

SEASONAL VARIABILITY OF HEAVY METAL CONTENT IN THE ATMOSPHERE OF KETU-MILE 12 AREA OF LAGOS - STATE, SOUTH - WESTERN NIGERIA USING *Polytrichum juniperinum* AS BIOMONITOR.

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ABSTRACT

This research reports the seasonal variability results of some heavy metals (Zn, Pb, Cr, Ni and Cu) present in Ketu-Mile 12 area, Lagos - State using moss plant (*Polytrichum juniperinum*) as a bioindicator. The samples of the Moss specie were collected randomly for wet (March - August, 2017) and dry seasons (September, 2016 - February, 2017) at ten different locations at Ketu-Mile 12 area, between 2 - 2.5 m high from unplastered buildings. 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). Results showed that Zinc (Zn) was the most abundant in all the sites while the least abundant is Cadmium (Cd) during the wet and dry season. During the dry season, the most polluted site was Ketu garage (2.0536mg/L) while Iyana school (0.2614mg/L) was the least polluted site. Similarly, Mile 12 Market (3.4303mg/L) was the most polluted site during the wet season while Kosofe (0.5358mg/L) was least polluted site. The average concentrations of the heavy metals at Ketu-Mile 12 during the dry and wet seasons and percentage concentration of the heavy metals were as follows respectively: Zn(3.5411mg/L; 80.1%), Pb(0.1696mg/L; 3.9%), Cd(0.0116mg/L; 0.3%), Ni (0.1374mg/L; 3.2%) and Cu(0.5080mg/L; 11.6%) and during the wet season were Zn(7.2496mg/L; 72.1%), Pb(0.5373mg/L; 5.3%), Cd(0.0442mg/L; 0.5%), Ni(0.2289mg/L; 2.3%) and Cu(1.9925mg/L; 19.8%). The sequence of bioaccumulation and distribution followed the pattern : Zn > Pb > Cu > Ni > Cd. Therefore, it was clearly seen that the heavy metal concentration during the wet season was greater than that during the dry season. There was a significant difference in the level of each heavy metal in the atmosphere of Ketu -Mile 12 ($P < 0.05$). The concentration of some of the heavy metals present were greater than the Federal Ministry of Environment of Nigeria (FME) and World Health Organization (WHO) threshold limiting values suggesting that the study area was polluted.

Key words: Anthropogenic, bioaccumulation, bioindicator, concentrations, pollution, spectrophotometer.

INTRODUCTION

Increased human activities has considerably brought about increased pollution into the atmosphere in form of metallic chemical elements that have a relatively high specific gravity of at least 5 times the gravity of water, for example, Pb, Cr, Zn etc. this metallic elements are referred to as heavy metals. (Bolinski et. al. (2009)). 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)). Those that are of grave concern are the non-essential heavy metals like As, Pb, Cd and Cr which may be considered major air and land pollutants in areas where they are most concentrated (Moses et. al. (2009)). Although, heavy metals are natural components of the environment, metals such as Pb, Cd, Hg, Ni and As have no known or reported biochemical importance and their appreciable concentration could become potential lethal hazards. 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). The term bioindicator / biomonitor is used to refer to an organism or part of it that depicts the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes or concentrations. 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)). The background level of different pollutants varies between plant species. Mosses are often considered as plants for use as biomonitors or bioindicators of air pollutants. Using biological materials in the determination of environmental pollution as indicators is a cheap and reliable method. Mosses are cryptogams that thrive in a humid climate. Ectohydric mosses have been used as biomonitors - in most cases terricolous bryophytes. They possess many properties that make them suitable for monitoring air pollutants (Onianwa, 2001; Zechmeister et. al. (2003)). These species obtain nutrients from wet and dry depositions and they do not have real roots. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle, which makes their tissues to be easily permeable to water, minerals, gaseous pollutants in the atmosphere as well as metal ions, possession of tissues with negative charged groups which can act as efficient cation exchange (Adie et. al. (2014)), Large surface to weight ratio and their habit of growing in groups. In addition to these properties, the wide distribution and ease of collection makes moss efficient

metal accumulators and biomonitors (Spiric et. al. (2013)). Earlier, research works have shown that mosses have proven to be better bioindicators of pollution because they are more sensitive to atmospheric pollution (Kulartene and Defreitas, 2013). Other suitable properties include a slow growth rate, undeveloped vascular bundles, and minimal morphological changes during the mosses' lifetime, perenniality, wide distribution, ease of sampling and the possibility to determine concentrations in the annual growth segments (Poikolainen, 2004). 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); Ojiodu and Olumayede (2018); Ekpo et. al. (2012); Fatoba and

Oduekun (2004); Adebisi and Oyedeji (2012); Aniefiok et. al.(2014); Sa'idu (2015). The dense carpets that *Polytrichum juniperum* 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 the seasonal variability of some heavy metals (Ni, Cu, Pb, Cr and Zn) content in the atmosphere of Ketu - Mile 12 Area, determine the 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. It is hopeful that the study will provide baseline data on bioaccumulation of heavy metals (Ni, Cu, Pb, Cr and Zn).



Figure I: *Polytrichum juniperinum*

MATERIALS AND METHODS

Study Area

Sampling Locations

This study was conducted in Ketu - Mile 12 (N⁰.4332 & E3⁰.4594 - N⁰.6492 & E3⁰.4770) areas of Lagos state, namely Ile Ile, Owode - Elede, Kosofe, Iyana

school, Mile 12 Market, Ketu garage, Alapere, Agboyi, Ikosi road, Owode - Onirin and Oniru Market in Lagos Island (Control). The sampling points were at least 300m from main roads and 100m from minor roads.



Figure 2: GIS Map Showing the Sampling sites at Ketu- Mile 12 Area.

KEY : II= Ile Ile, OE = Owode- Elede, KO= Kosofe, IS = Iyana School, MM = Mile 12 Market, KG = Ketu garage, AL=Alapere, AG= Agboyi, IR= Ikosi road, OO= Owode-Onirin, OM= Oniru Market (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 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 *Polytrichum juniperinum* were 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 *Polytrichum juniperinum* was chosen because it was widespread across Mushin and can be found in all parts of the study Area. Sampling below canopy of shrubs and large-leaved 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 *Polytrichum juniperinum* 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 45⁰C 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%) HNO₃ : H₂O₂ (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 in moss plant (*Polytrichum juniperinum*) specie were evaluated by analysis of variance (ANOVA) together with mean, standard deviation of each metal. T-test 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 *Polytrichum juniperinum* at Ketu- Mile 12 during dry and wet seasons.

Location	Season	Zinc (mg/l)	Lead (mg/l)	Cadmium (mg/l)	Nickel (mg/l)	Copper (mg/l)
Sample		$F_{10,132} = 20.830$ (<0.001)	$F_{10,132} = 14.278$ (<0.001)	$F_{10,132} = 4.629$ (<0.001)	$F_{10,132} = 11.900$ (<0.001)	$F_{10,132} = 7.798$ (<0.001)
Season		$F_{1,132} = 106.127$ (<0.001)	$F_{1,132} = 28.373$ (<0.001)	$F_{1,132} = 21.546$ (<0.001)	$F_{1,132} = 10.585$ (0.001)	$F_{1,132} = 82.082$ (<0.001)
Kosofe	Dry	1.113 ± 0.0475	0.0009 ± 0.0003	0.006 ± 0.0018	0.0001 ± 0.000	0.3215 ± 0.0644
	Wet	1.9659 ± 0.089	0.0001 ± 0	0.0194 ± 0.0029	0.0001 ± 0.000	0.5266 ± 0.1321
	t-test (p)	-8.453 (<0.001)	3.201 (0.009)	-3.972 (0.003)	-	-1.395 (0.193)
Agboyi	Dry	2.755 ± 0.3206	0.0009 ± 0.0003	0.006 ± 0.0018	0.149 ± 0.033	0.308 ± 0.0359
	Wet	11.4272 ± 0.2626	0.0073 ± 0.0009	0.0273 ± 0.0031	0.9987 ± 0.0308	0.8784 ± 0.1323
	t-test (p)	-20.925 (<0.001)	-7.061 (<0.001)	-5.927 (<0.001)	-18.803 (<0.001)	-4.161 (0.002)
Oniru Market(Control)	Dry	0.0027 ± 0.0008	0.0009 ± 0.0003	0.0009 ± 0.0003	0.2167 ± 0.0137	0.1317 ± 0.0421
	Wet	0.0027 ± 0.0008	0.0011 ± 0.0002	0.0009 ± 0.0003	0.2167 ± 0.0137	0.1317 ± 0.0421
	t-test (p)	0 (1.000)	-0.456 (0.658)	0 (1.000)	0 (1.000)	0 (1.000)
Ile Ile	Dry	3.3342 ± 0.5585	0.2577 ± 0.0611	0.0055 ± 0.0007	0.2982 ± 0.0444	0.74 ± 0.0784
	Wet	8.0655 ± 0.6343	0.4296 ± 0.1091	0.0262 ± 0.005	0.6434 ± 0.0823	3.0054 ± 0.3003
	t-test (p)	-5.598 (<0.001)	-1.374 (0.199)	-4.141 (0.002)	-3.694 (0.004)	-7299 (<0.001)
Ikosi Road	Dry	2.3001 ± 0.2672	0.0009 ± 0.0003	0.0009 ± 0.0003	0.0732 ± 0.0054	0.695 ± 0.0246
	Wet	3.7227 ± 0.3029	0.0001 ± 0	0.0377 ± 0.0103	0.1983 ± 0.0337	0.6901 ± 0.0698
	t-test (p)	-3.522 (0.006)	3.201 (0.009)	-3.564 (0.005)	-3.663 (0.004)	0.066 (0.949)

Alapere	Dry	4.9300 ± 0.4799	0.0009 ± 0.0003	0.016 ± 0.0063	0.0131 ± 0.0029	0.554 ± 0.1261
	Wet	9.5879 ± 0.2107	1.2179 ± 0.2929	0.0304 ± 0.0073	0.0227 ± 0.005	1.4798 ± 0.298
	t-test (p)	-8.888 (<0.001)	-4.154 (0.002)	-1.487 (0.168)	-1.676 (0.125)	-2.861 (0.017)
Ketu garage	Dry	7.8051 ± 0.6924	1.1121 ± 0.0443	0.059 ± 0.0483	0.381 ± 0.082	0.7893 ± 0.1817
	Wet	8.4287 ± 0.5643	1.1183 ± 0.1498	0.0445 ± 0.0208	0.0743 ± 0.0093	2.3543 ± 0.4355
	t-test (p)	-0.698 (0.501)	-0.040 (0.969)	0.276 (0.788)	3.717 (0.004)	-3.317 (0.008)
Mile 12 Market	Dry	2.0883 ± 0.5395	0.0009 ± 0.0003	0.0518 ± 0.0049	0.2 ± 0.0291	0.3972 ± 0.0949
	Wet	11.6 ± 0.3029	1.8354 ± 0.289	0.0935 ± 0.0213	0.2102 ± 0.0257	3.4205 ± 0.6888
	t-test	-15.374 (<0.001)	-6.348 (<0.001)	-1.912 (0.085)	-0.263 (0.798)	-4.348 (0.001)
OwodeElede	Dry	5.8751 ± 0.3491	0.0008 ± 0.0003	0.003 ± 0.0009	0.0001 ± 0.000	0.6838 ± 0.099
	Wet	7.0054 ± 0.4787	0.0866 ± 0.0144	0.1367 ± 0.0278	0.0001 ± 0.000	1.3482 ± 0.1298
	t-test (p)	-1.908 (0.086)	-5.977 (<0.001)	-4.806 (0.001)	-	-4.070 (0.002)
Iyana School	Dry	0.8277 ± 0.3258	0.0009 ± 0.0003	0.0056 ± 0.002	0.1075 ± 0.0469	0.2977 ± 0.0286
	Wet	9.4963 ± 0.1072	0.3283 ± 0.0681	0.034 ± 0.0064	0.0007 ± 0.0001	3.3711 ± 0.3713
	t-test (p)	-25.273 (<0.001)	-4.808 (0.001)	-4.219 (0.002)	2.277 (0.046)	-8.253 (<0.001)
OwodeOnirin	Dry	7.8804 ± 0.0926	0.6206 ± 0.0853	0.015 ± 0.0037	0.076 ± 0.0061	0.535 ± 0.0316
	Wet	8.4407 ± 0.5818	0.8861 ± 0.019	0.0615 ± 0.0117	0.323 ± 0.1707	4.5819 ± 0.6541
	t-test	-0.951 (0.364)	-3.039 (0.026)	-3.800 (0.003)	-1.446 (0.179)	-6.179 (<0.001)

NB: seasons with bold t-tests values are significantly different from each other at 5%

Table 2: Shows the average mean concentration of heavy metals (mg/l) in *Polytrichum juniperinum* at different locations of the Ketu-Mile 12 area during the dry season.

SAMPLE SITES/ LOCATIONS	ZINC(Zn)	LEAD(Pb)	CADMIUM(Cd)	NICKEL(Ni)	COPPER(Cu)
Kosofe	1.113	<0.0001	0.006	<0.0001	0.322
Agboyi	2.730	<0.001	0.006	0.149	0.308
Ile Ile	3.325	0.1251	0.006	0.298	0.742
Ikosi Road	2.3001	<0.001	<0.001	0.073	0.6950
Alapere	4.930	<0.001	0.016	0.0131	0.554
Ketu garage	7.8051	1.1121	0.014	0.381	0.956
Mile 12 Market	2.088	<0.001	0.0518	0.2000	0.405
Owode - Elede	5.8751	<0.001	0.003	<0.0001	0.675
Iyana school	0.900	<0.001	0.008	0.108	0.290
Owode - Onirin	7.8804	0.6200	0.015	0.076	0.535
Oniru Market	<0.005	<0.0010	<0.0010	0.2130	0.1060
Total Value	3.5411	0.1696	0.0116	0.1374	0.5080
UNEP, 2009	≤ 1.00	≤ 0.05	≤ 0.05	≤ 1.00	≤ 1.00

Table 3: Shows the average mean concentration of heavy metals (mg/l) in *Polytrichum juniperinum* at different locations of the Ketu-Mile 12 area during the wet season.

SAMPLE SITES/ LOCATIONS	ZINC(Zn)	LEAD(Pb)	CADMIUM(Cd)	NICKEL(Ni)	COPPER(Cu)
Kosofe	1.966	<0.0001	0.0194	<0.0001	0.6933
Agboyi	11.427	0.0073	0.0273	0.9987	0.8784
Ile Ile	8.066	0.4296	0.0262	0.6434	2.9954
Ikosi Road	3.723	<0.0001	0.0377	0.1983	0.6901
Alapere	9.588	1.2179	0.0304	0.0227	1.4798
Ketu garage	8.429	1.1183	0.0265	0.0743	2.3543
Mile 12 Market	11.600	1.8354	0.0852	0.2102	3.4205
Owode -Elede	7.005	0.0866	0.1367	<0.0001	1.3472
Iyana School	9.496	0.3283	0.0340	0.0007	3.3711
Owode - Onirin	8.441	0.8861	0.0615	0.1563	4.5819
Oniru Market	0.005	<0.0010	<0.0010	0.2130	0.1060
Total Value	7.2496	0.5373	0.0442	0.2289	1.9925
UNEP, 2009	≤ 1.00	≤ 0.05	≤ 0.05	≤ 1.00	≤ 1.00



Figure 3: GIS map of Ketu-Mile 12 showing the average mean concentration of heavy metals of each sample sites during the wet and dry seasons.

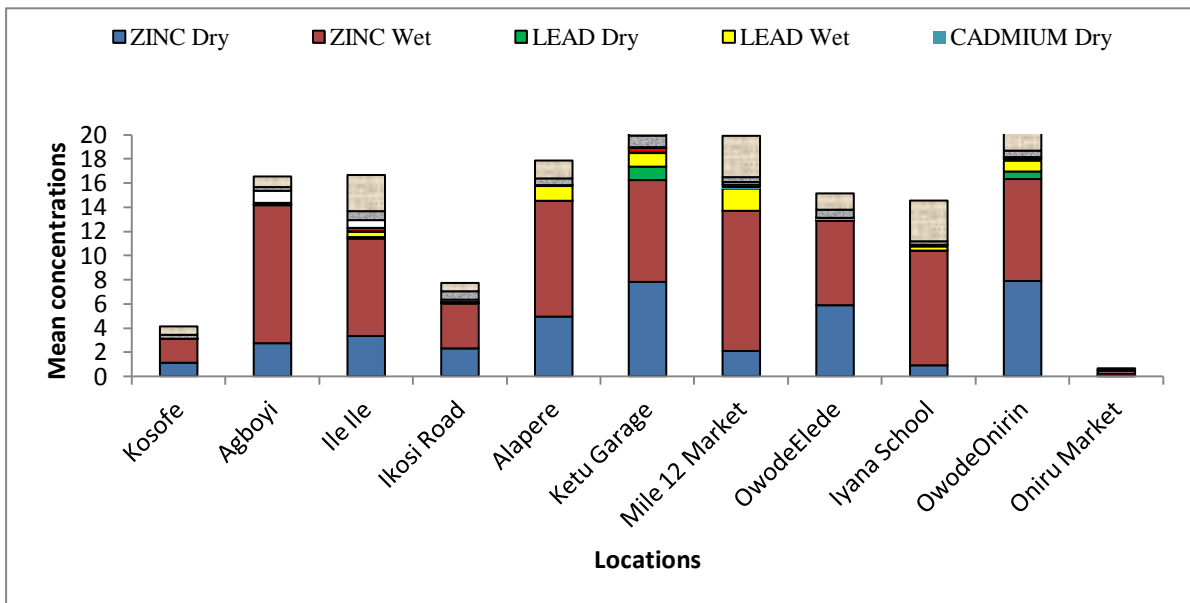


Figure 4: Distribution of heavy metals (mg/l) in *Polytrichum juniperinum* at different locations of Ketu-Mile 12 area during the wet and dry seasons.

DISCUSSION

The results of this research show that the main contributors to the pollution level of Ketu- Mile 12 during the wet and dry seasons were Zn (72.1 - 80.1)%, Pb (3.9 - 5.3)%, Cu (11.6 - 19.8) %, Ni (2.3 - 3.2)%, Cd (0.3 - 0.5)%. (Tables 2, 3). The most abundant heavy metal during the dry (3.5411mg/l) and wet (7.2496mg/l) seasons was Zinc while cadmium was the least abundant during the seasons: dry (0.0116mg/l) and wet (0.0442mg/l).(Figure 4).

The most and the least polluted sites during the dry season were Ketu garage (2.0536mg/l) and Iyana school (0.2614mg/l) respectively. Similarly, the most and the least polluted sites during the wet seasons were Mile 12 market (3.4303mg/l) and Kosofe (0.5358mg/l) respectively. The seasonal variation in Ketu- Mile 12 area were due to wash down of atmospheric heavy metals by rain and moisture to the soil which was absorbed by the Moss plant thereby increasing the level of heavy metals during the wet season.(Figure 3). There was a significant difference in the levels of heavy metals across the location in Ketu - Mile 12 area and across the wet and dry seasons ($p < 0.05$)(Table 1). The levels of Zn were highest at all locations during the seasons. This was due to the fact that Zinc was released to the atmosphere through metal production processes, from industrial combustion of coal, from waste incineration and improper disposal of sewage, corrosion of galvanized steels, scrap iron bars, wearing - off of tyre alloys on vehicles, alloys of Zinc composites. Small amounts are also released naturally from the earth's crust.(Figure 4). The trend in the levels of total

atmospheric heavy metals in the study area during the dry seasons was: Ketu garage > Owode elede > Owode - Onirin > Owode Elede > Alapere > Ile Ile > Agboyi > Ikosi road > Mile 12 Market > Kosofe > Iyana school > Oniru (Table 2). Similarly, during the wet seasons was: Mile 12 > Owode - Onirin > Agboyi > Iyana school > Ile Ile > Alapere > Ketu garage > Owode - Elede > Ikosi road > Kosofe. (Table 3). All the concentrations of the metals detected were higher than the control. 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. Mile 12 Market (11.600mg/l) and Owode Onirin(7.8804 mg/l) has the highest concentration of Zinc during the wet and dry seasons while the least concentrations were recorded at Kosofe (1.9659mg/l) and Iyana school (0.9000mg/l) respectively. Ketu garage has the highest concentration of Pb (1.1121mg/l), Ni (0.3810mg/l) and Cu(0.956mg/l) during the dry season. This was due to the presence of automobile workshops in the area, spillage of petrol and diesel, smoking of cigarette, paint chips from walls, disposal of used auto batteries and high vehicular activities in the area. Kosofe (<0.001mg/l) had the least concentration Pb. Mile 12 Market (1.8354mg/l) had the highest concentration of Pb during the wet seasons. Agboyi and Owode Onirin had the highest concentrations of Ni (0.9987mg/l) and Cu(4.5819mg/l) during the wet seasons respectively. This probably arose from combustion of fossil fuels, smelting of metals/steel and

oil activities also from wearing brass or bronze parts. The high concentration of Cd (0.0518mg/l) in Mile 12 Market during the dry season was due to high vehicular traffic congestion, commercial activities and the use of various old paint chips. Owode -Elede (1.367mg/l, 28.11%) had the highest concentration of Cd during the wet seasons while Kosofe (0.0194mg/l) had the least concentration (Figure 2). Despite, seasonal variation, the sequence of bioaccumulation and distribution followed the same pattern during the seasons thus: Zn > Cu > Pb > Ni > Cd. There was an increase in the level of bioaccumulation of these heavy metals from the dry to the wet seasons (Table 2,3). The results of this research agreed with the results obtained in some Nigerian cities and showed that concentration of heavy metals depended on the nature and activities of a place. (Adie et. al. (2014); Ekpo et. al. (2012); Ojiodu et. al. (2018)). The moss species *Polytrichum juniperinum* samples exhibited significant variation in the average levels of the heavy metals at different locations ($P_{\text{value}} < 0.05$). (Figure 1).

Though, Zn, Pb, Cu, Ni and Cd contribute 72.1 - 80.1; 3.9 - 5.3, 11.6 - 19.8; 2.3 - 3.2 and 0.3 - 0.5% respectively to the atmosphere of Ketu - Mile 12 area during dry and wet seasons, the high concentration of these heavy metals is as a result of commercial, vehicular and artisan activities which include improper disposal of waste/ sewage, galvanizing, smelting, fabricating of metals, combustion of fuel/oil, mechanical and engineering works etc. The high concentration of these metal pollution could be hazardous to human and plants existence, therefore,

there is need for constant environmental Monitoring of the Atmosphere of Ketu - Mile 12 area.

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