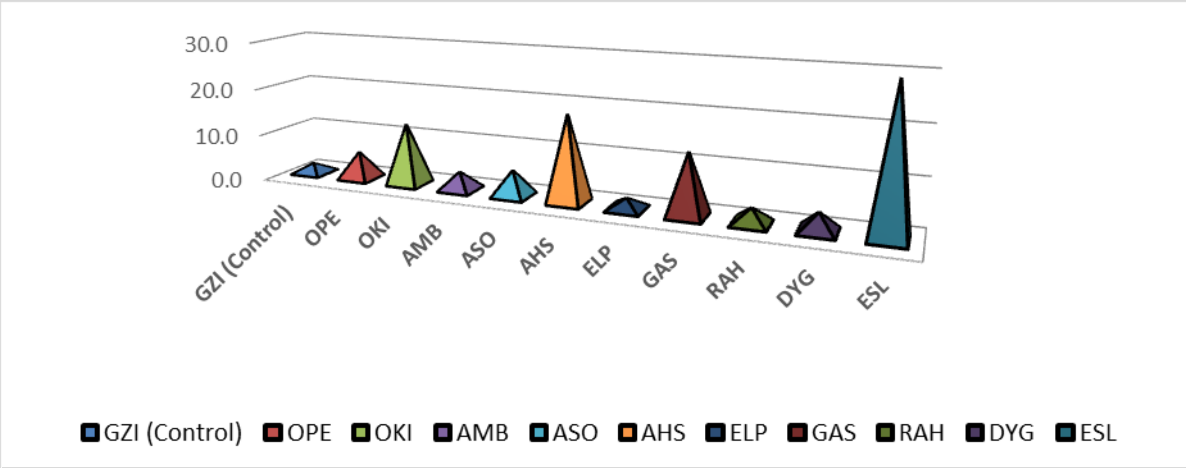

Figure 4: Total heavy metals in the sampling sites in Agbara Industrial Area.

Table 3:Mean Concentrations and Standard deviation of Heavy metals (mg/l) in *Sphagnum compactum in* Agbara Industrial Area.

MONTHS	Pb	Zn	Cd	Cu	Ni
September	16.404 ±0.72	69.530 ±1.98	0.274 ±0.54	6.820 ± 0.01	7.969 ±0.46
October	16.406 ± 0.87	69.531 ±1.34	0.276 ±0.67	6.821 ±0.06	7.967 ±0.65
November	16.414 ±0.76	69.540 ± 1.38	0.278 ±0.06	6.822 ±0.11	7.968 ±0.88
Mean Value	16.408 ±0.66	69.533 ±1.23	0.277 ±0.89	6.821 ±0.03	7.968 ±0.42

DISCUSSION

The most polluted site in Agbara Industrial Area is Eko Supreme Limited(29.871mg/l). This is as a result of anthropogenic activities going on in the site such as release of gases from near by industries, commercial, vehicular and automobile activities in and around the site . The highest percentage contribution of heavy metals(29.5%) was recorded at Eko Supreme Limited;this is due to the anthropogenic activities in this site some of which are waste burning, gases released by the industries around, fumes from numerous heavy duty vehicles. While the least percentage contribution(2.2%) was recorded at Elphatina.(Figure 4). Eko Supreme Limited site has the highest concentration of Zinc (20.207 mg/l) and Lead (8.165mg/l) while Elphatina (2.269 mg/I) which is the least polluted site has the least concentration of Zinc(1.581mg/l) and Lead(0.399mg/l)(Table 2). The most abundant heavymetal is Zinc(69.53mg/l) while the leastabundant heavymetal is Cadmium(0.274mg/l)**.** This can be attributed to the versatile use of zinc in the form of zinc oxide present in paints, rubber tyres, cosmetics, pharmaceuticals, wearing of brake lining, lossess of oil and cooling liquids from automobile, corrosion of galvanized steels, scrap iron bars and improper disposal of industrial waste in the area. There is a significant difference in the levels of zinc metal in Eko Supreme Limited compared to other sites.Similarly in Agbara Hotel & Suites and Gas Station, the level of zinc is significantly different from all other sites. Furthermore, in Opic Estate and Agbara Site Officesites the levels of zinc are not significantly different ($p > 0.05$). (Table 1). The high presence of Pbin Eko Supreme Limited may be due to the high commercial, automobile and vehicular activities in the area, spillage of petroleum products, smoking of cigarettes, paint chips from the walls of industrial buildings, careless discards of lead acid batteries used in automotives as well as the use of industrial grade and non-domestic paints by the surrounding industries. The level of Pbin Eko Supreme Limited is significantly different ($p < 0.05$) from all other sites; Agbara Hotels & Suites was different from all other sites except Oke-Ira and Agbara Site Office, etc. The highest concentrations of Copper(1.334 mg/l) and Nickel (5.370 mg/l) wererecorded in atmosphere of Agbara Hotels & Suites and Oke - Ira while Elphatina and Gas Station sites have the least concentrations of copper(0.249mg/l) and Nickel(0.102mg/l) respectively (Table 2). Copper has the highest concentration at Agbara Hotels & Suites(1.33mg/L), which may be due to the manufacturing of electrical cables, mining of metal, production of cans and the use of pesticides, combustion of fossil fuels, smelting of metals, vehicular emission, traffic congestion and industrial processes that uses these metals or their compounds. The level of Copper in Eko Supreme Limited and Agbara Hotels & Suites are significantly different from all other sites($p < 0.05$), while all others have mixed difference. The highest concentration of cadmium (0.137mg/l) was recorded at Opic Estate which may be due to the sewage and animal wastes dumped in the area. The levels of cadmium in Agbara Hotels & Suites and Eko Supreme Limited are significantly different from all other sites($p < 0.05$), while all other sites have mixed difference. Nickel has itshighest concentration at Oke - Ira (5.370mg/l). The concentration of nickel in this site may be as a result of fuel combustion from generators as well asfrequent bush burning in that surrounding. The level of nickel in Oke-Ira site is significantly different from all other sites($p < 0.05$), while the rest sites are not significantly different from each other($p > 0.05$) (Table 1). The moss,*Sphagnum compactum* (Figure 1) used in this research exhibited significant variation in the average levels of the metals in various sites in the study areas (Table 1).There was progressive increasein the level of bioaccumulation of these heavy metals from September to November. The amount of these heavy metals in Agbara Industrial Area were observed to follow the trend Zn > Pb > Ni > Cu > Cd (Table 3). The result of this research agrees with the results obtained in some Nigerian cities and showed that concentration of heavy metals depends on the nature of activities in the sites (Adie et al., 2014 ; Ekpo et al., 2012 ; Ojiodu and Elemike, 2017; Ojiodu and Olumayede, 2018a; Ojiodu et al., 2018b). The trend in the levels of total atmospheric heavy metals in the study area was: Eko Supreme Limited **(**29.5%) >Agbara Hotels & Suites (18.3%) >Oke - Ira (13.1%) >Gas Station (12.9%) >Opic Estate(5.8%)> Agbara Site Office(5.4%) > Abbey Microfinance Bank (3.8%) >Diya Gate(3.7%)> Rock of Ages Hospital (3.1%) >Elphatina (2.2%)> GZ Industries (control)(2.1%)(Figure 2). The level of heavy metals in the study area were far

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greater than the recommended limits of the Federal Ministry of Environment (FME), European Communities (EC) and United Nations Environmental Programme (UNEP) permissible level for heavy metals in the atmosphere.The concentration of heavy metals in all the sites washigher than the control values. This may be due to the fact that the control environment is a swampy forest vegetation with little or no anthropogenic activity(Figure 2).

Since, Zn, Pb, Ni, Cu and Cd contributes 68.8, 16.3, 7.7, 6.8 and 0.40% respectively to the atmosphere of Agbara Industrial area, the high significant levels of these heavy metals Zn, Pb, Ni, Cu and Cd obtained in the samples from Agbara Industrial area could be attributed to the emission of these heavy metals originating from gases released from near by industries, wearing of brake lining, losses of oil and cooling liquids, corrosion of galvanized steels, scrap iron bars, wearing of tyres, improper disposal of sewage, industrial waste, vehicular / commercial activities and industrial processes that uses these metals or their compounds within and around Agbara Industrial Area . The low concentration of Cd suggest low contributing factors to their spread and as well as the plant inability to preferentially accumulate these metals. Therefore, due to the high concentration of these metal pollution which could be very hazardous to human and plants existence, there is need for constant environmental monitoring of the atmosphere of Agbara Industrial Area.

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