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Heavy Metals in Epiphytic Lichens and Mosses of Oil–Producing Communities of Eket and Ibeno, Akwa Ibom State – Nigeria

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Abstract Epiphytic lichen (*Parmelia carperata*) and moss (*Polytrichum juniperinum, Calymperes erosum and Racopilum africanum*) samples were used as bioindicators and bioaccumulators of atmospheric heavy metals deposition in oil–producing host communities of Eket and Ibeno Local Government Areas of Akwa Ibom State – Nigeria. Sampling of lichen and moss species that are found to grow extensively and abundantly on the stems and branches of several plants was performed during September 2014 at 25 sampling location sevenly distributed over the two oil–producing host communities studied. Unwashed, oven dried and homogenized powdered lichen and moss samples were mineralized using wet digestion with 3:1 mixture of concentrated nitric acid and perchloric acid in Teflon beakers on a Gerhardt digestion hot plate. The concentrations of heavy metals and/or trace elements were determined by atomic absorption spectrometry (AAS) equipped with flame and/or graphite furnace systems. The concentration of heavy metals in lichen and moss samples ranged from 0.003 – 0.009 μg g^{-1} for Cadmium (Cd); 0.006 – 7.654 μg g^{-1} for Chromium (Cr); 1.120 – 1.999 μg g^{-1} for Cobalt (Co); 8.954 – 116.760 μg g^{-1} for Copper; 25.980 – 193.260 μg g^{-1} for Manganese (Mn); 2.268 – 23.783 μg g^{-1} for Nickel (Ni); 0.034 – 14.880 μg g^{-1} for Lead (Pb), and 26.230 – 98.780μg g^{-1} for Zinc (Zn).The mean concentration of heavy metals in the lichen and moss samples can be arranged in the decreasing order as follows: Mn > Zn > Cu > Ni > Cr > Pb > Co > Cd and the statistical analyses revealed that strong correlations exist between Cu–Pb, Cu–Zn, Pb–Ni and Mn–Zn concentrations. Some of the target heavy metals such as Cd, Cr, Mn, Ni and Zn were accumulated at higher concentrations in mosses compared to lichens from the same sampling location. There is some evidence that different site–specific characteristics affect the spatial distributions patterns and temporal trends of atmospheric deposition of heavy metals in the two oil–producing communities of Eket and Ibeno, Akwa Ibom State – Nigeria. However, a comparison with the previous study conducted in 2004by Ite et al. [1] showed a slightly decreasing trend of atmospheric heavy metal deposition and these results confirmed that air quality has not further deteriorated in the two oil–producing communities studied over the last 10 years.

Keywords: *heavy metals, lichen, moss, atomic absorption spectrometry, Oil–producing communities*

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1. Introduction

Heavy metals contamination of global environment arises from natural sources directly or indirectly from anthropogenic activities such as rapid industrialization, urbanization, energy generation, improper waste management and other local and/or regional anthropogenic sources. In the Nigeria's Niger Delta region, atmospheric heavy metal contamination has been a major environmental problem due to emissions from gas flaring associated with petroleum development, traffic–related emissions, combustion of fossil fuel, poor waste management strategies and local anthropogenic activities [1,2,3]. A large quantity of heavy metals associated with anthropogenic activities have been released into the atmosphere from where they can reach the soil environment and aquatic ecosystem through both dry and wet deposition processes. Apart from soil environment and aquatic ecosystem, atmospheric inorganic contaminants of natural origin or anthropogenic sources that contained heavy metals and/or trace elements such as Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn) at high concentrations could led to serious ecological consequences and pose human health risks [4]. Heavy metals are potentiallyhazardous to humans and various ecological receptors because of their toxicity, persistence, bioaccumulative and nonbiodegradable nature. Therefore, monitoring and evaluation of heavy metal

concentrations in soils, groundwater and atmospheric environment is imperative in order identify hazards to human health, to prevent bioaccumulation in the food chain and further degradation of the ecosystem [1,5]. According to Ite et al. [1] monitoring and assessment of heavy metals concentrations in theenvironment contribute towards effective understanding of biogeochemical processes and gauging ecosystem health.

Elemental analysis of lower plants, such as lichens and mosses, has become a powerful tool for biogeochemical prospecting, biomonitoring and assessment of spatial and/or temporal deposition patterns of atmospheric contaminants in several regions around the world [1,6-12]. Due to their physiological and morphologicalproperties [1,11,13,14,15,16], lichens and mosses have been widely used as bioindicators and bioaccumulators for assessing the atmospheric deposition of heavy metals and/or biological effects of airborne contaminants [10,16-31]. According to Shukla et al. [12], these lower (nonvascular) plants are long lived, having wide geographical distribution, and accumulate and retain many trace elements to concentrations that highly exceed their physiological requirements. Monitoring of the atmospheric quality of the ecosystem with lichens and mosses has been widely studied [1,6-42] and the concentrations of heavy metal contaminants in these lower plants may be directly correlated with environmental levels of trace elements [1,12]. According to Ite et al. [1], the use of lichens and mosses could provide information which may be used in assessment of spatial distribution patterns and temporal trend of atmospheric heavy metals deposition, identification of contaminants sources, assessment of potential environmental risks and/or human health risks associated with long–term exposure to ambient metals contamination. Although the use of lichens and mosses as bioindicators and bioaccumulators have been reported in several studies around the world, there are limited number of monitoring studies in the oil–producing communities in the Nigeria's Niger Delta region.

This study investigates the atmospheric heavy metals deposition using epiphytic lichen (*Parmelia carperata*) and moss (*Polytrichum juniperinum, Calymperes erosum and Racopilum africanum*) species that are found to grow extensively and abundantlyon the stems and branches of some plants in the oil–producing host communities of Eket and Ibeno Local Government Areas of Akwa Ibom State – Nigeria. The results obtained in this present study were compared with those obtained in the previous survey in 2004 [1], in order to evaluate temporal deposition trends and potential contamination of the atmospheric environment in the two oil–producing host communities studied. The suitability of lichens and mosses as bioindicators and bioaccumulators of atmospheric heavy metals deposition was assessed based on concentrations of trace elements measured in lichen and moss samples collected from the same sampling locations.

2. Materials and Methods

2.1. Materials

The chemicals, 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 and all the plastic and/or laboratory glassware were cleaned prior to use based on the procedure described by Ite et al. [1]. Sigma-Aldrich UK supplied the trace element standards and Lichen (trace elements) BCR® Certified Reference Material (CRM 482) used for analytical quality control. Prior to the experiment, the trace element standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg l^{-1} of each element obtained [1] and the range of concentrations of elements in the calibration solutions and detection limits were calculated.

2.2. Sampling, Sample Preparation and Analytical Procedure

Samples of epiphytic lichen (*Parmelia carperata*) and moss (*Polytrichum juniperinum, Calymperes erosum* and *Racopilum africanum*) were collected from various sampling locations in the oil–producing communities of Eket and Ibeno Local Government Areas of Akwa Ibom State (Figure 1). In September 2014, lichen and moss samples were collected from trunks of 3 isolated trees per sampling points at 1.5 – 2 m above the ground level [1,22] at 25 sampling locations evenly distributed over the two oil–producing host communities viz: Eket (Figure 2) and Ibeno (Figure 3) Local Government Areas of Akwa Ibom State – Nigeria. In order to enable comparison of the data from this present study with the previous study by Ite et al. [1], all of the sampling locations and biotope conditions were the same as those used in the 2004 pilot monitoring study. The general characteristic and major anthropogenic activities around the sampling locations have been previously described by Ite et al. [1]. Sampling and sample handling on the field and in the laboratory were carried using disposable polyethylene gloves for each lichen and moss sample in order to prevent any contamination.

In the laboratory, the unwashed samples of lichen and moss were cleaned from other extraneous materials(litter, dead leaves and tree bark) and oven dried at temperatures of 100°C for 24 h. Prior to elemental analysis, the homogenized powdered samples were prepared for atomic absorption spectrometry (AAS) technique based on the procedure described by Ite et al. [1]. In this present study, three replicates per lichen and moss sample were digested, and three replicate measurements per digest were performed in order to ensure precision and accuracy. The spectrophotometer (AAS; SOLAAR 939, ATI UNICAM) equipped with flame and/or graphite furnace system was optimized prior to the experiment, giving the recoveries of between 96 and 100 % depending on elements being analyzed [1]. In this present study, all analyses were carried out in triplicate and for each run, three blanks and a reference sample (Lichen BCR®CRM 482) were analysed using the same procedure [1]. The quality control for the AAS results was checked by analyses of a reference sample (Lichen BCR®CRM 482)which have been reported in the previous study by Ite et al. [1]and the measured values were in good agreement with the certified values. The results obtained for the heavy metal concentrations in lichen and moss samples were subjected to statistical analysis using statistical software package – SigmaPlot®, Version 12.5 (Systat Software Inc., USA). The descriptive statistical method was applied to the obtained data set to explain variations and the concentration of heavy metals in lichen and moss samples were expressed as micrograms per grams dry weight (µg g^{-1}).

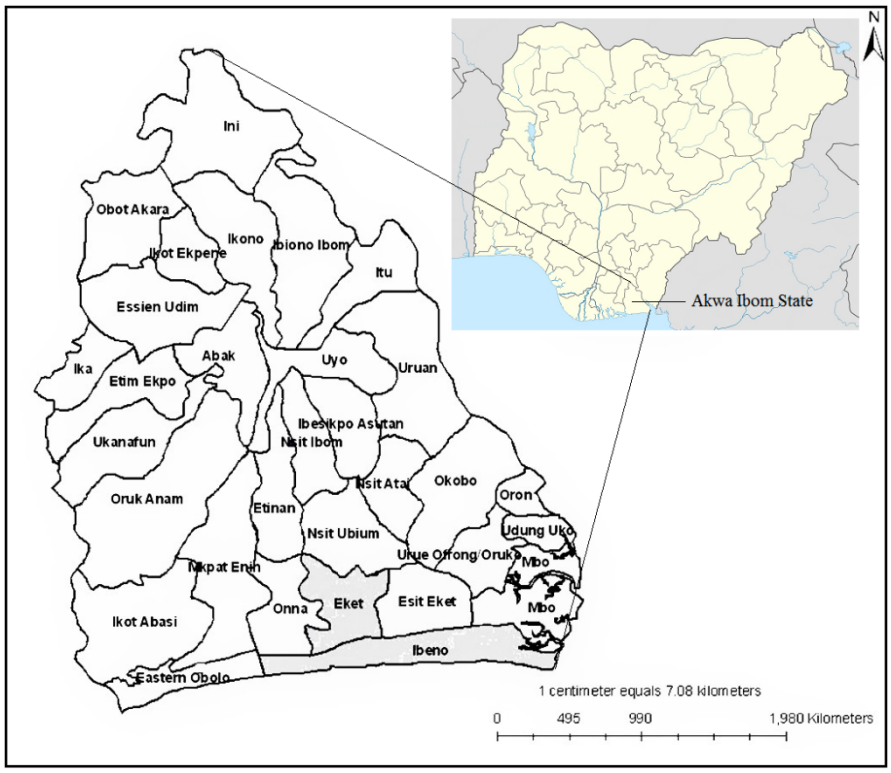

Figure 1. Map of Nigeria Showing the Location of Akwa Ibom State (Study Area: Oil–producing Communities of Eket and Ibeno Local Government Areas)

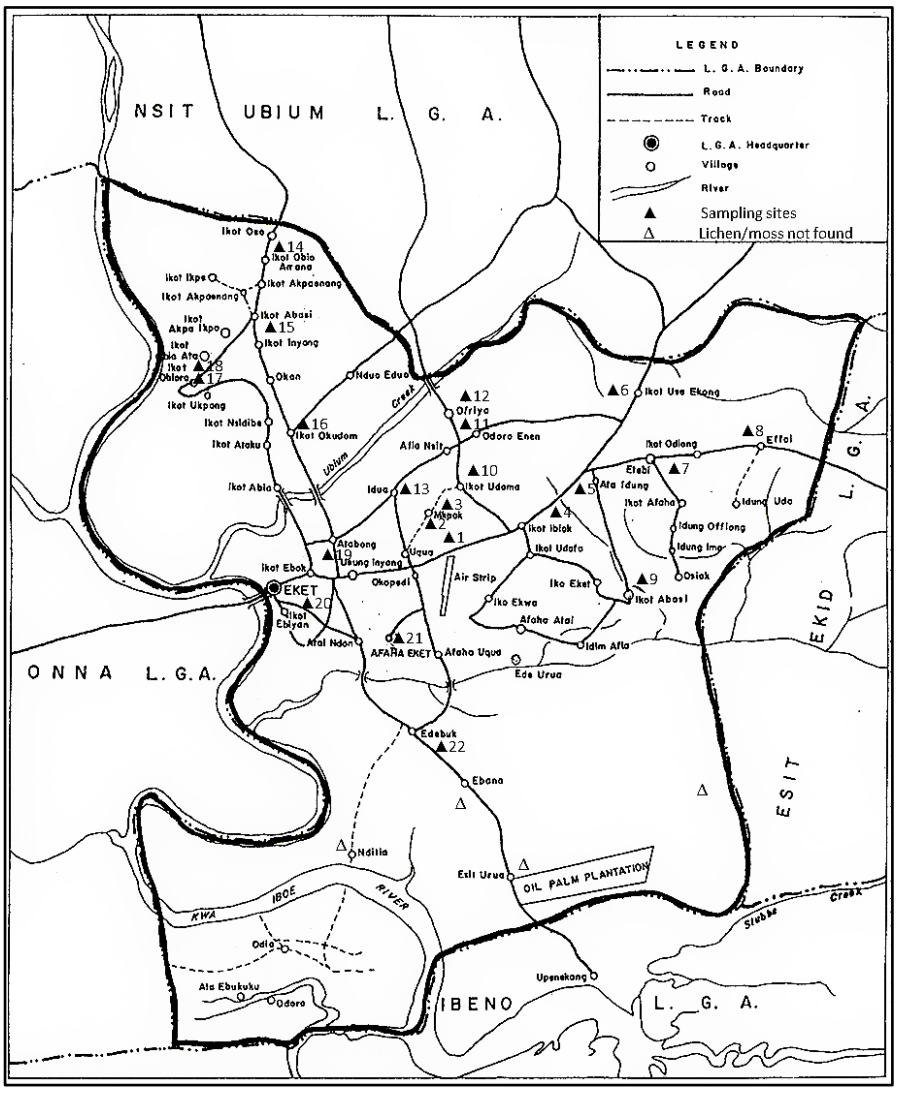

Figure 2. Map of Eket Local Government Area Showing the Location of Sampling Locations (Source: Ite et al. [1])

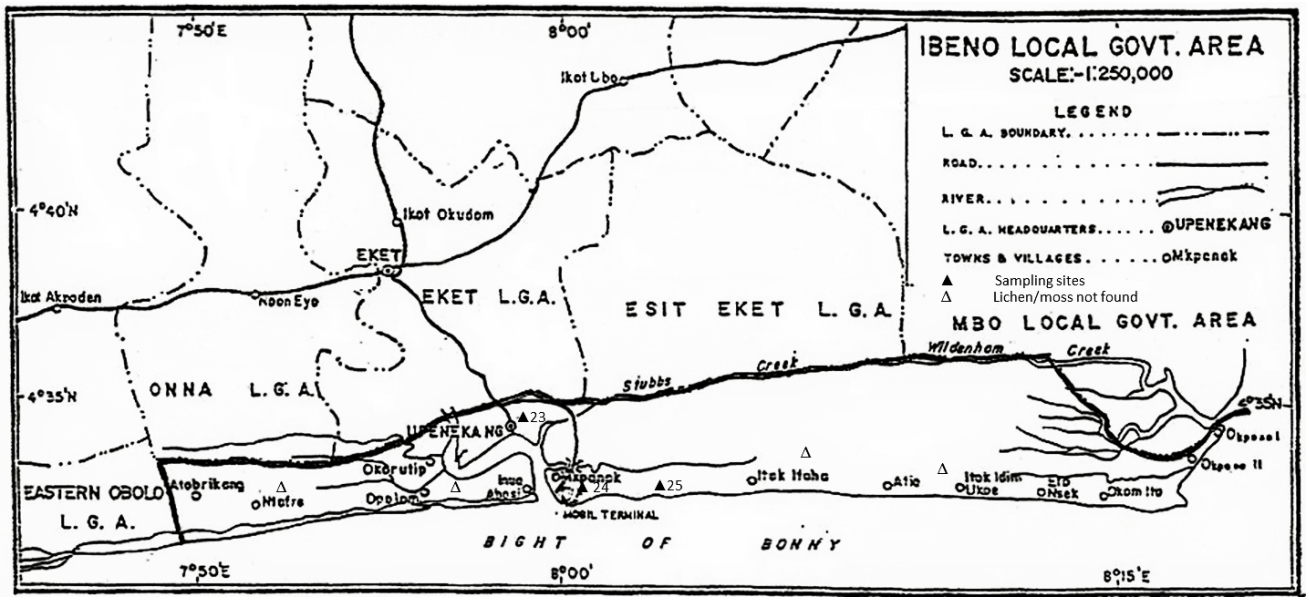

Figure 3. Map of Ibeno Local Government Area Showing the Location of Sampling Locations (Source: Ite et al. [1])

3. Results and Discussion

The concentration of heavy metals in lichen and moss samples at various sampling locations in the study area are presented in Table 1. Heavy metals concentrations in lichen and moss samples ranged from 0.003 – 0.099 μg g^{-1} for cadmium; 0.006 – 7.654 μg g^{-1} for chromium; 1.20 – 1.999 μg g^{-1} for cobalt; 8.954 – 116.760 μg g^{-1} for copper; 25.980 – 193.260 μg g^{-1} for manganese; 2.268 – 23.783 μg g^{-1} for nickel; 0.034 – 14.880 μg g^{-1} for lead, and 26.230 – 98.780 μg g^{-1} for zinc. From the results of analyses, the mean concentration of heavy metals in the lichen and moss samples can be arranged in the decreasing order as follows: Mn > Zn > Cu > Ni > Cr > Pb > Co > Cd.The results obtained in the present study are in agreement with the previous results obtained by Ite et al. [1] in a similar study which was carried out ten years ago in the same study areas. There were variations in the concentrations of heavy metals between samples collected from different sampling locations and the differences were statistically significant for most elements ($P < 0.01$). The data presented in Table 2 revealed very strong statistical significance of correlations between Cu–Pb, Cu–Zn, Pb–Ni and Mn–Zn concentrations [1]. In a direct comparison, elemental analysis reveals that most target heavy metals were accumulated in elevated concentrations in mossescompared to those measured in lichens from the same sampling location (Table 3). Apart from Co and Cu, the differences in concentrations of heavy metals between lichens and mosses from the same sampling locations were statistically significant ($P < 0.05$) for Cd, Cr, Mn, Ni, Pb and Zn, with mosses retaining higher concentrations compared to lichens (Table 3). Significant differences ($P < 0.05$) in concentrations of heavy metals between lichens and mosses have been reported in few related studies [1,32]. Although lichens and mosses accumulate particulates and dissolve chemical species through dry and wet deposition [6,19,32], heavy metals deposition in mosses are mostly associated the chemical composition of rain water [43,44]. In this present study, the high mean concentration of heavy metals in mosses may be attributed to the fact that mosses are long term integrator of atmospheric trace elements deposition and the absence of leaching results in rather stable high uptake efficiency [45].

Cadmium (Cd) concentrations in lichen and moss samples ranged from 0.003 to 0.099 μg g^{-1} with a mean concentration of 0.032 μg g^{-1} (Table 1). According to Ite et al. [1], the concentrations of Cd measured in lichen and moss samples were still at background levels at all the sampling locations with in the two oil–producing communities of Eket and Ibeno, Akwa Ibom State. The background concentrations of Cd in the range of 0.05 – 0.70 μg g^{-1} have been reported in related studies in Southwest region of Nigeria by Onianwa et al. [24,25]. In a previous study, Cd concentrations in the range of 0.001 – 0.092 μg g^{-1} have been measured in lichen and moss samples collected from oil–producing communities of Eket and Ibeno Local Government Areas [1]. Over the years, varying concentrations of Cd have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Cd in lichen and moss samples reported in other related studies include:0.06 – 2.24μg g^{-1} [31]; 0.06 – 33.60 μg g^{-1} [41,42]; 0.10 – 0.90 μg g^{-1} [38,39,40]; 0.16 – 6.13 μg g^{-1} [46]; 0.191 μg g^{-1} [33]; 0.047 – 0.162 μg g^{-1} [47]; 0.97 – 1.26 μg g^{-1} [48]; 0.34 – 1.07 μg g^{-1} [11]; 0.24 – 1.4 μg g^{-1} [35]; 0.10 – 0.64 μg g^{-1} [49], and 0.09 – 0.31 μg g^{-1} [37]. The highest concentration of Cd (0.099 μg g^{-1} measured in Sample M 10) can be attributed to localanthropogenic activities such as fossil fuels combustion and transport–relatedemissions [49], metal works and waste burning [1,4,24,37]. In this present study, the concentrations of Cd were not significantly correlated with concentrations of other heavy metals (Table 2) and the results obtained are in agreement with a previous study by Ite et al. [1].Although low concentrations of Cd in particulate form are normally found in ambient air [50], it has been reported that plants from unpolluted natural environments contain 0.01 – 0.3 μg g^{-1} Cd [7]. The background concentrations of Cd measured in this present study are within the range of values obtained in a previous study by Ite et al. [1]. Based on the comparison of results of this present study with the previous study [1], there has

been no further elevation in the atmospheric heavy metals depositionin the oil–producing communities of Eket and Ibeno over the past 10 years.Although the Cd contamination has been implicated as the cause of numerous human deaths [4], the concentration of Cd in lichens and mossescannot be used asa direct indicator of human exposure in the oil–producing communities studied.

Chromium (Cr) concentrations in lichen and moss samples ranged from 0.006 to 7.654 μg g^{-1} with a mean concentration of 3.398 μg g^{-1} (Table 1). The highest concentrations of Cr (>8 μg g^{-1}) were observed at rural sampling locations (Sample M 7 & M 14) compared to the lowest concentration of Cr (0.004 μg g^{-1}) measured at an urban sampling location(Sample M 19).The elevated concentrations of Cr measured at these sampling locationsare attributed to long–range transport of trace elements in ambient aerosols [51] and local anthropogenic activities near the sampling locations[1]. According to Ite et al. [1], several other sources such as deposition of windblown dust associated earth's crust and corrosion of metalsaround the sampling location might have contributed to the atmospheric contamination load. In a previous study, Cr concentrations in the range of 0.004 – 8.793 μg g^{-1} have been measured in lichen and moss samples collected from oil–producing communities of Eket and Ibeno Local Government Areas [1]. Over the years, varying concentrations of Cr have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Cr in lichen and moss samples reported in other related studies include: 2.46 – 35.00μg g^{-1} [31]; 2.68 – 22.00 μg g^{-1} [41,42]; 0.50 – 6.50 μg g^{-1} [38,39,40]; 1.4 – 2.6 μg g^{-1} [11]; 1.60 – 4.70 μg g^{-1} [35]; 3.6 μg g^{-1} [33]; 1.6 – 39.3 μg g^{-1} [34]; 2.62 – 6.69 μg g^{-1} [48]; 111 – 244 μg g^{-1} [52]; 1.20 – 3.01 μg g^{-1} [49]; 1.00 – 829.00 μg g^{-1} [20], and 0.07 – 2.54 μg g^{-1} [37].In this present study, the concentrations of Cr were not significantly correlated with concentrations of other heavy metals (Table 2) and the results obtained are in agreement with a previous study by Ite et al. [1]. The potential sources of human exposure to Cr are attributed to emissions associated with energy generation, traffic–related emissions, incineration of municipal wastes and other local anthropogenic activities [1,4,8,53]. Although it has been reported that the concentrations of Cr in urban air ranged from <10 ng m^{-3} to 50 ng m^{-3} [54], the background concentrations of Cr measured in this present study are within the range of values obtained in a previous study by Ite et al. [1]. The results ofCr concentrations measured in lichen and moss samples collected from the oil–producing communities of Eket and Ibeno Local Government Areas have revealed no further deterioration of air quality over the past 10 years.

Table 1. Heavy metals concentrations (*μg* 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	0.006 ± 0.04	6.816 ± 0.02	1.995 ± 0.02	18.980 ± 0.02	143.250 ± 0.02	7.998 ± 0.02	14.480 ± 0.02	92.620 ± 0.02
L 2*	0.042 ± 0.02	0.055 ± 0.02	1.891 ± 0.01	16.940 ± 0.01	163.719 ± 0.01	4.930 ± 0.01	0.998 ± 0.01	53.760 ± 0.01
M 3*	0.049 ± 0.06	2.06 ± 0.02	1.150 ± 0.01	17.618 ± 0.01	193.260 ± 0.01	5.190 ± 0.01	0.890 ± 0.01	78.770 ± 0.01
M 4	0.082 ± 0.02	1.038 ± 0.02	1.999 ± 0.01	11.700 ± 0.01	92.950 ± 0.01	23.7830 ± 0.01	2.958 ± 0.01	66.800 ± 0.02
M 5	0.005 ± 0.00	1.662 ± 0.02	1.250 ± 0.02	15.230 ± 0.01	98.130 ± 0.02	4.158 ± 0.01	4.950 ± 0.01	67.840 ± 0.01
M 6	0.006 ± 0.00	1.891 ± 0.02	1.909 ± 0.01	9.575 ± 0.01	61.350 ± 0.01	4.208 ± 0.01	0.058 ± 0.02	70.920 ± 0.01
M 7	0.003 ± 0.00	7.567 ± 0.02	1.950 ± 0.01	8.954 ± 0.01	56.859 ± 0.01	4.490 ± 0.01	4.628 ± 0.01	54.130 ± 0.01
M 8	0.058 ± 0.02	1.586 ± 0.02	1.725 ± 0.02	9.755 ± 0.01	78.890 ± 0.02	4.260 ± 0.01	0.034 ± 0.01	72.680 ± 0.02
M 9	0.067 ± 0.01	2.762 ± 0.02	1.676 ± 0.01	10.752 ± 0.01	56.600 ± 0.01	4.360 ± 0.01	0.062 ± 0.01	26.230 ± 0.01
M 10	0.099 ± 0.01	2.285 ± 0.02	1.550 ± 0.01	10.150 ± 0.01	84.030 ± 0.01	3.950 ± 0.01	0.041 ± 0.01	72.680 ± 0.01
L 11**	0.006 ± 0.01	6.724 ± 0.01	1.996 ± 0.01	10.860 ± 0.01	162.198 ± 0.01	4.480 ± 0.01	0.980 ± 0.01	83.960 ± 0.02
M 12**	0.007 ± 0.02	5.264 ± 0.02	1.293 ± 0.02	9.994 ± 0.01	165.980 ± 0.01	4.890 ± 0.01	1.890 ± 0.01	67.218 ± 0.01
M 13	0.008 ± 0.01	5.462 ± 0.02	1.882 ± 0.01	9.795 ± 0.01	156.898 ± 0.01	3.950 ± 0.01	2.812 ± 0.01	68.400 ± 0.01
M 14	0.010 ± 0.02	7.654 ± 0.02	1.910 ± 0.02	19.801 ± 0.01	174.380 ± 0.02	4.980 ± 0.01	6.854 ± 0.02	74.580 ± 0.01
M 15	0.007 ± 0.01	3.354 ± 0.02	1.675 ± 0.02	16.970 ± 0.02	176.530 ± 0.01	2.990 ± 0.01	2.640 ± 0.01	58.850 ± 0.02
M 16	0.059 ± 0.02	5.400 ± 0.02	1.600 ± 0.01	19.780 ± 0.01	145.230 ± 0.01	4.400 ± 0.01	2.875 ± 0.01	60.280 ± 0.01
L 17***	0.092 ± 0.02	0.505 ± 0.01	1.120 ± 0.01	19.982 ± 0.01	40.630 ± 0.01	2.632 ± 0.01	0.841 ± 0.01	59.850 ± 0.02
M 18***	0.096 ± 0.01	0.130 ± 0.02	1.137 ± 0.02	16.734 ± 0.01	39.949 ± 0.02	3.948 ± 0.02	1.686 ± 0.01	62.800 ± 0.01
M 19	0.009 ± 0.02	0.006 ± 0.02	1.975 ± 0.01	116.760 ± 0.02	109.930 ± 0.01	4.980 ± 0.01	14.880 ± 0.01	98.780 ± 0.02
M 20	0.007 ± 0.02	4.085 ± 0.02	1.885 ± 0.01	13.050 ± 0.01	109.890 ± 0.01	3.930 ± 0.01	3.958 ± 0.01	74.450 ± 0.01
M 21	0.004 ± 0.01	4.800 ± 0.02	1.985 ± 0.01	11.990 ± 0.02	68.988 ± 0.02	3.280 ± 0.01	4.989 ± 0.01	47.630 ± 0.01
M 22	0.004 ± 0.02	4.501 ± 0.02	1.899 ± 0.02	10.950 ± 0.01	98.680 ± 0.01	3.710 ± 0.01	3.964 ± 0.01	68.850 ± 0.01
M 23	0.006 ± 0.01	2.908 ± 0.02	1.789 ± 0.01	11.685 ± 0.01	25.980 ± 0.02	2.925 ± 0.01	2.870 ± 0.01	38.680 ± 0.02
M 24	0.003 ± 0.02	2.007 ± 0.02	1.850 ± 0.02	9.590 ± 0.02	25.990 ± 0.01	2.268 ± 0.02	2.425 ± 0.01	49.640 ± 0.01
M 25	0.068 ± 0.02	4.431 ± 0.02	1.998 ± 0.02	10.950 ± 0.01	68.410 ± 0.02	2.460 ± 0.01	0.052 ± 0.01	38.680 ± 0.02
Mean	0.032	3.398	1.723	17.530	103.900	4.927	3.312	64.363
Median	0.008	2.908	1.882	11.700	98.130	4.208	2.640	67.218
Min	0.003	0.006	1.120	8.954	25.980	2.268	0.034	26.230
Max	0.099	7.654	1.999	116.760	193.260	23.783	14.880	98.780
SD	0.035	2.382	0.301	21.010	52.190	4.091	3.883	16.560

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

Cobalt (Co) concentrations in lichen and moss samples ranged from 1.120 to 1.999 μg g^{-1} with a mean concentration of 1.723μg μg g^{-1} (Table 1). According to Ite et al. [1], the concentrations of Co measured in lichen and moss samples were still at background levels at all the sampling locations within the two oil–producing communities of Eket and Ibeno, Akwa Ibom State. The natural background concentrations of Co in the range of 1 to 40 ng m^{-3} have been reported in a study by Hamilton [55]. In a previous study, Cd concentrations in the range of 0.989 – 1.950 μg g^{-1} have been measured in lichen and moss samples collected from oil–producing communities of Eket and Ibeno Local Government Areas [1].Over the years, varying concentrations of Co have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Co in lichen and moss samples reported in other related studies include: 0.27 – 2.90μg g^{-1} [31]; 0.284 μg g^{-1} [33]; 0.28 – 0.55 μg g^{-1} [48]; 0.20 – 5.55 μg g^{-1} [49], and 3.33 – 5.63 μg g^{-1} [37]. The background concentrations of Co measured in this present study are within the range of values obtained in a previous study by Ite et al. [1]. However, the concentrations of Co were not significantly correlated with concentrations of other metals in measured in lichen and moss samples collected from the oil–producing communities of Eket and Ibeno Local Government Areas (Table 2). It is known that Co is closely related to Ni in both its chemical and biochemical properties. The elevated concentrations of Co at some of the sampling locations are attributed to anthropogenic sources such as transport–related emissions, wastes burning, combustion of fossil fuels and other local anthropogenic activities [1,4,56,57]. Although it behaviour in the environment is poorly understood, the concentration of Co measured in lichen and moss samples reflect the atmospheric deposition and the measured Cu concentrations cannot be used as adirect indicator of human exposure in the oil–producing communities studied.

Table 2. 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	-0.397	1.00						
Co	-0.439	0.275	1.00					
Cu	-0.100	-0.030	0.103	1.00				
Mn	-0.254	0.254	0.004	0.093	1.00			
Ni	0.245	-0.214	0.207	0.001	0.104	1.00		
Pb	-0.441	-0.153	0.327	0.662	0.180	0.138	1.00	
Zn	-0.200	-0.153	0.025	0.465	0.497	0.197	0.541	1.00

$P < 0.05$.

Table 3. Descriptive statistics of heavy metals concentrations (μg g^{-1} dry wt.) measured in lichen and moss samples from the same sampling location

Sample	Cd	Cr	Co	Cu	Mn	Ni	Pb	Zn
Lichen								
L 2*	0.042 ± 0.02	0.055 ± 0.02	1.891 ± 0.02	16.940 ± 0.02	163.719 ± 0.01	4.930 ± 0.01	0.998 ± 0.01	53.760 ± 0.01
L 11**	0.06 ± 0.01	6.724 ± 0.01	1.996 ± 0.01	10.860 ± 0.01	162.198 ± 0.01	4.980 ± 0.01	0.980 ± 0.01	83.960 ± 0.02
L 17***	0.092 ± 0.02	0.505 ± 0.01	1.120 ± 0.01	19.980 ± 0.01	40.630 ± 0.01	2.63 ± 0.01	0.841 ± 0.01	59.850 ± 0.02
Mean	0.047	2.428	1.667	42.78	122.19	4.18	0.939	65.86
Median	0.042	0.505	1.891	14.78	162.188	4.930	0.980	59.850
Min	0.006	0.055	1.120	10.860	40.630	2.63	0.841	53.760
Max	0.092	6.724	1.996	16.940	163.719	4.930	0.998	83.960
SD	0.043	3.727	0.478	3.103	70.62	1.342	0.086	15.97
Moss								
M 3*	0.049 ± 0.06	2.06 ± 0.02	1.150 ± 0.01	17.618 ± 0.01	193.260 ± 0.01	5.190 ± 0.01	0.8990 ± 0.01	78.770 ± 0.01
M 12**	0.007 ± 0.01	5.262 ± 0.02	1.293 ± 0.02	9.994 ± 0.01	165.980 ± 0.01	4.890 ± 0.01	1.890 ± 0.01	67.218 ± 0.01
M 18***	0.096 ± 0.01	0.130 ± 0.02	1.137 ± 0.02	16.734 ± 0.01	39.949 ± 0.02	3.948 ± 0.02	1.686 ± 0.01	62.800 ± 0.01
Mean	0.048	2.485	1.193	11.782	133.063	4.676	1.492	69.596
Median	0.049	2.06	1.150	16.734	165.980	4.890	1.686	67.218
Min	0.007	0.130	1.137	9.994	39.949	3.948	0.890	62.800
Max	0.096	5.264	1.293	17.618	193.260	5.190	1.890	69.596
SD	0.061	2.593	0.086	4.170	81.780	0.648	0.528	8.246

Copper (Cu) concentrations in lichen and moss samples ranged from 8.954 to 116.760 μg g^{-1} with a mean concentration of 17.538 μg g^{-1} (Table 1). The highest concentration of Cu (110.760 μg g^{-1}) measured at a sampling location along main road (Sample M 19) was significantly higher ($P < 0.05$) compared to other sampling locations (Table 1). Apart from the elevated concentration of Cu measured in Sample M 19, the background Cu concentrations in the range of> 8 – 30 μg g^{-1} measured at other sampling locations are in agreement with earlier studies by Ite et al. [1] and Onianwa et al. [25]. In a previous study, Cu concentrations in the range of 2.350 – 110.760 μg g^{-1} have been measured in lichen and moss samples collected from oil–producing communities of

Eket and Ibeno Local Government Areas [1]. Furthermore, background Cu concentrations in the range 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 [58]. Over the years, varying concentrations of Cu have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Cd in lichen and moss samples reported in other related studies include:2.00 – 10.60μg g^{-1} [31]; 0.90 – 21.30 μg g^{-1} [41,42]; 0.90 – 16.00 μg g^{-1} [38,39,40]; 8.10 – 38.10 μg g^{-1} [24]; 1.79 – 36.78 μg g^{-1} [46]; 0.91 μg g^{-1} [33]; 7.0 – 13.3 μg g^{-1} [34]; 11.40 – 96.00 μg g^{-1}[59]; 1.00 – 9.70 μg g^{-1} [11]; 3.8 – 14.0 μg g^{-1} [35]; 7.19 – 22.4 μg g^{-1} [49], and 1.60 – 26.30 μg g^{-1} [20]. Although it has been reported that average concentrations of Cu are usually well below 1 μg m^{-3}, higher concentrations may be found in polluted areas and/or urban areas [60,61,62]. The elevated concentrations of Cu herein reported at most of the sampling locations 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. [63]. 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 heavy metals (Table 2). The concentration of Cu measured in lichen and moss samples, which often depend on the proximity to major anthropogenic sources [1], reflect the atmospheric deposition associated traffic–related emissions, and other local anthropogenic sources. The elevated concentrations of Cu at some sampling locations are mainly attributed to emissions from vehicular traffic and metal works, however, Cu concentrations in lichen and moss samples cannot be used as a direct indicator of human exposure in the oil–producing communities studied.

Manganese (Mn) concentrations in lichen and moss samples ranged from 25.980 to 193.260 μg g^{-1} with a mean concentration of 103.972 μg g^{-1} (Table 1). Apart from the elevated concentrations of Mn measured at samplings locations in the urban areas, the concentrations of Mn measured in lichen and moss samples were still at background levels at all the sampling locations within the two oil–producing communities of Eket and Ibeno, Akwa Ibom State[1].It has been reported that the annual averages of manganese concentration are mainly in the range of 0.01 – 0.07 μg m^{-3}in urban and rural areas without significant contamination load [64,65]. The background concentrations of Mn in the range of 0.05 – 0.70 μg g^{-1} have been reported in related studies in Southwest region of Nigeria by Onianwa et al. [24,25]. In a previous study, Mn concentrations in the range of 10.530 – 153.320 μg g^{-1} have been measured in lichen and moss samples collected from oil–producing communities of Eket and Ibeno Local Government Areas [1].Over the years, varying concentrations of Mn have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Mn in lichen and moss samples reported in other related studies include:35.00 – 440.00μg g^{-1} [31]; 93.00 – 802.00 μg g^{-1} [24]; 3.91 – 244.47 μg g^{-1} [46]; 22.70 – 114.33 μg g^{-1} [35]; 38.20 μg g^{-1} [33]; 57.30 – 104.00 μg g^{-1} [48]; 25.80 – 208.00 μg g^{-1} [49], and 9.50 – 202.90 μg g^{-1} [20]. 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 2). The concentrations of atmospheric Mn in the rural areas are attributed to the contribution of vegetation inputs [19,20] and it has been reported thatthe Mn toxicity limits in plants are in the range of 400 – 1000 μg g^{-1} [66,67]. In this present study, the distribution of Mn is more regional compared to Zn and the atmospheric deposition of Mn is more frequently associated with transport–related emissions as well as air pollution particles of anthropogenic origin [1,4].

Nickel (Ni) concentrations in lichen and moss samples ranged from 2.268 to 23.783μg g^{-1} with a mean concentration of 4.091μg μg g^{-1} (Table 1). In this present study, the concentrations of Ni in lichen and moss samples were still at background levels at most of the sampling locations within the two oil–producing communities of Eket and Ibeno, Akwa Ibom State [1]. 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 [68]. The concentrations of ambient Ni in mosses collected from large part of Northern Europe are generally < 2 μg g^{-1} [28] and background concentrations of Ni of 3.50 – 13.50 μg g^{-1} have been reported in Nigeria [24,25]. In a previous study, Ni concentrations in the range of 1.425 – 21.730 μg g^{-1} have been measured in lichen and moss samples collected from oil–producing communities of Eket and Ibeno Local Government Areas [1]. Over the years, varying concentrations of Ni have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Ni in lichen and moss samples reported in other related studies include: 1.00 – 55.00μg g^{-1} [31]; 7.90 – 24.20 μg g^{-1} [41,42]; 1.10 – 1.80 μg g^{-1} [47]; 0.83 – 10.20 μg g^{-1} [69]; 1.65 – 1.73 μg g^{-1} [11]; 2.6 – 11.4 μg g^{-1} [35], and 1.48 – 3.90 μg g^{-1} [49]. Although the concentrations of Ni in this present study are in agreement with findings of Ite et al. [1], however, the reported Ni concentrations are significantly higher than the background concentration (< 0.5 μg g^{-1}Ni) reported for the Olympic National Park, Washington, U.S.A. [63]. In this present study, the concentrations of Ni were not significantly correlated with concentrations of other metals (Table 2). Apart from other local anthropogenic sources, the greatest contribution to atmospheric nickel contamination and/or elevated Ni concentrations in the present study is mainly associated with combustion of fossil fuels [1] in which nickel appears mainly as nickel sulphate, nickel oxide, and complex metal oxides containing nickel [4].

Lead (Pb) concentrations in lichen and moss samples ranged from 0.034 to 14.880 μg g^{-1} with a mean concentration of 3.312μg g^{-1} (Table 1). In this present study, the concentrations of Ni in lichen and moss samples were still at background levels at most of the sampling locations within the two oil–producing communities of Eket and Ibeno, Akwa Ibom State [1]. The highest concentrations of Pb (>14 μg g^{-1}) were measured at two sampling locations in the urban area with the highest vehicular traffic density, frequent traffic queues and various local anthropogenic activities. The background Pb concentrations in the range of 5.00 – 40.00 μg g^{-1} have been reported in few related studies in Nigeria [24,25]. In

a previous study, Pb concentrations in the range of 0.001 – 17.380 μg g^{-1} have been measured in lichen and moss samples collected from oil–producing communities of Eket and Ibeno Local Government Areas [1].Over the years, varying concentrations of Pb have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Pb in lichen and moss samples reported in other related studies include: 420.00 – 2000.00μg g^{-1} [31]; 6.35 – 52.40 μg g^{-1} [41,42]; 2.99 – 52.75 μg g^{-1} [46]; 15.90 μg g^{-1} [33]; 1.06 – 4.29 μg g^{-1} [47]; 27.30 – 50.80 μg g^{-1} [48]; 11.00 – 33.80 μg g^{-1} [11]; 4.03 – 44.60 μg g^{-1} [49]; 2.80 – 17.50 μg g^{-1} [20], and 3.10– 30.81 μg g^{-1} [37]. The Pb concentrations measured at most of the sampling locations in this present study are similar to background Pb concentration (3.6 μg g^{-1})reported for the Olympic National Park, Washington, U.S.A. [63]. The results obtained in this present study are consistent and in agreement with the previous findings by Ite et al. [1]. In this present study, the concentrations of Pb were significantly correlated with concentrations of Cu (r = 0.72) and Zn (r = 0.65) (Table 2). Apart from other local anthropogenic sources, the greatest contribution to atmospheric nickel contamination and/or elevated Pb concentrations in the present study is mainly associated with transport–related emissions and combustion of fossil fuels [1,49,70,71]. It has been reported 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 [4,72,73]. However, Pb concentrations measured in lichen and moss samples cannot be used as a direct indicator of human exposure in the oil–producing communities studied.

Zinc (Zn) concentrations in lichen and moss samples ranged from 26.230 to 98.780 μg g^{-1} with a mean concentration of 64.363 μg g^{-1} (Table 1). In this present study, the concentrations of Ni in lichen and moss samples were still at background levels at most of the sampling locations within the two oil–producing communities of Eket and Ibeno, Akwa Ibom State [1]. However, the highest Zn concentration (98.780 μg g^{-1}) was obtained at an urban sampling location with high vehicular traffic density, frequent traffic queues and other local anthropogenic activities.The background Zn concentrations of 26.30 – 153.00 μg g^{-1}have been reported in South West region of Nigeria [24] and Zn concentrations in the range of 23.530 – 130.600 μg g^{-1} have been reported inoil–producing communities in the South–South region of Nigeria [1]. Over the years, varying concentrations of Zn have been reported in many research studies that utilize lichens and mosses as bioindicators of trace elements in several regions across the world. The concentrations of Zn in lichen and moss samples reported in other related studies include: 13.00 – 94.00μg g^{-1} [31]; 16.10 – 69.60 μg g^{-1} [41,42]; 45.90 – 94.90 μg g^{-1} [38,39,40]; 3.40 – 68.22 μg g^{-1} [46]; 6.48 – 36.90 μg g^{-1} [47]; 37.00 – 101.00 μg g^{-1} [34]; 35.00 – 204.00 μg g^{-1} [52]; 39.00 – 69.00 μg g^{-1} [11]; 23.70 – 76.10 μg g^{-1} [35]; 14.50 – 41.80 μg g^{-1} [49]; 8.70 – 278.60 μg g^{-1} [20], and 23.50 – 68.24 μg g^{-1} [37]. The elevated concentrations Zn measured at most of the sampling locations in this present study are higher compared to background concentration (9 – 15 μg g^{-1}) reported for the Olympic [58,63] and Mt. Rainier National Park, Washington, U.S.A. [58]. Although the normal concentrations of Zn in plants are in the range of 10 – 100 μg g^{-1} [7], concentration of Zn in lichens > 100 μg g^{-1} is an indication of environmental contamination [36]. 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 2). Apart from other local anthropogenic sources, the greatest contribution to atmospheric zinc contamination and/or elevated Zn concentrations in the present study is mainly associated with transport–related emissions and combustion of fossil fuels [1,9,49,70,71].

4. Conclusions

The second study of atmospheric deposition of heavy metals and/or trace elements in oil–producing communities of Eket and Ibeno Local Government Area of Akwa Ibom State using lichens and mosses as bioindicators and bioaccumulators was conducted in 2014. The sampling network, lichen and moss species used in this study were chosen in the same manner as in the previous study conducted in 2004 by Ite et al. [1]. This present study has shown the variations in the concentrations and distribution patterns of atmospheric heavy metals deposition as reflected in lichen and moss samples. The concentrations of most target atmospheric heavy metals in lichen and moss samples were relatively higher in urban sampling locations compared to rural sampling locations. Apart from other local anthropogenic sources (e.g. solid waste disposal, metal corrosion and works, etc.), the greatest contribution to atmospheric heavy metal contamination and/or elevated heavy metal concentrations in the present study is mainly associated with transport–related emissions and combustion of fossil fuels. There is some evidence that different site–specific characteristics affect the spatial distributions patterns and temporal trends of atmospheric deposition of heavy metals in the two oil–producing communities of Eket and Ibeno, Akwa Ibom State – Nigeria. Comparison of the results obtained in this present study and those obtained in the 2004pilot monitoring study [1] suggested that the air pollution, along with some of the anthropogenic trace elements, has not significantly changed in the two oil–producing host communities of Eket and Ibeno, Akwa Ibom State – Nigeria. However, relatively precipitous decrease in the concentrations of atmospheric heavy metal deposition was observed at some of the sampling locations. This present study has shown the applicability of local epiphytic lichen and moss species as effective accumulative bioindicators and a valid method for measuring atmospheric heavy metals deposition and/or distribution in the oil–producing communities in the Nigeria's Niger Delta region. Although there has been no further deterioration of air quality in the area studied over the past decade, long–term exposure to elevated concentrations of ambient heavy metals may pose human health and environment risks. Since lichens and mosses cannot be used as a direct indicator of human exposure, there is a need to further investigate environmental and human health implications associated with atmospheric heavy metal deposition and subsequent contamination in the oil–producing Niger Delta region of Nigeria.

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