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Full Length Research Article

THE LEVEL OF HEAVY METALS IN THE ATMOSPHERE OF A MACROENVIRONMENT, LAGOS STATE, SOUTHWESTERN - NIGERIA USING MOSS PLANT(*DICRANIUM SCORPARIUM*) AS BIOINDICATOR

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ABSTRACT
The major objective of this study is to investigate the concentrations of some metals (Zn, Pb, Cd, Ni and Cu) content in moss plant (*Dicranum scoparium)* collected at different locations within Yaba College of Technology, Campus Lagos state, Southwestern - Nigeria. The samples of the plant were collected randomly between September and November, 2016 at 10 different locations at the Campus between 2 - 2.5 meters high from unplastered buildings in Lagos state. The samples were properly cleaned from all the debris, weighed and digested with a mixture of $HN0_3$ and H_2O_2 for 35 min. The concentrations of heavy metals were analyzed using Atomic Absorption Spectrophotometer (AAS) Perkin Elmer AA 200. Results obtained, showed that the average concentrations of the heavy metals at Yaba College of Technology Campus were: Zn 8.63574mg/l, 1.12618mg/l, Cu 0.51249mg/l, Ni 0.43252mg/l and Cd 0.02563mg/l which reflects 80.46; 10.49; 4.78; 4.03 and 0.24% respectively with the most abundant pollutant heavy metal being Zn in all the sites while the least abundant was Cd. Similarly, the most polluted site was Bakassi Hostel while the least polluted was the Staff Quarters. The levels of Zn and Pb were present in concentrations greater than the WHO threshold limiting values. There was a significant difference in the level of each heavy metal in the atmosphere of Yaba College of Technology Campus (P_V < 0.05).The sequence of bioaccumulation and distribution follows the pattern thus: Zn > Pb > Cu > Ni > Cd.

Keywords: Bioaccumulation, Pollution**,** Spectrophotometer, Bioindicator, Anthropogenic, Concentrations

INTRODUCTION
An environment consisting of two or more institutions is known as a Macroenvironment. Such institutions could be academic, financial, industrial etc. Since human activities are involved, Heavy metals are emitted into the atmosphere thereby causing adverse effect on the environment. The short term effects include conjunctive irritation, nose and throat discomfort, headache and sleeplessness, allergic skin reaction, nausea, fatigue and dizziness. While the long term adverse effects include loss of coordination, leukaemia, anaemia, cancer, liver damage, kidney and the central nervous system (Kim *et al.*, 2001; Eljarrat and Barcelo, 2003; Pohl *et al.*, 2003, Kerbachi *et al*., 2006). Atmospheric heavy metal contamination has been a major environmental problem in Lagos, Nigeria due to emissions from energy generation, vehicular traffic, combustion of fossil fuel and poor waste management strategies. Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. Several trace metals are emitted through the abrasion of tires (copper -Cu; Zinc - Zn, Cadmium - Cd) and brake pads(Antimony-Sb, copper - Cu), corrosion of metals (Vanadium-V, Iron-Fe, Nickel-Ni, Copper-Cu, Zinc-Zn, Cadmium-Cd), lubricant in oils (Vanadium-V, Zinc -Zn, Molybdenum - Mo, Cadmium - Cd) or fuel additives (Vanadium - V, Zinc - Zn, Cadmium- Cd, Lead - Pb) (Pacyna *et al*., 2001). The biotoxic effects of heavy metals refers to the harmful effects of heavy metals to the body when consumed above the bio-recommended limit. The following have been reported as general signs associated with cadmium, lead and zinc poisoning; gastrointestinal (GI) disorders diarrhea, stomatitis, tremo, hermoglobinuria, causing a rust - red colour to stool, ataxis, paralysis, vomiting and convulsion, depression and pneumonia when volatile vapors and fumes are inhaled.
The nature of the effect could be toxic (acute, chronic, sub-chronic), neurotoxic, carcinogenic, mutagenic and teratogenic (Young, 2005; Ferner, 2001; Ogwuegbu and Muhanga, 2005; Udedi, 2003; Nolan, 2001; Onianwa, 2001). Mosses are living organisms of the *plantae* kingdom and classified in the phylum *bryophyta.* They grow in forests, on rocks, on trees, bare soil, cracks of concrete side walls, on burnt bricks on abandoned automobiles, and uncompleted buildings (Adie *et al*., 2014).They are effective atmospheric pollution bioindicators as they take up nutrients and pollutants directly from the atmosphere since they have no root (Ruta and Dainius, 2010).Some plant species have developed specialized mechanisms of accumulate and regulate metals in their parts. These plants are generally used as biomonitor for air pollution monitoring, because they can indicate the presence of elements and their concentration gradients. 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 normally done through direct measurement by using electronic devices (Poykio *et al*., 2005).

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The use of bioindicators is of considerable interest because it allows measurements on a large scale, relatively quickly at low cost. Mosses possess many properties that makes them suitable for monitoring air pollutants. Nutrients uptake from the atmosphere is promoted by their weakly developed cuticles; most bryophytes are small and the leaves of many mosses and folious liverworts consists of only one cell layer. Substantial properties of mosses as good indicators are large surface to weight ratio, the slow growth rate and a habit of growing in groups. (Wang *et al*., 2008). Bryophytes are resistant to many substances which are highly toxic for their plants species. They are able to survive in such diverse and often extreme environment, these sedimentary organisms possess on equally diverse sets of physiological adaptations. Mosses have been shown to be capable of surviving complete desiccation and temperatures as extreme as 110°c (Fernandez *et al*., 2006, Dragovic and Mahailovic, 2009). 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 (Ojiodu and Elemike, 2017, 2018; Ojiodu and Olumayede, 2018; Ekpo *et al.*, 2012; Fatoba and Oduekun, 2004; Adebiyi and Oyedeji, 2012; Aniefiok *et al.,* 2014; Sa'idu, 2015). The dense carpets that *Dicranum scoparium* and other pleurocarpous mosses form on the ground have turned out to be very effective traps of heavy metals in precipitation and airborne particles. The objectives of this research are to assess and evaluate heavy metal presence in a macroenvironment using moss plant *Dicranum scoparium* as bioindicator, determine degree of bioaccumulation of heavy metals and determine whether there is a significant difference in the levels of heavy metals from one location to another within the study area

Figure 1: The Moss plant (*Dicranium scorparium*)

MATERIALS AND METHODS

Study Area / Sampling Locations
Yaba College of Technology, the center for this study, is a cradle of higher education in Nigeria is situated in Yaba Local Government Area of Lagos State. It is located on longitude 03^0 22E and latitude 06^0 30N and bounded to the North by Fadeyi, to the South by Fola Agoro, to the East by Shomolu and to the West by Herbert Macaulay Way. The present students population is about 15,000 while the total staff (both Academic and Non-Academic) strength is about 1600.The Campus is structured into Academic and Residential areas, with facilities such as Banks, Eateries, Business centers, Dry cleaning shops, Automobile workshops, Residential Buildings, Bukertaria etc.

Ten sampling sites were carefully chosen in the area, to reflect activities in the areas and based on the following criteria: accessibility, availability of open spaces and of course areas with minimal influence from traffic as well as industrial activities. The sampling points were at least 300 m from main roads and 100m from minor roads. The geo-referencing was carried out by using Garmin GPS MAP 76S.

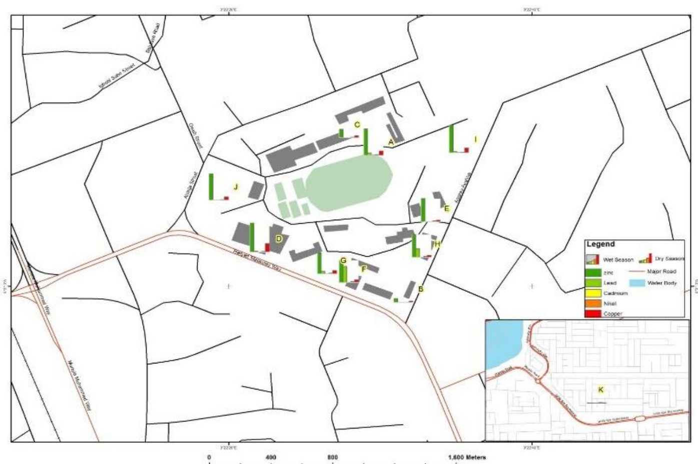

Figure 2: GIS Map of Yaba College of Technology, Campus showing the sampling sites.

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 chosen to reflect activities in the areas. The geo-referencing was carried out by using Garmin GPS MAP 76S.

Moss sampling
Samples of *Dicranum scoparium were* collected from ten sites within the studied area at least 10 meters apart, once in a month from September to November, 2016. The moss plant *Dicranum scoparium* was chosen because it is widespread across Yaba College of Technology, Campus 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 - 2.5m 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
Eleven samples of *Dicranum scoparium* mosses were cleaned from all debris (soil, leaves, and needles) dried at 45^0C to a constant weight (Blagnyte and Paliulis, 2010). Sample of the mosses (0.50g) were mixed with a mixture of 10ml nitric acid (65%) and 2ml of hydrogen peroxide (30%), 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).

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Mineralization conditions do not allow the total digestion of mineral particles and a filtration was necessary. Determination of the level of heavy metal ions 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.

Statistical Analysis

The results of heavy metal accumulation in *Dicranum scoparium* 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: Shows the mean concentration (mg/l) of Heavy metals at Yaba College of Technology, Campus

Location/Sites	Zinc(Zn) Mean + se	Lead(Pb) Mean + se	Cadmium(Cd) Mean + se	Nickel(Ni) Mean + se	Copper(Cu) Mean + se
Student Affair Unit	$8.43+ 0.93^{c}$	$0.48 + 0.07^{ab}$	$0.0001 + 0.00^{a}$	$0.11+ 0.04^{ab}$	$1.32 + 0.42^{bc}$
Old Bursary	$9.72+ 0.93^{c}$	$1.22 + 0.07^{c}$	$0.02 + 0.01^{a}$	$0.21 + 0.07^{ab}$	$1.61 + 0.11^{c}$
Staff Quarter	$3.55+ 0.73^{b}$	$0.0001+ 0.00^{a}$	$0.23 + 0.16^{b}$	$0.37+ 0.29^{ab}$	$0.82 + 0.07^{abc}$
Bakassi Hostel	$10.52 + 0.79^{c}$	$0.0001+ 0.00^{a}$	$0.0001 + 0.00^{a}$	$1.52 + 0.65^{c}$	$0.93 + 0.11^{abc}$
New Food Technology Building	$8.40 + 0.67^{c}$	$2.38 + 0.65^{d}$	$0.04 + 0.01^{a}$	$0.26+ 0.01^{ab}$	$0.76 + 0.11^{abc}$
Environmental Building	$8.15 + 0.65^{c}$	$0.0001+ 0.00^{a}$	$0.05 + 0.01^{a}$	$0.17+ 0.07^{ab}$	$0.54 + 0.11^{ab}$
Automobile Complex	$8.72 + 0.70^{c}$	$0.0001+ 0.00^{a}$	$0.0001 + 0.00^{a}$	$0.08 + 0.01^{a}$	$1.57 + 0.65^{c}$
Administrative Block	$9.96 + 0.65^{c}$	$0.0001+ 0.00^{a}$	$0.0001 + 0.00^{a}$	$0.44+ 0.11^{ab}$	$1.18 + 0.11^{bc}$
Science Complex	$9.43 + 0.65^{c}$	$0.33 + 0.07^{ab}$	$0.04 + 0.01^{a}$	$0.33+ 0.11^{ab}$	$1.10 + 0.07^{bc}$
Medical Centre	$9.56 + 0.65^{c}$	$0.72 + 0.11^{bc}$	$0.05 + 0.01^{a}$	$0.85+ 0.11^{ab}$	$1.34 + 0.42^{bc}$
Oniru(Control)	$0.01 + 0.00^{a}$	$0.01 + 0.01^{a}$	$0.0001 + 0.00^{a}$	$0.21+ 0.01^{ab}$	$0.11 + 0.01^{a}$
F - Statistics	$F_{10,22} = 20.423$ $p < 0.001$	$F_{10,22} = 13.778$ $p < 0.001$	$F_{10,22} = 1.885$ $p = 0.104$	$F_{10,22} = 3.587$ $p = 0.006$	$F_{10,22} = 2.702$ $p = 0.025$

NB: Sites with the same superscript along the columns (metals) are not significantly different at 5%

RESULTS AND DISCUSSION

Table 2: Shows the Characteristics and Co-ordinates of Monitoring Locations at Yaba College of Technology, Campus

SITE	LOCATION	COORDINATE	DESCRIPTION
1.A	Students Affairs Unit	6º32 10.1472N 3º21 13..2768E	Staff offices, Shops for Business and Commercial Activities.
2.B	Old Bursary	6º31 49.0146N 3º21 2.5164E.	A site with Staff offices and laboratories. Behind this site is a major busy high-way.
3.C	Staff Quarters	6º31 44.4072N 3º21 0.8166E	A Residential Area.
4.D	Bakassi Hostel	6º31 44.2992N 3º21 35.1360E	Students Residential Area with a high commercial Activities.
5. E	New Food Technology Building	6º3121.5034N 3º21 34.9230E	A site with laboratories, staff offices, Lecture hall, Metal dump. Behind this site is a major busy high- way.
6. F	Environmental Building	6º3137.6206N 3º21 39.1632E	Staff offices, Shops for Business and Commercial Activities.
7. G	Automobile Complex	6º31 36.9870N 3º21 36.5976E	A site for repairs and servicing of Vehicles.
8. H	Administrative Block	6º31 32.9550N 3º 21 18.7050E	A Site with Administrative offices Behind this site is a major busy high- way.
9. I	Science Complex	6º31 48.9930N 3º21 23.3130E	A site with staff offices, laboratories, Lecture hall and commercial activities.
10.J	Medical Centre	6º31 51.0204N 3º21 14.8680E	A site with offices, laboratories, Medical equipment/Instrumentation room, Pharmacy etc.
11.K	Oniru (Control)	6.433281N 3.459424E	Partly residential area. This area is surrounded with large body of water.

Table 3: Shows the Mean Concentrations of Heavy metals (mg/l) at different Locations at Yaba College of Technology, Campus using *Dicranum Scoparium* for September, October and November

Location /Sample Site	Zinc(Zn)	Lead(Pb)	Cadmium(Cd)	Nickel(Ni)	Copper(Cu)	Mean value
Students Affair Unit	9.7160	1.3177	0.0028	0.1595	1.2176	2.4837
Old Bursary	8.4288	1.6061	0.0168	0.2131	0.4811	2.14918
Staff Quarters	3.6240	0.8189	0.0636	0.0827	<0.0001	0.9179
Bakassi Hostel	10.1823	0.9282	<0.0001	1.5209	<0.0001	2.5263
New Food Technology Building	8.4045	0.7572	0.0399	0.2597	2.3776	2.3678
Environmental Building	8.1478	0.5657	0.0478	0.1744	<0.0001	1.7819
Automobile Complex	8.8916	1.5657	<0.0001	0.0756	<0.0001	2.1066
Administrative Block	9.9637	1.1841	<0.0001	0.4439	<0.0001	2.3184
Science Complex	9.4324	1.0955	0.0388	0.3290	0.3257	2.2443
Medical Centre	9.5663	1.330	0.0470	0. 8537	0.0217	2.36374
Oniru(Control)	<0.0050	0.1000	<0.0001	0.2130	< 0.0010	0.0650
Mean Value	8.6358	1.12618	0.02563	0.4325	0.51249	
UNEP, 2009	≤ 1.00	≤ 0.05	≤ 0.05	≤ 1.00	≤ 1.00	

Table 4: Shows the Mean Concentration and Standard deviation of the heavy metals (mg/l) at Yaba College of Technology, Campus.

MONTHS	Zn	Pb	Cd	Ni	Cu
September	8.7578 ± 1.92	1.12620 ± 0.34	0.02563 ± 0.83	0.4327 ± 1.64	0.51252 ± 0.36
October	8.6256 ± 0 .89	1.12618 ±1.26	0.02565 ± 0.12	0.4324 ± 0.95	0.51251 ± 1.74
November	8.54184 ± 1.12	1.12616 ± 0.73	0.02562 ± 1.45	0.4326 ± 0.33	0.51248 ± 0.47
Mean	8.64174 ± 0.44	1.12618 ± 1.02	0.02563 ± 0.42	0.4327 ± 0.64	0.51250 ± 0.32

The continuous monitoring and assessment of pollutant load in the environment should follow a radical approach as human and plant life are in great danger when the limits are exceeded. The present investigation has shown that Yaba College of Technology Campus is gradually becoming polluted with concentration of heavy metals in the atmosphere as presented in Table 3. The results of this analysis shows that the main contributors to the atmospheric pollution level of Yaba College of Technology Campus are Zn (80.46%), Pb (10.49%), Cu (4.78%) and to a lesser extent Ni (4.03%) and Cd (0.24%). The most abundant heavy metal in the atmosphere of Yaba College of Technology, Campus was Zn 39.14 mg/l while Ni 1.36mg/l was the least abundant. In each site, the moss species samples exhibited significant variation in the average levels of the metal at different locations (P_v< 0.05). There were progressive increase in the level of bioaccumulation from September to November but no significant difference in the level of bioaccumulation (P_v< 0.05) of each metal in the moss sample. The sequence of bioaccumulation and distribution follows the pattern thus: Zn > Pb > Cu > Ni > Cd. The results of this research agreed with the results obtained in some Nigerian cities and showed that concentration of heavy metals depend on the nature of activities of a place (Adie *et al.,* 2014; Saidu, 2015; Ojiodu and Olumayede, 2018). The most polluted site was Bakassi Hostel (2.5263mg/l) while the least polluted was the Staff Quarters (0.9179mg/l) of the mean concentrations of Heavy metals (mg/l) at different locations at Yaba College of Technology, Campus. Bakassi Hostel had the highest concentrations Zinc Zn (10.1823mg/l) and Nickel Ni (1.5209mg/l).The high concentration of Zn may be due to emission of zinc from paint chips from the walls of buildings, use of cosmetics including perfumes, pigments, corrosion of galvanized steel safety fence, wearing of iron etc; while the presence of nickel could be due to combustion of fossil fuels, smelting of metals/steel and oil activities. The Staff Quarters had the lowest value of heavy metals Zn 3.6240mg/l; Pb 0.0001mg/l; Cu 0.8189mg/l; Ni 0.0827mg/l; Cd 0.0636mg/l, this is because it is a residential area with little or no Metallic activities. High concentrations of Pb were recorded at the Old bursary (1.6061mg/l), Automobile Complex (1.5657mg/l) and the Students Affairs unit (1.3177mg/l), this was due to the high vehicular activities, Oil spill, generator fumes and paint chips from the walls of buildings within and around these locations. The New food Technology site had the highest concentration of Cu (2.3776mg/l) this was associated with release from corroding metal parts dump in the area. The highest concentration of Cd (0.0636mg/l) was recorded at the Staff Quarters. The presence of Cadmium (Cd) in this area arises from combustion of fossil fuels, smelting of metals and various old paint chips. The high significant levels of Zn, Pb and Cu obtained in the samples from Yaba College of Technology, Campus is an indication of heavy metals presence in the atmosphere which could be as a result of both vehicular activities within and around the Campus, generator fumes, paint chips from Walls of Buildings, use of cosmetics and metal dump. The low concentration of Cr and Ni suggest low contributing factors to their spread and as well as plant inability to preferentially accumulate these metals. The *Dicranum scoparium* specie used in this research exhibited significant variation in the average levels of the metals with various sites in the study areas (Figure 1). Since, there is a significant difference in the levels of heavy metals in the sampling sites, it shows that the heavy metals exerts different influence on the atmosphere of the studied sites. There were progressive increases in the levels of bioaccumulation from September to November, although not significant and T - test conducted showed (p > 0.05) (Table 4). This may account for the persistent anthropogenic activities in Yaba College of Technology, Campus (Table 2).The concentration of heavy metals in this study is high and exceeds the Federal Ministry of Environment, Nigeria (FME), European Communities (EC) and the WHO threshold limiting values. The trend in the levels of total atmospheric heavy metals in the study were: Bakassi Hostel > Students affairs Unit > New food Technology > Medical Centre > Administrative Block > Science complex > Old Bursary > Automobile Complex > Environmental Building > Staff Quarters > Oniru (Table 1). All concentration of the metals detected were higher than the control (Table 3). Furthermore, the level of Zinc metals in all the sites 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 was significant difference in the level of each heavy metal within each of the sites ($P_v < 0.05$ Table 1).

Conclusion

Mosses plants have proven to be excellent indicators of atmospheric pollution, as they reflect metals concentration gradient and sources of deposition. The results of this investigation had shown that Zn, Pb, Cu, Ni and Cd contributes 80.46; 10.49; 4.78; 4.03 and 0.249% to the atmosphere of Yaba College of Technology, Campus, Lagos State, Nigeria. Therefore, it is evident that the atmosphere of Yaba College of Technology, Campus is highly polluted with the analyzed heavy metals. The high concentration of these heavy metals could be attributed to vehicular activities within and around the Campus, generator fume, paint chips emanating from walls of Buildings, use of cosmetics and metal dump. As a result, there is need for continuous environmental monitoring and management of the atmosphere of Yaba College of Technology, Campus due to the high concentration of these metal pollution which could be very hazardous to human and plants existence

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