

Assessment of Foliose Epiphytic Lichen (*Parmelia sulcata*) as Bioindicators of Atmospheric Trace Metals Pollution in Lapai Metropolis, Niger State

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Abstract:

The levels of atmospheric trace metals were determined using foliose epiphytic lichens (*Parmelia sulcata*) samples collected in eight (8) different locations within the residential areas and two control locations outside the residential area of Lapai town in Lapai local government of Niger State. A stratified random sampling technique was adopted and the analysis of the samples with atomic absorption spectrophotometer (AAS) gives the concentration (mg/kg) range of the metals as follows; 1.123-7.837 for Fe, 4.579-6.62 for Pb, 0.210-2.152 for Cr, 0.491-1.171 g for Ni, 0.018-0.983 for Cd, 0.057-1.471 g Zn, 0.198-1.287 for Mn, and 0.098-2.583 for Cu but Selenium was not detected in all the samples. The levels of some of these metals were slightly higher than the recommended USEPA (1993) limits but lower than FEPA (1991) limits. However, the distribution of these metals was not uniform across the samples, though their level was still at the background and very low compared to the reports on similar studies from industrialized areas of South-south and South-west Nigeria and other European countries. The variation in concentration of these metals at $p \leq 0.05$ indicates their source is mainly anthropogenic in origin. Epiphytic lichens validate the cost-effectiveness of this method for evaluating, assessing, and identifying depositional sources of the metals in the environment. The study revealed the atmospheric trace metal concentration of the area under study to be at a threshold level and hence the environment is still very safe from atmospheric trace metal pollution.

Keywords: Epiphytic, Bioindicators, Tolerant, Lichen, Variation, Anthropogenic.

I. INTRODUCTION

Air pollution is an important environmental problem that threatens human existence and it's conceived as the release of different foreign substances into the atmosphere in the form of gas, liquid, or solids, at concentrations that are harmful to lives and can disrupt the ecological equilibrium (Cansaran-Duman, et al., 2012; Akabueze et al., 2012). The earth's environmental media co-exist in perfect equilibrium; only pollution episodes distort such equilibrium balance, thereby affecting the activities of the biotic and abiotic components in direct association with these media (Borrego et al., 2003).

The enormous strain on the atmosphere results from growing industrialization, urbanization, and increasing population. A polluted atmospheric environment poses a severe risk to both living and non-living compared to other environmental media (Carson et al., 1995). This is because, pollutants released into the atmosphere can be transported and deposited at locations far from their sources and can also undergo physical, chemical, and photochemical transformations which ultimately determine their fate and atmospheric concentrations (Garty, 1993; Hipolito et al., 2003).

Toxic air pollutant gets into the human biological tissue mainly through respiration, though they can also be ingested or absorbed through the skin (Borrego et al., 2003). World

Health Organization (WHO) statistics show that 70% of the world's urban dwellers suffer from the tremendous effects of polluted air. However, only 10% breathe the air of marginal quality. Hence, in developed countries, an estimated 0.5-1.0 million people die prematurely each year as a result of exposure to air contamination (Kojima, 2001). Generally, these countries still have a low level of air contamination compared to developing countries such as Nigeria (Martinez et al., 2003).

The cumulative effect of atmospheric pollution on the deterioration of both human health and the environment calls for intense government, industrial, and scientific efforts throughout the world today (Owaga et al., 2003). The depositions of atmospheric air pollutants of different kinds and nature are influenced by natural geochemical processes and numerous anthropogenic emission sources (Tsafe et al., 2010).

Trace metals are the most common and persistent chemical elements with a specific gravity at least 5 times the specific gravity of water and occurring naturally at $1.000\mu\text{gg}^{-1}$ or less in the earth's crust (Abdullateef et al., 2014). They are non-biodegradable, detoxified, and removed by metabolic activities once dispersed in the environment. These lead to their subsequent build-up to toxic levels or bioaccumulation in the ecosystem (Abdullateef et al., 2014). Bioaccumulation of

trace metals in man, animals, and plants results in metal poisoning (Audu and Lawal, 2005). Monitoring and assessment of trace metal concentrations in the environment contribute to an effective understanding of biogeochemical processes and gauging the healthy status of the ecosystem (Adriano, 2001).

Environmental bioindicators such as fungi, lichens, mosses, plant leaves, and tree bark can be used to evaluate atmospheric trace metals depositions (Bargagli et al., 2002). However, Lichens have been defined as the most 'efficient control system' for air pollution monitoring and assessment (Conti and Cecchetti, 2001) due to their high sensitivity and ability to store pollutants in their biological tissues.

Lichens have numerous advantages as biomonitors when compared to higher plants (Bargagli, 1998), and they are not differentiated into true leaves and root systems and rely on atmospheric dry and wet deposition for their mineral nutrition, most especially epiphytic lichen. These plants have a durable life span, ion exchange properties, high surface-to-volume ratio, slow growth rate, lack cuticles, and do not have variability in morphology throughout the growing season (Giordano et al., 2005). These enhance their use as passive as well as an active reliable integrator of atmospheric depositions (Sloof, 1993).

Lichens accumulate metals through the trapping of metal particles at intercellular spaces or uneven surfaces, intercellular absorption, and effective ion exchange mechanisms (Figueira et al., 2002; Jalkanen et al., 2000). Element retention in lichen depends on the number and nature of the extracellular binding sites, tissue age, growth condition Giordano et al, (2004), and also concentrations of trace elements in atmospheric deposition (Grodzińska et al., 2003).

Lichen does not offer selective enrichment of individual metals as such accumulated metals are easily accessible with analytical devices like AAS. The sole concern about the air pollution threats was due to the increased mortality rate, morbidity, and multifarious effect of air pollutants in our environment. For this reason, it becomes a necessity to carry out a regular systematic assessment and evaluation study to determine the extent and possible anthropogenic source of trace metals in our environment. Thus, this study is to investigate, assess and evaluate the atmospheric trace metals levels in Lapai Metropolis, Niger State using epiphytic foliose lichens (*Parmelia sulcata*).

II. MATERIALS AND METHODS

All plastics and glass wares were cleaned by soaking in dilute HNO₃ (10%) for 5 min and rinsed with distilled water before use. Standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg l⁻¹ of a compound containing each element of interest.

STUDY AREA

Lapai is about 56 Km East of Minna, Niger State Capital, Nigeria. The town lies on latitude 9° 03' 00" North and longitude 6° 34' 00" East with 162 meters elevation above the

sea level and covers a land mass of 3,051 km² with an estimated population of 12,859 at the 2006 census (NPC, 2006). The metropolis is situated in a rural setting, and the major occupation of the people is agriculture activities, mechanical activities and blacksmithing. A major federal road Suleja-Bida express way passes through the center of the town with dense traffic due to heavy-duty trucks plying the road at high frequency (250 trucks per hour). The locational map of the study area is shown in Figure 1.

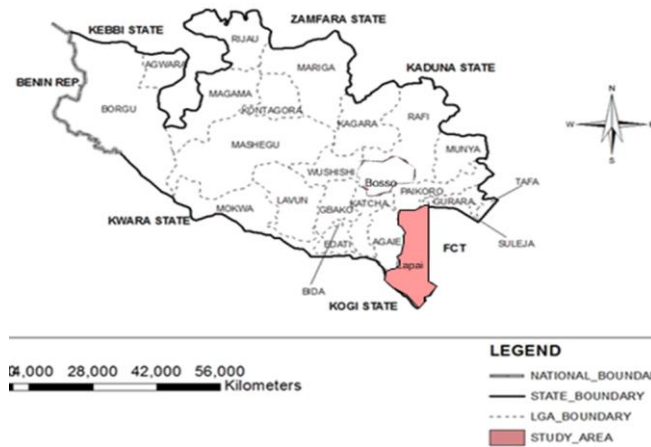


Figure 1: Map of Niger State showing Lapai Local Government Area, Nigeria (Source: Ministry of Lands and Housing, Minna (2018)).

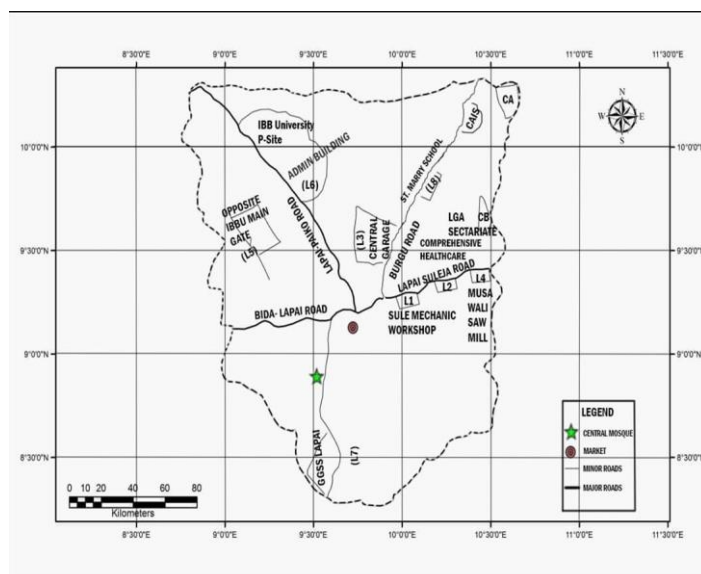


Figure 2: Map of Lapai Metropolis, Niger State, Nigeria Showing Sampling Locations.

SAMPLE COLLECTION AND PREPARATION

Lichen sampling was made according to the protocol given by Cansaran-Duman et al., (2009) but with slight modifications. Epiphytic foliose lichens species (*Parmelia sulcata*) family were collected from bark substrates of three different domestic tree plants which include Gamhar (*Gmalina, Arborea*), Neem (*azadirachta Indica*), and Cashew (*Anacardium Occidentale L*) within the study area. The suitability of this common species *Parmelia sulcata* as a quantitative biomonitor of atmospheric

depositions has been proven by Joyce and Sloof (1995). The lichens were sampled at 10 sampling locations consisting of 8 sample locations and two control locations. The sampling locations were arranged in a grid network covering the areas of suspected emission sources and random sampling was adopted. The samples were labeled as follows; L1, L2, L3, L4, L5, L6, L7, L8, CA, and CB. The control (CA and CB) was sampled 3 km and 5 km respectively away from the residential area and characterized by trees and other dense vegetative covers. The sample was identified in the Department of Biology, Ibrahim Babangida University Lapai, and Niger State.

SAMPLE DESCRIPTION

The table below shows the various sampling locations labeled and date of collection.

TABLE 1: SAMPLE DATE, SAMPLE ID, AND SAMPLE

S/N	Sample ID	Sample Locations
1	L ₁	Sule Mechanic Work Shop
2	L ₂	Opposite Comprehensive Health Care around Mechanic Work Shops
3	L ₃	Central Motor Garage
4	L ₄	Musa Wali Saw Mill
5	L ₅	T- junction Opposite IBBUL Main Gate, along Lapai-Minna Road
6	L ₆	Inside IBBUL Permanent Site, Beside Admin Block
7	L ₇	Opposite Government Girls Day Secondary School Lapai
8	L ₈	Along Burugu Road, Beside St. Marry Secondary School, Lapai
9	C _A	Control (A) 3km Behind College of Arabic and Islamic Studies
10	C _B	Control (B) 5km Back of Lapai Secretariat.

The Control locations A and B were located 3 km and 5 km respectively away from the residential area and characterized by trees and other vegetative cover.

SAMPLE PREPARATION/TREATMENT

The sample preparations and treatment were carried out by the method described by Kapu et al, (1991) and Gabriel et al. (2011) but slightly modified in this present study. In the laboratory, the lichen samples were separated from the bark substrates with nylon tweezers and washed with distilled water to remove adhering sand, dust, and other impurities. The washed samples were then dried to a constant weight at 60 oC in an oven and cooled in a desiccator, then ground and homogenized with agate mortar and pestle and finally freeze-dried for 24 hours, ready for analytical analysis.

SAMPLE DIGESTION

Homogenized samples (1.00 g) each were treated with a 12 cm³ mixture of concentrated nitric acid and perchloric acid at a 5:1 ratio (10 cm³ 70 % HNO₃: 2 cm³ 70 % HClO₄) using Teflon beakers on a digestion hot plate. The temperature indicator was placed inside digestion beakers while the beakers were loosely covered to avoid atmospheric contamination and the mixture was gently heated to 80 oC and gradually the temperature was then raised to 150 oC to achieve complete dissolution. The emission of white fumes

from the mixtures indicated the completion of the digestion processes. The digest (10 cm³) was then diluted with 20 cm³ distilled water and allowed to cool, then filtered through a Whatman 541 filter paper into a 50 cm³ volumetric flask, and made up to volume with distilled water (Gabriel et al., 2011). A blank solution was also prepared using the same sample preparation procedure without the samples.

CALIBRATION AND ANALYSIS OF SAMPLE

Strictly adhering to the instrument manufacturer’s instruction, appropriate steps were taken to calibrate the Atomic Absorption Spectrophotometer (AAS) (Model Sens AA GBC Scientific Equipment PTY Ltd Dendonong, Australia) by the analysis of element standard solutions. The instrument reading was set to zero and subsequently, the absorbance of each standard solution was then measured. For each standard, the measured absorbance values are plotted against known concentration enabling a calibration curve to be constructed. Sample solutions with high absorbance were further diluted to known volumes with distilled water before measurements. Subsequently, a calibration curve of absorbance against concentration was obtained from which individual sample concentration can be extracted directly. The analysis of sample solutions was carried out and the levels of chromium (Cr), Nickel (Ni), copper (Cu), Lead (Pb), Iron (Fe), Zinc (Zn), Manganese (Mn) and cadmium (Cd) were determined using AAS.

DATA ANALYSIS

The results of triplicate analyses obtained were subjected to statistical treatment using statistical software (MINITAB Model 16.0). Analysis of variance using one-way (ANOVA) was done to determine any significant difference in the level of trace metals across the study locations.

III. RESULTS AND DISCUSSION

The mean of the individual trace metal concentrations obtained from the analyses of the lichen samples are presented in Table 2.

TABLE 2: MEAN CONCENTRATIONS OF TRACE METALS IN LICHENS IN MG/KG (MEAN ± SD).

Locations	Cr	Ni	Cu	Pb	Fe	Zn	Mn	Cd
L1	^b 2.152±0.003	^d 0.491±0.005	^c 0.098±0.005	^a 4.579±0.010	^a 7.247±0.004	ND	^c 1.278±0.153	ND
L2	^b 2.148±0.003	ND	ND	ND	^a 7.837±0.006	^c 1.471±0.192	ND	^d 0.271±0.011
L3	^{cd} 0.456±0.346	ND	^c 0.617±0.006	^a 6.394±0.004	^b 2.367±0.019	ND	^d 0.287±0.029	^c 0.983±0.301
L4	^b 1.263±0.003	ND	^d 0.285±0.008	ND	^a 7.688±0.009	ND	ND	^c 0.817±0.094
L5	^b 1.331±0.006	ND	ND	ND	^a 1.781±0.008	ND	^b 1.223±0.101	^c 0.407±0.302
L6	ND	ND	^{cd} 0.74±0.583	^a 6.627±0.006	^b 4.043±0.011	^d 0.057±0.006	^d 0.198±0.030	^c 0.766±0.143
L7	^c 0.210±0.004	ND	ND	ND	^a 1.123±0.004	ND	ND	^b 0.419±0.100
L8	ND	ND	ND	ND	^a 4.967±0.987	ND	ND	^b 0.438±0.089
C _A	^b 0.356±0.006	ND	ND	ND	^a 6.822±1.497	^b 1.208±0.008	ND	^b 0.018±0.008
C _B	ND	^{bc} 1.11±0.003	^a 2.583±0.005	ND	^{ab} 1.89±0.665	ND	ND	^c 0.441±0.990

ND=Not Detected

The mean levels of Iron (Fe) in all the samples were found to be 7.247, 7.837, 2.367, 7.688, 1.781, 4.043, 1.123, 4.967, and 1.899 mg/kg for L1, L2, L3, L4, L5, L6, L8, CA, and CB respectively (Figure 1). The highest level of, 7.837 mg/kg was obtained in L2 and the lowest level of 1.123 mg/kg w in L7. The relatively high levels of Fe in L1, L2, L4, L6, L8, and CA were because Fe still represents the most abundant element of many plants including lower plants like lichens, and makes up the second most abundant metal in the earth's crust, which account for about 5 % (Kamble, et al., 213). Although, the high level of Fe in L1, L2, L4, L6, L8, and CA was in agreement with the report of Frati et al. (2005); the distribution of Fe as anthropogenic pollutants originates mainly from soil particles. High Fe concentrations of 202 mg/kg and 103 mg/kg in both soil and grass respectively were reported by Ho and Tai (1998), which they attributed to dust particles deposited on plant surfaces and roadside dust.

Although, there are other pollution sources as well which include repair and maintenance services at mechanic workshops, road traffic, sawdust from the sawmills, construction sites, and rusting of Fe from iron and steel scraps. The mean concentration of Fe found in this work was still lower than 438 mg/kg gotten from lichen samples in a study carried out around gas treatment plants in Akwa Ibom State (Jeran et al., 2003). A high concentration of Fe was also reported by Ozgur et al. (2007) which ranged from 331-436 mg/kg, in ten different species of lichens from the roadside in the eastern black sea region of Turkey. Mendel et al. (2005), Pandey et al. (2002), Jeran et al. (2003), Tuzen (2002), Lopi et al. (1999),

and Lopi et al. (2000) also reported levels of iron in lichens and moss of the ranges of 54.3-598, 1282-23035, 676-1220, 75.1-192.1, 1800, and 182-737 mg/kg respectively, which are all higher than the range recorded in this work.

The mean levels of Lead (Pb) found in the samples were 4.579, 6.394, and 6.627 mg/kg for L1, L3, and L6 respectively. For samples L2, L4, L5, L7, L8, CA, and CB, Pb concentration was below detection limit. The highest value of Pb was obtained in L6, while the lowest value 4.579 mg/kg was in L1. The value of Pb found in L1, L3, and L6 suggest some level of anthropogenic emission sources. The emission could be influenced by high traffic density and mechanical activities at location L1, exhaust from cars and smoke in cooking restaurants, mechanical activities, rust from damaged cars at L3, and exhaust from traffic density and suspended aerosol from agricultural activities in farmlands at L6. Similar concentration ranges of 2.74-5.15 mg/kg and relatively higher ranges of 3.19-9.16 mg/kg Pb in lichen were reported by Fatabo et al. (2012). The values of Pb obtained in this work were higher than 0.01 mg/kg reported by Obiakor and Ezeonyeji, (2013) in the study of heavy metals depositions in an industrial area of Southeastern Nigeria. The mean concentration of Pb in these three Samples L1, L3, and L6 was in agreement with the report of Olowoyo and Van Herendeen (2010), which suggests Pb is a major pollutant due to its persistence in the environment. The mean values of Chromium (Cr) in the samples were 2.152, 2.148, 0.456, 0.456, 1.263, 1.331, 0.210, and 0.356 mg/kg in L1, L2, L3, L4, L5, L7, and CA respectively as seen in table 1. The amount of Cr in L8 and CB was below the detection limit.

The highest value of Cr (2.152 mg/kg) was recorded in L1 while the lowest value of 0.210 mg/kg was obtained in L7. The relatively high mean value of Cr in some of the samples compared to the control samples CA with a mean value of 0.356 mg/kg indicates variation in anthropogenic emissions source. The source of Cr across the sample locations ranges from local point sources such as metal work, mechanical activities at the automobile workshops, wear and tear in car tires and other components, metal corrosion, and roadside dust due to traffic density. However, several works reported varying concentrations of Cr in lichen samples. The values of Cr obtained in this present study were lower compared to the range of values reported in a similar study using lichens samples by Aniefiok et al. (2014) (0.004-8.79 mg/kg), Lopi et al. (2000) (1.6-39.3 µg/g), Pandey et al. (2002) (111-244 mg/kg) but similar to 0.03-4.23 mg/kg reported by Ekpo et al., (2012) and (1.4-26 mg/kg) by Grodzinska et al. (2003) Therefore, the concentration of Cr obtained was considered still within the permissible limit of 0.01 mg/kg by EPA (1999).

The mean concentration of Nickel (Ni) was 0.491mg/kg in L1 and 1.171 mg/kg in CB. Ni was not detected in L2, L3, L4, L5, L6, L7, L8 and CA. Nickel is reported to be emitted through the combustion of plant base materials (EC, 2001) which conformed with the relatively high value of Ni found at CB compared to L1 as in Table 1. The value of Ni recorded in L1 could probably be from wear and tear or corrosion of alloys containing Ni, especially stainless steel (alloy wheels in cars). The level of Ni found in this study was in good agreement with the report of Ozgur (2007), where Ni level was below the detection limits in some of the lichen samples but found concentrations range of 1.480-3.90 mg/kg in others of the lichen samples.

The mean value of copper (Cu) in the lichen samples ranges from 0.098-2.583 mg/kg, with the highest value in CB and the lowest mean value detected in L1. The levels of Cu in some of these samples were attributed to vehicular emission and roadside dust which conforms to the report of Farmaki and Thomas, (2008), that Cu in the environment comes from vehicular emission and re-suspended road dust. Another source of Cu in the environment includes Cu-containing dust from metal corrosion and wind transport of debris particles and Wang et al. (2009), attributed the concentration of Cu in the environment to intensive traffic density. The high value of Cu in CB was due to wind dispersion and agricultural activities like the burning of bushes and the use of agrochemicals. The level of Cu reported by Fatabo et al. (2012) in a similar work, ranged from 5.83-7.36 mg/kg and 6.86-7.76 mg/kg for Lagos and Ogun States respectively. Also, a similar study reported the level of Cu across ten different species of Lichens range between 7.19-22.4 mg/kg (Ozgur, 2007) which considerably higher than the levels of Cu recorded in this present study (table 1) but Elaigwu et al. (2007) in a similar study reported a very similar concentration range of 0.0726-1.4092 mg/kg to the values obtained in this work.

The concentrations of cadmium (Cd) vary across the samples without a significant difference ($p > 0.05$). In L1, Cd was not detected shown in Table 1. Cadmium concentrations of 0.721,

0.983, 0.817, 0.407, 0.766, 0.419, 0.438, 0.018, and 0.441 mg/kg were obtained for L2, L3, L4, L5, L6, L8, CA, and CB respectively. The highest value of 0.983 mg/kg was obtained in L3 while the lowest value of 0.018 mg/kg was recorded for CA. Cd level in the study lichen samples was relatively high compared to the range of 0.0000-0.0487 mg/kg reported by Elaigwu et al. (2007) in a similar study, but still lower than 1.85-5.31 mg/kg and 3.77-8.70 mg/kg reported by Fatabo et al., (2014) in similar lichen samples in Lagos and Ogun states respectively. The levels were also higher than the concentration reported by Aniefiok et al., (2014) in lichen and moss which ranged from 0.001-0.092 mg/kg. The source of Cd in these samples most probably was anthropogenic activities, ranging from the combustion of fossil fuel, due to the proximity of some of these sample locations to high traffic, especially L2, L3, L4, L5, L6; as well as metal works and burning Cd containing substances. The level of Cd in the environment can also be pointed to the burning of vegetation exudates, forests mass, and slough (EC 2001) which can be responsible for the level of Cd in the control sample CB. The source of Cd recorded in L4 was attributed to saw dust particle deposits from the sawmill factory and road traffic.

The level of zinc (Zn) was found to be 1.471, 0.057, and 0.208 mg/kg in L2, L6, and CA respectively. The highest mean concentration of 1.471 mg/kg was found in L2, while the lowest mean value of 0.057 mg/kg was found in L6. Zn was not detected in sample L1, L3, L4, L5, L7, L8, and CB. Traffic density and local anthropogenic activities including the burning of components in cars, motorcycles, and metal works were attributed to zinc level in L2. The rusting of metal containing zinc and dispersion of particles by wind can accounts for the level of Zn in L6 and CA. However, the level of zinc found in this study was still lower than the range of 23.530-130.600, 0.0098-1.5782, 6.48-36.90, 23.530-68.24 mg/kg, reported by Aniefiok et al. (2014), Elaigwu et al. (2007), Jozwik (1990), and Aksoy et al. (2010) respectively.

The mean values of Mn were found to be 1.278, 0.287, 1.223, and 0.198 mg/kg; for L1, L3, L5, and L6 respectively. The level of Mn in L2, L4, L7, L8, CA, and CB were below the detection limit. Manganese levels in L1, L3, L5, and L6 could be associated with local anthropogenic activities, such as the repair of cars and motorcycle components at mechanic workshops and re-suspended dust particles. Similar studies have reported varying levels of Mn in lichen samples to range from 20-1021, 38.20, 57.30-104.00, and 22.7-114 mg/kg by Pandey et al. (2002), Lopi et al. (1999), Jeran et al. (2002), and Mendel et al. (2005) respectively, which are higher than the values of Mn obtained in this work. Although, the permissible limits of Mn in plant ranges between 400-1000 mg/kg due to its very low toxicity effect (Kula et al., 2012; Zhu et al., 2011).

The values of Fe obtained from samples in this study were all higher than the 0.3 mg/kg USEPA (1993) permissible limits, but far lower than the 20 mg/kg recommended permissible limits reported by Federal Environmental Protection Agency (FEPA, 1991). The levels of Pb were as higher than the zero permissible limits given by USEPA (1993) and 1.0 mg/kg permissible limits recommended by FEPA (1991). Although,

the levels of Pb were still lower than the 5-57 µg/g range given by Sardans and Penuelas (2005) in a similar work using the Moss *Hypnum compresfome*.

The levels of Cr in the samples were slightly higher than the 0.01 mg/kg permissible limits recommended by FEPA (1991) while the level of Ni was within the 0.2-2.7 mg/kg reported by WHO (1986) in vegetable plants and given recommended permissible limits of 1-1.8 mg/kg in plants.

The levels of Cu found were far lower than the 50-150 mg/kg limits given by (EC, 1991) council directives and also lower than the 20-115 mg/kg range recommended by Sardans and Penuelas (2005). Similarly, the levels of Cd in L2, L3, L4, L7, L8, CA, and CB were higher than the 0.005 mg/kg USEPA (1993) permissible limits but lower than 1.0 mg/kg FEPA (1991) limits and 1-3 mg/kg recommended by EC council (1986) directives 86/278/EEC. Though the level of Cd in sample L2, L7, L8, and CB fall within the range of 0.10-0.58 mg/kg given by Sardans and Penuelas (2005) in a similar study using the Moss *Hypnum compresfome*. The high Cd content in L4 was attributed to particles from the sawmill factory and dust particles from road traffic and agricultural activities.

The level of Zn in L2 and CA were slightly higher than the 1.0 mg/kg permissible limit given by FEPA (1991) but lower than the 5 mg/kg recommended by USEPA (1993) and 30-150 mg/kg given by Sardans and penuelas (2005) measured in a similar study. Kula et al. (2012) and Zhu et al., (2012) give the recommended permissible limits of Mn in Plants to range between 400-1000 mg/kg due to its very low toxicity effects. Though, the levels of Mn in this study stands far below the recommended limit stated above.

IV. CONCLUSION

The The statistical variation in the distribution of trace metal levels in the study area showed that their depositions was mainly engineered local anthropogenic sources; such as repair at the mechanical workshop, sawdust from sawmill factories, agricultural activities, particles from rusting of scrabs and construction sites, emission from vehicular traffic, burning of waste, and fossil fuel combustion. The average concentration of the metals of interest viz; Cr, Ni, Cu, Pb, Fe, Mn, and Cd were slightly higher than USEPA (1993) limits but lower than FEPA (1991) limits. Although, the concentration ranges of these metals were ithin the tolerant limits and also very low compared to the report of a similar study carried out in an industrial area of south-south and south-west Nigeria and other European countries.

The validity of foliose epiphyte lichens (*Parmalia sulcata*) as a suitable cost-effective and efficient bio-monitoring tool for the evaluation of atmospheric trace metals and air quality assessment cannot be overemphasized. The trace metal of in interest in this study were detected in the sample substrate at variable concentration across the study area but the level of these metals was still within the USEPA, FEPA, EPA and WHO recommended tolerant limits However, this study revealed the atmospheric trace metal level of the area under study to be at a threshold level and hence the environment is still very safe from atmospheric trace metal pollution.

V. REFERENCES

- Abdullateef, B., Kolo, B. G., Waziri, I and Idris, M.A. (2014). Levels of Heavy Metals in Soil as Indicator of Environmental Pollution in Maiduguri, Borno State, Nigeria Bill Environmental Pharmacological Life Science, 3 (11); 133-136.
- Adriano, D. C., (2001). Trace elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals, New York; Berlin; Heidelberg: Springer. 867.
- Akabueze, C. I., Tsafe, A. I., Itodo, A. U., Uba, A., and Tambuwal, A. D. (2012) Influence of Climate and Height on the Levels of Sulphur Dioxide (SO₂) in Sokoto High Traffic Density and Near Atmosphere Region, World Environment, 2(3): 51-55.
- Aksoy A., Leblebici, Z and Halici, M. G. (2010). "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., Springer Netherlands, 59-70.
- Aniefiok, E. I., Imaobong, I. U., Udo, J. I. (2014) Distribution of Some Atmospheric Heavy Metals in Lichen and Moss Samples, American Journal of Environmental Protection, 2 (1): 22-31.
- Audu, A. A. and Lawal, A.O. (2005). Variation in Metal Contents of Plants in Vegetable Garden Sites in Kano Metropolis, Journal of Applied Science and Environmental Management, 10 (2):105-109.
- Bargagli, R. (1998). Trace elements in Terrestrial Plants, An Eco-Physiological Approach to Biomonitoring and Bio recovery, Springer, Berlin.
- Borrego, C., Miranda A. I., Coutinho, M., Ferreira J, and Carvalho A. C (2003). Air Quality Management in Portugal: Needs and Available tools, proceedings of an International Workshop Organized by International Atomic Energy Agency, Azores Islands, Portugal 28th August- 3rd September 2000, 36-54.
- Cansaran-Duman D., Aras S., Atakol O, Atasoy I. (2012) Accumulation of Trace Elements and the Assessment of the Genotoxicity in the Lichen *Pseudevernia furfuracea* Transplanted to a Polluted Site in Ankara, Ekoloji, 21 (85): 1-14.
- Cansaran-Duman, D., Atakol, O., Atasoy, I., Kahya, D., Aras, S. and Beyaztas, T. (2009). Heavy Metal Accumulation in *Pseudevernia Furfuracea* from the Karabük iron-steel factory in Karabük, Turkey. Z Naturforsch C, 9/10-64c, 717-723.
- Carson, P.G., Neubauer, K.R., Johnston, M.V., Wexler, A.S (1995). "On-line chemical analysis of aerosols by Rapid Single-Particle Mass Spectrometry", Journal of Aerosol Sciences, 26, 535-545.
- Conti, M. E. and Cecchetti, G. (2001). Biological monitoring: lichens as bioindicators of air pollution assessment—a review, Environmental Pollution, 114, 471-492.

- EC (European Communities) (1986) Directives 86 278 EEC on the protection of the Environment and in particular of the soil when Sludge is used EEC, Brussels.
- EC (European Communities) (1986). Directives 86 278 EEC on the protection of the Environment and in particular of the soil when Sludge is used EEC, Brussels.
- Ekpo, B. O., Uno U. A., Adie A. P. and Ibok U. J. (2012). comparative study of the level of trace metals in moss species in some cities of Niger Delta Region of Nigeria, *International Journal of Applied Science and Technology*, 2(3): 127-135.
- Elaigwu S. E., Ajibola V. O and Falaranmi F. M (2007) Studies on the impact of Municipal Waste Dumps on Surrounding and air Quality of two Cities in Northern Nigeria, *Journal of Applied Sciences*, 7:421-425.
- European Communities (EC), (2001) Ambient air Pollution by As, Cd and Ni Compounds-Official Publications of the European Communities, 10-318.
- Farmaki, E.G., and Thomaidis, N.S. (2008). Current status of the metal pollution of the environment of Greece- a review. - *Global Nest* 10(3): 366-375.
- Fatoba, P. O., Ogunkunle, C. O., and Okewole, G. A. (2012). Mosses as biomonitors of heavy metals deposition in the atmosphere, *International Journal of Environmental Science*, 1(2):56-62.
- FEPA (1991) Guidelines and Standards for Environmental Pollution Control in Nigeria, 33
- Figueira, R., Sergio, C. and Sousa, A.J., (2002). Distribution of trace metals in moss biomonitors and assessment of contamination sources in Portugal, *Environmental Pollution*, 118:153-163.
- Frati, L., Brunialti, G., & Loppi, S. (2005). Problems related to lichen transplants to monitor trace element deposition in repeated surveys: a case study from Central Italy, *Journal of Atmospheric Chemistry*, 52:221-230.
- Gabriel, S., Ion, V.P., Anca, G., Cristiana, R., Ioan, A. D., Iulia B. and Raluca, S. (2011). Identification of Air Pollution Elements in Lichens used as Biomonitors, By the XRF and AAS methods, *Romanian Journal of Physics*, 56(1): 240-249
- Gary, J., (1993). Lichens as biomonitors for heavy metal pollution, In B. Merkert (ed), *Plants as Biomonitors. Indicators for heavy metals in the terrestrial environment*, VCH, Weinheim, New York: VCH D, 193-264.
- Giordano, S., Adamo, P., Sorbo, S. and Vingiani, S. (2005). Atmospheric trace metal pollution in the Naples urban area based on results from moss and lichen bags. *Environmental Pollution* 136:431-442.
- Giordano, S., Sorbo, S., Adamo, P., Basile, A., Spagnuolo, V. and Castaldo C. R. (2004) Biodiversity and trace elements content of epiphytic bryophytes in urban and extra-urban sites of southern Italy, *Plant Ecology* 170, 1-14.
- Grodzińska, K., Frontasyeva, M., Szarek-Łukaszewska, G., Klich, M., Kucharska-Fabiś, A., Gundorina, S. F. and Ostrovnaya, T. M. (2003). "Trace Element Contamination in Industrial Regions of Poland Studied by Moss Monitoring," *Environmental Monitoring and Assessment*, 87(3): 255-270.
- Hipolito, C.S., and Frietas, M.C. (2003). A chemical Speciation study in Aerosol Sample, *Proceedings of an International Workshop Organized by International Atomic Energy Agency, Azores Islands, Portugal 28th August- 3rd September 2000*; 215-218.
- Ho, Y. B. and Tai, K. M. (1998). Elevated Lead and Other Metals Levels in Roadside Soil and Grass and their Use to Monitor Aerial Deposition in Hong Kong, *Environmental pollution*, 49:37-51.
- Jalkanen, L., Mäkinen, A., Hasan, E., and Juhanoja, J., (2000). The Effect of Large Anthropogenic Particulate Emissions on Atmospheric aerosols deposition and Bioindicators in the Eastern Gulf of Finland region, *The Science of the Total Environment*, 262:123-136.
- Jean, Z., Raćimović, R., Bati, F. and Mavsar, R. (2002). 'Lichens as integrating air pollution monitors, *Environmental Pollution*, 120, 107-113.
- Joyce, E. S. (1995). Pattern recognition in lichens for source apportionment, *Journal of Atmospheric Environment*, 29(3):1995,333-343.
- Jozwik, Z. (1990). "Heavy metals in tundra plants of Bellsund area, Spitsbergen" *Polish Polar Research*, 11: 401-409.
- Kapu, M. M., Ipaye, M. M., Ega, R. A. I., Akanya, H. O., Balauabe, M. L. and Schaeffer, D. J. (1991). Lichen as Biomonitor of Aerial Fall out of Heavy Metal in Zaria, Nigeria, *Bill Environmental Contamination and Toxicology*, 47: 413-416.
- Kojima, M. L. (2001). *Urban Air Quality Management World Bank*, Washington D.CK
- Kula, E., Hrdlicka, Hedbávný, P. J. and Pavel, Š. (2012). Various content of manganese in selected forest tree species and plants in the undergrowth, *Beskydy*. 5:19-26.
- Lopi, S., Pirintsos, S. A., and De Dominicis, V. (1999). Soil contribution to elemental Composition of Epiphytic Lichens (Tuscany, Central Italy), *Environmental Monitoring and Assessment*, 58:121-131.
- Loppi, S., Putortù, E., Pirintsos, S.A. and De Dominicis, V. (2000). "Accumulation of Heavy Metals in Epiphytic Lichens near a Municipal Solid Waste Incinerator (Central Italy)," *Environmental Monitoring and Assessment*, 61 (3):361-371.
- Martinez, T., Lartigue, J., Avila-Perez, P., Zarazua, G., Cabrera L., Tejada, S., and Ramirez, A. (2003). Atmospheric Metallic Pollutants in the Metropolitan Zone of Mexico Valley, *Proceedings of an International Workshop Organized by International Atomic Energy Agency, Azores Islands, Portugal 28th August- 3rd September 2000*; 299-307.
- Mendel, D, Tuzen M, Yazici, K, and Soylak, M, (2005). Heavy Metals in Lichens from Roadside and Industrial Zone in Trabzon, Turkey, *Bullarious Environmental Contamination Toxicology*, 74:190-194.

- National Population Commission (2006). National and State Population and Housing Tables, Priority Tables. Vol. II
- Obiakor, M. O. and Ezeonyejaku, C. D. (2013). Spatial Biomonitoring of Trace Element Contamination and Atmospheric Quality Assessment, American Journal of Life Science Resource, 1(2): 67-73.
- Olowoyo, J. O., Van Heerden, E. (2010). Trace element concentrations from lichen transplants in Pretoria, South African Environment. Science Pollution Resource.
- Owega, S., Evans, G.J., Jovis, .R.E., Tsai, J., Kremer, E. and Tan, .P.V. (2003). Lams, Laser Ablation/Ionization mass spectrometry for Aerosol characterization and source apportioning, proceedings of an international workshop Organized by International Atomic Energy Agency Azores Islands, Portugal 28th August- 3rd September 2000; 77-86.
- Ozgur, D. U., Kadir, K., Mustafa, T., and Mustafa, S. (2007). Trace Metals Level in Lichen Samples from Roadsides in East Black Sea Region Turkey, Journal of Biomedical and Environmental Sciences, 20: 203-207.
- Pandey, V., D. K. Upreti, R. Pathak, and A. Pal (2002) "Heavy metal accumulation in lichens from the Hetauda industrial area Narayani zone Makwanpur District, Nepal," Environmental Monitoring and Assessment, 73 (3): 221-228.
- Sardans, J. and Penuelas, J. (2005). Trace metal Accumulation in Moss *Hypnum cupressiforme* Hedw and the tree *Quercus ilex* L. and *Pinus halepensis* Mill, In Catalonia, Chemosphere, 60: 1293-1307.
- Sloof, J. E., (1993). Biomonitoring Trace Elements Air pollution, Ph.D. The thesis is the Delft University of Technology, Interfaculty Institute Delft 191.
- Sloof, J. E., (1995). Lichens as Quantitative Biomonitors for Atmospheric Trace-Elements Deposition using Transplants, Atmospheric Environment, 29, 11–20.
- Tsafe, A. I., Abdulrahman, F. W., Zuru, A. A., and Ayodele, J. T. (2010). "Atmospheric Level of SO₂ in Sokoto Metropolis, Nigeria" Nigerian Journal of Basic and Applied Science, 18(1): 101-105.
- United States Environmental Protection Agency (U.S. EPA) (2002). Lead Compounds Technology Transfer Network-Air Toxics Website. Online at: <http://www.epa.gov/cgi-bin/epaprintonly.cgi>.
- USEPA, (1993). Regional Environmental Monitoring and Assessment Program, RE-MAP, Cincinnati.
- Wang, Z.M., Song, K.S., Zhang, B., Liu, D.W., Ran, C.Y., Zhang, S.M., Luo, L., and Zhang, C.H. (2009). Spatial variability and affecting factors of soil nutrients in crops land of Northeast China. - Plant, Soil and Plant, 55: 110-120.
- WHO, (1984). Guideline for Drinking Water Quality Volume 2: Health Criteria and Supporting Information, 63-315.
- Zhu F., Qu L., W. Fan W., Qiao M., Hao H. and Wang X, (2011). "Assessment of heavy metals in some wild edible mushrooms collected from Yunnan Province, China," Environmental Monitoring and Assessment, 179 (1-4):191-199.
- Kamble, R. K., Thakare, M. G., & Ingle, A. B. (2013). Iron in the environment. Indian Journal of Environmental Protection, 33:881-888.