



## Funaria hygrometrica moss as Bioindicator of Atmospheric Pollution of Heavy Metals in Makurdi and Environs, North Central Nigeria

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### Abstract

Samples of *Funaria hygrometrica* moss were collected at eleven (one of which was a control) different locations in Makurdi town and analyzed for their heavy metals contents. The concentrations of eight heavy metals; lead (Pb), copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni), manganese (Mn), zinc (Zn), and iron (Fe) were determined using a flame atomic absorption spectrophotometer (FAAS). The mean levels and standard deviation of heavy metals in the moss samples were found to be: Pb (0.575±0.74 µg/g); Cu (2.034±3.59 µg/g); Cr (0.296±0.22 µg/g); Fe (18.955±12.61 µg/g); Cd (0.001±0.007 µg/g); Ni (0.002±0.003 µg/g); Zn (2.362±1.49 µg/g); Mn (0.287±0.39 µg/g). Iron had the highest average concentration of 18.955µg/g while Cd had the least average concentration of 0.001µg/g. The amount of these metals were observed to follow the trend Fe> Zn>Cu>Pb>Cr>Mn>Ni>Cd. Statistical analysis showed a significant correlation ( $r = 0.988$ ;  $p < 0.01$ ) in the samples collected at commercial and industrial areas. Also, there was a significant correlation in metal levels collected at residential and industrial areas ( $r = 0.996$ ;  $p < 0.01$ ). In a similar way, a positive correlation existed between the levels of metals in commercial and residential areas ( $r = 0.997$ ;  $p < 0.01$ ). There was a strong correlation at 0.05 significance between Cd, Cr, Mn, Ni and Cu while the correlation of Fe, Pb and Zn was insignificant in all the studied locations. From the results, iron (Fe) was found to be the most abundant metal in the study area. Heavy metals pollution load in the analyzed samples was in the order; industrial> commercial> residential. The results showed that Makurdi atmosphere is not polluted with respect to these heavy metals based on NESREA (National Environmental Standards and Regulations Enforcement Agency) standards.

**Keywords:** *Funaria hygrometrica*, bio-monitors, bio-indicators, heavy metals, atmospheric pollution.

### Introduction

Mosses are living organisms of the plantae kingdom and classified in the phylum bryophyta. They grow in forests, on rocks, on trees, bare soil, cracks of concrete side walls, on burnt bricks on abandoned automobiles, and uncompleted buildings. They are effective atmospheric pollution bioindicators as they take up nutrients and pollutants directly from the atmosphere since they have no root system<sup>1</sup>. Mosses are extensively used as biomonitor for air pollution monitoring, because they can indicate the presence of elements and their concentration gradients<sup>2</sup>. Generally, bryophytes, especially mosses are ubiquitous as they are equipped with some structural adaptive strategies that enable them to grow successfully where they occur. Moreover their ability to grow on substrates or areas which are inhospitable to higher plants exclude them from intense competition and this gives them an added advantage to serve as good bio indicators<sup>3</sup>. Recent progress in environmental pollution studies has changed our understanding of bryophytes as useful plants<sup>4</sup>. Bryophytes are efficient accumulators of heavy metals due to some properties which includes lack of true root system that makes them to depend largely on atmospheric

deposition for their mineral element requirement, lack of cuticle layer, which makes their tissues to be easily permeable to water, minerals, gaseous pollutants in the atmosphere as well as metal ions, possession of tissues with negatively charged groups which can act as efficient cation exchangers<sup>5</sup>. In addition to these properties, the wide distribution and ease of collection makes bryophytes efficient metal accumulators and bio-monitors<sup>6</sup>. Earlier research works have shown that mosses have proven to be better bio-indicators of pollution because they are more sensitive to atmospheric pollution<sup>7</sup>.

Environmental pollution by heavy metals is usually as a result of activities related to industrialization, including combustion of fuels, or other temperature driven reactions associated with vehicular performances. Some fuel additives such as Cd, Pb, Cu, and Zn are released into the atmosphere and carried to the soil through rainfall and wind<sup>8</sup>. Although heavy metals are natural components of the environment, metals such as Pb, Cd, Hg, Ni and As have no known or reported biochemical importance and their appreciable concentration could become potential lethal hazards<sup>9</sup>. A range of these metals found in the environment are harmful to living organisms. Cadmium is

mostly encountered in cadmium-nickel battery production, although it continues to be used in paints as well as in plastic production where it is an effective stabilizing agent. Occupational exposure to cadmium can occur through metal refining processes, where cadmium is often associated with copper and can be released into the atmosphere during heating. Individuals exposed to cadmium can develop osteoporosis, anemia, eosinophilia, emphysema, and renal tubular damage. Long-term cadmium toxicity can produce *Itai-Itai* disease, in which individuals suffer from bone fractures, severe pain, proteinuria, and severe osteomalacia<sup>10</sup>. It is known that Cu is an essential element, yet it may be toxic to both humans and animals when its concentration exceeds the safe limits, and its concentration in some human tissues such as thyroid can be changed depending on the tissue state. Iron is vital for almost all living organisms, participating in a wide variety of metabolic processes, including oxygen transport, DNA synthesis, and electron transport<sup>11</sup>. It is known that adequate iron in a diet decreases the incidence of anemia. Chromium originates from combustion of fossil fuel and industrial activities. Chromium toxicity can cause irritation of respiration system, perforation of nasal passages and lung cancer, chronic exposure may also lead to liver and kidney damage<sup>12</sup>. The concentration of Pb found in various environmental compartments bordering a roadway is a function of a number of factors, including distance and meteorology<sup>13</sup>. Pb constitutes over 20% of total mass of fine particles emitted from cars, burning leaded gasoline. Approximately 75% of Pb contained in leaded gasoline is emitted directly to the atmosphere. However, it has been recorded that only 25% of Pb emitted by vehicle are in coarse fraction and thus deposited close to roads. The remaining 75% is in fine fraction and so may remain airborne hence contaminating areas more remote from the point of its emission<sup>13</sup>. Two Swedish scientists Åke Rühling and Germund Tyler in 1960 discovered that mosses are good bio-indicators of heavy metal pollution in the atmosphere. After this successful discovery, many European countries have used mosses in national and multinational surveys of atmospheric-metal deposition<sup>14</sup>.

Makurdi is a rapidly growing city located between latitudes 7° 44' and 8° 00' N and longitudes 8° 00' and 8° 33' E in the Lower Benue River Basin, a major agricultural zone in North Central Nigeria. It is the capital city of Benue State and doubles as the headquarters of Makurdi Local Government Area (LGA). Makurdi LGA has an approximate land mass of 804.35 km<sup>2</sup> and an estimated population of 297,398 inhabitants. The inhabitants are engaged in rural, peri-urban and urban agriculture, industrial, and other human activities. The city is itself bisected by the Benue River into the North - and South-Bank areas. The soils are derived from Precambrian basement complex rocks and quaternary alluvial deposits of the Benue River as parent materials. The range of annual rainfall is 1200 – 1650 mm and is distributed between March/April and October /November, followed by a marked dry season (of up to 4 months). Daily global irradiation and mean hours of insulation are, respectively,

314 – 433 calcm<sup>2</sup>day<sup>-1</sup> and 4.00 – 7.74h<sup>15</sup>. The city has witnessed influx of people from neighboring towns, as the state capital. This has increased the concentrations of motor vehicles and some industries over time. Therefore, this research work was aimed at appraising the concentrations of some heavy metals in *Funaria hygrometrica* harvested from the streets of Makurdi town to ascertain the level of pollution by these metals.

The quest for civilization and modernization has direct bearing on the environment in which man lives. There is therefore the necessity to periodically audit the environment for man's continuous healthy living. Such exercise will reveal the extent to which the habitat has been impacted. This would equally help in identifying the prevailing danger and thus enable the authorities to take necessary steps by checkmating the release of pollutants in the environment. This research work was therefore designed to assess heavy metals anthropogenic impact on the environment in Makurdi using *Funaria hygrometrica* moss.

## Material and Methods

**Sampling:** *Funaria hygrometrica* samples were harvested between March and April of 2013. Samples were collected from 10 different locations within Makurdi town and outskirts. These include: Industrial Layout, Naka Road; Ministry of Works and Housing, old GRA; Agbe Village; Fiidi village; Agboughoul village, behind Makurdi Modern Market; Mechanic village, Apir; Federal Housing Estate, North Bank; Wurukum Market; Community Secondary School, Wadata; and Behind NUJ, Ankpa Ward. The control sample was collected at Makurdi Zoological Garden, Benue State University. Sample locations were categorized as residential, commercial and industrial based on prevailing human activities. *Funaria hygrometrica* moss samples were collected randomly from the walls of burnt bricks, on trees, rooftop of buildings and walls of concrete buildings, along busy streets within the sampled area. Samples were collected with local wooden hand trowel into polyethylene bag and labeled accordingly. The samples were taken to the laboratory for further treatment.

**Preparation and Analysis of Samples:** Impurities adhering to the surface of the moss sample were removed very carefully under dry conditions. Only the green and greenish brown parts of the moss plants were used. The moss plants were later dried in an oven at a temperature of 75 °C for 48 hours. The ground sample (1.0 g) was weighed and digested with 5.0 cm<sup>3</sup> of a mixture of nitric acid and perchloric acid in the ratio (4:1) in a water bath (Clifton water bath, Nickel-Electro Ltd, Weston-s-mare Somerset, England, serial NO: 92525) at 60°C until a yellow straw solution was obtained. The temperature was then increased to 120°C until there was complete dissolution of the sample. The resulting solution was completely evaporated and re-dissolved in 10 cm<sup>3</sup> 0.1M HNO<sub>3</sub>. The solution was then filtered through an acid washed Whatman filter paper (cat no: 1001 110, Lot no: 231175.) into a 25 cm<sup>3</sup> volumetric flask and then diluted to the mark with deionized water. Metal

concentrations were determined by atomic absorption spectrophotometer (Biotech Engineering Management Co., Ltd. (UK) FAAS Phoenix 986).

## Results and Discussion

Concentrations and the means as well as standard deviations of heavy metals in the moss samples are presented in Table 2. Figure 2 presents the average concentrations of the heavy metals and figure 3 pictures the levels of the heavy metals in the study area in relation to their levels in other Nigerian cities<sup>16</sup>. Correlation statistics of the metals in industrial, residential and commercial areas are presented in tables 2, 3 and 4 respectively, while table 5 is the correlation of the average values of the metals. In most of the samples, Ni was found below detection limits (BDL), indicating low release of the metal in the environment. Nickel's highest concentration of 0.011 $\mu$ g/g was detected at the mechanic village, an area characterized by high automobile and industrial activities. Trace amounts of the metal were found in samples ILN and MMK. Other sources of the metal in these locations could be traced to activities such as fabrication and welding of metals, disposal of spent auto-batteries, and spent lubricating oils (SLO) and various paint wastes and pigments<sup>17</sup>.

The concentration of nickel obtained from this study is far less than reported from other cities in Nigeria<sup>16,18</sup>.

Ni in the Atmosphere originates from the combustion of fossil fuels, smelting and volcanoes. It is also found that combustion of oil and incineration of waste contributes more than 70% of total Ni to the atmosphere from manmade sources followed by refining process with 17% (IPCS, 1991b). Continuous and prolonged exposure to Ni can produce dermatitis and disorders in the respiratory system and it is a possible carcinogen<sup>13</sup>.

Only one site (MCV), an industrial area indicated trace amount (0.007  $\mu$ g/g) of cadmium. Activities leading to wear and tear of tyres and vulcanization are the principal sources of cadmium in the environment<sup>10,16</sup>.

The results of Zn concentrations in the moss plant within Makurdi metropolis ranged from 0.998  $\mu$ g/g in FHE (Residential) to 5.980  $\mu$ g/g MCV (Industrial). The concentration of Zn obtained in this study agrees with the results obtained in some Nigerian cities and showed that concentration of heavy metals depend on the nature of activities of a place in the following pattern; industrial area > commercial area > residential area<sup>11</sup>.

The highest concentration of 12.012  $\mu$ g/g was found at MCV, a site characterized by high vehicular activities, while the lowest concentration of 0.052  $\mu$ g/g was observed at CSS a commercial area. Copper in the environment is associated with release from corroding metal parts derived from engine wear, brushing and metal bearing<sup>19</sup>.

Manganese was present in all the samples and varies from 0.052  $\mu$ g/g in NUJ (Residential) to 1.009  $\mu$ g/g in MWH (Industrial).

Manganese contamination in the studied samples was comparatively lower than was reported in other cities in Nigeria<sup>16</sup>, but higher than was reported by Fatoba P.O. et al<sup>11</sup>. The deficiency of manganese in the human body can produce severe skeletal and reproductive abnormalities in mammals. High doses of manganese produce adverse effects primarily on the lungs and on the brain<sup>20</sup>.

Similarly, iron was detected in all the samples and varies from 9.001  $\mu$ g/g in CSS (Commercial) to 46.215  $\mu$ g/g in MCV (Industrial). Iron, a dominant component of steel is ubiquitous in household, commercial and industrial materials. Its concentration in the environment varies as the nature of human activities in the locality. Although Fe recorded the highest concentration in the moss samples in this study, but relatively low compared with the results from different cities in Nigeria<sup>16</sup> and thousands of times lower than values obtained by in china<sup>21</sup>. The variation of Fe concentration in moss plant within the study area also followed the similar pattern of industrial area > commercial area > residential area reported by Fatoba P.O. et al<sup>11</sup>.

Chromium recorded the lowest concentration of 0.012  $\mu$ g/g in FDV (Residential) and highest of 0.675  $\mu$ g/g in MCV (Industrial). The presence of Cr in an environment is associated with the industrial uses of battery and paints and the indiscriminate disposal of waste containing paint and batteries<sup>22</sup>. The existence of Cr in roadside soil may be due to the tire erosion<sup>23</sup>.

Contrary to expectations, lead was not detected in CSS (commercial). However, it varies in other samples from 0.035  $\mu$ g/g in NUJ (residential) to 1.352  $\mu$ g/g in MCV (industrial).

Elevated concentrations of Pb, in roadside soil and vegetation were reported to vary with traffic densities<sup>24</sup>. Levels of heavy metals in bark and fruit of trees along roads in Nigeria vary according to traffic volume<sup>22</sup>. Similarly, the concentration of Pb and, to some extent, a few other toxic elements are strongly correlated with traffic density<sup>20</sup>.

The average concentration of all the heavy metals under study in Makurdi recorded the highest concentration of 18.955 $\mu$ g/g for Fe while the least concentration of 0.001 $\mu$ g/g was recorded for Cd. The amount of these metals in Makurdi were observed to follow the trend of Fe > Zn > Cu > Pb > Cr > Mn > Ni > Cd. This observation is similar to that obtained in Czech Republic<sup>10</sup>.

The result of analysis of trace metals has revealed that for almost all the metals investigated, the preponderance of Fe over the other elements is as a result of its abundance in the materials releasing metals to the environment. The higher concentration of iron obtained from this study is similar to the result obtained in some Nigerian Cities though relatively lower when compared

with the iron concentration in these cities. Generally, the concentrations of all metals under this investigation were lower than the concentrations of in some cities in Nigeria<sup>16</sup>. However, the variation of these metal concentrations of moss plant in Makurdi showed a similar variations pattern with the variation of these metals in Aba, Port Harcourt, Eket and Calabar (Table 4).

This implies that the increasing concentration of one will cause the other to diminish. A strong positive correlation was found between Pb and Mn ( $r = 0.911$ ;  $P < 0.05$ ), and between Zn and Cu ( $r = 0.990$ ,  $P > 0.01$ ). This implies that Zn and Cu come from the same sources of pollution.

In table 5, Ni and Cd show no correlation with other metals. The other metals all show strong positive correlation ( $r = 1.00$ ;  $P < 0.01$ ) among themselves, suggesting same source derivation and direct relationships in their concentrations.

Statistical analysis (table 5) reveal inter-correlation among metals analyzed. Chromium correlates strongly ( $r = 0.999$ ;  $P <$

$0.05$ ) with cadmium and copper. Similarly, Ni shows significant correlation ( $r = 1.00$ ;  $P < 0.05$ ) with Cr and Cu, and at ( $r = 0.998$ ;  $P = 0.05$ ) and with Cd at ( $r = 0.997$ ;  $P = 0.05$ ) with Mn. This strong inter-correlation among metals implies same pollution sourcing. These points to the fact that, the presence of these metals in the atmosphere could be traceable to vehicular emissions, metallurgical processes or refuse incineration, oil combustion and processing of oil products<sup>25</sup>.

### Conclusion

From the results, Iron (Fe) was found to be the most abundant metal in the study area. The presence of all the metals was found to be most abundant in the Mechanic Village. Also, the industrial areas accounted for the greatest amounts of these metals in atmosphere, in comparison to commercial and residential areas, a result which is much expected because of the high traffic density and industrial activities in these areas. Heavy metals pollution in the area follows the pattern; industrial > commercial > residential. However, the study reveals that Makurdi is not as polluted as other Nigerian cities<sup>16</sup>.

**Table-1**  
**Description of sample locations**

S/N	Sampling location	Sample ID	Location description	Co-ordinates
1	Community Secondary School Wadata Area	CSS	Commercial	7 <sup>0</sup> 44'N and 8 <sup>0</sup> 30'E
2	Wurukum market	WRK	Commercial	7 <sup>0</sup> 43'N and 8 <sup>0</sup> 33'E
3	Mechanic village, Apir Road, Kanshio Area	MCV	Industrial	7 <sup>0</sup> 39'N and 8 <sup>0</sup> 33'E
4	Ministry of Works and Housing	MWH	Industrial	7 <sup>0</sup> 44'N and 8 <sup>0</sup> 32'E
5	Industrial layout, Naka Road	ILN	Industrial	7 <sup>0</sup> 41'N and 8 <sup>0</sup> 33'E
6	Agboughoul Village, behind Modern Market	MMK	Residential	7 <sup>0</sup> 44'N and 8 <sup>0</sup> 32'E
7	Behind NUJ	NUJ	Residential	7 <sup>0</sup> 43'N and 8 30'E.
8	Federal Housing Estate, North Bank	FHE	Residential	7 <sup>0</sup> 45'N and 8 <sup>0</sup> 34'E
9	Agbe village	AGV	Residential	7 <sup>0</sup> 43'N and 8 <sup>0</sup> 30'E
10	Fiidi village km 9 opposite Airforce Base	FDV	Residential	7 <sup>0</sup> 43'N and 8 <sup>0</sup> 38'E
11	Benue State University, Makurdi	BSU	Control	7 <sup>0</sup> 43'N and 8 <sup>0</sup> 34'E

**Table-2**  
**Concentration of heavy metals in Funaria hygrometrica in the study area**

Sample ID	Ni (µg/g)	Cd (µg/g)	Zn (µg/g)	Cu (µg/g)	Mn (µg/g)	Fe (µg/g)	Cr (µg/g)	Pb (µg/g)
AGV	BDL	BDL	1.552	0.971	0.072	10.931	0.221	0.089
CSS	BDL	BDL	1.721	0.052	0.079	9.001	0.062	BDL
FDV	BDL	BDL	1.921	1.072	0.102	11.672	0.012	0.823
MCV	0.011	0.007	5.980	12.012	0.998	46.215	0.675	1.352
MWH	BDL	BDL	1.628	0.982	1.009	13.930	0.324	0.052
MMK	0.002	BDL	1.721	1.072	0.059	10.992	0.431	0.044
NUJ	BDL	BDL	1.782	0.993	0.052	11.062	0.321	0.035
FHE	BDL	BDL	0.998	0.461	0.072	13.901	0.049	0.049
ILN	0.006	BDL	2.381	1.821	0.342	32.935	0.551	1.301
WRK	BDL	BDL	3.931	0.901	0.082	28.913	0.311	2.007
BSU	BDL	BDL	0.122	0.051	0.004	1.000	0.017	0.006
Average concentration	0.002±0.003	0.0007±0.001	2.362±1.49	2.034±3.59	0.287±0.39	18.955±12.61	0.296±0.22	0.575±0.74

BDL = below detection limits

**Table-3**  
**Correlation of heavy metals in the industrial area**

S/N		Ni	Cd	Zn	Cu	Mn	Fe	Cr	Pb
1	Ni	-							
2	Cd	.839	-						
3	Zn	.916	.987	-					
4	Cu	.874	.998*	.996	-				
5	Mn	-.067	.487	.340	.427	-			
6	Fe	.999*	.811	.895	.849	-.116	-		
7	Cr	.993	.770	.863	.812	-.181	.998*	-	
8	Pb	.906	.530	.660	.586	-.482	.926	.949	-

\*Correlation is significant at the 0.05 level (2 tailed)

**Table-4**  
**Correlation of heavy metals in the residential area**

S/N		Ni	Cd	Cr	Cu	Fe	Mn	Pb	Zn
1	Ni	-							
2	Cd	.000	-						
3	Cr	.705	.000	-					
4	Cu	.344	.000	-.470	-				
5	Fe	-.319	.000	-.653	-.932*	-			
6	Mn	-.362	.000	-.811	.056	.219	-		
7	Pb	-.226	.000	-.625	.347	-.028	.911*	-	
8	Zn	.229	.000	.417	.990**	-.921*	.067	.379	-

\*Correlation is significant at the 0.05 level (2 tailed) \*\*Correlation is significant at the 0.01 level (2 tailed)

**Table-5**  
**Correlation of heavy metals in the commercial area**

S/N		Ni	Cd	Zn	Cu	Mn	Fe	Cr	Pb
1	Ni	-							
2	Cd	.000	-						
3	Zn	.000	.000	-					
4	Cu	.000	.000	1.000**	-				
5	Mn	.000	.000	1.000**	1.000**	-			
6	Fe	.000	.000	1.000**	1.000**	1.000**	-		
7	Cr	.000	.000	1.000**	1.000**	1.000**	1.000**	-	
8	Pb	.000	.000	1.000**	1.000**	1.000**	1.000**	1.000**	-

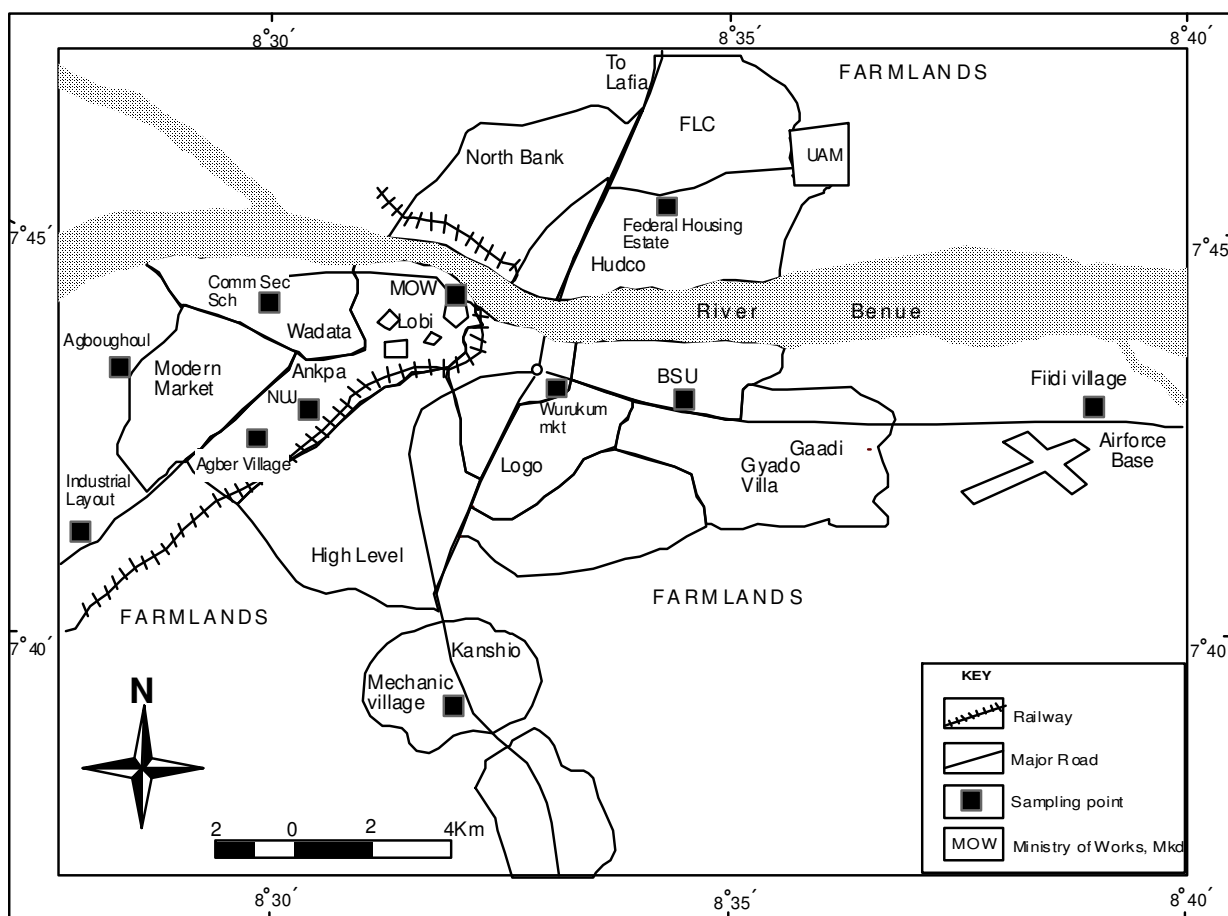
\*\* Correlation is significant at the 0.01 level (2-tailed).

**Table-6**  
**Inter-correlation of heavy metals in *Funaria hygrometrica* in the study area**

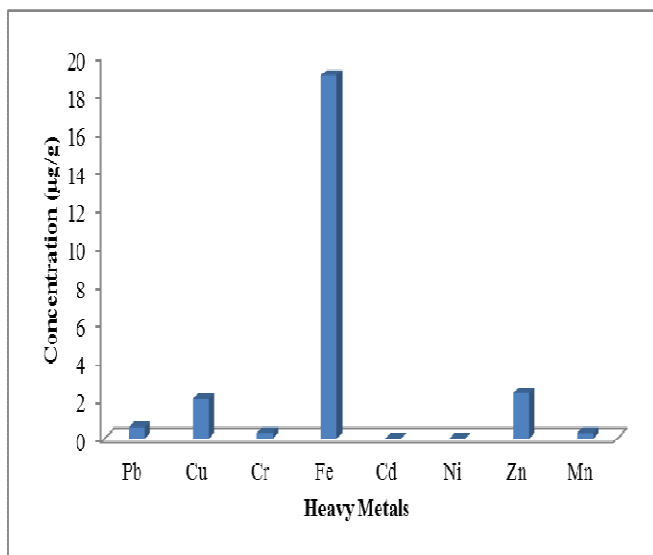
	Industrial	Commercial	Residential
Industrial	-		
Commercial	.988**	-	
Residential	.996*	.997**	-

S/N		Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	Cd	-							
2	Cr	.999*	-						
3	Cu	.996	.999*	-					
4	Fe	.928	.907	.91	-				
5	Mn	1.000*	.998	.995	.933	-			
6	Ni	.998*	1.000*	.1.000*	.905	.997*	-		
7	Pb	.396	.346	.312	.709	.407	.340	-	
8	Zn	.722	.683	.657	.927	.730	.679	.921	-

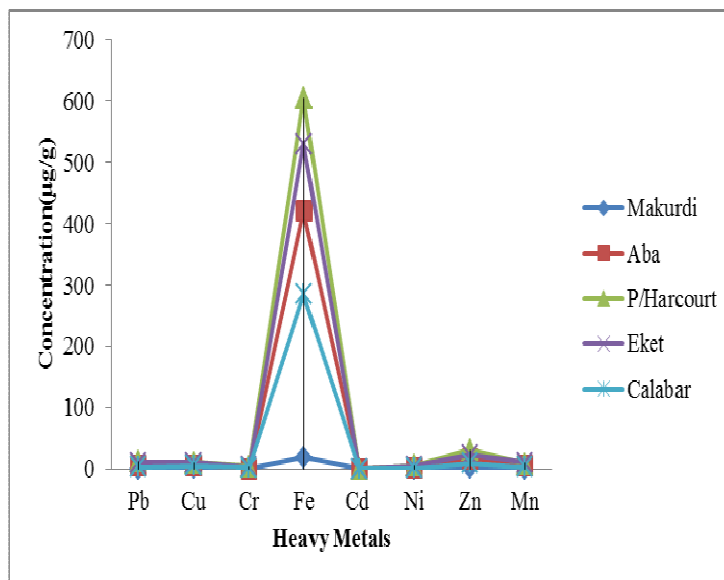
\* Correlation is significant at the 0.05 level (2-tailed).



**Figure-1**  
**Map of Makurdi showing sample points**



**Figure-2**  
Average concentrations of heavy metals in *Funaria hygrometrica* moss in Makurdi



**Figure-3**  
Comparison of heavy metal concentrations obtained in Makurdi with some Nigerian Cities

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