The Bioscientist: Vol. 1(1):99-105, May, 2013.
Available online at http://www.bioscientistjournal.com

Full Length Research Paper

Heavy Metal Depositions around some Petroleum Product Depots in Nigeria, using Mosses as Biomonitors.

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ABSTRACT
This study was aimed at assessing atmospheric depositions of heavy metals around Nigerian NNPC depots using the moss (*Barbula lambarenensis*). Concentrations of 7 elements (Cd, Pb, Ni, Cu, Cr, Fe and Zn) were determined in the moss samples by Flame Atomic Absorption Spectrophotometry analysis. Nickel concentrations in the moss samples across the depots, except Mosimi NNPC depot were highest ($p<0.05$). A comparison of the metal depositions among the depots revealed that elemental contents of the mosses were significantly the same ($p<0.01$) in all the depots except for Cd and Cu in Ibadan and Mosimi NNPC depots respectively. This could be attributed to fact that Ibadan depot is situated close to residential areas with major input of Cd from domestic wastes incineration while Mosimi depot serves several other depots around it, so vehicular activities was greater and also the release of Cu. Generally, the pollution level of these depots is high and this calls for their proper monitoring to reduce workers exposure to heavy metal hazards.

Keywords:- Heavy metals, atmospheric deposition, biomonitor, pollution, monitoring

1.0 INTRODUCTION

The rapid increase in urbanization and industrialization in Nigeria in the past decades has led to sharp increase in the use of petroleum products for energy generation. This initiated the establishment of the Nigeria National Petroleum Corporation (NNPC) with the mission to ensure security of supply of petroleum products to the domestic market at low operating costs. The Nigerian National Petroleum Corporation (NNPC) has evolved different strategies for effective distribution of refined products to different parts of Nigeria (NNPC, 1999). There are about 5,000 km long pipelines and about 20 oil depots industrial facilities for the storage of petrochemical products and from where they are transported to end-users (NNPC, 1999; Adewuyi *et al*., 2011).

The increased activities in these petroleum depots have resulted in extensive environmental pollution arising blowouts, leakages from tanks or tanker trunk, dumping of waste petroleum products and deposition of heavy metal particulates in air and aerosols. Leakages and spills associated with loading and offloading of petroleum products in these depots, as well as washing of oil storage tanks, have adverse impact on the environment (Rasmussen, 1976; Orubu *et al*., 2004). These impacts according to Uzoekwe and Oghosanine (2011), depend primarily on the petroleum products, its concentration after release and the biotic community that is exposed. This is because refined products show higher toxicity compared to crude oil due to the altered metal speciation and introduction of new metals to the matrix in the process of refining.

Several trace metals are emitted through the abrasion of tires (Cu, Zn, Cd) and brake pads (Sb, Cu), corrosion (V, Fe, Ni, Cu, Zn, Cd), lubricating oils (V, Cu, Zn, Mo, Cd) or fuel additives (V, Zn, Cd, Pb) (Pacyna and Pacyna, 2001) that occur on a daily basis in these petroleum depots . Most of the trace metals are emitted in particulate form (Molodovan *et al*.,

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2002) and accumulate in the smaller particles (Espinosa *et al*., 2001) with high potentials of bio-accumulation and bioconcentrations in humans and plants around deposition areas.

The objective of this study was to use native ectohydric mosses to assess the particulate metal depositions of Cd, Pb, Cu, Cr, Fe, Zn and Ni within four Nigerian NNPC depots in southern Nigeria. Ectohydric mosses are important in biomonitoring of atmospheric pollution due to their ability to trap suspended pollutants with their body surfaces.

2.0 MATERIALS AND METHODS

2.1 Moss Sampling

Eighty composite ectohydric moss samples (*Barbula lambarenensis*) were collected from four Nigerian National Petroleum Corporation (NNPC) depots in south-west and north-central regions of Nigeria. The depots are Ibadan NNPC depot, Oyo state (southwest); Mosimi NNPC depot, Ogun state (southwest); Ore NNPC depot, Ondo state (southwest) and Ilorin NNPC depot, Kwara state (north-central). The moss sampling procedure was according to Nordic guidelines (Kubin *et al*., 2000). Green parts of the mosses with their substrates removed were dried to constant weight at 40^{o} C in an oven for some hours and labeled for chemical analysis (Frontasyeva *et al*., 2004).

2.2 Chemical Analysis

One (1g) of each of the homogenized moss samples were wet-digested in a microwave oven, using Nitric-Perchloric acid (4:1 v/v) digestion described by Batagarawa and Lawal (2010). The digest was filtered through a Whatman filter No 42 into a - 50 ml volumetric flask and made up to the mark with deionized water. Determination of Cd, Pb, Cu, Cr, Fe, Zn and Ni was carried out by Atomic Absorption Spectrophotometry using Buck Scientific 210VGP. Quality control was ensured by carrying out simultaneous analysis of blank solution and reference material-IAEA 336 alongside the moss samples after every 10^{th} digestion and the percentage recoveries of heavy metals from the reference material were within the range of 75%-105%.

2.3 Statistical Analysis

The data generated were subjected to statistical analysis. Means were compared with the Analysis of Variance (ANOVA) and the means were separated with Duncan's Multiple Range Test (DMRT).

3.0 RESULTS

3.1 Heavy metal depositions in the four selected NNPC depots.

Mean Cd and Pb contents (6.13 mg/kg and 5.53 mg/kg respectively) of moss samples from Ibadan NNPC depot were significantly lower than Ni and Cu contents (7.45 mg/kg and 7.05 mg/kg) but greater than Cr, Fe and Zn contents ($p<0.05$) (Table 1). This indicates that Ni and Cu contributed largely to the metal pollution of Ibadan NNPC depot while Cr, Fe and Zn pose no threat. There are several outliers in the distribution of Fe and Zn in the moss samples collected at the Ibadan NNPC depot as indicated by the high values of coefficient of variation (80% and 66.7% respectively) (Table 1).

Table 1: Heavy metal content (mg/kg) of native mosses within Ibadan NNPC depot

Element	Cd	Pb	Ni	Cu	Cr	Fe	Zn
n	21	21	21	21	21	21	21
Mean	6.13†^{b}	5.53^{b}	7.45^{a}	7.05^{a}	0.18^{c}	0.10^{c}	0.03^{c}
Standard deviation	2.41	1.92	0.97	0.57	0.05	0.08	0.02
CV%	39.3	34.7	13.0	8.08	27.7	80	66.7
Minimum	2.06	2.92	6.06	5.98	0.11	0.01	0.01
Maximum	9.68	8.93	9.02	8.02	0.27	0.32	0.08

† – Mean values with different superscripts are significantly different at $p<0.05$; CV- Coefficient of variation

Heavy metal contents of the sampled mosses in Mosimi NNPC depot showed that mean values Cd, Pb, Ni and Cu (9.01 mg/kg, 8.62 mg/kg, 7.81 mg/kg and 7.64 mg/kg) respectively were

The Bioscientist: Vol. 1(1):99-105, May, 2013.
Available online at http://www.bioscientistjournal.com

statistically the same but greater than the Cr, Fe and Zn contents (0.26 mg/kg, 0.16 mg/kg and 0.03 mg/kg) respectively at p<0.05 (Table 2). The major contributors to the metal pollution of Mosimi NNPC depot were Cd, Pb, Ni and Cu. Coefficient of variation indicated that Pb, Fe and Zn distribution values in the moss samples showed a great dispersion from the mean values due to the several outliers in the distribution (Table 2).

Table 2: Heavy metal content (mg/kg) of native mosses within Mosimi NNPC depot

Element	Cd	Pb	Ni	Cu	Cr	Fe	Zn
n	23	23	23	23	23	23	23
Mean	9.01†^{a}	8.62^{a}	7.64^{a}	7.81^{a}	0.26^{b}	0.16^{b}	0.03^{b}
Standard deviation	3.12	13.85	0.72	1.03	0.07	0.19	0.02
CV%	34.6	160.6	9.42	13.2	26.9	118.7	66.7
Minimum	2.91	2.04	6.92	5.88	0.11	0.02	0.01
Maximum	20.72	71.01	9.02	8.98	0.41	0.61	0.08

† – Mean values with different superscripts are significantly different at p<0.05; CV- Coefficient of variation

Table 3 showed that the mean concentration of Cd (5.37 mg/kg) in the moss samples from Ore NNPC depot was significantly lower than the mean values of Ni, Cu and Pb (7.23 mg/kg, 7.01 mg/kg and 6.57 mg/kg) respectively but greater than the mean values of Cr, Fe and Zn (0.25 mg/kg, 0.13 mg/kg and 0.03 mg/kg) (p<0.05) respectively. Contributions of Ni, Cu, and Pb depositions to Ore NNPC depot significantly increased the metal pollution status. Some outlier values were present in the concentration distributions of Pb and Fe as indicated in the coefficient values (41.4% and 46.1% respectively).

Table 3: Heavy metal content (mg/kg) of native mosses within Ore NNPC depot

Element	Cd	Pb	Ni	Cu	Cr	Fe	Zn
n	20	20	20	20	20	20	20
Mean	5.37†^{b}	6.57^{a}	7.23^{a}	7.01^{a}	0.25^{c}	0.13^{c}	0.03^{c}
Standard deviation	1.81	2.72	1.11	0.87	0.08	0.06	0.01
CV%	33.7	41.4	15.3	12.4	32	46.1	33.3
Minimum	0.09	2.66	5.62	5.88	0.12	0.08	0.02
Maximum	8.01	14.42	9.85	8.71	0.41	0.01	0.06

† – Mean values with different superscripts are significantly different at p<0.05; CV- Coefficient of variation

Table 4: Heavy metal content (mg/kg) of native mosses within Ilorin NNPC depot

Element	Cd	Pb	Ni	Cu	Cr	Fe	Zn
n	16	16	16	16	16	16	16
Mean	3.38†^{d}	6.22^{c}	7.97^{a}	7.28^{b}	0.28^{e}	0.11^{e}	0.06^{e}
Standard Deviation	1.49	1.37	0.54	0.64	0.15	0.03	0.01
CV%	44.1	22	6.77	8.79	53.6	27.3	16.7
Minimum	0.98	3.99	7.05	6.39	0.09	0.01	0.03
Maximum	6.02	8.79	9.22	8.31	0.72	0.14	0.08

† – Mean values with different superscripts are significantly different at p<0.05; CV- Coefficient of variation

There was significant variation in the mean values of the metal contents in the moss samples from Ilorin NNPC depot (p<0.05) (Table 4). The sequence of the distribution follows the pattern: Ni > Cu > Pb > Cd > Cr = Fe = Zn (p<0.05). Coefficient of variation indicated some outlier values in the distribution of Cd and Cr (44.1% and 53% respectively). The sole contributors to the pollution level of Ilorin NNPC depot were Ni, Cu and Pb and to a lesser extent Cd.

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3.2. Comparison of metal deposition among the four depots.

Cd content of mosses in Ibadan NNPC depot was significantly highest ($p<0.01$) while Mosimi and Ore NNPC depots had statistically the same Cd concentrations in the mosses ($p<0.01$). Ilorin depot had the least Cd concentration in the moss (Fig. 1).

There was no significant difference at $p<0.01$ in the Pb, Ni, Cr, Fe and Zn contents of the sampled mosses ($p<0.01$) (Fig. 1) in all the NNPC depots. Significant differences were recorded for Cu contents of sampled mosses in all the studied depots ($p<0.01$). Mosimi NNPC depot had significantly higher Cu content of mosses while the other three NNPC depots had statistically the same Cu contents (Fig. 1).

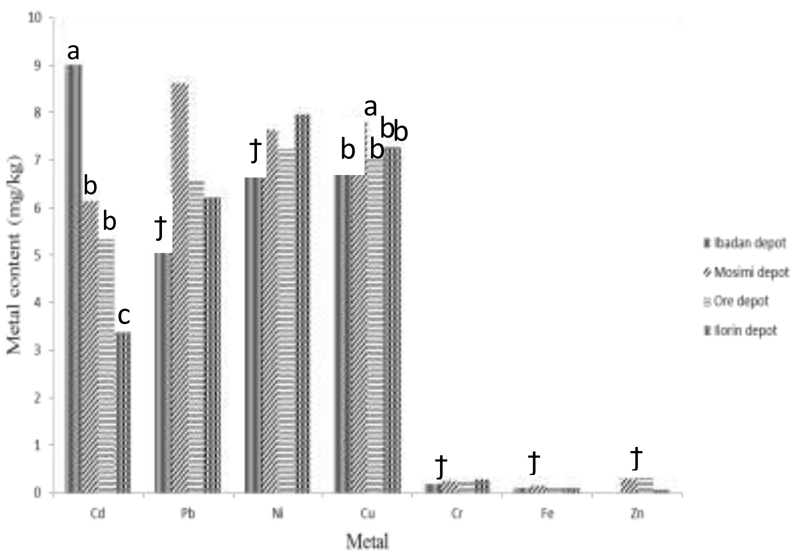

Fig. 1: Variations in metal contents of mosses among the different NNPC depots. (Bars with different letters are significantly different at $p<0.01$; † refers to no significant difference at $p<0.01$).

4.0. DISCUSSION

Nickel appeared to be the largest contributing metal pollutant to the environment of the NNPC depots and this could be related to various processes/activities at the depots that are releasing Ni particulates into the environment. Leetham *et al*. (1982) reported extremely high Ni level in Szazhalombetta due to its refinery and oil-fuelled power station while Poikolainen (2004) put forward that Ni and V are frequently associated with emissions from oil-refining industries. This shows that Ni is a major metal pollutant associated with oil and gas activities. Fatoba and Oduekun (2004) also reported highest Ni level among metal that were deposited in the environment of Ilorin city and this corroborated the aforementioned assertion that Ni deposition is related to oil and gas activities since an NNPC depot is located in the city.

Pollution of the atmospheric environment of these depots by Pb Cd and Cu is related to anthropogenic contamination sources. The environmental variables related to these elements are indirect measurements of contamination caused by human activity through heavy traffic exhausts caused by population density and various activities around these depots. Figueira *et al*. (2002) opined that fuel selling is an indirect source of Cu, Pb and Ni introduction into the environment. Pacyna and Pacyna (2001) also reported that large amount of Cu and Cd are emitted through the abrasion of tires, lubricating oils and brake pads of vehicles while Pb is released into the atmosphere through the use of fuel additives. The identification of outliers in the environmental data set of Mosimi (Pb, Fe and Zn) and Ibadan (Fe and Zn) NNPC depots showed that some outside input occurred. For instance, pollution contribution could come from pollutants dispersion from stacks of Lafarge-cement WAPCO that was within the same geographical location with Mosimi NNPC depot. In the same vein, contributions from scattered industries in Oluyole industrial estate which is contiguous with Apata municipal where Ibadan NNPC depot is situated.

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Detection of low Fe and Cr content in the moss samples from the four depots indicated that most deposited particulates on the mosses are not from crustal re-suspended materials but particulate matters directly released into the air either through exhaust from cars, fumes or gaseous releases from the depots. This was supported by Bargagli (1998) in his report that high content of Al and Fe in moss samples is generally an indication of high level soil dust pollution. Fe is normally considered a lithophilic element, while Cr is mainly of soil origin, and is related to parameters describing the soil typology and site conditions (Figueira *et al*., 2002).

The high level of Cd pollution of the atmosphere in Ibadan NNPC depot could not have resulted from the activities at the depot. It could also be ascribed to the fact that the NNPC depot is located near residential areas where various Cd-contaminated domestic wastes are released. Combustion of domestic waste is a regular occurrence in this area, particularly Apata municipal where Ibadan NNPC depot is located and this process significantly increases atmospheric Cd content. Awofolu (2005) stated that one of the sources of Cd release to the environment is incineration of municipal waste materials. This assertion was also supported by Olowoyo and van Heerden (2010) that Cd is released in the burning of household wastes. Ilorin NNPC depot environment happens to be least polluted with Cd because the depot is located far away from residential areas and input of Cd from domestic waste incineration was involved. The only source of Cd pollution was through the various activities within and around the depot in addition to the vehicular activities.

There was no significant difference in the level of pollution of the studied NNPC depots by Pb, Ni, Cr, Fe and Zn because the major sources of these pollutants are related to vehicular activities involved in loading of petroleum products resulting in high level of oil/fuel combustion. All these processes increase the depositions of Pb, Ni, Cr, Fe and Zn into the environment (Scerbo *et al*., 2001; Fatoba *et al*. 2012). Cu pollution of Mosimi NNPC depot was significantly higher than the other NNPC depots which possibly could have been similarly polluted because the sources of pollution are attributed to vehicular/traffic activities. However, there is always high traffic density at the Mosimi NNPC depot because it is the headquarters of the southwestern NNPC depots where petroleum products are transported to other depots, once supplies are received from the Atlas Cove jetty in Lagos. The high activities associated with this depot could result in the high Cu pollution of the environment.

CONCLUSION

There is evidence of high pollution of the studied NNPC depots by Ni, Cd, Pb and Cu. The concentrations of these heavy metals could only be attributed to the day-to-day activities around these depots. Monitoring, environmental safety and management of these depots are suggested due to the high concentration of these metal pollutants which could be very hazardous to human health when too much doses are bioaccumulated.

REFERENCES

Adeniyi, A.A. and Afolabi, J.A. (2002). Determination of total petroleum hydrocarbons and heavy metals in the soil within the vicinity of facilities handling refined products in Lagos Metropolis. *Environmental International*, 28: 79-82.

Adeniyi, A.A., Yusuf, K.A. and Okedeyi, O.O. (2008). Assessment of the exposure of two fish species to metal pollution in the Ogun river catchments, Ketu, Lagos, Nigeria. *Environmental Monitoring and Assessment*, 137:145-458.

Adewuyi, G.O., Etchie, O.T. and Ademulegun, O.T. (2011). Determination of total petroleum hydrocarbons and heavy metals in surface water and sediment of

The Bioscientist: Vol. 1(1):99-105, May, 2013.
Available online at http://www.bioscientistjournal.com

Ubeji River, Warri, Nigeria. *Bioremediation, Biodiversity and Bioavailability*, 5(1): 46-51.

Awofolu, O.R. (2005). A survey of trace metals in vegetation, soil and lower animal along some selected major roads in metropolitan city of Lagos. *Environmental Monitoring and Assessment*, 105:431-447

Bargagli, R. (1998). *Trace elements in terrestrial plants*. Springer Verlag, New York. 324pp.

Batagarawa, S.M. and Lawal, A.O. (2010). Determination of some heavy metal levels in Funaria hygrometric in Dutsinma town of Katsina State, Nigeria. *Journal of Applied Science and Environmental Management*, 14(30): 65-68.

Commendatore, M.G. and Esteves, J.L. (2004). Natural and anthropogenic hydrocarbons in sediments from the Chubut river (Patagonia, Argentina). *Mar. Pollut. Bull*., 48: 910-918.

Espinosa, A.J.F., Rodriguez, M.T. Barragan de la Rosa, F..J. and Sanchez, CJ. (2001). Size distribution of metals in urban aerosols in Seville (Spain). *Atmospheric Environment*, 35, 2595-2601.

Fatoba, P.O., Ogunkunle, C.O. and Olawepo, G.K. (2012). Assessment of atmospheric metal depositions in the industrial areas of the southwest of Nigeria. *Ethiopian Journal of Environmental Studies and Management*, 5(3): 260-267.

Fatoba, P.O. and Odekun, T. I. (2004). Assessment of Metal Deposition in Illorin

Metropolis using Mosses as Bioindicators. *Nigerian Journal of Pure and Applied Science*, 19: 1549-1552.

Figueira, R., Sergio, C. and Sousa, AJ. (2002). Distribution of trace metals in moss biomonitors and assessment of contamination sources in Portugal. *Environmental Pollution*, 118: 153-163.

Frontayeva, M.V., Galinskaya, T.Y. Krmar, M. Matavuly, M. Pavlov, S.S. Povtoresyko, E.A. Radnovic, D. and Steinnes, E. (2004). Atmospheric deposition of heavy metals in northern Serbia and bosnia-herzegovina studied by the moss biomonitoring, neutron activation analysis and GIS technology. *Journal of Radioanalytical and Nuclear Chemistry*, 259(1): 141-147.

Kubin, E., Lippo, H. and Poikolainen, J. (2000). Heavy metal loading. In: Mälkönen E (ed). Forest condition in a changing environment – The Finnish Case.- Forestry Sciences *65;* Kluwer Academic Publishers, Dordrecht, pp. 60-71.

Leetham, J.W., McNary, T.J., Dodd, J.L. and Lauenroth, W.K. (1982). Reponse of soil nematodes, rotifers and tardigrades to three levels of season long sulphur dioxide exposure. *Water, Air and Soil Pollution*, 17: 343-356.

Molodovan, M., Palacios, M.A. Gomez, M.M. Morrison, G. Rauch, S. McLeod, C. Ma, R. Caroli, S. Alimonti, A. Petrucci, F. Bocca, B. Schramel, P. Zischka, M. Pettersson, C. Wass, U. Luna, M. Saenz, J.C. and Santamaris, J. (2002). Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. *Science of the Total Environment*, 296: 199 – 208.

Nigerian National Petroleum Corporation (NNPC) (1999). Archived Report. Pp. 16-18.

Olowoyo, J.O. and van Heerden, E. (2010), Trace element concentrations from

The Bioscientist: Vol. 1(1):99-105, May, 2013.
Available online at http://www.bioscientistjournal.com

lichen transplants in Pretoria, South Africa. *Environmental Science and Pollution Research.* DOI 10.1007/s11356-010-0410-3

Orubu, C.O. Ayodele, O. and William, E. (2004). The Nigeria oil industry: environmental diseconomies, management strategies and the need for community involvement. *Journal of Human Ecology*, 16(3): 203-214.

Pacyna, J.M. and Pacyna, E.G. (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environmental Review*, 9: 269-298.

Poikolainen, J. (2004). Mosses, epiphytic lichens and tree bark as biomonitors for air pollutants-specifically for heavy metals in regional surveys. The Finnish Forest Research Institute, Muhos Research Station.

Rasmussen, D.V. (1976). Characterization of oil spill by capillary column gas chromatography. *Analytical Chemistry*, 48(11): 1536-1566.

Samara, C., Kouimtzis, T.H. Tsitouridou, R. Kanias, G. and Simeonov, V. (2003). Chemical mass balance source apportionment of PM_{10} in an industrialized urban area of northern Greece. *Atmospheric Environment*, 37(1): 41-54.

Scerbo, R., Ristori, T. Possenti, L. Lampugnami, L., Barale, R. Barghigiani, C. (2001), Lichen (*Xanthoria parientina*) biomonitoring of trace element contamination and air quality assessment in Pisa Province, Italy. *Total Environment*, 286:27-40

Uzoekwe, S.A. and Oghosanine, F.A. (2011). The effect of refinery and petrochemical effluent on water quality of Ubeji creek Warri, Southern Nigeria. *Ethiopian Journal of Environmental Studies and Management*, 4(2): 107-116.