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Trace Lead, Zinc and Copper Levels in *Barbula lambarenensis* as a Monitor of Local Atmospheric Pollution in Ile-Ife, Nigeria

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Abstract: Moss samples *Barbula lambarenensis* (P. Vard) were taken along major and minor roads of Ile-Ife, in the South Western part of Nigeria and were analysed after triple acid digestion for the trace metals: Lead, Zinc and Copper by Graphite Furnace Atomic Absorption spectrophotometry. The triplicate field data were averaged to yield mean concentrations at each sample location. The lead and zinc levels ranged from 196.8 (0.04)-108.5 (0.03) μg g^{-1} and from 593.1 (0.02)-35.0 (0.10) μg g^{-1} dry weight, respectively in the moss samples. These results from the analysis of the moss samples show that Pb and Zn levels were generally higher in areas with relatively high traffic density than low traffic density areas. Similar studies on Copper gave lower values (47.0 (0.01)-10.1 (0.01) μg Cu g^{-1}) dry weight in the samples which did not show any correlation with traffic density. Analysis of standard plant reference materials (BCR: CRM 062) gave results Pb 26.7 (0.10); Zn 17.4 (0.46) and Cu 45.8 (0.40) which are found to be in good agreement with the certified values for Pb 25.0 (1.5); Zn 16.0 (0.7) and Cu 46.6 (1.8). The average traffic volumes of the study area are 990 vehicles per hour and 520 vehicles per hour for high and low traffic density areas, respectively.

Key words: Trace metals, traffic density, Ile-Ife, *Barbula lambarenensis*

INTRODUCTION

Pollution of vegetation by metallic elements has been a subject of active investigation over the years. Lower plants, especially mosses and Lichens, are often used as indicators of atmospheric pollution[1-3]. It has been shown that vegetation is an important sink for atmospheric pollutants and its use in atmospheric pollution monitoring has been found to be simple and cheap[4]. As a result, many biological materials such as tree leaves, tree barks and tree rings have been used as bioindicators of atmospheric heavy metal pollution[5-8]. The measured levels of metals in these materials serve as index of the extent of pollution and as a basis for which explanations for many ecological phenomena can be formulated.

Motor vehicles introduce a number of toxic metals into the atmosphere which are later deposited on roadsides[9-11]. For example, lead emission from motor vehicles produces high concentrations of lead in road side dust[12] and vegetation adjacent to roadsides[13-15]. The release of lead from vehicle exhaust has been established and attributed to the addition of lead alkyl as an antiknock additive to gasoline to increase its octane number[16]. The implication of this is that high levels of lead and other heavy metals are emitted to the atmosphere along motor ways. This may lead to serious health consequences like impairment of circulatory, reproductive and nervous systems as well as kidney problems, more so that a large number of the populace in Nigeria are susceptible to traffic pollution problems because their daily activities bring them near the roadside. In this regards, school children, traffic warders, livestock and street hawkers are most directly susceptible[16-18]. Furthermore, Zinc is emitted into the environment as a result of wear from tires of automobiles and motor vehicles emission due to Zinc-containing additives in lubricating oils. Copper on the other hand is an essential component of motor vehicle parts such as break linings. It is also emitted into the environment as a result of wear and tear[6,7].

Present study reported the levels of Lead, Zinc and Copper in *Barbula lambarenensis* taken close to some major and minor roads of Ile-Ife town, Nigeria using Graphite Furnace Atomic absorption spectrophotometry. *Barbula lambarenensis* is found widely grown naturally on different kinds of substrate e.g. concrete wall, ground surfaces etc. of Ile-Ife. The moss samples analysed serve as indicators of trace metals concentrations in the environment of this ancient city, for which no such previous data have been reported. This plant was considered in this study for aerial deposition of metals because of their large area cation-exchange properties and

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the fact that they derive their water and nutrients almost exclusively from air. They usually form an extensively dense green patch or a soft velvet-like carpet[19].

MATERIALS AND METHODS

Sample and sample collection: Palace road, Enuwa is the central part of Ile-Ife. It is a tourist centre; hence traffic density is high on the road. Ondo road and Ibadan/Ilesa road are the two major busy roads of Ile-Ife apart from the palace road and represent areas of heavy traffic density. NITEL road sample serve as the pollution free reference point being remote from traffic flow. Thus the sampling points designated (X_1-X_6) and (X_7-X_{10}) are locations of high traffic density and low traffic density, respectively.

Moss samples (*Barbula lambarenensis*) were collected along some major and minor roads of Ile-Ife. Samples were collected close to the road and were carefully scraped from the substrate with a treated stainless steel pen-knife[7]. The moss samples were kept in labelled polythene bags and taken to the laboratory avoiding contamination during sampling, transport and storage.

Analysis: The moss samples were placed in a pre-treated Teflon beaker and dried in the oven (Gallenkamp, England) at about 80°C for about 24 h to constant weight and was ground to uniform size in a mortar to pass through 80-mesh sieve. All reagents used for digestion were of analytical grade. About 0.5 g of the sieved moss sample was accurately weighed into teflon beaker [previously soaked in 10% nitric acid (Hopkins and Williams Chadwell Heat, Essex England) for 24 h and later rinsed with deionized water]. This was placed on hot plate maintained at 100°C and the samples were digested in a triple acid system viz. 2 cm^3 perchloric acid (Koch-Light Laboratories Haverhill Suffolk England), 10 cm^3 hydrofluoric acid (Hopkins and Williams Chadwell Heat, Essex England) and 20 cm^3 nitric acid. The residue left was further digested with 2 cm^3 of conc. HCl (May and Baker, Limited, Dagenharm England) on the hot plate. Furthermore, the final residue obtained was dissolved in a 4 cm^3 2.5M HCl and the concentrate brought up to the mark in a 50 cm^3 volumetric flask with de-ionized water[20].

The worked-up moss samples were analysed for the Pb, Zn and Cu contents by Graphite Furnace Atomic Absorption spectrophotometry (Chemtech Analytical UK) at the Centre for Energy Research and Development of the Obafemi Awolowo University, Ile-Ife, Nigeria. Measurements were made at 217.0, 213.9 and 324.7 nm for lead, zinc and copper, respectively. The slit widths were 2cm for Zn, 3cm for Pb and 2cm for Cu. The instrument was operated as per the instrument's handbook and data were acquired on a Gateway 2,000 PC system using the Alphaster software. The instrument was calibrated using mixed calibration standard solutions obtained by stepwise dilution of stock standard solution prepared from the pure analytical grade salt of the metal. As control, a blank experiment was carried out following the same procedure described above, omitting the sample. The background correction was carried out by subtracting concentrations of Pb, Zn and Cu obtained from AAS analysis of the blank from those for the samples.

Determination of precision and accuracy : The analytical quality control included determination of limit of detection of the technique-AAS for each of the element-Pb, Zn and Cu. The quantity of the standard analytes aspirated into the equipment, gave rise to a reading equal to twice the standard deviation of six measurements of 5 mg L^{-1} analyte[21]. The accuracy of the analytical technique (AAS) was evaluated by analysing a certified standard reference material BCR: CRM 062, trace elements in plant *Olea europaea* [Commission of the European communities Bureaus of reference Brussels] after the triple acid system digestion of the plant following the procedure described above.

Data analysis: The standard deviation for each element from replicate measurements was determined. The mean values were used for the subsequent general evaluation of data. The student t-test[22] was used to demonstrate significant difference between two means of elements (i.e. Pb, Zn, Cu) from high and low traffic density sites using the equation:

$$t = \left[\frac{\bar{x}-\bar{y}}{s}\right]\left[\frac{N_1N_2}{N_1+N_2}\right]^{1/2}$$

RESULTS AND DISCUSSION

The detection limits and precision found for lead, zinc and copper using AAS-technique are presented in Table 1. The detection limit ranged from 0.001-0.009 ppm. Precision of the results can be adjudged satisfactory for all the elements from the low values of relative standard deviations obtained which varied from 1.50-2.86%. Comparison between the elemental values observed in this study with certified actual values for the reference material *Olea europaea* BCR: CRM 062 are presented in Table 1. The results are in good agreement with the certified values. Good levels of precision were also obtained with a range of elemental standard deviation of 0.10-0.46 compared with certified values of 0.7-1.8.

The results of the chemical analysis for elemental concentrations in moss *Barbula lambarenensis* of Ile-Ife are presented in Table 2. The results are for the two series

Table 1: Results of control analyses of certified reference materials CRM 062 (trace elements in plant *Olea europaea*) and the detection limits of the AAS technique

	Olea europaea (CRM 062)			
Element	Certified value	Observed (this study)	Detection Limit	%R.S.D
Pb	25.0 (1.5)	26.7 (0.10)	0.004	2.30
Zn	16.0 (0.7)	17.4 (0.46)	0.009	1.50
Cu	46.6 (1.8)	45.8 (0.40)	0.001	2.86

Note: Concentrations are in μg g^{-1} of triplicate analyses. Values in parenthesis are standard deviation, R.S.D = Relative Standard Deviation

Table 2: Levels of lead, zinc and copper in Nigerian *Barbula lambarenensis* at high traffic and low traffic density sites of Ile-Ife

		Concentration* of elements (μg g^{-1} of dry weight)		
Sample number	Sample location	Pb	Zn	Cu
X_1	Diganga Hotel (Ibadan Road)	196.8 (0.04)	170.2 (0.01)	18.0 (0.01)
X_2	Lagere Road	143.1 (0.08)	168.4 (0.02)	32.6 (0.02)
X_3	OAU** Teaching Hospital (Ilesa Road)	151.7 (0.01)	102.2 (0.01)	20.1 (0.02)
X_4	Lexy's place (Ondo Road)	136.3 (0.04)	593.1 (0.02)	28.6 (0.01)
X_5	School of Science (Ondo Road)	132.5 (0.01)	107.0 (0.01)	18.3 (0.03)
X_6	Palace Road (Enuwa)	188.0 (0.05)	206.3 (0.01)	25.0 (0.01)
X_7	Famia Road	113.1 (0.02)	74.4 (0.01)	47.0 (0.01)
X_8	Oke Amola Road	108.5 (0.04)	101.6 (0.02)	28.4 (0.01)
X_9	Ilare Road	121.0 (0.06)	56.3 (0.02)	24.2 (0.04)
X_{10}	Nitel Road	14.7 (0.04)	35.0 (0.10)	10.1 (0.01)
Mean (SD)		130.3 (0.48)	161.5 (1.53)	25.2 (0.09)

*Concentrations are means of triplicate analysis. Values in parenthesis are standard deviations **Obafemi Awolowo University (OAU)

Table 3: Statistical analysis of lead, zinc and copper contents of Nigerian *Barbula lambarenensis* collected from two areas of different traffic density levels of Ile-Ife, with traffic volume

Traffic sites	Lead	Zinc	Copper	Average traffic volume (Vehicles h^{-1})
High density				
Mean (μg g^{-1})	158.07	224.53	23.77	990
Coefficient of variation (%)	17.40	82.59	24.21	
Low density				
Mean (μg g^{-1})	89.33	66.83	27.43	520
Coefficient of variation (%)	56.50	11.76	56.52	
t-value	2.83	1.65	0.38	

The t-critical = 2.365 at 8 degrees of freedom and 95% probability level ($P<0.05$)

of heavy and low traffic pollution areas. It is obvious from Table 2 that there is a marked variation of concentration of Pb, Zn and Cu with traffic volume. Moss samples of relatively high traffic density such as Ibadan road, Ilesa road and Ondo road (X_1-X_6) generally have higher values of Pb and Zn for each sample analysed compared to those of low traffic density sites (X_7-X_{10}) which is an indication of an enhanced level in the surrounding atmosphere. The values of lead obtained for high traffic density areas ranged from 132.5 (0.01) to 196.8 (0.04) μg Pb g^{-1}, whilst lead in samples from low traffic density areas range from 14.7 (0.04) to 121.0 (0.06) μg Pb g^{-1} (Table 2). The same trend observed for Pb was also observed for Zn in moss samples of Ile-Ife (Table 2). It is perhaps not surprising that Zn level obtained from X_4 moss samples taken from Lexy's Place Ondo road was the highest (593.1 (0.02) μg Zn g^{-1}) for all samples analysed. This can be attributed to the presence of road side motor workshops located close to the sampling site which may be an additional source of this contaminant apart from the high traffic density along this busy road. It is a common practice for road side mechanics to dispose off their wastes/effluent, particularly lubricating oils directly into the environment untreated and these lubricating oils contain Zinc dialkyl dithiophosphate[6]. Expectedly NITEL road sample X_{10} (a low density residential area) where the traffic density is very low had the least concentration of the three heavy metals compared to other areas already mentioned above (Table 2).

From Table 2, the values of Zn and Pb are consistently higher than the values of Copper. Similar observation had been reported in road side tree barks[7]. These authors reported consistently low values of Cu (16.0-51.2 μg Cu g^{-1}) compared to that of Zn (33.5-68.9 μg Zn g^{-1}) for tree barks of a polluted area. Besides the generally low values of Cu compared to Pb and Zn in all the samples, the Cu levels follow no specific trend from low to high traffic density areas. The low values of Copper reported in this study compared to those of Pb and Zn and the non-dependence of the Cu concentration on traffic density suggest different sources for Pb and Zn on the one hand and Cu on the other hand. The sources of Copper are probably varied and may be from other sources besides motor traffic. Soil and depositions as a result of refuse and tyre burning which is commonly practiced in the study area are probable sources of Copper in the moss samples.

Table 3 shows the mean concentration of Pb, Zn and Cu in the moss samples of the two groups of high traffic density and low traffic density sites with their coefficient of variation. The average traffic volume of the site with high traffic density was 990 vehicles h^{-1} while that of low traffic density was 520 vehicles h^{-1}. In this Table, there is an increasing trend in the mean concentration of Pb and Zn in moss samples from low to high traffic density. The student t-test demonstrates significant difference between the two means of lead, Zinc and Copper from both groups of traffic sites which shows the difference between the samples taken from high and low polluted sites.

The suitability of moss *Barbula lambarenensis* as indicator of aerial Pb and Zn burdens has been demonstrated in this study. The source of aerial Pb and Zn appears to be from motor traffic while copper probably has natural source. The results of this study may therefore allay the fear of copper poisoning especially for the livestock during grazing on grass and pecking of associated soil along the highway which is a common practice in the study area, but high levels of Pb and Zinc reported may give cause for concern.

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REFERENCES

1. Rühling, A. and G. Tyler, 1968. An ecological approach to the lead problem. Bot. No., 121: 321-342.
2. Thomas, W., 1986. Representativity of mosses as biomonitor organisms for the accumulation of environmental chemicals in plants and soils. Ecotox. Environ. Safety, 11: 339-346.
3. Goodman, G.T. and T.M. Roberts, 1971. Plants and soil as indicators of metals in the Air. Nature, 231: 287-292.
4. Clyde, A.H., 1971. Vegetation: A sink for atmosphere pollutants. J. Air pollut. Control Assoc., 21: 341.
5. Valko Vic, V., D. Rendic and E.K. Biegert, 1979. Trace element concentration in tree rings as Indicators of environmental pollution. Environ. Int., 2: 27.
6. Osibanjo, O. and S.O. Ajayi, 1980. Trace metal levels in tree barks as indicators of atmospheric pollution. Environ. Int., 4: 239-244.
7. Fatoki, O.S. and E.T. Ayodele, 1991. Zinc and copper levels in tree barks as indicators of environmental pollution. Environ. Int., 17: 455-460.
8. Fatoki, O.S., 1987. Colorimetric determination of lead in tree leaves as indicators of atmospheric pollution. Environ. Int., 13: 369-373.
9. Williamson, S.J., 1973. Fundamentals of air pollution Reading, MA: Addison-Wesley.
10. Cannon, H.L. and J.M. Bowels, 1962. contamination of vegetation by tetraethyl lead. Science N.Y., 137: 565.
11. Moore, J.W. and E.A. Moore, 1976. Environmental Chemistry. New York: Academic press, USA.
12. Ogunsola, O.J., A.F. Oluwole, O.I. Asubiojo, H.B. Olaniyi, F.A. Akeredolu, O.A. Akanle, N.M. Spyron, N.I. Ward and W. Ruck, 1994. Traffic pollution: preliminary elemental characterisation of road side dust in Lagos, Nigeria. Sci. Total Environ., 146/147: 175-184.
13. Motto, H.L., R.A. Daines, D.M. Chilko and C.K. Motto, 1970. Lead in soils and plants: its relationship to traffic volume and proximity to high ways. Environ. Sci. Technol., 4: 231-237.
14. Cannon, H.L. and J.M. Bowels, 1962. Contamination of vegetation by tetraethyl lead. Science, 137: 765-766.
15. Oyedele, D.J., I.B. Obioh, J.A. Adejumo, A.F. Oluwole, P.O. Aina and O.I. Asubiojo, 1995. Lead contamination of soils and vegetation in the vicinity of a lead smelter in Nigeria. Sci. Total Environ., 172: 189-195.
16. Ogunsola, O.J., A.F. Oluwole, I.B. Obioh, O.I. Asubiojo, F.A. Akeredolu, O.A. Akanle and N.M. Spyrou, 1993. Analysis of suspended air particulates along some motorways in Nigeria by PIXE and EDXRF. Nuclear instruments and Methods in Physics Research, B79: 404-407.
17. Arah, A.R.O. and J.N. Nwankwo, 1987. Lead-free gasoline in Nigeria: an Update, paper presented at the 1987 Int. Seminar on the petroleum Industry and the Nigerian Environment. Owerri.
18. Fatoki, O.S., 2000. Trace Zinc and Copper concentration and surface soils: A measurement of local atmospheric pollution in Alice. South Africa. Int. J. Environ. Studies, 56: 501-513.
19. Dutta, A.C., 1974. Botany for Degree Students. (4th Edn.), pp: 614.
20. Nyagababo, J.T. and J.W. Hamya, 1986. The deposition of lead, cadmium, zinc and copper from motor traffic on Brachiaria Enimi and soil along a major Bombo road in Kampala City. Int. J. Environ. Studies, 27: 115-119.
21. Ogunfowokan, A.O. and O.A. Fakankun, 1998. Physicochemical characterisation of effluent from Beverage Processing Plants in Ibadan Nigeria. Int. J. Environ. Studies, 54: 145-152.
22. Miller, J.C. and J.N. Miller, 1988. Statistics for Analytical Chemistry, R.A. Chelmers and M. Masson Ed. Ellis Horwood Ltd. Halsted press a division of John Wiley and Sons, New York, USA., pp: 55-58.