American Journal of Environmental Protection, 2014, Vol. 2, No. 1, 22-31
Available online at http://pubs.sciepub.com/env/2/1/5

DOI:10.12691/env-2-1-5

Distribution of Some Atmospheric Heavy Metals in Lichen and Moss Samples Collected from Eket and Ibeno Local Government Areas of Akwa Ibom State, Nigeria

Aniefiok E. Ite[1,3,*], Imaobong I. Udousoro[2], Udo J. Ibok[1]

[1]Faculty of Natural and Applied Sciences, Akwa Ibom State University, P.M.B., Uyo, Akwa Ibom State, Nigeria
[2]Department of Chemistry, University of Uyo, P.M.B., Uyo, Akwa Ibom State, Nigeria
[3]Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom
*Corresponding author: aniefiokite@yahoo.co.uk

Received December 11, 2013; Revised March 01, 2014; Accepted March 10, 2014

Abstract The atmospheric deposition of some heavy metals was investigated using lichen (*Parmelia caperata*) and moss (*Polytrichum juniperinum, Calymperes erosum and Racopilum africanum*) samples collected from two oil–producing host communities viz Eket and Ibeno Local Government Areas of Akwa Ibom State, Nigeria. Lichen and moss samples were analysed using atomic absorption spectrometry equipped with flame and graphite furnace after decomposition using acid digestion technique. The concentrations of heavy metals in lichen and moss samples ranged from 0.001 – 0.092 μg g^{-1} for cadmium (Cd); 0.004 – 8.793 μg g^{-1} for chromium (Cr); 0.989 – 1.950 μg g^{-1} for cobalt (Co); 2.350 – 110.760 μg g^{-1} for copper (Cu); 10.530 – 153.320 μg g^{-1} for manganese (Mn); 1.425 – 21.730 μg g^{-1} for nickel (Ni); 0.001 – 17.380 μg g^{-1} for lead (Pb), and 23.530 – 130.600 μg g^{-1} for zinc (Zn). The statistical significance of correlations between Cu–Pb, Cu–Zn, Pb–Ni and Mn–Zn concentrations confirmed anthropogenic sources mainly due to emissions from vehicular traffic, fossil fuel combustion, solid waste disposal and other local anthropogenic activities. In a direct comparison, some of the target heavy metals such as Cd, Cr, Mn, Ni and Zn were accumulated at higher concentrations in moss samples compared to lichen from the same sampling site. The results obtained reveal important contributions towards understanding of heavy metal deposition patterns and provide baseline data that can be used for potential identification of areas at risk from atmospheric heavy metals contamination in the region. The use of epiphytic lichens and mosses provides a cost–effective approach for monitoring regional atmospheric heavy metal contamination and may be effectively used in large scale air pollution monitoring programmer.

Keywords: *atmospheric deposition, heavy metals, lichen, moss, atomic absorption spectrometry, akwa ibom state, nigeria*

Cite This Article: Aniefiok E. Ite, Imaobong I. Udousoro, and Udo J. Ibok, "Distribution of Some Atmospheric Heavy Metals in Lichen and Moss Samples Collected from Eket and Ibeno Local Government Areas of Akwa Ibom State, Nigeria." *American Journal of Environmental Protection*, vol. 2, no. 1 (2014): 22-31. doi: 10.12691/env-2-1-5.

1. Introduction

Atmospheric heavy metal contamination has been a major environmental problem in Nigeria's Niger Delta region due to emissions from gas flaring associated with petroleum development, energy generation, vehicular traffic, combustion of fossil fuel and poor waste management strategies. Heavy metals (or trace elements) are defined as chemical elements having density greater than 5 g cm^{-3} [1,2] and are toxic components of particulate matter. Some of these elements such as cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn) are micronutrients required by plants [3,4]. In addition, low concentrations of chromium (Cr) and antimony (Sb) are essential for normal metabolic functioning of animals [5,6]. The non–essential metals and/or metalloids such as mercury (Hg), cadmium (Cd), lead (Pb), arsenic (As), chromium (Cr), and antimony (Sb) are toxic in either chemically combined or elemental forms. Apart from emissions from natural sources (meteoric, biogenic, terrestrial, marine, volcanic, forest fires, erosion and surface winds), heavy metals from anthropogenic sources are introduced into the environment mainly via three routes: (i) deposition of atmospheric particulates, (ii) disposal of metal enriched sewage sludge and sewage effluents and (iii) emissions from automobiles, metal mining, petroleum production and fossil fuel combustion. Combustion of fossil fuels is the principal anthropogenic

source of Be, Co, Hg, Mo, Ni, Sb, Se, Sn and V, as well as a large contributor of As, Cr, Cu, Mn and Zn, while industrial metallurgical processes produce the largest emissions of As, Cd, Cu, Ni and Zn [7]. However, other sources and mechanisms such as re-suspension of local soil dust, through rainfall precipitation and leaching from higher plants might significantly contribute to atmospheric deposition of heavy metals [8,9].

Monitoring and assessment of heavy metals concentrations in the environment contribute towards effective understanding of biogeochemical processes and gauging ecosystem health. Elemental analysis of vegetation has become a powerful tool for biogeochemical prospecting, biomonitoring and study of the environment [2,5,10,11,12,13]. In particular, lichens and mosses have been widely used as bioindicators for assessing the atmospheric deposition of heavy metals and/or biological effects of airborne contaminants [12,14-25]. Lichens and mosses have neither cuticle nor transport systems and obtain their nutrients and airborne contaminants directly from the atmosphere through cell walls. These non–vascular plants usually have slow growth rate with rapid rate of atmospheric absorption and/or accumulation of potentially high concentrations of trace elements without apparent damage to the plant [26,27,28]. Uptake of heavy metals in these lower plants depends on the simple process of ion exchange and concentrations of trace elements in atmospheric deposition [13,27]. Although the use of lichens and mosses as bioindicators has been reported in some parts of Nigeria [21,22,23,24,29,30], there is a limited record in Nigeria's Niger Delta region. However, lichens and mosses are evergreen plants which can be surveyed/ sampled for assessment of heavy metal deposition on a regional scale throughout the year. Measurement of the bioaccumulation of heavy metals in the lichen and moss samples could provide information which may help in the assessment of environmental risk and human health hazards in the Niger Delta region.

This study investigates the concentrations of atmospheric heavy metals using epiphytic lichen and moss samples collected from Eket and Ibeno Local Government Areas of Akwa Ibom State, Nigeria. The concentrations of heavy metals in lichen and moss samples were used to assess the potential contamination of the atmospheric environment in the region.

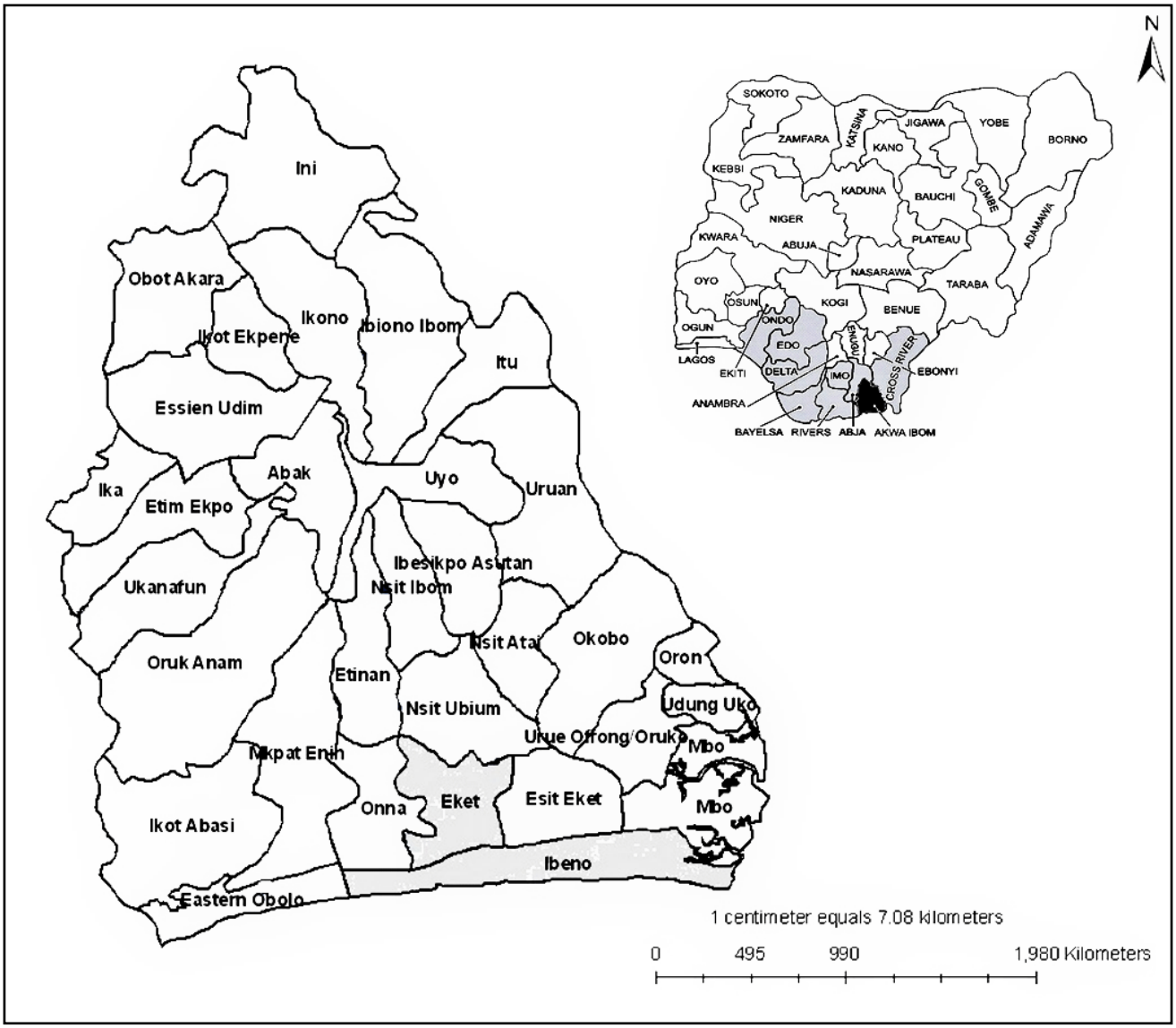

Figure 1. Map of Akwa Ibom State showing the location of the study areas (Eket and Ibeno Local Government Areas)

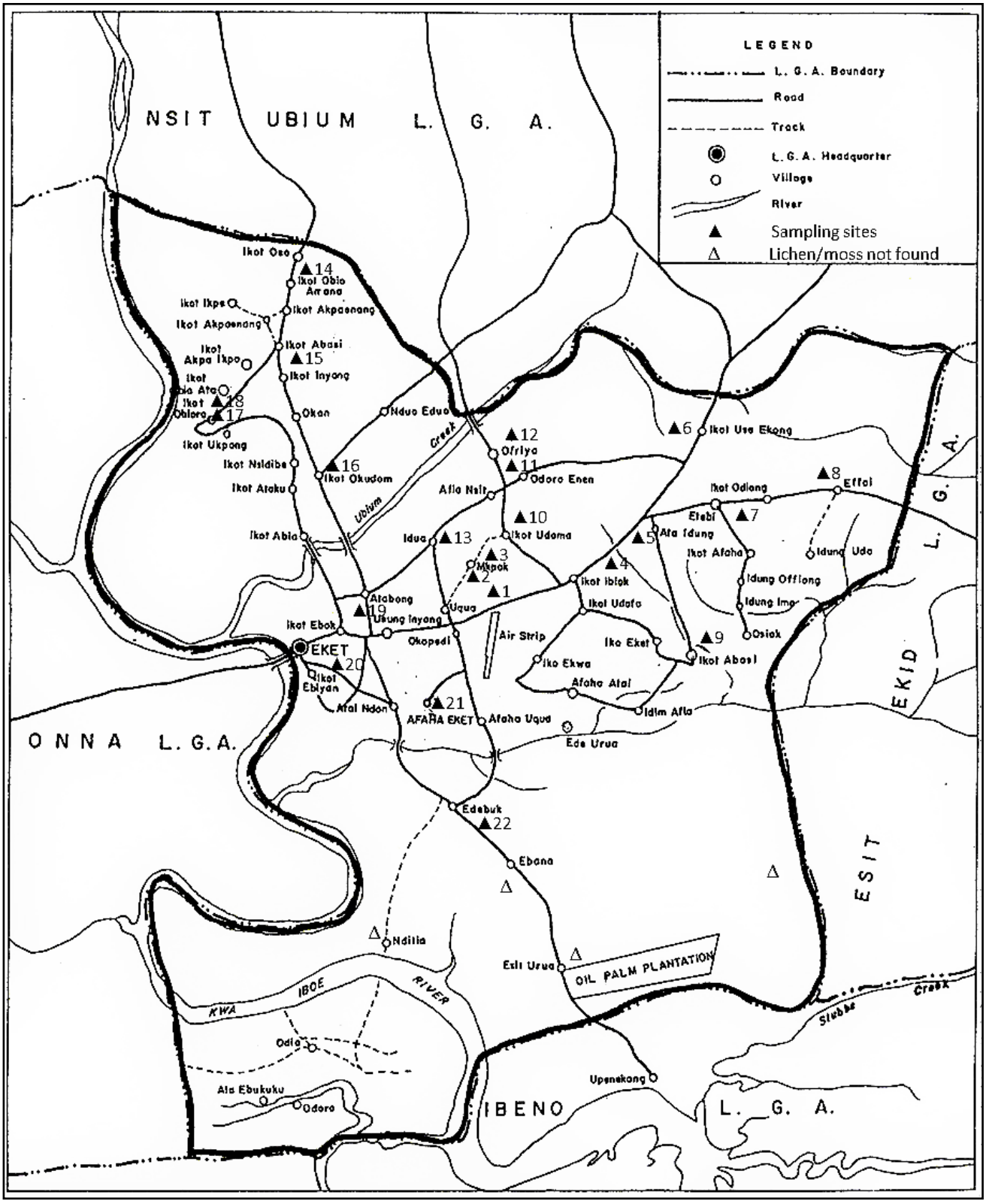

Figure 2. Map of Eket Local Government Area showing the location of sampling sites

2. Materials and Methods

2.1. Materials

Nitric acid (HNO_3) and perchloric acid ($HClO_4$) used for sample decomposition by wet acid digestion procedure were of supra pure quality (Merck, UK). Double deionised water was used for all dilutions (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity). All the plastic and glasswares were cleaned by soaking in dilute HNO_3 (10%) and were rinsed with distilled water prior to use. The trace element standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg l^{-1} of each element obtained from Sigma-Aldrich, UK. Sigma-Aldrich UK supplied the Lichen (trace elements) BCR® Certified Reference Material (CRM 482) used for analytical quality control.

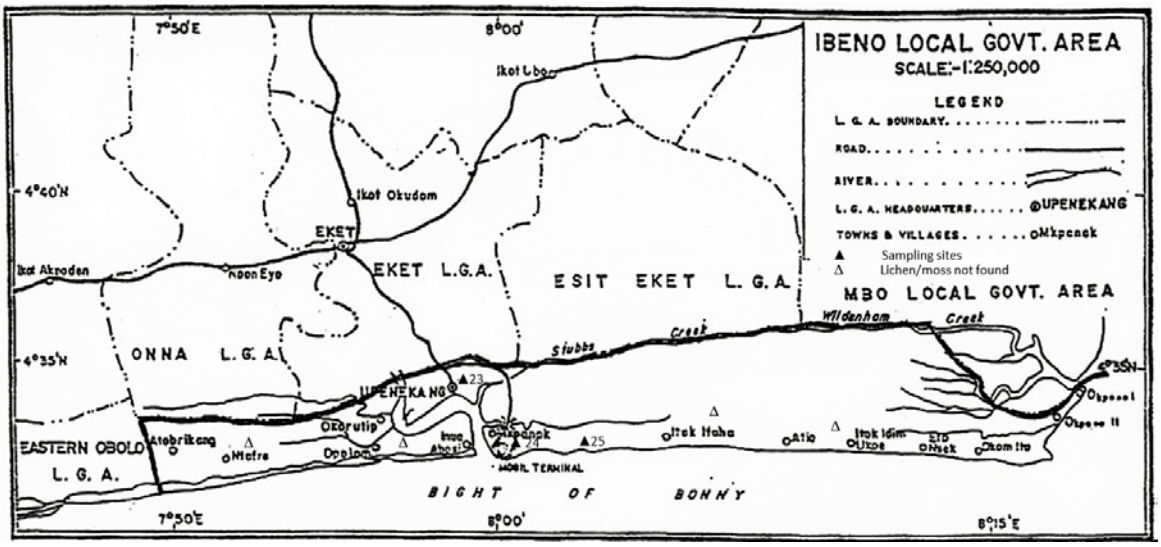

Figure 3. Map of Ibeno Local Government Area showing the location of sampling sites

Table 1. General characteristics and anthropogenic activities around the sampling sites

Sampling sites	Locality	Specie	Scientific name	Substrate	Anthropogenic activity
M 1	176 Eket – Oron Road, Eket	Moss	Racopilum africanum	Magnifera indica (Mango)	High vehicular traffic, airstrip & municipal waste burning
L 2	# 5 Route 2, Mkpok Housing Estate, Eket	Lichen	Permelia caperata	Magnifiera indica (Mango)	Residential estate: fossil fuel combustion & waste burning
M 3	# 5 Route 2, Mkpok Housing Estate, Eket	Moss	Racopilum africanum	Magnifiera indica (Mango)	Residential estate: fossil fuel combustion & waste burning
M 4	Lutheran Primary School, Ikot Ibiok	Moss	Racopilum africanum	Magnifiera indica (Mango)	High vehicular traffic, metal works & waste burning
M 5	10 Ata Idung Afaha Eket, Eket-Oron Road	Moss	Calymperes erosum	Elaeis guineensis (Oil palm)	Medium vehicular traffic & metal works (welding)
M 6	Uncultivated farm land, Ikot Use Ekong	Moss	Polytrichum juniperinum	Elaeis guineensis (Oil palm)	Remote rural settlement: peasant farming
M 7	Ikot Odiong, Eket	Moss	Racopilum africanum	Elaeis guineensis (Oil palm)	Domestic waste burning & automobile repairs
M 8	Effoi Village, Eket	Moss	Racopilum africanum	Citrus sinensis (Orange)	Low vehicular traffic & Domestic waste burning
M 9	Ikot Abasi, Eket	Moss	Racopilum africanum	Magnifera indica (Mango)	Low vehicular traffic & Domestic waste burning
M 10	Ikot Udoma, Eket	Moss	Racopilum africanum	Elaeis guineensis (Oil palm)	Low vehicular traffic & Domestic waste burning
L 11	Ofriyo Road, Ofriyo - Eket	Lichen	Pleurozium caperata	Unidentified flowering plant	Low vehicular traffic & Domestic waste burning
M 12	Ofriyo Road, Ofriyo - Eket.	Moss	Racopilum africanum	Unidentified flowering plant	Low vehicular traffic & Domestic waste burning
M 13	98 Idua Road, Idua, Eket	Moss	Racopilum africanum	Magnifiera indica (Mango)	Metal works, automobile repairs & waste burning
M 14	Ikot Obio Amana, Eket-Etinan Highway	Moss	Calymperes erosum	Magnifiera indica (Mango)	Metal works, Municipal & domestic waste burning.
M 15	Ikot Inyang, Okon, Eket-Etinan Highway	Moss	Racopilum africanum	Magnifiera indica (Mango)	Petrol station, automobile repairs & waste burning
M 16	Ikot Okudom - Okon, Eket-Etinan Highway	Moss	Racopilum africanum	Magnifiera indica (Mango)	High vehicular traffic & fossil fuel combustion
L 17	Ikot Obioro, Okon Eket	Lichen	Parmelia caperata	Elaeis guineensis (Oil palm)	Remote rural settlement: peasant farming
M 18	Ikot Obioro, Okon Eket	Moss	Racopilum africanum	Elaeis guineensis (Oil palm)	Remote rural settlement: peasant farming
M 19	52 Atabong Road, Eket	Moss	Racopilum africanum	Cola spp (Kola)	High vehicular traffic, metal works & auto–repairs
M 20	High Court 2, Barracks Road, Eket	Moss	Racopilum africanum	Magnifera indica (Mango)	Business district: metal works & waste burning
M 21	15C Marina Road, Afaha Eket	Moss	Polytrichum juniperinum	Elaeis guineensis (Oil palm)	High vehicular traffic & fossil fuel combustion
M 22	Primary school, Edebuk, QIT Road	Moss	Polytrichum juniperinum	Magnifera indica (Mango)	High vehicular traffic & fossil fuel combustion
M 23	Judiciary Magistrate Court, Iwuo-Achang	Moss	Calymperes erosum	Elaeis guineensis (Oil palm tree)	Fossil fuel combustion & waste burning
M 24	100 Jetty street, Iwuo Okpom, Mkpanak	Moss	Calymperes erosum	Elaeis guineensis (Oil palm tree)	Emissions from power plant, gas flaring & venting
M 25	Ibeno Beach, Mkpanak, Ibeno	Moss	Calymperes erosum	Elaeis guineensis (Oil palm tree)	Industrial power generation, gas flaring & venting

2.2. Sampling and Analytical Procedure

This study was conducted in the vicinity of two oil–producing host communities viz Eket and Ibeno Local Government Areas, in the coastal area of Akwa Ibom State (Figure 1). Akwa Ibom State is located in the South–South geopolitical zone and is one of the major oil–producing states in Nigeria's Niger Delta region. Eket Local Government Area occupies the South central territorial part of Akwa Ibom State (Figure 2; 4°33'N, 4°45'N and 7°52'E, 8°02'E) and based on data from 2006 Nigeria's national census [31], it is home to 172, 856 people and various oil and gas servicing companies. Ibeno Local Government Area occupies the largest Atlantic coastline of more than 129 km in Akwa Ibom State (Figure 3; 4°32' 02''N, 4°36'02''N and 7°48''E, 8°17'42''E) and based on data from 2006 Nigeria's national census [31], it is home to 74, 840 people and ExxonMobil Producing Nigeria Unlimited – Qua Iboe Terminal (QIT). Apart from gas flaring and venting associated with petroleum exploration and production in the Nigeria's Niger Delta [32], fossil fuel combustion and emissions from vehicular traffic are the main sources of atmospheric heavy metals in most host communities in Akwa Ibom State. In September 2004, lichen (*Parmelia caperata*) and moss (*Polytrichum juniperinum, Calymperes erosum and Racopilum africanum*) samples were collected from various sampling sites at Eket and Ibeno Local Government Areas. The general characteristic and major anthropogenic activities around the sampling sites are presented in Table 1. Lichen and moss samples were collected from trunks of 3 isolated trees per sampling points at 1.5 – 2 m above the ground level [19]. The lichen and moss samples were cleaned from mechanical impurities and dried at temperatures of 100°C for 24 h.

The oven dried samples were homogenized by grinding in agate mortars and stored in polyethylene bottles prior to elemental analysis. In the laboratory, 1 g of each powdered sample was mineralized with 20 ml mixture of concentrated nitric acid and perchloric acid at a 3:1 ratio (15 ml 70% $HN0_3$: 5ml 70% $HCl0_4$) using Teflon beakers on a Gerhardt digestion hot plate. The beakers were loosely covered to avoid atmospheric contamination and the digestates were heated until the nitric acid boils off and white fumes from perchloric acid indicated the end of digestion. The digestates (5 ml) were diluted with 20 ml distilled deionized water, filtered through a Whitman 541 filter paper into a volumetric flask and the final volume in each flask was adjusted to 100 ml with distilled deionized water. A series of blank samples were prepared using the same digestion method and the filtrates were analysed for concentrations of trace metals.

The total concentrations of heavy metals in lichen and moss samples were determined using atomic absorption spectrophotometer (AAS; SOLAAR 939, ATI UNICAM) equipped with flame and graphite furnace. The digestates were directly introduced into the flame with continuous aspiration through polyethylene tubing and the concentration of the object element was obtained from the calibration plot. The concentrations of trace metals in the extracts were determined by comparing the absorbance of the standard metal solution and accuracy of the results was checked by analysis of the Lichen BCR® CRM 482. The concentrations of heavy metals in lichen and moss samples were expressed on dry weight basis (μg g^{-1}). All analyses were carried out in duplicate and for each run, two blanks and a reference sample were analysed using the same procedure in order to ensure precision and accuracy of the analytical methods.

2.3. Statistical Analysis

The results obtained for the heavy metal concentrations in lichen and moss samples were subjected to statistical analysis. Variance in the data set was tested for statistical significance through analysis of variance (ANOVA) and correlation coefficients between the elements were determined by the Pearson product–moment using SigmaPlot® 12.5 (Systat Software Inc.).

Table 2. Background concentrations of trace metals (μg g^{-1} dry wt.) in the Lichen BCR® Certified Reference Material (CRM 482). Values are the mean (n=12) ± standard deviation (SD)

	Cd	Cr	Co	Cu	Mn	Ni	Pb	Zn
Certified ($\mu g\ g^{-1}$)	0.56 ± 0.02	4.12 ± 0.15	0.32 ± 0.03	7.03 ± 0.19	33.0 ± 0.5	2.47 ± 0.07	40.9 ± 1.4	100.6 ± 2.2
Found ($\mu g\ g^{-1}$)	0.56 ± 0.02	4.10 ± 0.12	0.32 ± 0.01	6.78 ± 0.34	32.0 ± 1.2	2.58 ± 0.15	39.9 ± 1.3	99.2 ± 4.7
Recovery %	100	100	100	96	97	100	98	99

3. Results and Discussion

The concentrations of heavy metals in the Lichen BCR® CRM 482 (Table 2) reveal that there were no significant differences between measured values and certified values for the reference material ($P > 0.05$). The measure of good agreement between the results obtained and certified values of the reference material indicates high precision of the analytical methods and accuracy of the results. The concentrations of heavy metals in lichen and moss samples at various sampling sites in the study area are reported in Table 3. Heavy metals concentrations in lichen and moss samples ranged from 0.001 – 0.092 μg g^{-1} for cadmium; 0.004 – 8.793 μg g^{-1} for chromium; 0.989 – 1.950 μg g^{-1} for cobalt; 2.350 – 110.760 μg g^{-1} for copper; 10.530 – 153.320 μg g^{-1} for manganese; 1.425 – 21.730 μg g^{-1} for nickel; 0.001 – 17.380 μg g^{-1} for lead, and 23.530 – 130.600 μg g^{-1} for zinc. There were variations in the concentrations of heavy metals between samples collected from different sampling sites and the differences were statistically significant for most elements ($P < 0.01$). The data revealed very strong statistical significance of correlations between Cu–Pb, Cu–Zn, Pb–Ni and Mn–Zn concentrations (Table 4). In a direct comparison, elemental analysis reveals that most target heavy metals were present in elevated concentrations in moss samples compared to those in lichen from the same sampling site (Table 5).

Table 3. Heavy metals concentrations ($\mu g\ g^{-1}$ dry wt.) in lichen and moss samples. Values are the mean ($n=2$) ± standard deviation (SD)

Sample	Cd	Cr	Co	Cu	Mn	Ni	Pb	Zn
M 1	0.002 ± 0.04	5.816 ± 0.02	1.175 ± 0.02	18.180 ± 0.02	113.250 ± 0.02	6.480 ± 0.02	16.700 ± 0.02	87.700 ± 0.02
L 2*	0.027 ± 0.02	0.005 ± 0.02	0.989 ± 0.01	15.240 ± 0.01	53.710 ± 0.01	3.230 ± 0.01	0.695 ± 0.01	49.070 ± 0.01
M 3*	0.046 ± 0.12	2.305 ± 0.02	1.150 ± 0.01	7.618 ± 0.01	153.320 ± 0.01	3.390 ± 0.01	0.860 ± 0.01	74.570 ± 0.01
M 4	0.064 ± 0.02	1.038 ± 0.02	1.950 ± 0.01	11.700 ± 0.01	92.950 ± 0.01	21.730 ± 0.01	2.425 ± 0.01	60.300 ± 0.01
M 5	0.002 ± 0.00	1.662 ± 0.02	1.250 ± 0.01	15.230 ± 0.01	19.130 ± 0.01	3.050 ± 0.01	4.550 ± 0.01	64.430 ± 0.01
M 6	0.005 ± 0.00	1.801 ± 0.02	1.301 ± 0.01	6.575 ± 0.01	41.350 ± 0.01	2.700 ± 0.01	0.001 ± 0.01	69.420 ± 0.01
M 7	0.001 ± 0.00	8.793 ± 0.02	1.550 ± 0.01	7.950 ± 0.01	25.850 ± 0.01	3.850 ± 0.01	4.225 ± 0.01	46.030 ± 0.01
M 8	0.051 ± 0.02	1.385 ± 0.02	1.725 ± 0.01	8.575 ± 0.01	63.700 ± 0.01	3.350 ± 0.01	0.001 ± 0.01	69.780 ± 0.01
M 9	0.059 ± 0.01	3.462 ± 0.02	1.475 ± 0.01	9.675 ± 0.01	33.600 ± 0.01	2.550 ± 0.01	0.050 ± 0.01	23.530 ± 0.01
M 10	0.092 ± 0.01	2.285 ± 0.02	1.350 ± 0.01	10.150 ± 0.01	74.030 ± 0.01	3.050 ± 0.01	0.001 ± 0.01	70.780 ± 0.01
L 11**	0.004 ± 0.01	2.205 ± 0.02	1.516 ± 0.01	8.660 ± 0.01	132.160 ± 0.01	2.600 ± 0.01	0.870 ± 0.01	81.590 ± 0.01
M 12**	0.004 ± 0.01	4.126 ± 0.02	1.293 ± 0.01	7.676 ± 0.01	131.510 ± 0.01	3.980 ± 0.01	1.390 ± 0.01	63.180 ± 0.01
M 13	0.007 ± 0.01	3.462 ± 0.02	1.500 ± 0.01	8.575 ± 0.01	116.800 ± 0.01	3.450 ± 0.01	2.210 ± 0.01	65.800 ± 0.01
M 14	0.009 ± 0.02	8.654 ± 0.02	1.910 ± 0.01	17.780 ± 0.01	131.280 ± 0.01	4.680 ± 0.01	6.050 ± 0.01	72.100 ± 0.01
M 15	0.005 ± 0.01	2.354 ± 0.02	1.375 ± 0.01	5.570 ± 0.01	106.530 ± 0.01	2.750 ± 0.01	2.500 ± 0.01	55.650 ± 0.01
M 16	0.050 ± 0.02	5.400 ± 0.02	1.600 ± 0.01	17.780 ± 0.01	115.230 ± 0.01	4.200 ± 0.01	2.025 ± 0.01	60.280 ± 0.01
L 17***	0.082 ± 0.02	0.205 ± 0.02	1.120 ± 0.01	14.490 ± 0.01	10.530 ± 0.01	1.430 ± 0.01	0.541 ± 0.01	55.250 ± 0.01
M 18***	0.086 ± 0.02	2.307 ± 0.02	1.137 ± 0.01	9.830 ± 0.01	29.910 ± 0.01	3.045 ± 0.01	1.306 ± 0.01	58.700 ± 0.01
M 19	0.008 ± 0.02	0.004 ± 0.02	1.675 ± 0.01	110.760 ± 0.01	79.830 ± 0.01	4.750 ± 0.01	17.380 ± 0.01	130.600 ± 0.01
M 20	0.005 ± 0.02	4.085 ± 0.02	1.625 ± 0.01	11.050 ± 0.01	90.780 ± 0.01	2.830 ± 0.01	3.550 ± 0.01	68.350 ± 0.01
M 21	0.001 ± 0.02	3.669 ± 0.02	1.575 ± 0.01	9.650 ± 0.01	49.030 ± 0.01	2.480 ± 0.01	4.200 ± 0.01	41.430 ± 0.01
M 22	0.001 ± 0.02	4.501 ± 0.02	1.750 ± 0.01	4.650 ± 0.01	95.680 ± 0.01	3.310 ± 0.01	3.010 ± 0.01	65.250 ± 0.01
M 23	0.004 ± 0.02	2.908 ± 0.02	1.350 ± 0.01	7.475 ± 0.01	15.780 ± 0.01	2.425 ± 0.01	2.350 ± 0.01	31.980 ± 0.01
M 24	0.003 ± 0.02	2.007 ± 0.02	1.450 ± 0.01	2.350 ± 0.01	13.790 ± 0.01	1.425 ± 0.01	1.825 ± 0.01	44.530 ± 0.01
M 25	0.056 ± 0.02	4.431 ± 0.02	1.925 ± 0.01	9.650 ± 0.01	59.310 ± 0.01	2.100 ± 0.01	0.001 ± 0.01	± 0.01
Mean	0.027	3.155	1.469	14.274	73.962	3.953	3.149	61.948
Median	0.007	2.354	1.475	9.650	74.030	3.050	2.025	63.180
Min	0.001	0.004	0.989	2.350	10.530	1.425	0.001	23.530
Max	0.092	8.793	1.950	110.760	153.320	21.730	17.380	130.600
SD	0.031	2.284	0.264	20.524	43.737	3.855	4.488	20.883

*, **, *** Samples of lichen and moss from the same site; L = Lichen; M = Moss

Table 4. Pearson correlation coefficient (r) of concentrations of heavy metals in lichen and moss samples

	Cd	Cr	Co	Cu	Mn	Ni	Pb	Zn
Cd	1.00							
Cr	-0.302	1.00						
Co	-0.078	0.352	1.00					
Cu	-0.084	-0.244	0.145	1.00				
Mn	-0.165	0.258	0.215	0.056	1.00			
Ni	0.170	-0.065	0.379	0.085	0.236	1.00		
Pb	-0.396	0.162	0.073	0.717	0.175	0.169	1.00	
Zn	-0.161	-0.167	0.057	0.709	0.483	0.147	0.653	1.00

$P < 0.05$

Table 5. Descriptive statistics of heavy metals concentrations ($\mu g\ g^{-1}$ dry wt.) measured in lichen and moss samples from the same sampling site

Sample	Cd	Cr	Co	Cu	Mn	Ni	Pb	Zn
Lichen								
L 2*	0.027 ± 0.02	0.004 ± 0.02	0.989 ± 0.01	15.240 ± 0.01	53.710 ± 0.01	3.230 ± 0.01	0.695 ± 0.01	49.070 ± 0.01
L 11**	0.004 ± 0.01	2.205 ± 0.02	1.516 ± 0.01	8.660 ± 0.01	132.160 ± 0.01	2.600 ± 0.01	0.870 ± 0.01	81.590 ± 0.01
L 17***	0.082 ± 0.02	0.205 ± 0.02	1.120 ± 0.01	14.490 ± 0.01	10.530 ± 0.01	1.430 ± 0.01	0.541 ± 0.01	55.250 ± 0.01
Mean	0.038	0.805	1.208	12.797	65.467	2.420	0.702	61.970
Median	0.027	0.205	1.120	14.490	53.710	2.600	0.695	55.250
Min	0.004	0.004	0.989	8.660	10.530	1.430	0.541	49.070
Max	0.082	2.205	1.516	15.240	132.160	3.230	0.870	81.590
SD	0.040	1.217	0.274	3.602	61.661	0.913	0.165	17.270
Moss								
M 3*	0.046 ± 0.12	2.305 ± 0.02	1.150 ± 0.01	7.618 ± 0.01	153.320 ± 0.01	3.390 ± 0.01	0.860 ± 0.01	74.570 ± 0.01
M 12**	0.004 ± 0.01	4.126 ± 0.02	1.293 ± 0.01	7.676 ± 0.01	131.510 ± 0.01	3.980 ± 0.01	1.390 ± 0.01	63.180 ± 0.01
M 18***	0.086 ± 0.02	2.307 ± 0.02	1.137 ± 0.01	9.830 ± 0.01	29.910 ± 0.01	3.045 ± 0.01	1.306 ± 0.01	58.700 ± 0.01
Mean	0.045	2.913	1.193	8.375	104.913	3.472	1.185	65.483
Median	0.046	2.307	1.150	7.676	131.510	3.390	1.306	63.180
Min	0.004	2.305	1.137	7.618	29.910	3.045	0.860	58.700
Max	0.086	4.126	1.293	9.830	153.320	3.980	1.390	74.570
SD	0.041	1.051	0.087	1.261	65.864	0.473	0.285	8.182

Cadmium (Cd) concentrations in lichen and moss samples ranged from 0.001 to 0.092 μg g^{-1} with a mean concentration of 0.027 ± 0.031 μg g^{-1} (Table 3). The concentrations of Cd in lichen and moss samples were still at background levels at all the sampling sites. The background concentrations of Cd of 0.05 – 0.70 μg g^{-1} have been reported in related studies in other regions in Nigeria [21,22]. Several studies have reported varying

concentrations of Cd in lichen and moss samples. Examples of the concentrations of Cd in lichen and moss samples obtained from other studies include 0.16 – 6.13 μg g^{-1} [33]; 0.191 μg g^{-1} [34]; 0.047 – 0.162 μg g^{-1} [35]; 0.97 – 1.26 μg g^{-1} [36]; 0.34 – 1.07 μg g^{-1} [13]; 0.24 – 1.4 μg g^{-1} [37]; 0.10 – 0.64 μg g^{-1} [38], and 0.09 – 0.31 μg g^{-1} [39]. In the present study, the highest concentration of Cd of 0.092 μg g^{-1} obtained at Ikot Udoma (Sample M 10, Table 1) can be attributed to anthropogenic activities such as combustion of fossil fuels and emissions from motor vehicles [38], metal works and waste burning [21,39]. The concentrations of Cd were not significantly correlated with concentrations of other metals (Table 4). Plants from unpolluted natural environments contain 0.01 – 0.3 μg g^{-1} Cd [10] and ambient air usually has a low concentration of Cd in particulate form [40]. The background concentrations of Cd measured in this study are within the range of values obtained in similar studies in the developed countries like United State of America (U.S.A) and Europe.

Chromium (Cr) concentrations in lichen and moss samples ranged from 0.004 to 8.793 μg g^{-1} with a mean concentration of 3.155 ± 2.284 μg g^{-1} (Table 3). The highest concentrations of Cr were observed in rural settlement at Ikot Odiong (8.793 μg g^{-1}) and Ikot Obio Amana (8.654 μg g^{-1}) compared to the lowest concentration of Cr of 0.004 μg g^{-1} measured at Atabong Road, which is an urban site with high anthropogenic activities (Table 1). The highest concentrations of Cr at these rural sites are attributed to long–range transport of trace metals in ambient aerosols [41] and local point sources such as a metal works, automobile workshop and wastes incineration located near the sampling sites. In addition, aerial fallout of windblown dust contribution from metal corrosion and soil of the study area might have increased the contamination load of the surrounding atmosphere. Several studies have reported varying concentrations of Cr in lichen and moss samples. Examples of the concentrations of Cr in lichen and moss samples obtained from other studies include 1.4 – 2.6 μg g^{-1} [13]; 1.60 – 4.70 μg g^{-1} [37]; 3.6 μg g^{-1} [34]; 1.6 – 39.3 μg g^{-1} [42]; 2.62 – 6.69 μg g^{-1} [36]; 111 – 244 μg g^{-1} [43]; 1.20 – 3.01 μg g^{-1} [38]; 1.00 – 829.00 μg g^{-1} [17], and 0.07 – 2.54 μg g^{-1} [39]. Apart from subtle relationship with Co, the concentrations of Cr were not significantly correlated with concentrations of other metals in the present study (Table 4). It has been reported that the concentrations of Cr in urban air ranged from <10 ng m^{-3} to 50 ng m^{-3} [44]. The potential sources of human exposure to Cr are attributed to emissions from power plants [5,45], incineration of municipal wastes, metal works (e.g. welding and chrome-plating, etc.) and application of anti–corrosion paints.

Cobalt (Co) concentrations in lichen and moss samples ranged from 0.989 to 1.950 μg g^{-1} with a mean concentration of 1.469 ± 0.264 μg g^{-1} (Table 3). The concentrations of Co in lichen and moss samples were still at background levels at all the sampling sites. The natural background concentrations of Co is in the order of 1 pg m^{-3} and concentrations up to 40 ng m^{-3} have been reported in urban areas [46]. Several studies have reported varying concentrations of Co in lichen and moss samples. Examples of the concentrations of Co in lichen and moss samples obtained from other studies include 0.284 μg g^{-1} [34]; 0.28 – 0.55 μg g^{-1} [36]; 0.20 – 5.55 μg g^{-1} [38], and 3.33 – 5.63 μg g^{-1} [39]. Apart from subtle relationship with Ni, the concentrations of Co were not significantly correlated with concentrations of other metals in the present study (Table 4). Co is closely related to Ni in both its chemical and biochemical properties. The elevated concentrations of Co at some of the sampling sites are attributed to anthropogenic sources such as emissions from automobile exhausts, metal works, wastes burning, combustion of fossil fuels, and industrial emissions such as gas flaring and venting [47,48]. The behaviour of anthropogenic Co in the environment is poorly understood and there is limited baseline information to support wider and long–term environmental impacts.

Copper (Cu) concentrations in lichen and moss samples ranged from 2.350 to 110.760 μg g^{-1} with a mean concentration of 1.469 ± 0.264 μg g^{-1} (Table 3). The highest concentration of Cu of 110.760 μg g^{-1} was measured at a sampling site at Atabong Road (Table 1) and was significantly higher ($P < 0.05$) compared to concentrations of Cu at other sampling sites (Table 3). The background Cu concentrations of 10 – 30 μg g^{-1} measured at other sampling sites are in agreement with earlier study by Onianwa [22] and concentrations of 0.6 – 1.0 μg g^{-1} have been measured in *Alectoria* lichens in Mt. Rainier and Olympic National Park, Washington, U.S.A [49]. Several studies have reported varying concentrations of Cu in lichen and moss samples. Examples of the concentrations of Cu in lichen and moss samples obtained from other studies include 8.10 – 38.10 μg g^{-1} [21]; 1.79 – 36.78 μg g^{-1} [33]; 0.91 μg g^{-1} [34]; 7.0 – 13.3 μg g^{-1} [42]; 11.40 – 96.00 μg g^{-1} [50]; 1.00 – 9.70 μg g^{-1} [13]; 3.8 – 14.0 μg g^{-1} [37]; 7.19 – 22.4 μg g^{-1} [38], and 1.60 – 26.30 μg g^{-1} [17]. Few studies have reported that average concentrations are usually well below 1 μg m^{-3}, but higher concentrations may be found in urban or otherwise polluted areas [51,52,53]. The elevated concentrations of Cu herein reported at most of the sampling sites in the present study are much higher than background concentration of Cu 4.8 μg g^{-1} obtained for the Olympic National Park, Washington, U.S.A. [54]. Apart from significant correlations with Pb ($r = 0.72$) and Zn ($r = 0.71$), the concentrations of Cu were not significantly correlated with concentrations of other metals (Table 4). The elevated concentrations of Cu at some sampling sites, which often depend on the proximity to major anthropogenic sources, are attributed to emissions from vehicular traffic, metal works and other local anthropogenic source such as Cu–containing dust from metal corrosion.

Manganese (Mn) concentrations in lichen and moss samples ranged from 10.530 to 153.320 μg g^{-1} with a mean concentration of 73.962 ± 43.737 μg g^{-1} (Table 3). The concentrations of Mn in lichen and moss samples were still at background levels at most of the sampling sites. The elevated concentrations of Mn were measured at samplings sites in the urban areas compared to the rural areas (Table 3). In urban and rural areas without significant manganese contamination, annual averages of manganese concentration are mainly in the range of 0.01 – 0.07 μg m^{-3} [55,56]. Several studies have reported varying concentrations of Mn in lichen and moss samples. Examples of the concentrations of Mn in lichen and moss samples obtained from other studies include 93.00 –

802.00 μg g^{-1} [21]; 3.91 – 244.47 μg g^{-1} [33]; 22.70 – 114.33 μg g^{-1} [37]; 38.20 μg g^{-1} [34]; 57.30 – 104.00 μg g^{-1} [36]; 25.80 – 208.00 μg g^{-1} [38], and 9.50 – 202.90 μg g^{-}1 [17]. Apart from significant correlation with Zn (r = 0.48), the concentrations of Cu were not significantly correlated with concentrations of other metals in the present study (Table 4). The concentrations of Mn in the ambient air in the rural areas are probably reflecting the contribution of vegetation inputs [16,17]. However, it is known that Mn toxicity limits in plants are in the range of 400 – 1000 μg g^{-1} [57,58]. The atmospheric deposition of Mn is associated with local and/or anthropogenic activities in the urban areas and the distribution of Mn is more regional compared to Zn.

Nickel (Ni) concentrations in lichen and moss samples ranged from 1.425 to 21.730 μg g^{-1} with a mean concentration of 3.953 ± 3.855 μg g^{-1} (Table 3). The concentrations of Ni in lichen and moss samples were still at background levels at most of the sampling sites. According to Norseth and Piscator [59], atmospheric concentrations of Ni may range from 6 – 17 ng m^{-3} in suburban areas and 120 –170 ng m^{-3} in the industrialized regions and large cities. The background concentrations of Ni of 3.50 – 13.50 μg g^{-1} have been reported in few related studies in other regions in Nigeria [21,22]. In the large part of northern Europe, the concentrations of ambient Ni in mosses are generally less than 2 μg g^{-1} [25]. Several studies have reported varying concentrations of Ni in lichen and moss samples. Examples of the concentrations of Ni in lichen and moss samples obtained from other studies include 1.10 – 1.80 μg g^{-1} [35]; 0.83 – 10.20 μg g^{-1} [60]; 1.65 – 1.73 μg g^{-1} [13]; 2.6 – 11.4 μg g^{-1} [37], and 1.48 – 3.90 μg g^{-1} [38]. The values herein reported for most of the sampling sites in this present study are much higher than the background Ni concentration of < 0.5 μg g^{-1} reported for the Olympic National Park, Washington, U.S.A. [54]. Apart from subtle relationship with Co, the concentrations of Ni were not significantly correlated with concentrations of other metals in the present study (Table 4). The elevated concentrations of anthropogenic Ni in the urban areas are attributed to emissions from vehicular traffic, power generation plants, combustion of fossil fuel and incineration of municipal wastes.

Lead (Pb) concentrations in lichen and moss samples ranged from 0.001 to 17.380 μg g^{-1} with a mean concentration of 3.149 ± 4.488 μg g^{-1} (Table 3). The concentrations of Pb in lichen and moss samples were still at background levels at most of the sampling sites. The highest Pb concentrations of 16.70 μg g^{-1} and 17.38 μg g^{-1} were measured at the urban sites with the highest vehicular traffic density, frequent traffic queues and various anthropogenic activities (Table 1). The background concentrations of Pb of 5.00 – 40.00 μg g^{-1} have been reported in few related studies in other regions in Nigeria [21,22]. Several studies have reported varying concentrations of Pb in lichen and moss samples. Examples of the concentrations of Pb in lichen and moss samples obtained from other studies include 2.99 – 52.75 μg g^{-1} [33]; 15.90 μg g^{-1} [34]; 1.06 – 4.29 μg g^{-1} [35]; 27.30 – 50.80 μg g^{-1} [36]; 11.00 – 33.80 μg g^{-1} [13]; 4.03 – 44.60 μg g^{-1} [38]; 2.80 – 17.50 μg g^{-1} [17], and 3.10 – 30.81 μg g^{-1} [39]. The values obtained at most of the sampling sites in this study are similar to background Pb concentration of 3.6 μg g^{-1} reported for the Olympic National Park, Washington, U.S.A. [54]. Apart from significant correlation with Cu (r = 0.72) and Zn (r = 0.65), the concentrations of Pb were not significantly correlated with concentrations of other metals in the present study (Table 4). The elevated concentrations of Pb reported in the present study are mainly attributed to emissions from vehicular traffic [38,61,62], exhaust gases associated with fossil fuel combustion, metal works, automobile repairs and municipal wastes incineration. However, it is important to note that long–term exposure to Pb contamination (>5 μg g^{-1}) may cause complex human health effects such as chronic and/or peripheral neuropathy especially in children [63,64].

Zinc (Zn) concentrations in lichen and moss samples ranged from 23.530 to 130.600 μg g^{-1} with a mean concentration of 61.948 ± 20.883 μg g^{-1} (Table 3). The concentrations of Zn in lichen and moss samples were still at background levels at most of the sampling sites. The highest concentration of Zn of 130.60 μg g^{-1} was obtained at Atabong Road, an urban site with high vehicular traffic density, frequent traffic queues and other local anthropogenic activities (Table 1). The elevated concentrations herein reported at most of the sampling sites in this study are higher than Zn concentration of 9 – 15 μg g^{-1} reported for the Olympic [49,54] and Mt. Rainier National Park, Washington, U.S.A. [49]. The background Zn concentrations of 26.30 – 153.00 μg g^{-1} have been reported in South West region of Nigeria [21]. Several studies have reported varying concentrations of Zn in lichen and moss samples. Examples of the concentrations of Zn in lichen and moss samples obtained from other studies include 3.40 – 68.22 μg g^{-1} [33]; 6.48 – 36.90 μg g^{-1} [35]; 37.00 – 101.00 μg g^{-1} [42]; 35.00 – 204.00 μg g^{-1} [43]; 39.00 – 69.00 μg g^{-1} [13]; 23.70 – 76.10 μg g^{-1} [37]; 14.50 – 41.80 μg g^{-1} [38]; 8.70 – 278.60 μg g^{-1} [17], and 23.50 – 68.24 μg g^{-1} [39]. Although the normal concentrations of Zn in plants are in the range of 10 – 100 μg g^{-1} [10], concentration of Zn in lichens > 100 μg g^{-1} is an indication of environmental contamination [65]. Apart from significant correlations with Cu (r = 0.72) and Pb (r = 0.65), the concentrations of Zn were not significantly correlated with concentrations of other metals in the present study (Table 4). The significant correlations among most of the elements such as Fe, Zn, Pb, Cr, Ni and Cu are considered as indicative of vehicle emissions airborne deposition [11,66]. The elevated concentrations of Zn deposition reported in the present study are attributed to emissions from vehicles, fossil fuel combustion, wastes incineration, metal works and rapid corrosion of zinc roofs in the Niger Delta region.

The differences in concentrations of heavy metals between lichens and mosses were statistically significant (P < 0.05) for Cd, Cr, Mn, Ni, Pb and Zn, with mosses retaining higher concentrations than lichens except for Co and Cu (Table 5). In a similar study, Loppi and Bonini [67] reported significant differences (P < 0.05) in concentrations of heavy metals between lichens and mosses for Al, B, Fe, Hg, Pb, Sb, and Zn, with mosses retaining higher values than lichens except for Hg and Zn. Although lichens and mosses accumulate particulates and dissolve chemical species through dry and wet deposition [2,16,67], heavy metals deposition in mosses are more closely related to the chemical composition of rain water

[68,69]. Further, sea–spray or sea salt aerosols may contribute about 10% of total trace element emissions to the atmosphere [69,70]. Apart from strong marine influence that can affect metal deposition [71], emissions from gas flaring systems and acid precipitation might have affected the distribution of some heavy metals in epiphytic lichen and moss species at some of the sampling sites.

4. Conclusions

This study has shown the variations in the concentrations of heavy metals in lichen and moss samples and the distribution of certain heavy metals has shown that deposition patterns are mainly dominated by local and/or regional anthropogenic sources peculiar in the studied area. The concentrations of most target heavy metals in lichen and moss samples were relatively higher in urban sites compared to rural sites. Apart from gas flaring and venting associated with petroleum production that influence air quality in the Niger Delta region, statistical correlations confirmed that emissions from vehicular traffic, fossil fuel combustion, solid waste disposal and other local anthropogenic activities greatly contribute to atmospheric heavy metal contamination in this region. Epiphytic mosses are better accumulative bioindicators for some target atmospheric heavy metals such as Cd, Cr, Mn, Ni and Zn compared to lichens. Depending on speciation and bioavailability, long–term exposure to elevated concentrations of ambient heavy metals may pose a threat to human health and the environment. This study has made important contributions toward the understanding of atmospheric metal distribution patterns and the obtained baseline data can be used for identification of spatial and temporal changes in the distribution of atmospheric heavy metals in the studied area. The use of epiphytic lichens and mosses provides a cost–effective approach for monitoring regional atmospheric heavy metal contamination and may be effectively used in large scale air pollution monitoring programme.

References

[1] Lepp, N. W., Effects of heavy metal pollution on plants. Vol.1, Effects of trace metals on plant function, London: Applied Science Publishers, 1981.

[2] Adriano, D. C., Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals, p. pp. 867, New York; Berlin; Heidelberg: Springer, 2001.

[3] Akbulut, M., S. Calisir, T. Marakoglu, and H. Coklar, “Chemical and technological properties of European cranberrybush (Viburnum opulus L.) fruits,” Asian Journal of Chemistry, 20 1875-1885, 2008.

[4] Ross, H., “On the use of mosses (Hylocomium splendens and Pleurozium schreberi) for estimating atmospheric trace metal deposition,” Water, Air, & Soil Pollution, 50 (1). 63-76, 1990.

[5] Markert, B. A., Plants as biomonitors : indicators for heavy metals in the terrestrial environment, Weinheim; New York: VCH, 1993.

[6] Misra, S., and D. Mani, Soil pollution, New Delhi: APH Publishing Corp., 2009.

[7] Pacyna, J. M., "Source Inventories for Atmospheric Trace Metals," Atmospheric Particles, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems R. M. Harrison and R. E. van Grieken, eds., pp. 385 - 423: Wiley, Chichester, UK, 1998.

[8] Michaelis, W., “Wet and dry deposition of heavy metals,” Technische Mitteilungen, 79 (5-6). 266-271, 1986.

[9] Tuncel, G., “Wet and dry deposition fluxes of major ions in the Eastern Mediterranean, Black Sea and Central Anatolia,” Map Technical Report Series (133). 1-34, 2001.

[10] Allen, S. E., Chemical analysis of ecological materials, Oxford: Blackwell Scientific Publications, 1989.

[11] Ward, N. I., “Multielement contamination of British motorway environments,” Science of the Total Environment, 93 393-401, 1990.

[12] Markert, B. A., A. M. Breure, and H. G. Zechmeister, Bioindicators and biomonitors: principles, concepts and applications, Amsterdam; Boston: Elsevier, 2003.

[13] Grodzińska, K., M. Frontasyeva, G. Szarek-Łukaszewska, M. Klich, A. Kucharska-Fabiś, S. F. Gundorina, and T. M. Ostrovnaya, “Trace Element Contamination in Industrial Regions of Poland Studied by Moss Monitoring,” Environmental Monitoring and Assessment, 87 (3). 255-270, 2003.

[14] Rühling, A, and G. Tyler, “An ecological approach to the lead problem,” Botaniska Notiser, 122 248-342, 1968.

[15] Tyler, G., "Moss analysis – a method for surveying heavy metal deposition."

[16] Steinnes, E., “A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals,” Science of the Total Environment, 160-161 243-249, 1995.

[17] Abdullah, M. Z., A. B. Saat, and Z. B. Hamzah, “Assessment of the impact of petroleum and petrochemical industries to the surrounding areas in Malaysia using mosses as bioindicator supported by multivariate analysis,” Environmental Monitoring and Assessment, 184 (6). 3959-3969, 2012.

[18] Markert, B., “Definitions and principles for bioindication and biomonitoring of trace metals in the environment,” Journal of Trace Elements in Medicine and Biology, 21, Supplement 1 77-82, 2007.

[19] Klos, A., M. Rajfur, I. Sramek, and M. Waclawek, “Use of Lichen and Moss in Assessment of Forest Contamination with Heavy Metals in Praded and Glacensis Euroregions (Poland and Czech Republic),” Water Air and Soil Pollution, 222 (1-4). 367-376, 2011.

[20] Pino, A., A. Alimonti, F. Botre, C. Minoia, B. Bocca, and M. E. Conti, “Determination of twenty-five elements in lichens by sector field inductively coupled plasma mass spectrometry and microwave-assisted acid digestion,” Rapid Communications in Mass Spectrometry: RCM, 21 (12). 1900-1906, 2007.

[21] Onianwa, P. C., and S. O. Ajayi, “Heavy metal contents of epiphytic acrocarpous mosses within inhabited sites in Southwest Nigeria,” Environment International, 13 (2). 191-196, 1987.

[22] Onianwa, P. C., S. O. Ajayi, O. Osibanjo, and A. Egunyomi, “Accumulation patterns of heavy metals in forest mosses from the south-west region of Nigeria,” Environmental Pollution Series B, Chemical and Physical, 11 (1). 67-78, 1986.

[23] Onianwa, P. C., and A. Egunyomi, “Trace metal levels in some Nigerian mosses used as indicators of atmospheric pollution,” Environmental Pollution Series B, Chemical and Physical, 5 (1). 71-81, 1983.

[24] Kakulu, S. E., “Biological monitoring of atmospheric trace metal deposition in North-Eastern Nigeria,” Environmental Monitoring and Assessment, 28 (2). 137-143, 1993.

[25] Rühling, A., Atmospheric heavy metal deposition in Europe: estimations based on moss analysis, Copenhagen: Nordic Council of Ministers, 1994.

[26] Sawidis, T., G. A. Zachariadis, J. Stratis, and E. Ladukakis, “Mosses as Biological Indicators for Monitoring of Heavy Metal Pollution,” Fresenius Environmental Bulletin, 2 193-199, 1993.

[27] Sawidis, T., M. K. Chettri, G. A. Zachariadis, J. A. Stratis, and M. R. D. Seaward, “Heavy metal bioaccumulation in lichens from Macedonia in Northern Greece,” Toxicological and Environmental Chemistry, 50 (1-4). 157-166, 1995.

[28] Garty, J., "Lichens as Biomonitors for Heavy Metal Pollution," Plants as biomonitors: indicators for heavy metals in the terrestrial environment, B. A. Markert, ed., pp. 193-264, Weinheim; New York: VCH, 1993.

[29] Bako, S. P., S. Afolabi, and I. I. Funtua, “Spatial distribution and heavy metal content of some bryophytes and lichens in relation to air pollution in Nigeria's Guinea Savanna,” International Journal of Environment and Pollution, 33 (2). 195-206, 2008.

[30] Fatoba, P. O., and T. I. Oduekun, "Assessment of metal deposition in Ilorin metropolis using mosses as bioindicators," Nigerian Journal of Pure and Applied Science, 19 1549-1552, 2004.

[31] NPC, 2006 Population and Housing Census of the Federal Republic of Nigeria: National and State Population and Housing Tables, Federal Republic of Nigeria - Abuja: National Population Commission (NPC), 2009.

[32] Ite, A. E., and U. J. Ibok, "Gas Flaring and Venting Associated with Petroleum Exploration and Production in the Nigeria's Niger Delta," American Journal of Environmental Protection, 1 (4). 70-77, 2013.

[33] Jozwik, Z., "Heavy metals in tundra plants of Bellsund area, Spitsbergen," Polish Polar Research, 11 401-409, 1990.

[34] Loppi, S., S. A. Pirintsos, and V. De Dominicis, "Soil Contribution to the Elemental Composition of Epiphytic Lichens (Tuscany, Central Italy)," Environmental Monitoring and Assessment, 58 (2). 121-131, 1999.

[35] Riget, F., G. Asmund, and P. Aastrup, "The use of lichen (Cetraria nivalis) and moss (Rhacomitrium lanuginosum) as monitors for atmospheric deposition in Greenland," The Science of the total environment, 245 (1-3). 137-148, 2000.

[36] Jeran, Z., R. Jacimovic, F. Batic, and R. Mavsar, "Lichens as integrating air pollution monitors," Environmental Pollution, 120 (1). 107-113, 2002.

[37] Mendil, D., M. Tuzen, K. Yazici, and M. Soylak, "Heavy metals in lichens from roadsides and an industrial zone in Trabzon, Turkey," Bulletin of Environmental Contamination and Toxicology, 74 (1). 190-194, 2005.

[38] Uluozlu, O. D., K. Kinalioglu, M. Tuzen, and M. Soylak, "Trace metal levels in lichen samples from roadsides in East Black Sea region, Turkey," Biomedical Environmental Sciences, 20 (3). 203-207, 2007.

[39] Aksoy, A., Z. Leblebici, and M. G. Halici, "Biomonitoring of Heavy Metal Pollution Using Lichen (Pseudevernia furfuracea (L.) Zopf.) Exposed in Bags in a Semi-arid Region, Turkey," Plant Adaptation and Phytoremediation, M. Ashraf, M. Ozturk and M. S. A. Ahmad, eds., pp. 59-70: Springer Netherlands, 2010.

[40] Nordberg, G. F., K. Nogawa, M. Nordberg, and L. T. Friberg, "Chapter 23 - Cadmium," Handbook on the Toxicology of Metals (Third Edition), G. F. Nordberg, B. A. Fowler, M. Nordberg and L. T. Friberg, eds., pp. 445-486, Burlington: Academic Press, 2007.

[41] Schroeder, W. H., M. Dobson, D. M. Kane, and N. D. Johnson, "Toxic Trace Elements Associated with Airborne Particulate Matter: A Review," JAPCA, 37 (11). 1267-1285, 1987.

[42] Loppi, S., E. Putortì, S. A. Pirintsos, and V. De Dominicis, "Accumulation of Heavy Metals in Epiphytic Lichens Near a Municipal Solid Waste Incinerator (Central Italy)," Environmental Monitoring and Assessment, 61 (3). 361-371, 2000.

[43] Pandey, V., D. K. Upreti, R. Pathak, and A. Pal, "Heavy metal accumulation in lichens from the Hetauda industrial area Narayani zone Makwanpur District, Nepal," Environmental Monitoring and Assessment, 73 (3). 221-228, 2002.

[44] Langard, S., and M. Costa, "Chapter 24 - Chromium," Handbook on the Toxicology of Metals (Third Edition), G. F. Nordberg, B. A. Fowler, M. Nordberg and L. T. Friberg, eds., pp. 487-510, Burlington: Academic Press, 2007.

[45] Harte, J., Toxics A to Z: A Guide to Everyday Pollution Hazards, Berkeley: University of California Press, 1991.

[46] Hamilton, E. I., "The geobiochemistry of cobalt," Science of the Total Environment, 150 (1-3). 7-39, 1994.

[47] Kim, J. H., H. J. Gibb, P. Howe, and M. Sheffer, Cobalt and inorganic cobalt compounds: Concise International Chemical Assessment Document, No 69 9789241530699 9241530693, World Health Organization, Geneva, 2006.

[48] Gál, J., A. Hursthouse, P. Tatner, F. Stewart, and R. Welton, "Cobalt and secondary poisoning in the terrestrial food chain: Data review and research gaps to support risk assessment," Environment International, 34 (6). 821-838, 2008.

[49] Frenzel, R. W., G. W. Witmer, and E. E. Starkey, "Heavy metal concentrations in a lichen of Mt. Rainier and Olympic National Parks, Washington, USA," Bulletin of Environmental Contamination and Toxicology, 44 (1). 158-164, 1990.

[50] Tüzen, M., "A Comparison of Sample Preparation Procedures for the Determination of Heavy Metals in Lichen Samples by GFAAS," Analytical Letters, 35 (10). 1667-1676, 2002.

[51] Georgopoulos, P. G., A. Roy, M. J. Yonone-Lioy, R. E. Opiekun, and P. J. Lioy, "Environmental copper: its dynamics and human exposure issues," Journal of Toxicology and Environmental Health. Part B, Critical Reviews, 4 (4). 341-394, 2001.

[52] Sweet, C. W., S. J. Vermette, and S. Landsberger, "Sources of toxic trace elements in urban air in Illinois," Environmental Science & Technology, 27 (12). 2502-2510, 1993.

[53] Romo-Kröger, C. M., and F. Llona, "A case of atmospheric contamination at the slopes of the Los Andes mountain range," Atmospheric Environment. Part A. General Topics, 27 (3). 401-404, 1993.

[54] Wiersma, G. B., M. E. Harmon, G. A. Baker, and S. E. Greene, "Elemental composition of Hylocomium splendens Hoh Rainforest Olympic National Park Washington, USA," Chemosphere, 16 (10-12). 2631-2645, 1987.

[55] WHO, Air Quality Guidelines for Europe, 2nd ed., p. pp. 273, Copenhagen, Denmark: World Health Organization, Regional Office for Europe, 2000.

[56] Pace, T. G., and N. H. Frank, Procedures for estimating probability of nonattainment of a PM10 NAAQS using total suspended particulate or inhalable particulate data, Research Triangle Park, N.C.: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division, 1984.

[57] Kula, E., P. Hrdlička, J. Hedbávný, and P. Švec, "Various content of manganese in selected forest tree species and plants in the undergrowth," Beskydy, 5 (1). 19-26, 2012.

[58] Zhu, F., L. Qu, W. Fan, M. Qiao, H. Hao, and X. Wang, "Assessment of heavy metals in some wild edible mushrooms collected from Yunnan Province, China," Environmental Monitoring and Assessment, 179 (1-4). 191-199, 2011.

[59] Norseth, T., and M. Piscator, "Nickel," Handbook on the Toxicology of Metals, L. Friberg, G. Nordberg and V. B. Vouk, eds., pp. 541-553, Amsterdam; New York: Elsevier/North-Holland Biomedical Press, 1979.

[60] Allen-Gil, S. M., J. Ford, B. K. Lasorsa, M. Monetti, T. Vlasova, and D. H. Landers, "Heavy metal contamination in the Taimyr Peninsula, Siberian Arctic," Science of the Total Environment, 301 (1-3). 119-138, 2003.

[61] Divrikli, U., M. Soylak, L. Elci, and M. Dogan, "Trace Heavy Metal Levels in Street Dust Samples from Yozgat City Center, Turkey," Journal of Trace and Microprobe Techniques, 21 (2). 351-361, 2003.

[62] Pacyna, J. M., and T. E. Graedel, "Atmospheric Emissions Inventories: Status and Prospects," Annual Review of Energy and the Environment, 20 (1). 265-300, 1995.

[63] Klaassen, C., Casarett & Doull's Toxicology: The Basic Science of Poisons, Seventh Edition, New York: McGraw-Hill, 2007.

[64] Goyer, R. A., and T. W. Clarkson, "Toxic effects of metal," Casarett and Doull's Toxicology : The Basic Science of Poisons, C. D. Klaassen, ed., pp. 931-979, New York: McGraw-Hill, 2007.

[65] Adamo, P., S. Giordano, S. Vingiani, R. Castaldo Cobianchi, and P. Violante, "Trace element accumulation by moss and lichen exposed in bags in the city of Naples (Italy)," Environmental Pollution, 122 (1). 91-103, 2003.

[66] Garty, J., R. Ronen, and M. Galun, "Correlation between chlorophyll degradation and the amount of some elements in the lichen Ramalina duriaei (de not.) Jatta," Environmental and Experimental Botany, 25 (1). 67-74, 1985.

[67] Loppi, S., and I. Bonini, "Lichens and mosses as biomonitors of trace elements in areas with thermal springs and fumarole activity (Mt. Amiata, Central Italy)," Chemosphere, 41 (9). 1333-1336, 2000.

[68] Bargagli, R., Trace elements in terrestrial plants: an ecophysiological approach to biomonitoring and biorecovery: Springer, 1998.

[69] Reimann, C., J. H. Halleraker, G. Kashulina, and I. Bogatyrev, "Comparison of plant and precipitation chemistry in catchments with different levels of pollution on the Kola Peninsula, Russia," Science of the Total Environment, 243-244 169-191, 1999.

[70] Allen, A. G., E. Nemitz, J. P. Shi, R. M. Harrison, and J. C. Greenwood, "Size distributions of trace metals in atmospheric aerosols in the United Kingdom," Atmospheric Environment, 35 (27). 4581-4591, 2001.

[71] Coskun, M., E. Steinnes, M. Coskun, and A. Cayir, "Comparison of Epigeic Moss (Hypnum cupressiforme) and Lichen (Cladonia rangiformis) as Biomonitor Species of Atmospheric Metal Deposition," Bulletin of Environmental Contamination and Toxicology, 82 (1). 1-5, 2009.