ASSESSMENT OF MOSS PLANTS AS BIO-MONITORS OF AIRBORNE HEAVY METALS IN SELECTED TOWNS OF NORTHWESTERN NIGERIA

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Abstract: Significant contribution of air pollution to the diminished health status of the exposed human populations has become a matter of global concern. This work was designed to study the use of moss species as bio-monitors of airborne heavy metals in some towns of northwestern Nigeria (Birnin gwari, Zaria, Kano and Ringim). Moss sampling was carried out during the dry and wet seasons from various substrates. Heavy metal content of Cobalt (Co), Nickel (Ni), Copper (Cu), Cadmium (Cd), Lead (Pb), Chromium (Cr) and Zinc (Zn) in the samples were determined using Fast Sequential Atomic Absorption Spectrometer (Varian AAS 240FS). Results show that Kano had the highest mean concentrations of 4 of the 7 heavy metals analyzed; these were Cu (68.65 ppm), Cd (2.56 ppm), Cr (96.75 ppm) and Pb (67.39 ppm). Kano had the highest concentrations of almost all the major pollutants, while Ringim had the least of the majority of metals. Ni, Cu, Cd, Cr and Co showed relatively higher accumulation values in the wet season than the dry season, while Pb and Zn had higher values in the dry season but this was statistically not significant in any case. The study has shown that *Bryum coronatum, Fissidens grandifolius* and *Hyophila crenulata* are bioindicators/biomonitors of heavy metals in the studied locations with *B. coronatum* as the most effective, having highest metal accumulation capacity.

Keywords: Bioaccumulation, biomonitoring, bryophytes, heavy metals, Northwestern, Nigeria

Introduction

Air pollution has become a matter of global concern, particularly in developing countries, mainly due to various anthropogenic activities (Zechmeister *et al.*, 2003). This contribute to the diminished health status of the exposed human populations, forest decline, loss of agricultural productivity, etc. and has been a cause of increasing public concern throughout the world (Smodis, 2003; Bako *et al.*, 2008). The quick development of industry, motor transport and urbanization caused a dramatic increase in dust emissions containing heavy metals. As ecologists focused their attention on threats posed by heavy metals and other atmospheric pollutants to the biotic and abiotic environment, the search for sensitive and cheap biological methods for assessing the environmental level of heavy metals, most especially the toxic ones like Cd, Pb and Hg became intensified (Zechmeister *et al.*, 2003).

The suitability of bryophytes for the indication and monitoring of atmospheric heavy metal deposition is based on their accumulation of the metals. This depends on their morphological and physiological properties (Pyatt *et al.*, 1999). They possess rhizoids in place of real roots so that they cannot take enough nutrients from the soil; nutrient uptake from the atmosphere is promoted by weakly developed cuticle and one-cell-thick leaves; large surface to weight ratio improves absorption; slow growth rate, enables them to accumulate pollutants over time; perenniality; wide distribution and ease of sampling are other attributes (Zechmeister *et al.*, 2003; Chakrabortty and Paratkar, 2006). It is possible to make deductions as to the presence of various air pollutants and their levels on the basis of the occurrence and chemical constitution of epiphytic plants such as lichens and bryophytes (Pyatt *et al*., 1999; IAEA, 2000; IAEA, 2003).

Apart from the monitoring of emissions from local hot spots such as the vicinities of industrial complexes, mines and highways (Onianwa and Ajayi, 1987; Fatoba and Oduekun, 2004; Dymitrova, 2009; Ekpo *et al*., 2012), mosses have also been used for extensive regional surveys in various parts of the world (IAEA, 2000; Chen *et al*., 2010; Ekpo *et al*., 2012). This technique has proved rapid and reliable in identifying metal emission and deposition gradients over vast areas. Mosses are abundant in Nigeria and an earlier survey by Onianwa and Egunyomi (1983) has shown the local species to be suitable for biomonitoring atmospheric heavy metal pollution. Onianwa and Ajayi (1987) have surveyed the southwest region of Nigeria using various species of mosses collected from forest sites and inhabited sites in the region. Other studies in the use of mosses as environmental biomonitors in parts of Nigeria have been reported (Kakulu, 1993; Fatoba and Oduekun, 2004; Bako *et al*., 2008; Adebiyi and Oyedeji, 2012; Ekpo *et al*., 2012).

However, use of biomonitors in monitoring environmental quality in the West African region is limited (Bako *et al.*, 2008). In northwestern region of Nigeria, it is suspected that the buildup of air pollutants may be anticipated as a result of obvious polluting sources such as agricultural practices, urbanization, rapid industrialization and the resulting heavy traffic. However, quantitative documentation of this over extended areas of the region has not been done. This study was therefore is designed to evaluate the suitability of naturally occurring moss species in monitoring of heavy metal disposal and accumulation pattern in some parts of northwestern Nigeria.

Materials and Methods

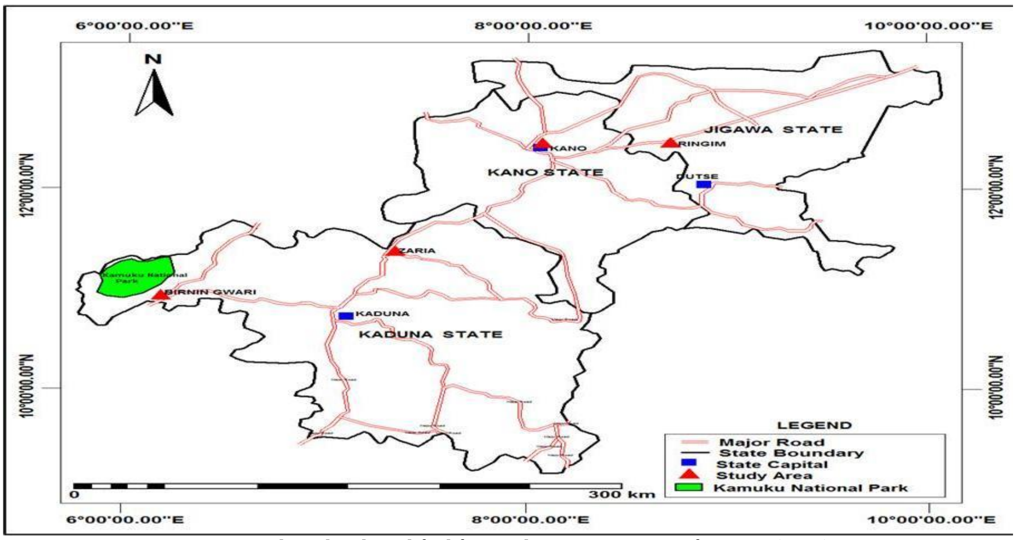
Selection of study sites

Sites selected in each location/area were located at least 300 meters from main roads, densely populated areas and other direct source of pollutants. This was to assist in the collection of samples in the areas suspected to be of low deposition of all the pollutants, and also to avoid collection of samples from areas of pollution sources. Wherever possible, the site selection for this study took into consideration the reproducibility of results and other environmental factors such as accessibility, availability of open spaces, and of course areas with minimal local influence from traffic as well as other anthropogenic activities.

Location and description of study areas

The study areas as shown in Fig. 1 are Kano, Zaria, Ringim and Birnin Gwari all in northwestern region of Nigeria. Kano is located at 12˚ 00′ 00.00″ N and 8˚ 31′ 00.00″ E. It has a substantial number of industries, with commercial activities, heavy traffic density, densely populated and highly urbanized. Zaria located at 11˚ 04′ 54.91″ N and 7˚ 42′ 57.44″ E is less industrialized, but with heavy traffic density, densely populated and highly urbanized.

Ringim (12˚ 08′ 50.14˝ N and 9˚ 10′ 09.27˝ E) is more of a rural setting and not industrialized, with moderate traffic density, moderately populated and urbanized. The Kamuku National Park in Birnin Gwari on the other hand is relatively "pollution free" with very little human activities and is located at 10˚ 40′ 00.00˝ N and 6˚ 32′ 00.00˝ E.



Source: Adapted and Modified from Administrative Map of Nigeria (2015)

Fig. 1: Location of the study areas

Sampling of Moss species

Moss sampling was carried out randomly during the dry and wet seasons. Specifically samples were collected monthly in three months of dry season and in three months of wet season. For each month, moss samples were collected from at least six sites with six replicates of each species, in each location selected. The moss species were collected from 2 to 2.5 m high from the ground on trees, cemented and un-cemented walls, and such structures within the sampling area. The samples were placed in small brown envelopes and labeled accordingly with field notes. They were then taken to the Herbarium unit, Department of Botany, University of Ibadan – Nigeria for proper identification.

Preparation of samples

The method of Shakya *et al.* (2001) was used. Foreign materials adhering to the surface of the moss samples were removed carefully by shaking the plant materials with hand under dry conditions. Only the green and greenish brown parts of the plants were left for analysis since they were generally intended to represent a period of about 3-5 years. Their metal content is considered to reflect the atmospheric deposition during that period (Ruhling and Steinnes, 1998). The samples were first thoroughly washed with double-distilled water 3 times. They were then dried at 60℃ in an oven for 48 hours after which they were ground in a porcelain mortar to obtain fine particles and stored in polythene bags ready for analyses. The mortar was carefully cleaned and cleared of all possible trace of previous sample before the next to avoid contamination.

Determination of heavy metals

Each representative sample (0.5 g) was transferred into an open quartz tube for digestion, with three replications in each case. Concentrated 5ml HNO_3 and HCl were added to each tube in the ratio 3:1 and the mixture heated at 160°C for about 2 h. The solution was allowed to cool and then filtered through Whatman type 589/2 filter paper and the volume of the filtrate was diluted to 100 ml with deionized water. The metal contents in the filtrates (Co, Ni, Cu, Cd, Pb, Cr, and Zn) were determined using Fast Sequential Atomic Absorption Spectrometer (Varian AAS 240FS) (Sawidis *et al*., 1993; Chettri, 1997).

Data analysis

Mean levels of the pollutants at the period of sampling for all locations and for all moss species were calculated. ANOVA was used to test for differences in individual concentrations in each species found and in the different locations. Duncan's Multiple Range Test (DMRT) was used to separate the means where they were significantly different. T-test was used to determine seasonal variability of mean levels of pollutants in moss species.

Results and Discussion

Mean levels of heavy metal concentrations in different Moss species in parts of northwestern Nigeria

The mean heavy metal concentrations in different moss species are summarized in Table 1. There is a significant difference in the uptake and accumulation of all the metals by different moss species ($p < 0.05$), and most of the species in turn showed preference for certain heavy metals. *Bryum coronatum* had the highest concentrations of four (4) of the seven (7) analyzed metals. These were Cu (57.95±38.03 ppm), Pb (99.88±32.19 ppm), Cr (52.88±46.94 ppm), and Zn (559.44±389.03); *Fissidens grandifolius* had the highest concentrations of Ni (31.86±3.13 ppm) and Co (18.24±3.40 ppm) while *Fabronia pilifera* had the highest concentration of Cd (1.58±1.12 ppm). *Hyophila crenulata* had the second highest concentrations of Cu, Pb, Cr and Co. There was no accumulation of Cr and Co recorded in *Fabronia pilifera*. Zn concentration was higher than other heavy metals in all the species while Cd had the least concentration in all. In general, the trend of accumulation in the moss species was in the following order: Zn > Pb, Cr, Cu > Ni > Co > Cd. Comparison of individual metal concentrations of different moss plants at different locations were given in Figs. 2 – 8 to give an overview of best moss species for each heavy metal in each location.

Table 1: Mean levels of heavy metal concentrations (ppm) in different moss species in parts of northwestern Nigeria

Moss species	Heavy metals						
	Ni	Cu	Cd	Pb	Cr	Zn	Co
H. crenulata	9.59±0.56[bc]	36.13±10.59[b]	0.9±0.51[b]	30.97±14.49[b]	40.73±15.40[b]	122.19±42.89[c]	4.34±1.46[b]
B. lambarenensis	10.36±1.18[b]	17.2±7.69[c]	0.17±0.10[d]	30.14±8.77[b]	25.89±10.26[c]	95.83±47.31[cd]	3.56±0.49[b]
B. coronatum	10.86±0.35[b]	57.95±38.03[a]	1.52±1.32[a]	99.88±32.19[a]	52.88±46.94[a]	559.44±389.03[a]	4.43±2.21[b]
S. subjulaceum	9.91±0.79[bc]	16.4±0.84[c]	0.29±0.25[d]	26.3±5.28[c]	27.3±2.07[c]	119.94±56.79[c]	2.33±2.01[c]
B. leptophyllum	11.68±2.30[b]	16.54±1.15[c]	0.8±0.21[b]	24.56±3.35[c]	11.71±1.52[e]	71.06±5.16[d]	2.12±0.21[c]
E. pobeguinii	8.7±1.04[c]	17.19±0.54[c]	0.85±0.20[b]	28.45±3.19[b]	20.39±6.04[d]	64.2±11.43[d]	3.72±0.78[b]
F. pilifera	7.56±0.76[c]	13.61±1.31[d]	1.58±1.12[a]	25.41±3.42[c]	0±0.00	163.13±20.55[b]	0±0.00
F. grandifolius	31.86±3.13[a]	7.47±0.16[e]	0.54±0.07[c]	12.5±2.11[d]	4.15±0.55[f]	16.86±3.02[e]	18.24±3.40[a]

Means followed by the same superscripts along the columns are not significantly different (p≥0.05); Ni=Nickel, Cu=Copper, Cd=Cadmium, Pb=Lead, Cr=Chromium, Zn=Zinc, Co=Cobalt

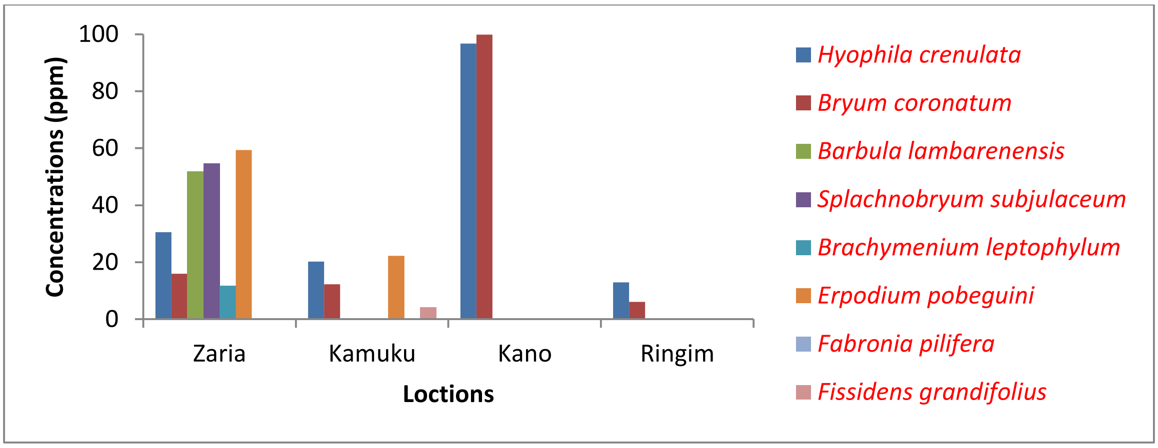


Fig. 2: Accumulation of Cr by different moss species at different locations of northwestern Nigeria

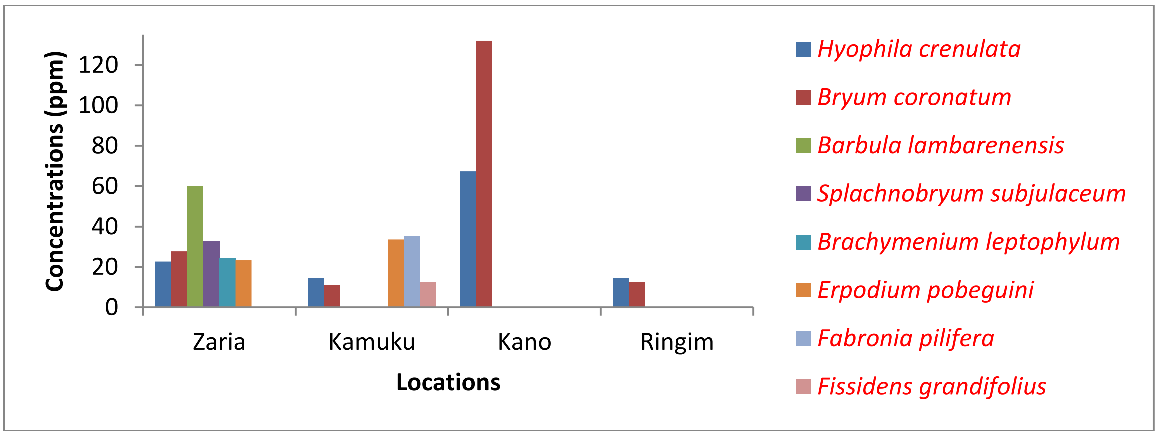


Fig. 3: Accumulation of Pb by different moss species at different locations of northwestern Nigeria

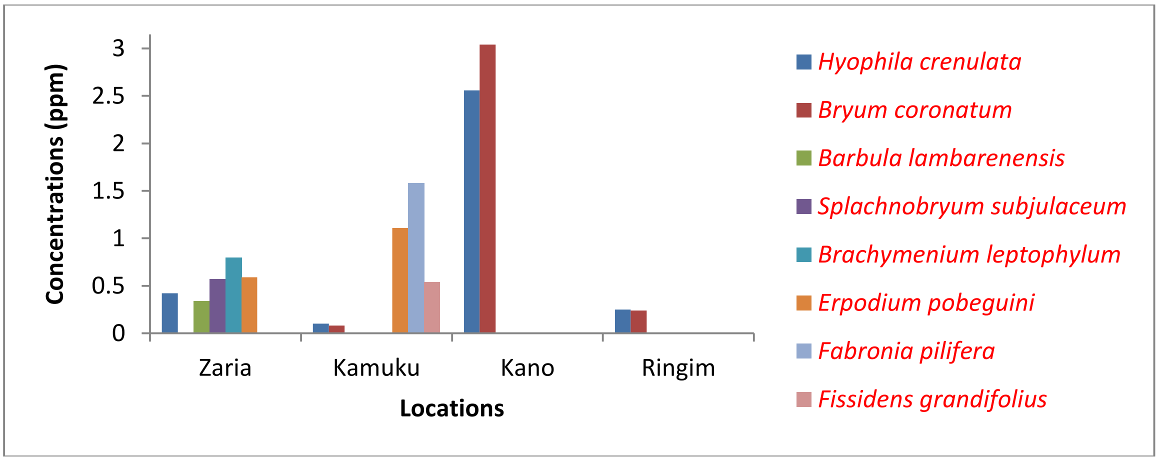


Fig. 4: Accumulation of Cd by different moss species at different locations of northwestern Nigeria

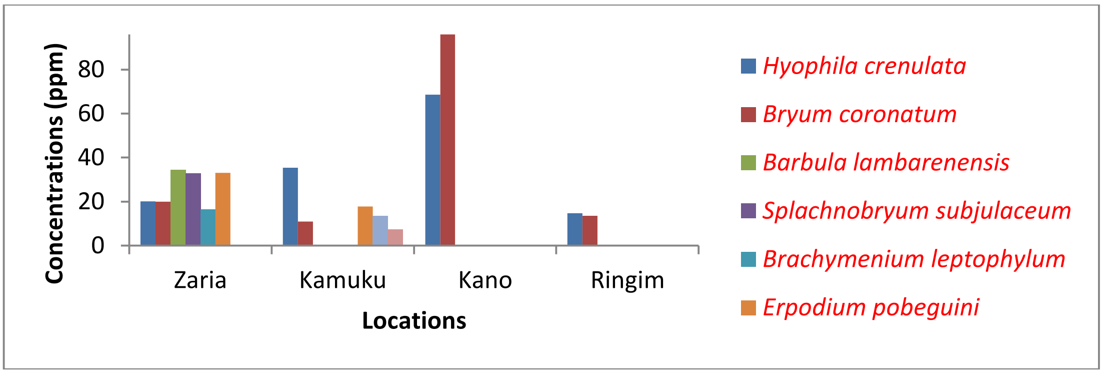


Fig. 5: Accumulation of Cu by different moss species at different locations of northwestern Nigeria

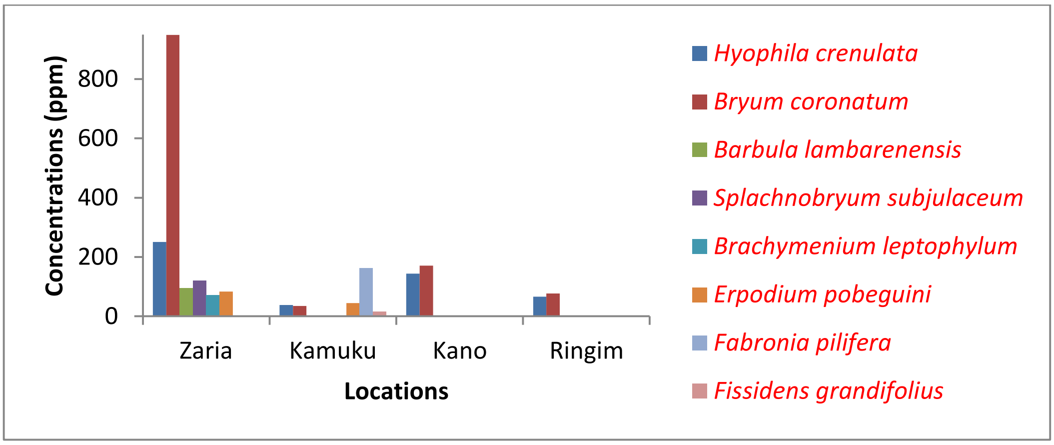


Fig. 6: Accumulation of Zn by different moss species at different locations of northwestern Nigeria

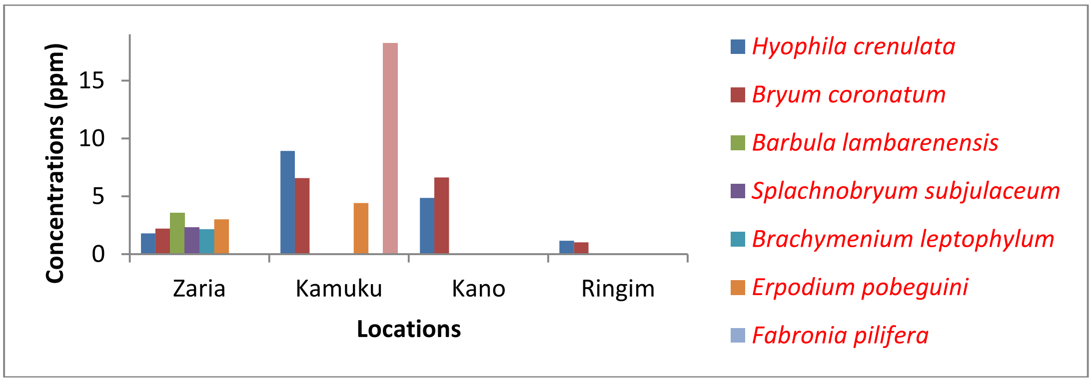


Fig. 7: Accumulation of Co by different moss species at different locations of northwestern Nigeria

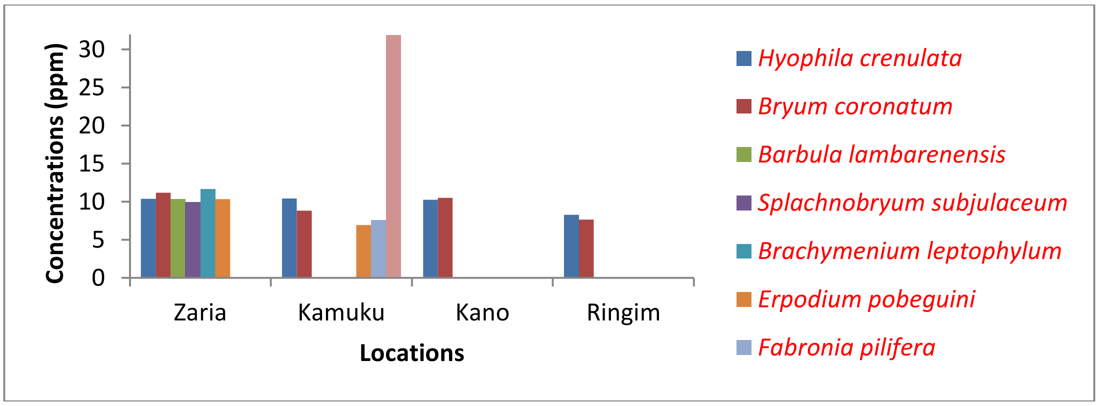


Fig. 8: Accumulation of Ni by different moss species at different locations of northwestern Nigeria

Variations in the level of accumulation of individual metals in moss species could be as a result of differences in their morphological and physiological characteristics and growth habit. Interspecies comparison of specific heavy metal contents by Chen *et al*. (2010) indicated that the biological characters such as living form and morpha had a great influence on accumulative capacity even if collected from the same biotope. Most moss species had different accumulation capacity even for the same heavy metal element. It could also be a function of the differential ion exchange potentials of the species, with particular reference to the cation exchange capacity and formation of chelates by the metals (Crist *et al*., 1996; Zechmeister *et al*., 2003; Chakrabortty and Paratkar, 2006). The high bioaccumulation of heavy metals by *Bryum coronatum, Hyophila cenulata,* and *Fissidens gandifolius* may be due to their morphology and growth form, in that their leaves are compactly arranged, growing in tufts, which must have facilitated them to trap different suspended particulate matter. The dense canopy of mosses acts as an efficient filter in trapping airborne particles and ultimately higher element concentrations (Herpin *et al*., 2001). The moss species studied in this work were washed to ensure that only the metal content accumulated in them is measured. Markert *et al*. (1996) listed some moss species such as *Bryum radiculosum, Aloina aloides, Tortella flavovirens, Scleropodium purum* and *Polytrichum formosum* selected for biomonitoring of atmospheric pollution in the Czech and Slovak Republics; and the genus *Bryum* was also found to be good in this study. There was no apparent accumulation of Cr and Co in *Fabronia pilifera* in our study. It may be that the species had low affinity to these metals. The variation in the accumulation pattern of the heavy metals among the different species might be due to the differences in binding affinity of the metals to the moss species (Rasmussen, 1978). It might thus result in different affinities of mosses for different heavy metals even within the same genus due to the varying cell wall contents. One can also predict the suitable moss species that may be used as a biomonitor for a single trace element, or a group of trace elements. It is very difficult for any other approach to obtain such a detailed picture of variations in time and space at a reasonable cost (Chakrabortty and Paratkar, 2006). The reason for lowest concentration of Cd in all cases might be that it is a trace element (Chen *et al*., 2010). In general, the trend of accumulation in the moss species was in the following order: Zn > Pb, Cr, Cu > Ni > Co > Cd which is in agreement with the findings of Chen *et al*. (2010).

Mean levels of heavy metal concentrations in different locations of northwestern Nigeria

A summary of the mean levels of seven (7) heavy metal concentrations in all locations is given in Table 2. The concentrations of all the heavy metals varied significantly ($p < 0.05$) both within and among the study locations. Species found across all locations were used for comparison among the various locations. Kano had the highest mean concentrations of 4 of the 7 heavy metals analyzed. These were Cu (68.65±5.3 ppm), Cd (2.56±1.26 ppm), Cr (96.75±20.28 ppm) and Pb (67.39±50.06 ppm); Zaria had the highest concentration of Zn (250.47±107.34 ppm) while Kamuku had the highest of Co (8.91±2.33). From the concentrations, it was clear that Kano was more contaminated with almost all the heavy metals investigated, followed by Zaria and then there was less contamination in Kamuku and Ringim. In general, the mean concentration of Zn was highest and that of Cd was the lowest in all locations. The overall pattern of abundance of each metal and in each location was in the following order: Zn > Cr, Cu, Pb > Ni > Co > Cd.

Higher concentrations of the various pollutants in Kano may be as a result of substantial number of industries compared to other locations, heavy traffic and more human activities as it is one of the most populous cities in Nigeria. It is the center of commercial activities in the country. High mean values of the metals in the area may be due to the high emission of these metals in the air. Shakya *et al*. (2001) carried out a study on the appraisal of some mosses for biomonitoring airborne heavy metals in Kathmandu Valley situated in the middle part of the Himalayan range. They indicated the most severely contaminated sites with Cd, Cr and Pb to be the areas with high vehicular movement and high population density. This is also in agreement with the work of Chen *et al*. (2010) who compared heavy metal accumulation capacity of some indigenous mosses in Southwest China (a case study of Chengdu city). Their conclusion was that atmospheric pollution of heavy metals in Wangjiang Park was relatively more serious than that of Ta Zishan Park and Cultural Park, which may be result of steel industry, heavy traffic and more human activities near Wangjiang Park. The amount of heavy metals originating from natural sources in the atmosphere is small as compared with the anthropogenic flux of these elements (Zechmeister *et al*., 2003). The elevated concentration of Zn in Zaria may be attributed to the presence of large crop fields and agricultural activities where spraying is usually undertaken, especially around PZ area almost throughout, sometimes by irrigation, which agrees with the work of Shakya *et al.* (2001) who observed high mean value of Zn outside the ring road in southeastern part of Kathmandu Valley and related that to the agricultural activities around the Valley. Even though Kamuku had relatively less anthropogenic activity, Co concentration was somewhat high which is probably due to its proximity to the only highway that links the northern and southern part of the country, always with large vehicles conveying goods and passengers. This is comparable to the work of Shakya *et al.* (2001) who showed high vehicular movement to be one of the reasons of high metal contamination in some sites in Kathmandu valley.

Table 2: Mean levels of heavy metal concentrations (ppm) in different locations of northwestern Nigeria

Heavy metals	Locations: Zaria	Kamuku	Kano	Ringim
Ni	10.38±1.17[a]	10.45±1.63[a]	10.25±0.79[a]	8.29±0.62[b]
Cu	20.09±4.8[c]	35.38±24.41[b]	68.65±5.3[a]	14.77±1.23[d]
Cd	0.42±0.08[b]	0.10±0.02[c]	2.56±1.26[a]	0.25±0.01[bc]
Pb	22.70±1.29[b]	14.59±3.69[c]	67.39±50.06[a]	14.44±1.84[c]
Cr	30.59±5.55[b]	20.2±7.99[c]	96.75±20.28[a]	12.99±6.92[d]
Zn	250.47±107.34[a]	38.41±3.75[d]	144.38±8.5[b]	66±11.17[c]
Co	1.78±1.29[c]	8.91±2.33[a]	4.87±0.83[b]	1.16±0.14[c]

Means followed by the same superscripts along the rows are not significantly different ($p \geq 0.05$)

Table 3: Seasonal variation in the mean level of metal concentrations (ppm) in parts of northwestern Nigeria

Heavy Metals	Dry	Wet	P value	Remark
Nickel (Ni)	9.09±2.45	12.39±2.00	0.32	NS
Copper (Cu)	22.69±3.50	38.85±4.56	0.41	NS
Cadmium (Cd)	1.02±0.20	1.08±0.33	0.93	NS
Lead (Pb)	39.09±7.62	34.49±3.43	0.84	NS
Chromium (Cr)	28.08±6.55	36.59±3.22	0.72	NS
Zinc (Zn)	112.89±10.12	91.62±4.66	0.72	NS
Cobalt (Co)	3.68±1.20	6.58±1.56	0.33	NS

NS=Not Significant ($p \geq 0.05$)

Seasonal variation in the levels of heavy metal concentrations in different locations of northwestern Nigeria

Table 3 shows the seasonal variation in the mean levels of metal concentrations. Ni, Cu, Cd, Cr and Co showed relatively higher accumulation values in the wet season than the dry season, while Pb and Zn had higher values in the dry season but this was statistically not significant in any case with $p > 0.05$.

Bryophytes possess a number of characteristics that make them suitable for use as biomonitors of air pollutants. They are usually very long lived and their morphology does not vary with season (Chakrabortty and Paratkar, 2006). Ni, Cu, Cd, Cr and Co showed relatively higher accumulation values in the wet season than in the dry season, while Pb and Zn had higher values in the dry season but these were not statistically significant in any case. This could be a result of the moss plants accumulating the pollutants continuously for a somewhat long period, and rain not likely to be wash what is already in them. In a study carried out in Galicia (Northwest Spain) using moss for biomonitoring metal deposition by Fernandez and Carballeira (2002), no significant differences were found in the concentrations of all the elements studied among the seasons, which agreed with the present findings. The results are also in agreement with the work of Onianwa *et al*. (1986) on the accumulation pattern of heavy metals in forest mosses from the southwestern region of Nigeria who reported that comparison of data on wind and wet precipitation for parts of the region with the metal accumulation gradients did not show any correlation. However, it contradicts the findings of Ekpo *et al*. (2012) whose results showed the mean levels of trace metals to be higher in the wet season than in the dry season.

Conclusions

Heavy metals (Co, Ni, Cu, Cd, Pb, Cr, and Zn) were present in the environments of all the study locations, at the time of sampling. There was significant variation in the concentrations of all the pollutants both within and among locations and moss species. Kano had the highest concentrations of almost all the major pollutants, while Ringim had the least of the majority of the pollutants. Hence, the study has shown that *Bryum coronatum*, *Fissidens grandifolius* and *Hyophila crenulata* are bioindicators/biomonitors of heavy metals in the studied locations with *B. coronatum* as the most effective.

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