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Full Length Research Paper**Mosses as Biomonitors of Heavy Metal Deposition in the Atmosphere****Fatoba Paul Ojo, Ogunkunle Clement Oluseye^{*} and Okewole Grace Abiola***Department of Plant Biology, University of Ilorin, Ilorin, Nigeria.***ABSTRACT**

87 moss samples with the entrapped thin soil particle/dust layers on the substrates were collected from different locations in guinea savanna and tropical rain forest biomes of Southern Nigeria during the dry season of the year 2007. The moss plants sampled were identified and the collected samples (plants and entrapped soil) were digested and analyzed for Pb, Cu, Zn, Fe, Cd and Cr concentrations with Atomic Absorption Spectrophotometric Method so as to assess the bio monitoring potentials of these mosses. The concentrations of the different heavy metals of the entrapped soil particles on the substrates and moss plants were correlated with Carl Pearson's Correlation Coefficient. Identification of the moss plants showed *Barbula lambarenensis*, *Hyophila involuta*, *Thuidium gratum*, *Octoblepharum albidium* and *Calymperes afzelii*. *B. lambarenensis* and *H. involuta* were the most encountered species in the collected samples and they also occurred on the most polluted substrates. The results of the analyzed moss samples showed a range of 0.22– 10.68ug/g for Pb, 2.22– 26.62 ug/g Cu, 9.75– 65.43ug/g Zn, 111.6-961.9ug/g Fe, 0.01-2.70ug/g Cd and 0.00– 1.73 ug/g Cr. Those of the entrapped soil particles gave 0.00–12.21ug/g, 4.87-28.21ug/g, 10.48-74.18ug/g, 126.7-978.2ug/g, 0.01-1.83 ug/g and 0.00-1.07ug/g for Pb, Cu, Zn Fe, Cd and Cr respectively. The correlation coefficient (r) between the entrapped soil particles and moss samples were r = 0.39 for Pb, r =0.85 for Cu, r =0.66 for Zn, r = 0.62 for Fe, r =0.94 for Cd and r =0.73 for Cr. All these r values except that of Pb were high and statistically significant at 5% level of probability suggesting that mosses can be used effectively to monitor the levels of these six heavy metals in the atmosphere.

INTRODUCTION

The biosphere is heavily loaded with different pollutants via the industrial discharges, agricultural practices, combustion, vehicular wears and tears, poor waste management etc. This situation was further worsened by desert encroachment with its attending global warming leading to imbalance ecosystem. Many plants and even animals have been used as bio- monitors but of all, lichens and mosses were found to be the most suitable. For example, epiphytic mosses and lichens have been used by researchers as bio-monitors e.g. Lopp *et al.* (2000); Pandev (1995); Weirsberg (1988) and Verga *et al.* (1993). Verga *et al.* (1993) also reported the use of some higher plants such as *Nicotiana*, *Capsella*, *Poa*, and *Pinus*. Moreover, tilland was identified as a useful bio monitor of air pollution (Bargagi *et al.*, 1993)

The effects of environmental pollutants can be estimated by using bio monitors which can either be bio- indicators or bio- accumulators. The bio-indicators reflect the state of the environment with their occurrence (absence or presence), frequency, abundance, vitality, reactions and responses change under certain environmental conditions (Smith *et al.*, 2000). The bio-accumulators are used in the quantification of the pollutants in question, in time and in space. The use of lichens and mosses have been found suitable, easy and cheap in detecting the possible emission sources of heavy metals or radioactive pollutants (Smith *et al.*, 2000). They further reported that mosses are great bio-accumulators because they have high absorbing and ion exchange capacities such that the concentrations of heavy metals in mosses closely correlated with atmospheric depositions.

Bleuel *et al.* (2005) reported that if a significant change is detected during bio-monitoring, this information will be used as corrective measures that will return the system to the

normal condition where the parameters measured are within their natural range of variability. Since the ultimate goal of environmental pollution is to assess and monitor the state of the whole ecosystem, it is therefore reasonable to identify species of mosses that will be useful in this respect. Evaluation of the concentrations of heavy metals in different species of lichen has been used to establish the levels of contaminations as a result of human activities in Antarctic (Adamson and Seppett, 1990; Bargagi *et al.*, 1993; Kanda and Inoue, 1994; Olechi, 1991; Poblet *et al.*, 1987; Shears, 1995; Upreti and Pandev, 1994; 2000). The Bulgarian Antarctic Program has initiated studies on trace elements in lichens (Chipev and Kovachev, 1996) and mosses (Yurukova and Ganeva, 1999) towards establishing baseline concentration and monitoring.

Heavy metals and other pollutants have serious implications on the ecosystem such as green house effect caused by CH₄ released from combustion and landfill, CO₂ from combustion etc. These pollutants make the air unsafe, cause serious ailments such as cancer, heart problem. It is therefore necessary for the status of these pollutants to be monitored and determined from time to time. A close observation may reveal one or more species as bio-indicator(s) of the environment, which it's or their presence or absence and morphology will indicate serious information about the environment.

This study was designed to assess the environmental pollution status of southern part of Nigeria with the use of mosses and depict the relationship between these plants and their substrates

MATERIALS AND METHODS

87 moss samples with the entrapped soil particles at the base (substrates) were collected from different locations in Ilorin, North-central Nigeria; Adeyemi College of Education, Ondo, South-south Nigeria; Government Secondary School, Ado Ekiti, South-west; International Institute for Tropical Agriculture, Ibadan, South-west Nigeria and Redemption Estate, Mowe, South-west Nigeria. The samples were collected into separate well-labelled envelopes brought to the laboratory for further analyses. The collections were done during the dry season: January and February 2008 so as to exclude the removal of these elements by precipitation, stem flow, erosion or flooding. Moss samples collected were identified using all the diagnostic and morphological features. The substrates were carefully removed from the bases of the plants into separate well-labeled envelopes. These plants and the substrates were subjected to wet digestion method, filtered and put into separate sample bottles. Each filtrate was subjected to Pb, Cd, Cr, Cu, Zn, and Fe analyses with the use of Atomic Absorption Spectrophotometer. Data generated were subjected to Carl Pearson's Correlation Coefficient so as to establish if any, relationship exists between these substrates and the occurring plants with respect to the analyzed heavy metals. This is also to justify the possibility of the usage of these plants as bio-monitors.

RESULTS

Five different moss species: *Barbula lambarenensis*; *Hyophila involuta*; *Thuidium gratum*; *Calymperes afzelii*; *Octoblepharum albidum* were identified in the collected samples. The most occurred mosses are *B.lambarenensis* and *H. involuta*. The different concentrations of the analyzed heavy metals are shown in Figures 1-6. Figure 1 shows the concentrations of Pb in the analyzed moss plants. A range of 0.22-15.5ug/g of Pb was found in the plants analyzed. All the samples that have more than 7ug/g were collected from the drainages and roadsides and were colonized by *Barbula lambarenensis* and *Hyophila involuta*. The substrates gave a range of 0-12.2ug/g of Pb showing that the substrates have lesser concentrations. 0.01-2.70ug/g of Cd was observed in the moss samples (Fig.2) and 0-0.83ug/g in the substrates meaning that the plants and the substrates had less than 3.0ug/g of Cd. Observations have it that samples with high Pb and Cd concentrations were those collected on sandcrete materials around Global Soaps and Detergent Company, Ilorin and these were colonized by *B. lambarenensis* and *H. involuta*. Cr concentrations in the collected moss samples were less than 2ug/g and ranged between 0 and 1.73ug/g (Figure 3) whereas the substrates ranged between 0 and 1.07ug/g

The concentration of Zn in the moss plants is shown in Figure 4. A range of 9.75-65.43ug/g of Zn was observed in the sampled mosses while the substrates have a range of 10.48 -74.18ug/g. The Zn contents of the substrates tend to be higher than those of the mosses. Moreover, Figure 5 shows the Cu contents of the sampled moss plants. 2.22-26.62ug/g and 4.87-28.21ug/g was observed in the mosses and samples respectively. However, these samples have less than 30ug/g Cu. A range of 111.6-964.9ug/g of Fe was

encountered in the analyzed plants while the substrates have 126.7-978.2ug/g. Cr<Cd<Pb<.Cu<Zn<Fe trend was observed in both the plants and substrate. Comparative study of the heavy metal contents of the substrates and the moss plants showed that the concentrations of Pb, Cd and Cr were higher in the plants than the substrates but the reverse were for those of Zn, Cu and Fe. The correlation coefficient (r) of the concentrations in mosses and substrates gave Pb(0.39), Cd(0.94), Cr(0.73), Cu(0.85), Zn(0.66) and Fe(0.62). All except Pb had high correlation coefficients of more than 0.60.

DISCUSSION

The occurrence of moss plants on any substrate depends on the pH; nutrient content, physical nature, and moisture content of the substrates. Some of these plants are phorophyte specific. Although, these plants are rootless but equipped with some survival strategies that enable them to cope in their environments. Gradzinski (1990) identified three types of bio indicators: true indicator (pollutants damage the plants proportionally to their concentrations), scales of indicator species (appear or disappear in respect of the pollutants) and accumulator (accumulates potentially toxic pollutants). Mosses have an advantage of being the least sensitive to the major pollutants (Bates, 2000;2002). However, Sergio (1987) indicted SO₂ and heavy metals in the disappearance and changes in the flora around urban and industrial areas.

Heavy metals reduce chlorophylls a and b concentrations, inhibit photosynthesis temporarily; increase respiration and cause substantial intracellular loss of potassium from *Rhytidiadelphus squarrosus* (Neolith and Chemical Ltd, 1988). Fatoba and Udoh (2008) found that heavy metals reduce chlorophyll a, b and total chlorophyll contents in mosses. Herpin *et al.*(1996) reported that Cd and Cr have harmful effects and toxicity on organisms. Gupta and Devi (1994) reported that increasing Cd concentration led to inhibition of 1st and 2nd generation spores, abnormal protonemal development and abnormal sporangia in *Pteris vittata*. Couto *et al* (2004) reported that certain bryophytes do well in highly polluted areas than less polluted and some are associated with high pollution sites than others. Metals such as Pb, Cd, and Cr that accumulated in the mosses than the substrates are those that are challenging to the plants (Cuoto *et al.*, 2004). Others that are more in the substrates than the plants are essential elements that are naturally present in the soil even though at higher concentration that can be damaging to the plants. Although, mosses are exposed to different concentrations of these heavy metals but, without much pronounced or negative effects. This is in agreement with the observation of Kakulu (1993) who confirmed that mosses are tolerant to heavy metals. This tolerance was attributed to the ability of these plants to accumulate toxic elements (Brown,1984; Kovacs *et al.*,1993; Rao,1982).The tolerance can be attributed to their metal uptake mechanism extracellularly and ion exchange capacities (Richardson,1981). Bleuel *et al.* (2005) found that tillands were able to intercept air particles and to accumulate them on their leaf surfaces.

Heavy metal concentration varied greatly in moss samples, depending on environmental impact (Chipev, 2006; Herpin *et al.*, 1996). Poblet *et al.* (1997) reported that the concentrations of Cd, Cr, Cu, Fe, Ni, Pb, V and Zn found in mosses varied greatly with the air quality. The following ranges of heavy metals per dry weight: Cd (0.25-2.75ug/g); Cr(0.7.33ug/g); Cu(3.824.3ug/g); Fe(2406761ug/g); Ni(0.9719.86ug/g); Pb(5.337.9ug/g); V(0.70-46.69ug/g); Zn(22.6-94.0ug/g) (Gjengedal *et al.*,1990; Oleehi *et al.*,1998; Poblet *et al.*,1997). Although, the result obtained in this study compared favourably with the results of these researchers but the values reported in this study tend to be lower. The low values may be attributed to low industrial activities in these areas. The high values of Cd, Cr, Fe, Ni, and Zn encountered in Szazhalombatta were due to its oil refinery and oil fuelled power station and in Danaujvaries because of its steel industry (Gjengedal *et al.*, 1990). Some of the enriched elements in mosses may originate from natural sources such as re suspension of soil and road dust (K, Ca), leaching from living or dead plants tissues (Mg, Zn) and partly from anthropogenic sources (Vargha, 1988). Vargha (1988) identified Br, Sb, As, Mo, and Zn as indicators of fossil fuel combustion processes including vehicle exhausts. This may also be responsible for the Zn concentration found in this study. Heavy metal levels are differently connected with emission from industrial centres for example, high Cd, Cr, Fe, Ni and Zn could be due to oil refinery and oil-fuelled power station or steel industry (Gjengedal *et al.*, 1990; Leetham, 1982).The different concentrations of the heavy metals investigated in this study may also be hinged on these reasons.

The use of Pb as antiknock additives in gasoline in many parts of the world, have resulted to its release from vehicular exhaust and contaminates the roadside environment (Smith, 1976). Pb-containing particulates often settle onto roadside vegetation by sedimentation, impaction and interception resulting in high Pb content in the vegetation (Ho and Tai,1985) .Moreover, Mn ,Cu, Fe ,Zn, and Cd are also contaminants of the roadsides (Ward *et al.*,1977; Kovacs *et al.*,1982). Lagerwerff and Specht (1990) reported that these metals are released into roadsides through the wears and tears of vehicles.Cd mainly spread to the environment through the use of phosphate fertilizers and emissions from metal industry (Herpin *et al.*, 1996).They reported that the Cd content of mosses in Europe was less than 0.3ug/g in unpolluted areas. An average of 1ug/gCd was reported for roadside soil (Ho and Tai, 1988) while Lagerwerff and Specht (1970) and Ho and Tai (1985) found the Cd in roadsides being generally low. Therefore some of the areas under study are relatively polluted.

The main source of Cr is iron and steel mills and the baseline level of Cr was lower than 1ug/g in unpolluted region (Herpin *et al.*, 1996).The areas under study may be assumed Cr unpolluted considering the lower concentration resulting from the absence of the major sources of Cr. Ho and Tai (1988) reported that Zinc is normally present in uncontaminated plants up to approximately 100ug/g and they reported 43-276ug/g Zn in roadside grasses in Hongkong. With this, the study areas may be considered

unpolluted as the concentration encountered in this study was less than 100ug/g.Ho and Tai (1988) reported that local soil in Hongkong has a baseline level of 5 to 10ug/g Cu. Ward *et al.* (1977) reported a range of 16-31ug/g Cu for 5 species of grass used in monitoring interchange in Auckland, New Zealand. The Cu concentration found in this study agreed favourably with the findings of Ward *et al.* (1977). Ho and Tai (1988) reported high concentration of Fe in both the soil and the grass samples. However, Hopke *et al.* (1980) found high levels of Fe in the grass samples which they attributed to considerable amount of dust particles deposited on the plant surface and roadside dust. Leetham *et al.* (1982) reported that the Fe content in mosses collected from unpolluted areas is generally lower than 500ug/g. It is therefore logical to say that some of the study areas are polluted.

The use of Pearson Correlation Coefficient between pollutants and monitors has been used to assess the potential of tillands as biomonitor by Trapp *et al.* (1990). Chipev and Kovachev (2006) found that the heavy metal concentrations of *Brachythecium* spp and *Eurhynchium* spp in Belgrade positively correlated with the local topsoil samples. In the same way, results of this study agreed favourably with this finding. The concentration of heavy metals encountered in this study may be attributed to anthropogenic impact through vehicular traffic, industrial and combustion. A possible relationship exist between the concentration of metals (Cd, Cr, Cu, Fe, Ni, Pb, V, Zn) measured in mosses and those of Tardigrade species detected in the same samples (Meininger and Spatt, 1997). Lau and Luk (2001) reported a good correlation between air quality in Hongkong and leaves of *Bauhinia*.

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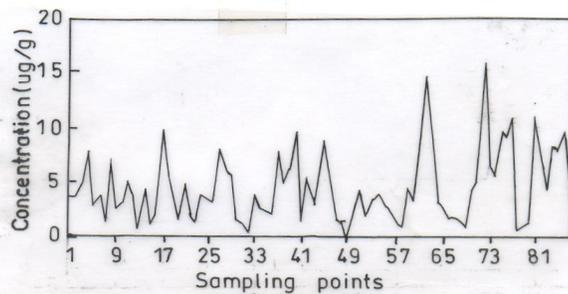


Fig.1 The concentration of Lead(ug/g) in moss samples

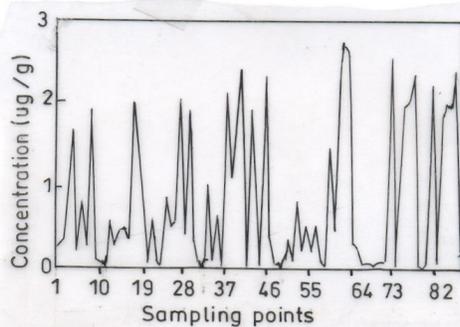


Fig 2 The concentration of Cadmium(ug/g) in moss samples.

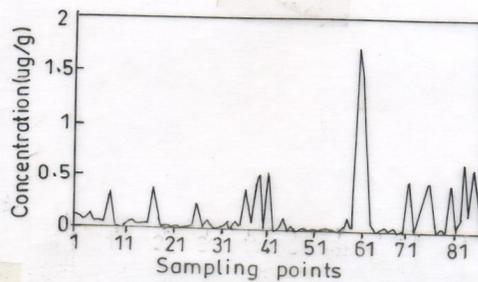


Fig. 3 The concentration of Chromium (ug/g) in moss samples

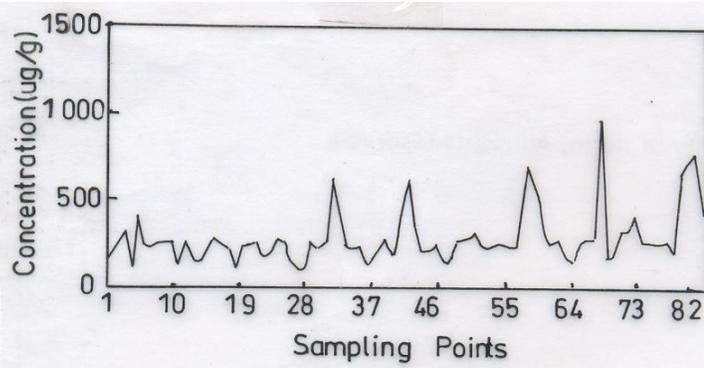


Fig. 4 The concentration of Iron (ug/g) in moss samples

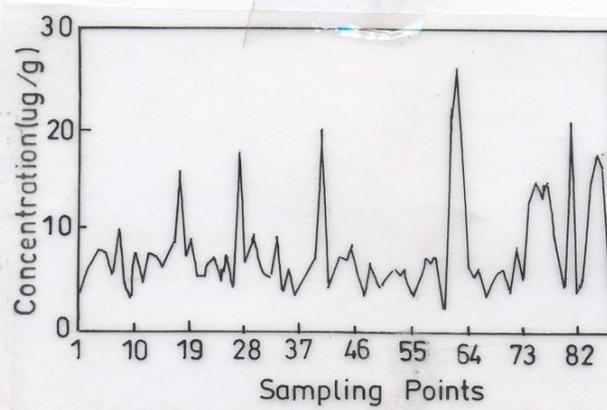


Fig. 5 The concentration of Copper (ug/g) in moss samples

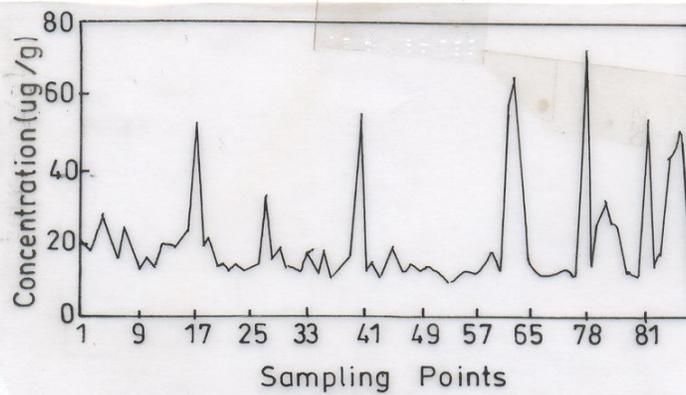


Fig. 6 The concentration of Zinc (ug/g) in moss samples

