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TEMPORAL VARIABILITY OF HEAVY METAL CONTENT IN THE ATMOSPHERE OF MUSHIN AREA OF LAGOS - STATE, SOUTHWESTERN - NIGERIA USING *Barbulaindica (*Hook*) spreng.var.indica* AS BIOINDICATOR

C. C. Ojiodu [1*], E. E. Elemike [2], A. O. Eruola [3] and E. M. Ikegwu [4]

[1,3]Department of Chemical Science, Yaba College of Technology, Yaba – Lagos, Nigeria
[2]Department of Chemistry, College of Science, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria
[4]Department of Statistics, Yaba College of Technology, Yaba – Lagos, Nigeria
**Corresponding Author: ojiodu1966@yahoo.com , 08138335470.*

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ABSTRACT
This research reports the results of some heavy metal content (Zn, Pb,Cd, Ni and Co) in Mushin area of Lagos - State using the moss plant Barbulaindica (Hook) spreng.var.indica as bioindicator. The samples of the Moss plant were collected randomly from September to November, 2016 at ten different locations at Mushin area between 2 to 2.5 metres high from unplastered buildings in Lagos 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 $HN0_3$ and H_2O_2 for 35 min. The concentrations of the five heavy metals were determined using Atomic Absorption Spectrophotometer (AAS). Results of the analysis, shows that the average concentration of the heavy metals at Mushin are: Zn 23.477mg/l,53.9%; Pb 4.240mg/l,9.74%; Cd 0.195mg/l,0.45%; Ni 4.418mg/l, 10.15% and Co 11.191mg/l,25.71%. The most abundant pollutant heavy metal was Zn in all the sites while the least abundant was Cd. Levels of some of the heavy metals were present in concentrations greater than WHO (2001) threshold limiting values. The most polluted site is Olorunshogo 11.809mg/l while the least polluted is Shoremekun 1.2765mg/l. The sequence of bioaccumulation and distribution follows the pattern: Zn > Co > Ni > Pb > Cd. 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. There is a significant high level of each heavy metal in the atmosphere of Mushin areas ($P_{value} < 0.05$).

Keywords: **A**nthropogenic, bioaccumulation, bioindicator, concentrations, pollution**, s**pectrophotometer.

INTRODUCTION
Mushin being a local government area in Lagos, is located 10 km north of the city core, adjacent to the main road Ikeja. It is largely a congested residential area with inadequate sanitation and low quality housing, that had 633,009 inhabitant at the 2006 census. After the 1960 independence from Great Britain, there were large migrations to the sub urban areas. This led to extensive overcrowding. In addition, the rise of industrialization in

Nigeria, Mushin has become one of the largest beneficiaries of the industrial expansion. Their local commercial enterprise include spinning and weaving of cotton, shoe manufacturing, bicycle and motorized cycle assembly, alongside with production of milk.

Heavy metals are the stable metals or metalloids whose density is greater than $4.5gcm^3$, namely Pb, Cu, Ni, Cd, Zn, Hg and Cr, etc (Chopra *et al*, 2009). Metals of high atomic mass that cannot be processed by living organisms due to toxicity are commonly known as heavy metals (Duffus, 2007) . 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. Those that are of grave concern are the non - essential heavy metals lie As, Pb, Cd and Cr which may be major air and land pollutants in areas where they are most concentrated (Moses *et al*, 2009). Their dispersion and transport in the atmospheric layers may be exacerbated by human activities and natural phenomenon. Exposure to this type of toxic metals is a health hazard for humans (Cao *et al*, 2009). The primary sources of heavy metal pollution are the burning of fossil fuels, smelting of metal ores, municipal wastes, fertilizers, pesticides and sewage (Rai, 2009). Although, individual metals exhibit specific signs of toxicity, the following have been reported; gastrointestinal (GI) disorders, diarrhea, stomatitis tremor, hermoglobinuria causing a rust-red color to stool, ataxis, paralysis, vomiting and convulsion, depression and pneumonia when volatile vapors and fumes are inhaled as general signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminum. The term bioindicator is used to refer to an organism or a part of it that depicts the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes or concentrations. Biomonitoring consists of the use of responses of individual plants or plant associations at several biological organization levels in order to detect or predict changes in the environment and to follow their evolution as a function of time. Biological monitoring of airborne contaminants has made a great progress since the early observations of environmentally induced stress on plants and its applications have grown to an extent hardly envisaged just a few decades ago (Kuang, *et al*, 2007). But, it is important to note that a unique species that can be a suitable bioindicator for biomonitoring of toxic metal pollution all over the world has not been found yet. For this reason, different species of mosses are useful as bioindicators in different parts of the world (Coskun, 2006).

Mosses posses many properties that make them suitable for monitoring air pollutants. These species obtain nutrients needed for vital processes from wet and dry deposition and they do not have real roots. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle, most bryophytes are small and the leaves of many mosses and folious liverworts consist of only one cell layer. Substantial properties of mosses as good biomonitor are: large surface to weight ratio, there slow growth rate, and a habit of growing in groups. Other suitable properties of mosses include minimal morphological changes during the mosses life time, ease of sampling, an ability to survive in highly polluted environment and the possibility to determine concentrations in the annual growth segments (Cenci *et al*, 2003;Ceburnis *et al*, 2002; Poikalainen, 2004; Wang *et al*, 2008). Some plants species are sensitive to single pollutants or to mixtures of pollutants. Those species or cultivars are likely to be used in order to monitor the effects of air pollutant, as

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bioindicator plants. They have a great advantage to show clearly the effects of phytotoxic compounds present in the ambient air. As such, they are ideal for demonstration purposes. However, they can also be used to monitor temporal and spatial distributions of pollution effects (Temmerman *et al*, 2005). Suitable biomonitors, which meet the requirements, make continuous monitoring and even retrospective monitoring of air pollution possible at relatively low cost. Ekpo *et al*, (2012) carried out a comparative study of the levels of trace metals in moss species in some cities of the Niger Delta Region of Nigeria where twelve trace metals were revealed. Their levels have been determined and show significant variation from metal and from location to location. This probably shows difference in the kind of anthropogenic activities in the region. Lambe *et al*, (2013) studied air pollution in Macedonia and reported the increasing trends in the elemental content in mosses are connected with anthropogenic source, such as Cd, Pb, Ni, and Zn, in the elemental content in mosses are connected with anthropogenic source, such as Cd, Pb, Ni and Zn, in the period from 2000 to 2005 except for Cr. Whil the result from 2010 showed a lower elemental content in the mosses for the mentioned elements than the results obtained in 2005. Onianwa,(2001) reviewed the literature on the use of mosses for monitoring atmospheric metal pollution. The objectives of this research are to investigate the distributions of some metals (Ni, Cu, Pb, Cr and Zn) in *Barbulaindica (Hook)spreng.var.indica* plants in Mushin. This is to establish uptake and bioaccumulation of metals by *Barbulaindica (Hook)spreng.var.indica*, thereby evaluate their potential use as indicator of air quality metal pollution in the atmosphere. It is hopeful that the study will provide baseline data on bioaccumulation of heavy metals(Ni, Cu, Pb, Cr and Zn) and determine temporal variability of heavy metals(Ni, Cu, Pb, Cr and Zn) from one location to another within the study area.

Figure 1: *Barbulaindica (Hook)spreng.var.indica*

MATERIALS AND METHODS

Study Area / Sampling Locations

This study was conducted in Mushin ($N6^0$ 31 21.5N 3^0 21 0.8E - $N6^0$ 32 10.1N 3^0 21 36.6 E) areas of Lagos state, namely Olosha, Ladipo, Olorunshogo, Abiodun, Labinjo , Imoru, Shoremekun, Luth road, Akintan, Oke and Oniru in Lagos Island (Control). The sampling points were at least 300m from main roads and 100m from minor roads.

Figure 2: GIS Map of Mushin Showing the Concentrations of Heavymetals in Barbulaindica (Hook)spreng.var.indica.

KEY: A= Olosha, **B** = Ladipo**, C=** Olorunsogo**, D=** Abiodun **E** = Labinjo, **F=** Imoru, G= Shoremekun, H= Luth road, I = Akintan, J = Oke, K= Oniru (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 *Barbulaindica (Hook) spreng.var.indica* collected from Ten sites(10) within the studied area at least 10 metres apart, once in a month from September to November, 2016. The moss plant *Barbulaindica (Hook) spreng.var.indica* was chosen because it is widespread across Mushin and can be found in all parts of the study Area.

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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 *Barbulaindica (Hook)spreng.var.indica* was 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 45^0C 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_20_2 (4:1), digestion was performed using hot plate for 35minutes. After mineralization, samples were left to cool till room 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 *Barbulaindica (Hook)spreng.var.indica* 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 metals and sites.

Table 1: **Statistical analysis on the mean concentration of heavy metals(mg/l) in *Barbulaindica (Hook)spreng.var.indica* in Mushin Area.**

Locations / Sites	N	Zn	Pb	Cd	Ni	Co
		Mean ± std dev.	Mean ± std dev.	Mean ± std dev.	Mean ± std dev.	Mean ± std dev.
Olosha	6	4.034 ± 1.523^b	0.709 ± 0.142^d	0.039 ± 0.006^f	0.278 ± 0.142^{ab}	0.192 ± 0.134^a
Ladipo	6	6.754 ± 0.634^c	0.59 ± 0.005^c	0.008 ± 0.004^{bc}	0.34 ± 0.127^{ab}	0.298 ± 0.129^{ab}
Olorunshogo	6	7.363 ± 3.615^c	0.8 ± 0.141^e	0.016 ± 0.005^d	0.63 ± 0.141^e	1.333 ± 0.645^e
Abiodun	6	0.398 ± 0.127^a	1.233 ± 0.128^f	0.027 ± 0.004^e	0.528 ± 0.063^{de}	0.968 ± 0.013^{cd}
Labinjo	6	0.269 ± 0.268^a	0.001 ± 0.00^a	0.001 ± 0.00^a	0.226 ± 0.143^a	1.394 ± 0.099^e
Imoru	6	1.002 ± 0.001^a	0.56 ± 0.064^c	0.001 ± 0.00^a	0.254 ± 0.003^{ab}	1.214 ± 0.129^{de}
Shoremekun	6	0.006 ± 0.002^a	0.001 ± 0.00^a	0.001 ± 0.00^a	0.473 ± 0.005^{cd}	0.876 ± 0.191^c
Luth road	6	0.006 ± 0.002^a	0.161 ± 0.014^b	0.082 ± 0.007^g	0.573 ± 0.142^{de}	1.288 ± 0.063^e
Akintan	6	0.006 ± 0.002^a	0.001 ± 0.00^a	0.013 ± 0.006^{cd}	0.478 ± 0.064^{cd}	0.915 ± 0.003^c
Oke	6	0.006 ± 0.002^a	0.087 ± 0.052^{ab}	0.006 ± 0.002^{ab}	0.379 ± 0.095^{bc}	0.489 ± 0.064^b
Oniru (Control)	6	1.088 ± 0.001^a	0.068 ± 0.001^a	0.001 ± 0.00^a	0.248 ± 0.001^a	0.262 ± 0.001^{ab}
Test statistics		$F_{10,55} = 32.714$; $p < 0.001$	$F_{10,55} = 182.020$; $p < 0.001$	$F_{10,55} = 203.865$; $p < 0.001$	$F_{10,55} = 11.827$; $p < 0.001$	$F_{10,55} = 26.362$; $p < 0.001$

Table 2: Concentrations of heavy metals (mg/l) in *Barbula indica (Hook) spreng.var. indica* at different Locations of Mushin.

LOCATION	Zn	Pb	Cd	Ni	Co
Olosha	5.022	0.709	0.039	0.277	0.266
Ladipo	6.755	0.586	0.009	0.34	0.035
Olorunsogo	9.030	0.800	0.015	0.63	1.334
Abiodun	0.397	1.233	0.028	0.527	0.967
Labinjo	0.181	<0.001	<0.001	0.225	1.377
Imoru	1.002	0.56	<0.001	0.253	1.157
Shoremekun	<0.0005	<0.001	<0.001	0.474	0.800
Luth road	<0.0005	0.161	0.082	0.573	1.287
Akintan	<0.0005	<0.001	0.0132	0.478	0.916
Oke	1.088	0.068	<0.001	0.247	0.262
Oniru(Control)	<0.005	<0.001	<0.001	0.213	0.106
Total value	23.477**(53.9)**	4.240 **(9.74)**	0.195 **(0.45)**	4.418 **(10.15)**	11.191 **(25.71)**
Mean value	**2.3477**	**0.424**	**0.0195**	**0.4418**	**1.1191**
UNEP, 2009	**≤ 1.00**	**≤0.50**	**≤ 0.50**	**≤ 1.00**	**≤ 1.00**

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

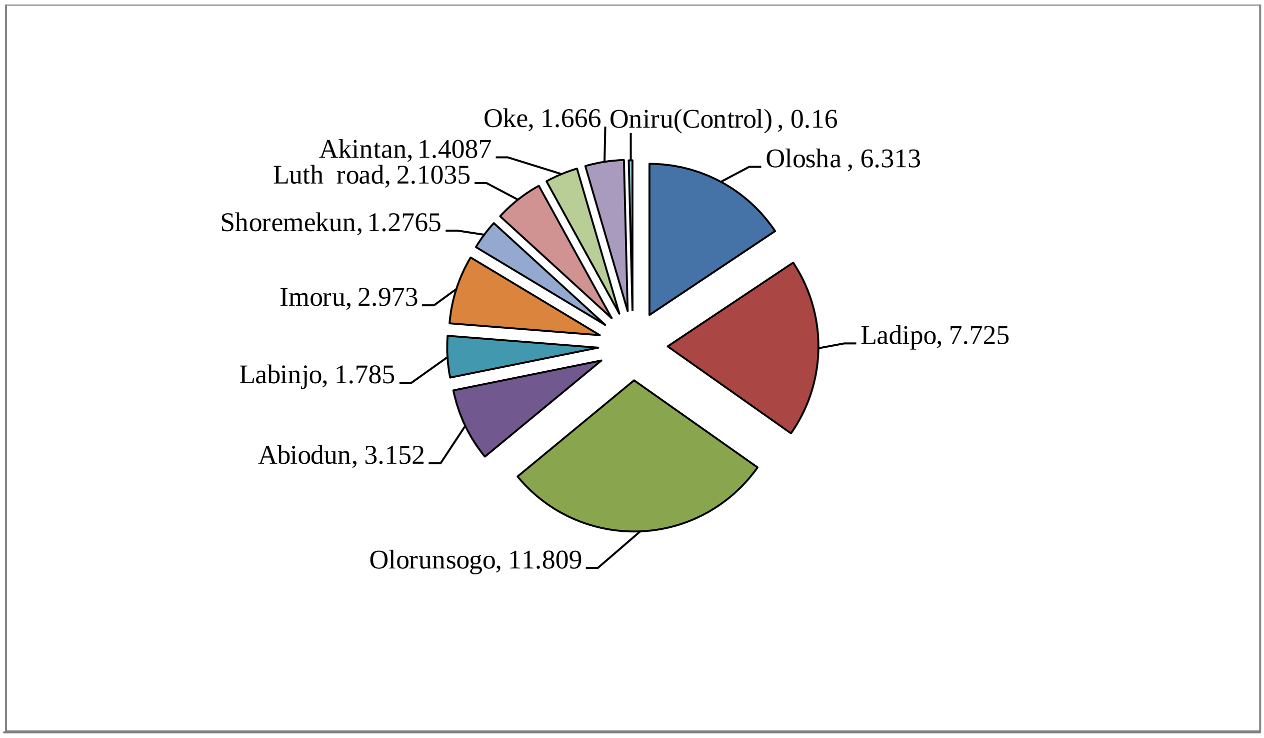

Figure 3: Distribution of heavy metals (mg/l) in *Barbulaindica (Hook)spreng.var.indica* in the sampling sites in Mushin.

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Table 3: Mean Concentrations and Standard deviation of Heavy metals (mg/l) *Barbulaindica (Hook)spreng.var.indica* in Mushin.

MONTHS	Zn	Pb	Cd	Ni	Co
September	23.365 ± 0.62	4.220 ± 0.11	0.175 ± 1.21	4.209 ± 0.34	11.180 ± 2.22
October	23.589 ± 0.91	4.250 ± 0.32	0.205 ± 0.33	4.418 ± 0.23	11.211 ± 2.37
November	23.476 ± 1.01	4.260 ± 0.74	0.206 ± 0.57	4.627 ± 0.36	11.182 ± 0.45
Mean Value	23.477±0.46	4.243±0.12	0.195 ± 0.67	4.488±0.94	11.191 ± 0.76

DISCUSSION

The most polluted site in Mushin is Olorunshogo (11.8091mg/l). This is as a result of anthropogenic activities going on in the site such as release of contaminated gases from nearby company, commercial, vehicular and automobile activities in and around the site . Olorunshogo site has the highest concentration of Zinc (9.030 mg/l) while Shoremekun Street (1.2765 mg/I) is the least polluted site with the least concentration of Zinc (< 0.0005 mg/l)(Table 2). The presence of Zinc is may be due to emission of Zinc originating from wearing of brake lining, lossess of oil and cooling liquids, corrosion of galvanized steels, scrap iron bars, wearing of tyres and improper disposal of sewage in the area. Apart from Labinjo, Shoremekun and Akintan street (<0.0001mg/l) with the least concentrations of lead, Abiodun street has the highest concentration of Pb (1.233 mg/l) which is above WHO (2001) threshold limit due to the high commercial, automobile and vehicular activities in the area, spillage of petroleum products, smoking of cigarette, paint chips from the walls and disposal of used auto batteries. The highest concentration of Cadmium (0.082 mg/l) and Nickel (0.573 mg/l) was recorded in atmosphere of Luth road while Labinjo, Imoru and Oke sites has the least concentrations of cadmium(<0.001mg/l). Labinjo site has the highest concentrations of Colbalt (1.377mg/l) and the least concentration of Nickel (0.225mg/l) (Table 2). The presence of Cadmiun, Nickel and Colbalt in these sites arises from combustion of fossil fuels, smelting of metals, vehicular emission, traffic congestion and industrial processes that uses these metals or their compounds. The amount of these heavy metals in Mushin were observed to follow the trend Zn > Co > Ni > Pb > Cd(Table 3). The result of this research agrees with the results obtained in some Nigerian cities and showed that concentration of heavy metals depend on the nature of activities in the sites (Adie *et al*, 2014 ; Ekpo *et al*, 2012 ; Ojiodu *et al*, 2017). The *Barbulaindica (Hook) spreng.var.indica* specie (Figure 1) used in this research exhibited significant variation in the average levels of the metals with various sites in the study areas (Table 1). There were progressive increases in the levels of bioaccumulation from September to November, although not significant ($p > 0.05$)(Table 3). This may account for the persistent anthropogenic activities in the Mushin area (Table 2). The average levels of Zinc, Lead, Cadmium, Nickel and Cobalt are significantly different in different sites ($p < 0.05$). There is a significant difference between the levels of Zinc at Ladipo and Olorunsogo compared to other sites in Mushin ($p > 0.05$) (Table 1). However, the Zinc levels in all other sites apart from Olosha, Ladiopo and Olorunsogo are not significantly different from each other and the control. The average level of lead from Labinjo, Shoremekun and Akintan were not significantly different from the control while other locations showed clear differences. However, the average lead levels at Luth road and Oke are not significantly different from each other. Apart from Labinjo, Imoru, Shoremekun and Oke where the levels of Cadmium were not significantly different from the control, there is significant difference between the levels of Cadmium in all other sites ($P_{value} < 0.05$) (Table 1). Apart from Olosha, Ladipo, Labinjo and Imoru where the levels of Nickel were not significantly different from the average levels of Nickel at the Control, the levels of Nickel in other sites in Mushin were significantly different. The average level of Cobalt in Olosha, Ladipo, Shoremekun and Oke sites were not significantly different from the control while the remaining sites were significantly different from the control. The trend in the levels of total atmospheric heavy metals in the study are : Olorunshogo > Ladipo > Olosha > Abiodun > Imoru > Luth road > Labinjo > Oke > Akintan > Shoremekun > Oniru (Figure 2) . Furthermore, the level of heavy metals in the study area were far 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. There is a significant difference in the level of each heavy metals within each of the sites($P_{value} < 0.05$) (Table 1). The concentration of heavy metals in all the sites were higher than the control values(Table 2).

Since, Zn, Pb, Cd, Ni and Co contributes 53.9; 9.74; 0.45; 10.15 and 25.71% respectively to the atmosphere of Mushin, the high concentration of this heavy metals could be attributed to the emission of these heavy metals originating from wearing of brake lining, lossess of oil and cooling liquids, corrosion of galvanized steels, scrap iron bars, wearing of tyres, improper disposal of sewage , vehicular / commercial activities and industrial processes that uses these metals or their compounds within and around Mushin. 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 Mushin.

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