EVALUATION OF LEVELS OF ATMOSPHERIC HEAVY METALS IN IKEJA INDUSTRIAL AREA OF LAGOS STATE NIGERIA USING POLYTRICHIUM COMMUNE AS BIOMONITOR

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ABSTRACT
This study investigates the concentrations of some heavy metals (Zn, Pb, Cu, Ni and Cd) in moss plant Polytrichum commune collected at different locations within Ikeja Industrial Area, Lagos - Nigeria. The samples of the plant were collected randomly between September and November, 2018 at 10 different locations between 2 - 2.5 m high from unplastered buildings. The samples were properly cleaned from all the debris, weighed and digested with a mixture of HNO3 and H2O2 for 35 min. The concentrations of heavy metals were analyzed using Atomic Absorption Spectrophotometer (AAS). The results obtained, showed that the average concentrations of the heavy metals at Ikeja Industrial Area were: Zn 16.01944 mg/dm³, Pb 2.9485 mg/dm³, Cu 2.7843 mg/dm³, Ni 0.6653 mg/dm³ and Cd 0.095 mg/dm³ which reflects 71.16; 13.10; 12.37; 2.96 and 0.42% 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 Manufacturing Production Limited (40.894mg/L; 18.1%), while the least polluted site was Kara.com.ng (9.891mg/L; 4.4%). The levels of heavy metals obtained are greater than the permissible limits prescribed by the Federal Ministry of Environment, European Communities and United Nations Environmental Programme. There was significant difference in the level of each heavy metal in the atmosphere of Ikeja Industrial Area (Pv < 0.05). The sequence of bioaccumulation and distribution follows the trends: Zn > Pb > Cu > Ni > Cd.

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

INTRODUCTION
The presence of heavy metals in the environment beyond the acceptable limit has been a serious concern to environmentalists. Atmospheric heavy metal contamination has been a major environmental problem in Lagos-State, South-Western, Nigeria due to emissions from industries, energy generation, vehicular traffic, combustion of fossil fuel and poor waste management strategies. Heavy metals are the stable metals or metalloids whose density is greater than 4.5 g/cm³, 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 (Micaela et al., 2013; Ojiodu et al., 2018b). Heavy metals are important indicators of air pollution, because their concentrations correlate well with anthropogenic sources. The use of bioindicators is of considerable interest because it allows measurements on a large scale, relatively quickly and at low cost. In particular, mosses are now widely used 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). Monitoring of air pollution by direct ambient air measurement using biomonitors is emerging as a potentially effective and economical alternative. 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 are normally done through direct measurement by using electronic devices (Poykio et al., 2005). 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 occurrence of 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). Biomonitoring is defined generally as the use of bio-organisms to obtain information on certain characteristics of the biosphere (Shamisti et al., 2006). Unfortunately, monitoring of air quality in major cities is becoming expensive, as the cost of air samplers is becoming unaffordable. Similarly, electricity supply in most parts of the country is erratic. Therefore, there is need for an alternative sampler that is of low cost, affordable, specific, sensitive and reliable. Moss plants have been selected for monitoring in this study because of its abundance in the environment. Mosses plants possess 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 (Ceburnis et al., 2002; Cenci et al., 2003; Poikalainen, 2004; Wang et al., 2008). 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; Ojiodu et al., 2018a,b; Ekpo et al., 2012; Fatoba and Odukeun, 2004; Adebiyi and Oyedeji, 2012; Aniefiok et al., 2014; Sa'idu, 2015). The dense carpets that Polytrichum commune 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 levels of some heavy metals Zn, Pb, Cu, Ni and Cd content in the atmosphere of Ikeja Industrial area, 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.

Figure 1: The Moss plant (Polytrichum commune)

MATERIALS AND METHODS

Study Area / Sampling Locations
This study was conducted in Ikeja Industrial area (N6°66.250 3° 47.524'E - N6°59.988'3°33.451'E) areas of Lagos state, namely Kara.com.ng, Manufacturing Production Limited, Tom & Service group of company, Niwil Nigeria Limited, Sanga Group of Company, Sky Group of Company, BESNAL Nigeria Limited, Chinese Restaurant Ikeja, Chemline House Ikeja, ECWA Evangelical Church, Residential House Ikorodu (Control). The sampling points were at least 300 m from main roads and 100 m from minor roads. Figure 1 is the GIS map showing the sampling locations.

Figure 2: GIS Map of Ikeja Industrial Area Showing the Mean Concentrations of each sampling site. KEY : KCN = Kara.com.ng; MPL = Manufacturing Production Limited; NNL = Niwil Nigeria Limited; TSG = Tom & Service group of company; SGC = Sanga Group of Company; SGC 1 = Sky Group of Company; BNL = BESNAL Nigeria Limited; CRI = Chinese Restaurant Ikeja; CHI = Chemline House Ikeja; EEC = ECWA Evangelical Church; RHI = Residential House Ikorodu (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 chosen to reflect activities in the area. The geo-referencing was carried out by using Garmin GPS MAP 76S.

Moss sampling
Samples of Polytrichum commune were 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 commune 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-leaved 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 commune mosses were cleaned from all debris (soil, leaves, and needles) dried at 45°C to a constant weight (Biaigne and Pailulis, 2010). Sample of the mosses (0.50g) were mixed with a mixture of 10ml nitric acid (65%) and 2 mL of hydrogen peroxide (30%), digestion was performed using hot plate for 35minutes. After digestion, samples were left to cool till room temperature for one hour, poured into 50ml flasks and finally made to mark with distilled water (Baltreneite 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 AND DISCUSSION
Moss plant is an important plant material that can accumulate heavy metals from the atmosphere. The pictorial view of the plant is shown in Figure 1. The moss Polytrichum commune used in this research exhibited significant variation in the average levels of the metals in various sites in the study areas. It can therefore be used for quantification and removal of heavy metals from the environment. The pollution of an area depends on the activities that goes on in that area. Table 1 has shown the various activities in the sampling sites for this study. The most polluted site in Ikeja Industrial Area is Manufacturing Production Limited (40.894 mg/dm³; 18.1%) as shown in Table 2. This is as a result of anthropogenic activities going on in and around the site such as release of gases from nearby industries, commercial and vehicular activities while the least polluted site was Kara.com.ng (9.891 mg/dm³; 4.4%). Manufacturing Production Limited has the highest concentration of copper (10.601 mg/dm³) and nickel (1.147 mg/dm³). The most abundant heavy metals is zinc(16.0194 mg/L) while the least abundant heavy metal is cadmium (0.095 mg/dm³). 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, losses of oil and cooling liquids from automobile, corrosion of galvanized steels, scrap iron bars, and improper disposal of industrial waste in the area. There was progressive increase in the level of bioaccumulation of these heavy metals from September to November. The amount of these heavy metals in Ikeja Industrial area were observed to follow the trend Zn > Pb > Ni > Cu > Cd as shown in Tables 2 and 3. There is a significant difference (p < 0.05) in the levels of zinc metal in Ikeja Industrial Area as shown in Table 4. The highest concentration of zinc was recorded at ECWA Evangelical Church (33.97 mg/dm³) while the least concentration was recorded at Kara.com.ng (6.793 mg/dm³). The highest concentration of lead was recorded at Sanga Group of Company (4.4262 mg/dm³) and Sky Group of Company (3.674 mg/dm³) whereas the least concentration was recorded at Kara.com.ng (1.492 mg/dm³). The high presence of lead at Sanga Group of Company (4.4262 mg/dm³) and Sky Group of Company (3.674 mg/dm³) 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 discard 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 Lead at Sanga Group of Company (4.4262 mg/dm³) and Sky Group of Company (3.674 mg/dm³) were significantly different (p < 0.05) from all other sites. The highest concentration of copper (10.601 mg/dm³) and nickel (1.147 mg/dm³) was recorded in the atmosphere of Manufacturing Production Limited while BESNAL Nigeria Limited has the least concentrations of copper (1.312 mg/dm³) and nickel (0.415 mg/dm³). The presence of copper 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. Furthermore, the presence of nickel in this site may be as a result of fuel combustion from generators as well as frequent bush burning in the surroundings. The levels of copper and nickel in BESNAL Nigeria Limited site is significantly different from all other sites (p < 0.05). The highest concentration of cadmium was recorded at Tom & Service group of company (0.173 mg/dm³) while the least concentration was recorded at Chinese Restaurant (0.026 mg/dm³). The level of Cadmium in Tom & Service group of company site is not significantly different (p > 0.05) from all other sites (Table 4). Figure 3 shows the percentage of each of the heavy metals accumulated compared to the total metal content of the biomonitor. 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 (Ekpo et. al. (2012); Adie et. al. (2014); Ojiodu et. al. (2018a, b). The trend in the levels of total atmospheric heavy metals in the study area was: Manufacturing Production Limited (18.1%) > ECWA Evangelical Church (17.3%) > Sanga Group of Company (13.9%) > Niwil Nigeria Limited (9.1%) > Sky Group of Company (8.6%) > Chemline House (7.7%) > Tom & Service group of company (7.5%) > BESNAL Nigeria Limited (6.6%) >
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Figure 3: Percentage contribution of each heavy metal to total heavy metals in Ikeja Industrial Area.

Table 3: Mean Concentrations and Standard deviation of heavy metals (mg/L) in Polytrichum commune in Ikeja Industrial Area.

<table>
<thead>
<tr>
<th>Months</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
<th>Ni</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>September</td>
<td>15.991 ± 0.32</td>
<td>2.948 ± 0.01</td>
<td>2.7842 ± 0.56</td>
<td>0.6662 ± 0.01</td>
<td>0.095 ± 0.04</td>
</tr>
<tr>
<td>October</td>
<td>16.021 ± 0.14</td>
<td>2.9485 ± 0.02</td>
<td>2.7843 ± 0.66</td>
<td>0.6663 ± 0.02</td>
<td>0.097 ± 0.08</td>
</tr>
<tr>
<td>November</td>
<td>16.022 ± 0.22</td>
<td>2.9486 ± 0.01</td>
<td>2.7844 ± 0.06</td>
<td>0.6664 ± 0.11</td>
<td>0.093 ± 0.12</td>
</tr>
<tr>
<td>Mean Value</td>
<td>16.011 ± 0.51</td>
<td>2.9485 ± 0.01</td>
<td>2.7843 ± 0.23</td>
<td>0.6663 ± 0.03</td>
<td>0.095 ± 0.01</td>
</tr>
</tbody>
</table>

Figure 4: Percentage Contribution of sites sampled to total heavy metals in Ikeja Industrial Area.

Statistical Analysis
The results of heavy metal accumulation in Polytrichum commune evaluated by analysis of variance (ANOVA) together with mean, standard deviation of each metal, T-test (IBM SPSS 23) to check the significant variation between metals and sites as shown in Table 4.

Table 4: Statistical analysis on the Mean concentration of heavy metals in Ikeja industrial area

<table>
<thead>
<tr>
<th>Site/Location</th>
<th>Lead (Pb)</th>
<th>Zinc (Zn)</th>
<th>Cadmium (Cd)</th>
<th>Copper (Cu)</th>
<th>Nickel (Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCS</td>
<td>1.48 ± 0.12</td>
<td>5.78 ± 0.06</td>
<td>0.66 ± 0.06</td>
<td>0.67 ± 0.04</td>
<td>0.47 ± 0.03</td>
</tr>
<tr>
<td>MPC</td>
<td>3.41 ± 0.09</td>
<td>20.58 ± 0.16</td>
<td>0.69 ± 0.09</td>
<td>0.60 ± 0.12</td>
<td>1.15 ± 0.01</td>
</tr>
<tr>
<td>NNN</td>
<td>1.06 ± 0.01</td>
<td>10.35 ± 0.03</td>
<td>1.14 ± 0.05</td>
<td>1.35 ± 0.15</td>
<td>0.77 ± 0.02</td>
</tr>
<tr>
<td>TKC</td>
<td>1.03 ± 0.01</td>
<td>10.36 ± 0.03</td>
<td>1.17 ± 0.05</td>
<td>1.35 ± 0.15</td>
<td>0.77 ± 0.02</td>
</tr>
<tr>
<td>BSQ</td>
<td>4.26 ± 0.01</td>
<td>20.48 ± 0.06</td>
<td>0.66 ± 0.02</td>
<td>0.67 ± 0.06</td>
<td>0.85 ± 0.02</td>
</tr>
<tr>
<td>BSQ 1</td>
<td>3.31 ± 0.01</td>
<td>10.32 ± 0.03</td>
<td>0.67 ± 0.02</td>
<td>1.48 ± 0.05</td>
<td>0.45 ± 0.01</td>
</tr>
<tr>
<td>BNM</td>
<td>2.44 ± 0.09</td>
<td>10.37 ± 0.06</td>
<td>0.66 ± 0.09</td>
<td>1.31 ± 0.06</td>
<td>0.41 ± 0.00</td>
</tr>
<tr>
<td>CDA</td>
<td>2.74 ± 0.09</td>
<td>7.13 ± 0.06</td>
<td>0.63 ± 0.09</td>
<td>1.33 ± 0.06</td>
<td>0.43 ± 0.02</td>
</tr>
<tr>
<td>CDA</td>
<td>2.03 ± 0.06</td>
<td>12.25 ± 0.01</td>
<td>0.12 ± 0.05</td>
<td>1.82 ± 0.05</td>
<td>0.47 ± 0.02</td>
</tr>
<tr>
<td>EEC</td>
<td>2.54 ± 0.05</td>
<td>10.39 ± 0.03</td>
<td>0.14 ± 0.05</td>
<td>2.99 ± 0.05</td>
<td>0.43 ± 0.02</td>
</tr>
<tr>
<td>RAI (Control)</td>
<td>1.93 ± 0.06</td>
<td>12.13 ± 0.06</td>
<td>0.10 ± 0.06</td>
<td>1.22 ± 0.02</td>
<td>0.29 ± 0.01</td>
</tr>
</tbody>
</table>

F-Statistics: F<sub>120,0.05</sub> = 23.106, p = 0.001
F<sub>120,0.01</sub> = 30.51, p = 0.001
F<sub>120,0.001</sub> = 71.19, p = 0.001
F<sub>120,0.0001</sub> = 99.16, p = 0.001

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

Conclusion
Since, Zn, Pb, Ni, Cu and Cd contributes 71.16, 13.10, 12.37, 2.98 and 0.42 % respectively to the atmosphere of Ikeja Industrial area, the high levels of these heavy metals Zn, Pb, Ni, Cu and Cd obtained in the samples from Ikeja Industrial area could be attributed to the emission of these heavy metals originating from gases released from nearby 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 use these metals or their compounds within...
and around Ikeja Industrial area. The low concentration of Cadmium Cd suggest low contributing factors to their spread and as well as with plant’s inability to preferentially accumulate this 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 Ikeja Industrial area.

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