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Full Length Research Article

TEMPORAL VARIABILITY OF HEAVY METAL CONTENT IN THE ATMOSPHERE OF KETU- MILE 12 AREA OF LAGOS - STATE, SOUTHWESTERN - NIGERIA USING MOSS PLANT POLYTRICHUM JUNIPERUM AS BIOINDICATOR

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ABSTRACT
The concentrations of the five heavy metals; Zinc (Zn), Lead (Pb), Cadmium (Cd), Nickel (Ni) and Copper (Cu) were determined using Atomic Absorption Spectrophotometer (AAS). Results of the analysis, shows that the average concentration of the heavy metals at Ketu - Mile 12 were : Zn 7.175mg/L; Pb 1.288mg/l; Cu 0.531mg/l; Ni 0.223mg/l and Cd 0.021mg/l which reflects Zn 77.67; Pb 13.94; Cu 5.75; Ni 2.41 and Cd 0.22 % with the most abundant pollutant heavy metal being Zn in all the sites while the least abundant was Cd. It was found that the highest concentration of each heavy metals in all the sites were as follow; Zn 14.93mg/l - Alapere; Pb 1.720mg/l - Ketu garage; Cd 0.118mg/l - Mile 12 market; Ni 0.458mg/l - Mile 12 and Cu 0.956mg/l - Ketu garage while the least concentration of heavy metals in all the sites were as follows: Zn < 0.005mg/l, Pb < 0.001mg/l), Cd < 0.001mg/l and Cu 0.106mg/l - Oniru, Ni 0.108mg/ - Iyana school. The most polluted site was Ikosi road 4.441 mg/l while the least polluted was Iyana School 0.327mg/l. The sequence of bioaccumulation and distribution follows the pattern thus: Zn>Pb>Cu>Ni >Cd.

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

INTRODUCTION
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. The extent of environmental changes over the last decades has given a new urgency and relevance to the detection and understanding of environmental change which has altered global biogeochemical cycling of heavy metals. Human activities such as industrial production, mining, agriculture and transportation release a high amount of heavy metals to the biosphere. The primary sources of heavy metal pollution are the burning of fossil fuels, smelting of metal like ores, municipal wastes, fertilizers, pesticides and sewage (Rai, 2009). 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 like As, Pb, Cd and Cr which may be major air and land pollutants in areas where they are most concentrated (Moses *et al.*, 2009) . Exposures to these types of toxic metals produces health hazard in humans (Cao *et al.*, 2009). Cadmium is toxic at extremely low levels. Several exposures may result to pulmonary odema and death (Young, 2005). Lead is the most significant toxic of all the heavy metals, and the inorganic forms are absorbed through ingestion by food and water, and in inhalation (Ferner, 2001). A notably serious effect of lead toxicity is its teratogenic effect (Udedi, 2003; Ogwuegbu and Muhanga 2005). Zinc is considered to be relatively non-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that results in impairment of growth and reproduction (Onianwa, 2001; Nolan, 2011). 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 and Govind, 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 normally done through direct measurement by using electronic devices (Poykio *et al.*, 2005). 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. They occur on every continent and in every location habitable by photosynthetic plants. Mosses have little or no developed cuticle. 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 root and 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 and Paratkar, 2006).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 *et al.*,2017; Ekpo *et al.*, 2012; Fatoba and Oduekun, 2004; Adebiyi and Oyedeji, 2012; Aniefiok *et al.,* 2014; Sa'idu, 2015). The dense carpets that Polythricum 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 temporal variability of some heavy metals content in the atmosphere of Ketu - Mile 12, determine the baseline levels and 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.

MATERIALS AND METHODS

Study Area / Sampling Locations

This study was conducted in Ketu - Mile 12 (N6^0 59 3^0 38E - N6^0 64 3^0 47E) areas of Lagos state, namely Ile ile, Owode - elede, kosofe, Iyana school, Mile 12 , Ketu guarage (Ikosi branch), Alapere, Agboyi, Ikosi road, Owode - Onirin and Oniru in Lagos Island. (Control). The sampling points were at least 300m from main roads and 100m from minor roads.

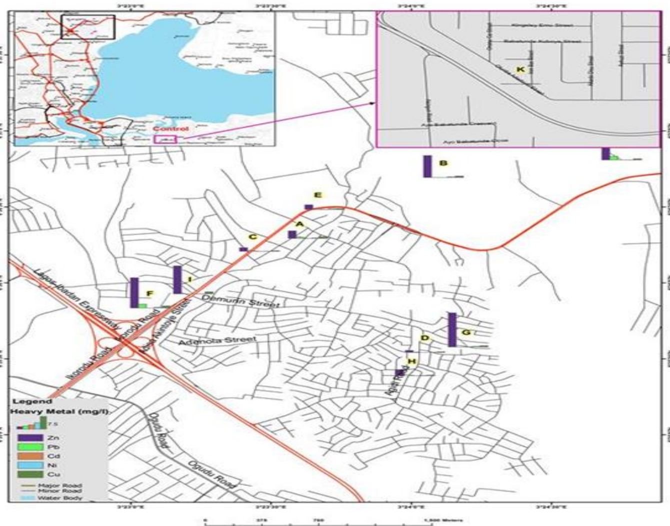

Figure 1: GIS Map of Ketu - Mile 12 Showing the Mean Concentrations of each sampling site.

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 Polytrichum juniperum collected from Ten sites within the studied area at least 10 metres apart, once in a month from September to November, 2016. The moss plant Polytrichum juniperum was chosen because it is widespread across Ketu - Mile 12 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 Polytrichum juniperum mosses were cleaned from all debris (soil, leaves, and needles) dried at 45^{0}C 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).

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.

Statistical Analysis

The results of heavy metal accumulation in Polytrichum juniperum 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 Statistical analysis on the means concentration of Heavy metals in Ketu - Mile 12 Area.

Locations/Sites	N	Zinc (Zn)	Lead (Pb)	Cadmium (Cd)	Nickel (Ni)	Copper (Cu)
		Mean + se	Mean + se	Mean + se	Mean + se	Mean + se
Ile – ile	6	$3.334 + 0.558^{a}$	$0.525 + 0.134^{a}$	$0.006 + 0.001^{a}$	$0.298 + 0.044^{cd}$	$0.740 + 0.079^{a}$
Owode elede	6	$9.688 + 0.909^{b}$	$0.001+ 0.0003^{a}$	$0.003 + 0.001^{a}$	$0.003 + 0.001^{a}$	$0.674 + 0.094^{a}$
Kosofe	6	$1.613 + 0.415^{a}$	$0.001+ 0.0003^{a}$	$0.006 + 0.002^{a}$	$0.071 + 0.010^{ab}$	$0.322 + 0.064^{a}$
Iyana school	6	$0.828 + 0.325^{a}$	$0.001+ 0.0003^{a}$	$0.006 + 0.002^{a}$	$0.107 + 0.047^{ab}$	$0.297 + 0.029^{a}$
Mile 12	6	$2.088 + 0.539^{a}$	$0.001+ 0.0003^{a}$	$0.118 + 0.056^{b}$	$0.458 + 0.084^{e}$	$0.397 + 0.094^{a}$
Ketu garage	6	$11.652 + 2.299^{b}$	$1.720 + 0.536^{b}$	$0.059 + 0.048^{a}$	$0.381 + 0.082^{de}$	$0.789 + 0.182^{a}$
Alapere	6	$14.930 + 1.998^{c}$	$0.001+ 0.0003^{a}$	$0.016 + 0.006^{a}$	$0.300 + 0.081^{cd}$	$0.553 + 0.126^{a}$
Agboyi	6	$2.755 + 0.321^{a}$	$0.001+ 0.0003^{a}$	$0.006 + 0.002^{a}$	$0.149 + 0.033^{ab}$	$0.308 + 0.036^{a}$
Ikosi road	6	$12.300 + 0.313^{bc}$	$0.001+ 0.0003^{a}$	$0.001 + 0.0002^{a}$	$0.073 + 0.005^{ab}$	$0.950 + 0.146^{ab}$
Owode – Onirin	6	$10.088 + 1.080^{b}$	$1.620 + 0.146^{b}$	$0.015 + 0.004^{a}$	$0.076 + 0.006^{ab}$	$0.535 + 0.032^{a}$
Oniru(Control)	6	$0.003 + 0.001^{a}$	$0.001 + 0.0003^{a}$	$0.001 + 0.0002^{a}$	$0.217 + 0.014^{bc}$	$0.106 + 1.045^{b}$
		$F_{10,55} = 26.328$, $p < 0.001$	$F_{10,55} = 15.125$, $p < 0.001$	$F_{10,55} = 3.723$, $p = 0.001$	$F_{10,55} = 9.193$, $p < 0.001$	$F_{10,55} = 1.718$, $p = 0.100$

NB: locations with the same superscript for each metal are not significantly different from each other

RESULTS AND DISCUSSION

Table 2: Shows the Characteristics and Co-ordinates of Monitoring Locations at Ketu - Mile 12 Area.

SITES NAME	CODE	CO-ORDINATES	SITE DESCRIPTION
1 Ile ile	Ie	N $6^{0'}$ 64.92 E 3^{0} 47.70'	A dump site for metals with a high traffic and vehicular activities. Guarage with abanXMdoned vehicles.
2 Owode - elede	Od	N 6^{0} 61.22' E 3^{0} 40.19''	Residential area with few welding shops, abandoned vehicles and filling stations.
3 Kosofe	Ks	N 6^{0} 60.41' E 3^{0} 39.09'	A residential area with few commercial and vehicular activities.
4 Iyana school	Is	N6^{0} 59.29' E3^{0} 40.19'	A residential area with a dumping site for metals, abandoned vehicles.
5 Mile 12	Mm	N6^{0} 60.89' E3^{0} 39.48'	An area with high commercial and vehicular activities.
6 ketu guarage	Kg	N6^{0} 59.78' E3^{0} 38.50'	Commercial and vehicular, Mechanical activities, abandoned vehicles, spillage of petrol and diesel and smoking of cigarettes.
7 Alapere	Ap	N6^{0} 59.04 E3^{0} 40.34	Residential area, fumes from exhausts of generators, metal works and present of filling stations.
8. Agboyi	Ag	N6 ^{0} 59.04 E 3^{0} 40.02	Residential area, metal works, fumes from generators with little vehicular activities.
9. Ikosi road	Ir	N 6^{0} 59.94 E 3^{0} 38.02	An area with filling stations, high commercial and vehicular activities, dump of scrap-metals.
10. Owode - Onirin	On	N 6^{0} 61.41 E 3^{0} 41.25	This is a site with dump of scrap-metals, Iron-bars, galvanized-metals, steel etc. high welding and mechanical activities, filling stations.
11. Oniru (Control)	Ou	N 6^{0} 43.32 E 3^{0} 45.94	Residential area. This area is surrounded with large body of water.

Table 3: Mean Concentration of Heavy metals at different Locations in Lagos (mg/l).

Location	Ni	Cu	Pb	Cd	Zn	Cr
V/I	7.99	6.62	3.49	-	-	0.29
Marine	7.39	7.03	3.19	-	-	0.13
Apapa	6.69	6.26	6.62	-	-	0.17
Ikeja	6.54	7.36	5.68	-	-	0.23
Oshodi	7.97	7.17	4.81	-	-	0.28
Ojota	8.01	6.76	6.63	-	-	0.24
Mile 2	8.20	5.83	9.16	-	-	0.32
Owode – Onirin	1.36	7.57	9.46	-	39.14	1.71

Source: Ekpo *et al.*, 2014

Table 4: Shows the mean Concentrations of Heavy metals (mg/l) at different Locations of Ketu - Mile 12 using Polytrichum juniperum for September, October and November.

LOCATION	Concentration (mg/l)					Mean value
	Zn	Pb	Cd	Ni	Cu	
Ile ile	3.325	0.525	0.006	0.298	0.742	**1.918**
Owode elede	9.688	<0.001	0.003	0.333	0.675	**2.675**
Kosofe	1.613	<0.001	0.006	0.071	0.322	**0.503**
Iyana school	0.900	<0.001	0.008	0.108	0.290	**0.327**
Mile 12	2.088	<0.001	0.118	0.458	0.405	**0.767**
Ketu garage	13.300	1.720	0.014	0.381	0.956	**3.274**
Alapere	14.930	<0.001	0.016	0.300	0.554	**3.950**
Agboyi	2.730	<0.001	0.006	0.149	0.308	**0.798**
Ikosi road	12.300	<0.001	<0.001	0.073	0.950	**4.441**
Owode Onirin	10.880	1.6200	0.015	0.076	0.535	**2.625**
Oniru (control)	<0.005	<0.001	<0.001	0.213	0.106	**0.160**
Mean value	**7.175**	**1.288**	**0.021**	**0.223**	**0.531**	
UNEP, 2009	**≤ 1.00**	**≤ 0.05**	**≤0.05**	**≤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.

Table 5: Shows the mean Concentration and Standard deviation of the heavy metals (mg/l) at Ketu- Mile 12.

MONTHS	Zn	Pb	Cd	Ni	Cu
September	7.150 ± 1.38	1.287 ± 0.87	0.023 ± 4.76	0.225 ± 0.69	0.531 ± 3.66
October	7.175 ± 1.96	1.288 ± 1.56	0.022 ± 2.45	0.223 ± 1.97	0.532 ± 2.37
November	7.200 ± 2.01	1.289 ± 0.74	0.021 ± 0.57	0.221 ± 2.24	0.531 ± 3.71
Mean	7.175 ± 1.52	1.288 ± 3.97	0.022 ± 1.98	0.223 ± 1.54	0.531 ± 5.59

The most polluted site in Ketu - Mile 12 is Ikosi - road (4.441mg/l). Alapere has the highest concentration of Zinc (14.93mg/l) while Iyana school (0.327mg/l) is the least polluted site with the least concentration of Zinc (0.900mg/l)(Table 4). The presence of Zinc is due to large depot of weared brakes, corrosion of galvanized steels, scrap iron bars, wearing - off of tyre alloys, alloys of Zinc composite and improper disposal of sewage in the area. Apart from Owode Onirin (1.6200mg/l) and Ile ile (0.525mg/l), Ketu garage has the highest concentration of Pb (1.720mg/l) which is above WHO (2001) threshold limit due to the high commercial and vehicular activities in the area, spillage of petroleum products, smoking of cigarette, paint chips from the walls and disposal of used auto batteries. Ketu garage which is associated with mechanical and automobile activities has the highest concentration of Cu (0.956mg/l) this is associated with release from corroding metal parts derived from engine wear, brushing and metal bearing and also from lubricating oil, used automobile batteries. The highest concentration of Cd (0.118mg/l) and Ni (0.458mg/l) was recorded in atmosphere of Mile 12 while Ikosi road and kosofe has the least concentrations of Cd (< 0.001mg/l) and Ni (0.071mg/l) respectively (Table 4). The presence of Cadmiun and Nickel in these areas arises from combustion of fossil fuels, smelting of metals, vehicular emission, traffic congestion and various old paint chips. The amount of these heavy metals in Ketu - Mile 12 were observed to follow the trend Zn > Pb > Cu > Ni > Cd (Table 5). This result is in agreement with that obtained by Adie *et al.,* 2014 and Sa, idu, 2015 who carried out a survey of heavy metals deposition in Makurdi and environs in north central and north - western part of Nigeria respectively using the moss monitoring method in which the trend was Fe > Zn > Pb > Cu > Cr > Mn > Ni > Cd, they reported that the results from the moss sample exhibited a significant variation in the levels of metal ion with type of sampling site. The Polytrichum juniperum specie used in this research exhibited significant variation in the average levels of the metals with various sites in the study areas. 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 5). This may account for the persistent anthropogenic activities in the Ketu - Mile 12 area (Table 2). The average levels of heavy metals obtain in this research is lower compared to other areas in Lagos, this may be due to Seasonal variation i.e in dry season when the research was carried out the atmospheric moisture content is low, there is no wash-down that will lead to bioaccummulation of heavy metals in the moss plant (Ekpo *et al.*, 2012) (Table 3). The average levels of Zinc, Lead, Cadmium and Nickel are significantly different in different sites ($p < 0.05$), while the average levels of Copper in each of the sites is not significantly different ($p > 0.05$). There is no significant difference between the levels of Zinc at Ile ile, Kosofe, Iyana school, Mile 12, Agboyi and Oniru, but they differ significantly from each other in Owode -

elede, Ketu guarage, Alapere and Owode Onirin, Ikosi - road. Also, there is no significant difference in the levels of Zinc at Alapere and Ikosi road, but there is significant difference in the levels of Zinc in all other sites (Table 1). There is no significant difference between the levels of lead at Owode Onirin and Ketu garage but there is a significant difference in the lead levels in all other sites (Table 1). In addition, the levels of cadmium in all the sites do not differ significantly from each other except Mile 12. There is significant difference in the levels of Copper and Nickel across all the studied sites ($p > 0.05$) (Table 1). The trend in the levels of total atmospheric heavy metals in the study are; Ikosi road > Alapere > Ketu garage > Owode elede > Owode - Onirin > Ile ile > Agboyi > Mile 12 > Kosofe > Iyana school > Oniru (Table 1). All concentration 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. 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 values in the control (Table 4). The high significant levels of Zn, Pb and Cu obtained in the samples from Ketu - Mile 12 area is as a result of vehicular and the activities of artisans in the area(Figure 1). The low concentration of Chromium Cr and Nickel Ni suggest low contributing factors to their spread and as well as plant inability to preferentially accumulate these metals. However , levels of some of the heavy metals were present in concentrations greater than WHO (2001) threshold limiting values which the range is Zn (0.02 - 0.1mg/l), Pb (0.005 - 0.03mg/l), Cd (< 0.0024mg/l), Ni (0.000002 - 0.05mg/l) and Cu (0.0025mg/l) while some of the heavy metals were within the range.

Conclusion

Since, Zn, Pb, Cd, Ni and Cu contributes 77.67; 13.94; 0.22; 2.41 and 5.75% to the atmosphere of Ketu - Mile 12. It is evident that the atmosphere of Ketu - Mile 12 is highly polluted with the Heavy metals. The high concentration of this heavy metals could be attributed to large depot of weared brakes, corrosion of galvanized steels, scrap iron bars, wearing of tyre alloys, alloys of Zinc composite and improper disposal of sewage, vehicular and Commercial activities within and around Ketu - Mile 12. Therefore, there is need for environmental Monitoring, safety and management of the Atmosphere of Ketu - Mile 12 to the high concentration of this metal pollution which could be very hazardous to human and plants existence.

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