Global Scientific JOURNALS

GSJ: Volume 8, Issue 4, April 2020, Online: ISSN 2320-9186

www.globalscientificjournal.com

Seasonal Variation in Accumulation of Atmospheric Heavy Metals in Bryophyte Moss around the Mining Areas of Ebonyi State, Southeast Nigeria

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Abstract

The seasonal variation in the accumulation of atmospheric heavy metals around the mining areas of Ebonyi state were assessed using bryophyte mosses as biomonitors. Moss samples were collected from various substrates at Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu mining areas across the State during the dry and wet seasons and analysed for the concentration of Al, Ca, Cd, Cu, Fe, K, Mg, Na, Pb, Zn, As, Mn and Hg by means of atomic absorption spectrometry (AAS). The results of the analysis showed varying order in the mean heavy metal concentration in the moss samples across the mining areas with Ihietutu Pb/Zn mining area having the order Al>K>Ca>Fe>Mg>Pb>Zn>Na>Cu>Mn>As>Cd>Hg; Amaokwe stone quarry area had Al>Ca>Mg>Fe>K>Cu>Na>Zn>Pb>Mn>Cd>As>Hg; Uburu/Okposi salt mining area had Na>Mg>Ca>K>Al>Fe>Zn>Cu>Pb>Hg>Mn>Cd>As; and Nkalagu limestone mining area had Ca>Mg>Al>Fe>K>Zn>Cu>Pb>Na>Mn>Hg>As>Cd. The result also showed that the dry season moss samples had higher concentration of all the analysed heavy metals than the wet season samples, due to their exposure to increased particulate emission replete with heavy metals and other pollutants, which has varying potential environmental and health effects. The study concludes that solid mineral mining activities results in the emission of pollutants containing heavy metals into the atmosphere, and that the monitoring of these emissions gives an understanding of their spatial and temporal distribution, their effects on the environment and human health, and how to minimise their effects. It therefore recommends proper air quality management through the reduction of dust emissions and use of safer processes. Dust control should also be built into every aspect of the mines planning and operation system so as to reduce air pollution and their potential adverse effects on the environment and human health.

Keywords: Bryophyte, Moss, Biomonitor, Heavy metals, Mining, Atmospheric pollution

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Introduction

Monitoring of air pollution using bioindicators is emerging as a potentially effective and more economical alternative method of air pollution measurements. This is especially relevant for monitoring large areas as was done in parts of Europe (Rühling, 1994; Harmens *et al.*, 2013; Godzik, 2020). Bryophytes are an important component of biodiversity, and they have proven to be suitable bioindicators. They are a group of non-vascular plants comprising mosses, hornworts and liverworts. Of these three, mosses have been widely used for biomonitoring. Mosses are green plants, without true roots, stems or leaves and lack cuticle and vascular system (Aziz and Khdir, 2016), which makes them unable to avoid heavy metal accumulation from atmospheric deposition (Cortis *et al*., 2016). Like all bryophytes, mosses are independent of the soil and their rhizoids only serve as anchor to the substratum. Mosses receive minerals and nutrients, including pollutants from rain and atmospheric particles through the entire surface of their cells; and their high cation exchange capacity ensures a predisposition toward sensitive response to the concentration levels of metals in the environment (Stafilov *et al.*, 2018).

The usefulness of mosses in determining trace and heavy metal concentrations in different geographical areas has been discussed and demonstrated in several studies (Ruhling and Tyler, 1968, Onianwa, 2001; Markert *et al*., 2003; Saxena *et al.,* 2008; Hristozova *et al*., 2014; Jovan, 2016; Balabanova *et al*., 2017; Abdullahi *et al*., 2018). Mosses have several advantages as biomonitors of heavy metal pollution. This is because they are widely distributed, their large surface-to-weight ratio improves adsorption, their slow growth rate lets them accumulate pollutants over a long period of time and the metal concentrations in the moss's tissues reflects the atmospheric deposition over time (Grodzinska and Szarek-Lukaszewska, 2001; Chakraborty and Paratkar, 2006; Jovan, 2016).

Heavy metals distribute widely in the environment as a result of a range of human and natural sources. Mineral mining and processing is one of the important human activities that release heavy metals into the environment and this occour during each stage of the mine cycle, especially during exploration, development, construction and operational activities (Ziadat *et al*., 2015; Garty and Garty-Spitz, 2015).

Mineral mining in Ebonyi State is associated with large scale excavation, blasting, crushing, transportation and deposition of the excavated materials, which forms large heaps of mining wastes (Peter *et al.*, 2018; Makwe, 2020). Each of these activities are accompanied by the release of dusts, which are made up of fine particulate matter that contain metals among other pollutants. These are easily dispersed by the wind and deposited on surfaces of materials and vegetation around the mining sites (Makwe, 2019). Monitoring of air pollution around the mining areas of Ebonyi State is therefore needed for the understanding of their spatial and temporal distribution, their effects on the environment and human health (Okobia, 2015), and importantly to minimize their harmful effects.

Most air pollution monitoring studies in Nigeria and indeed Ebonyi State were based on the use of automatic air samplers and high volume air samplers (Njoku *et al*., 2016; Okobia *et al*., 2017; Anake *et al*., 2018; Oni and Ana, 2019; Ezeja *et al*., 2020). These are active methods that gives an idea of trace-element atmospheric pollution only during the sampling time. It requires long-term sampling at a large number of sampling sites. The measurements also require sophisticated technical equipment which are expensive. Biomonitoring however, is a passive method and provides a measure of integrated exposure over a period of time. It does not require long term use of expensive sampling equipment; the sampling of organisms used as biological monitor is generally easier; the concentrations in the monitor organisms are higher than the system to be monitored and this improves the accuracy of measurements. In addition, most biomonitor organisms reflect external conditions averaged over certain periods of time. This becomes important when monitoring levels change rapidly with time (Chakrabortty and Paratkar, 2006). Reports on the use of biomonitors for air pollution studies are non-existent in Ebonyi State. It therefore necessitated this research, which investigates the accumulation of atmospheric heavy metals as well as their seasonal variation around the mining areas of Ebonyi State using moss samples collected from the mining sites and their environs as biomonitors.

Study Area

Ebonyi State is located in the Southeastern region of the Federal Republic of Nigeria. The state lies between latitude 5°43’30” and 6°46’30’’ North of the equator and between longitudes 7°36’00” and 8°28’30’’ East of the Greenwich Meridian. Ebonyi State occupies a landmass of approximately 6,400 square kilometers and lies in an area of moderate relief with elevations between 125m and 245m above sea level (Edeani *et al*., 2013).. It is physically bounded to the east by Cross River State, to the north by Benue State, to the west by Enugu State and to the south by Abia State (Annual Abstract of Statistics, 2012).

The climate of Ebonyi State is generally that of the humid tropical type with marked dry season and wet season. The wet season begins in March and ends in October while the dry season begins in November and ends in February, with monthly average ranges of 3.1mm in January to 270mm in July and annual averages from 1750mm in the northern parts to

2250mm in the southern parts of the state (Onwuemesi *et al*., 2013a). Temperature ranges from 25^{o}C to 33^{o}C in the dry season and 23^{o}C to 27^{o}C in the wet season (Annual Abstract of Statistics, 2012; Onwuemesi *et al.*, 2013b)

Ebonyi state is endowed with many minerals, the primary ones being lead, zinc, limestone, marble, salt and igneous rocks. These minerals occur in commercial quantity in different parts of the state (Akubugwo *et al*., 2007; MMSD, 2010; Chiadikobi *et al.*, 2011; Igwe *et al*., 2013; Fatoye and Gideon, 2013).

Ebonyi State is part of the rainforest region of southeastern Nigeria with evergreen vegetation (Akanwa *et al*., 2016). The 2006 national population census gave the population of Ebonyi State as 2,176,947 with an annual growth rate of 3.5%. (NPC, 2006). The population is largely rural (Akanwa *et al.,* 2016), with the major economic activity as farming. Another very important economic activity in the study area is mining (Uhuo, 2013), which was made possible because of the several solid minerals found in the State.

This study was carried out in four mining areas located in three Local Government Areas of Ebonyi State namely Ihietutu Pb and Zn mining site and Amaokwe stone quarry site in Ivo LGA, salt mining area of Uburu/Okposi in Ohaozara LGA and limestone mining area of Nkalagu in Ishielu LGA. The selected locations have the largest mining areas for the minerals studied (Lead, Zinc, granites, salt and limestone).

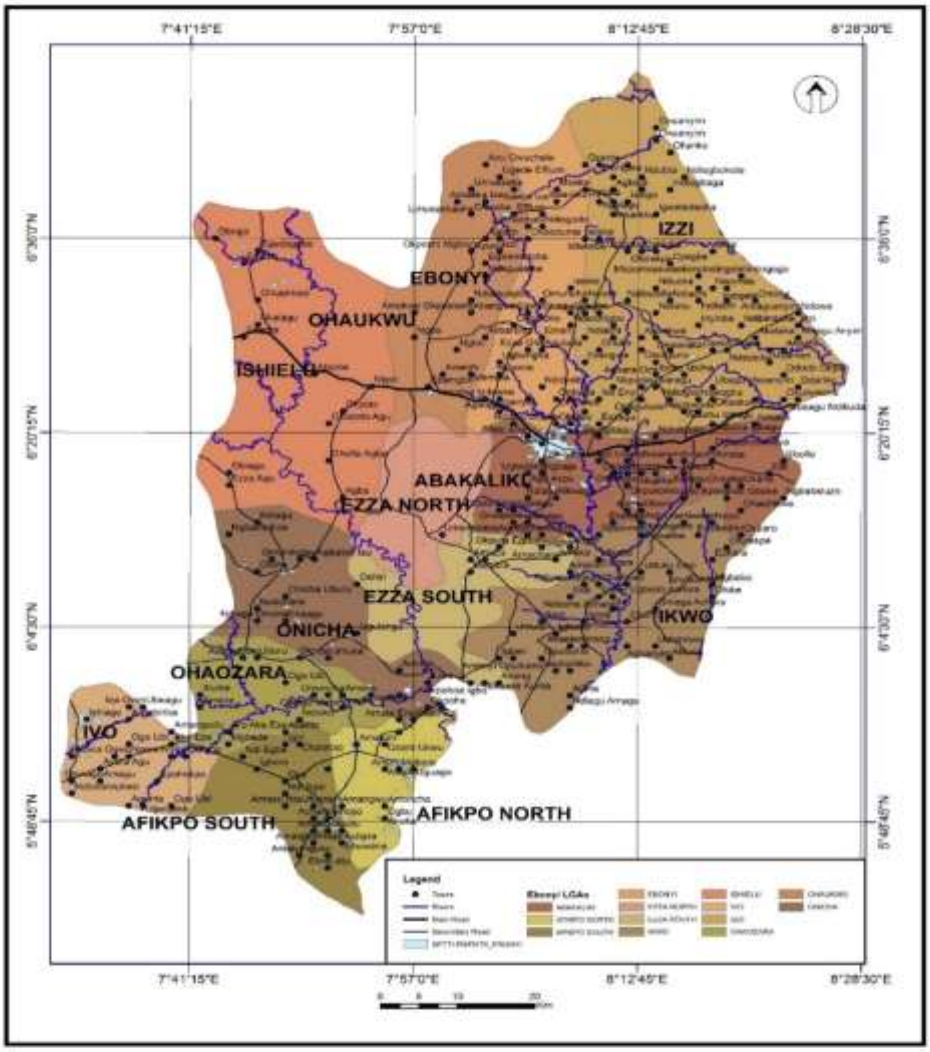


Fig. 1: Map of Ebonyi State showing the Local Government Areas
Source: National Space Research and Development Agency, 2018

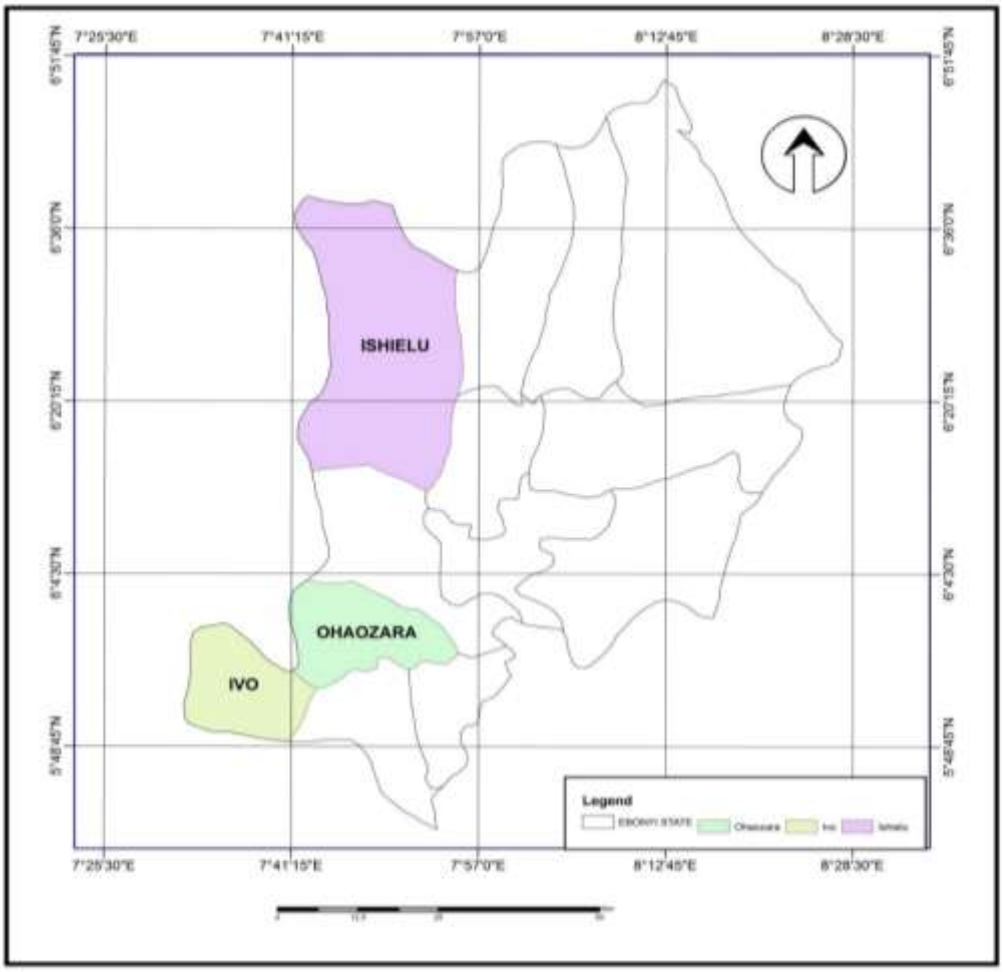


Figure 2: Map of Ebonyi State showing the Sample Local Government Areas
Source: NASRDA GIS Laboratory, 2018

Materials and Methods

Samples Collection

Moss sampling was carried out during the wet and dry seasons in 2018. The dry season samples were collected in the months of January and February and the wet season samples were collected in the months of July and August. Twelve sampling points, three from each mining area, distributed across the study area were selected. These comprised of Ihietutu Pb and Zn mining area, Amaokwe stone quarry area, Uburu/Okposi salt mining area and Nkalagu limestone mining area. The moss samples were picked up with a small plastic shovel. The green parts of the mosses were separated from the residual soil with plastic tweezers so as to avoid accelerated accumulation of pollutants on the leaves. The collected mosses were placed in separate well labelled envelopes, on which all the necessary identification data were written (Zepeda-Gomez *et al*., 2014). In collecting the samples care was taken to avoid contamination or losses by using tools and containers which will neither add to nor reduce the chemical composition of the samples (Hristozova *et al*., 2014). After collection the samples were transported to the laboratory where they were digested and analysed for heavy metals. Prescribed precautions were taken in the handling and transportation of the samples (Goudarzi, 2015).

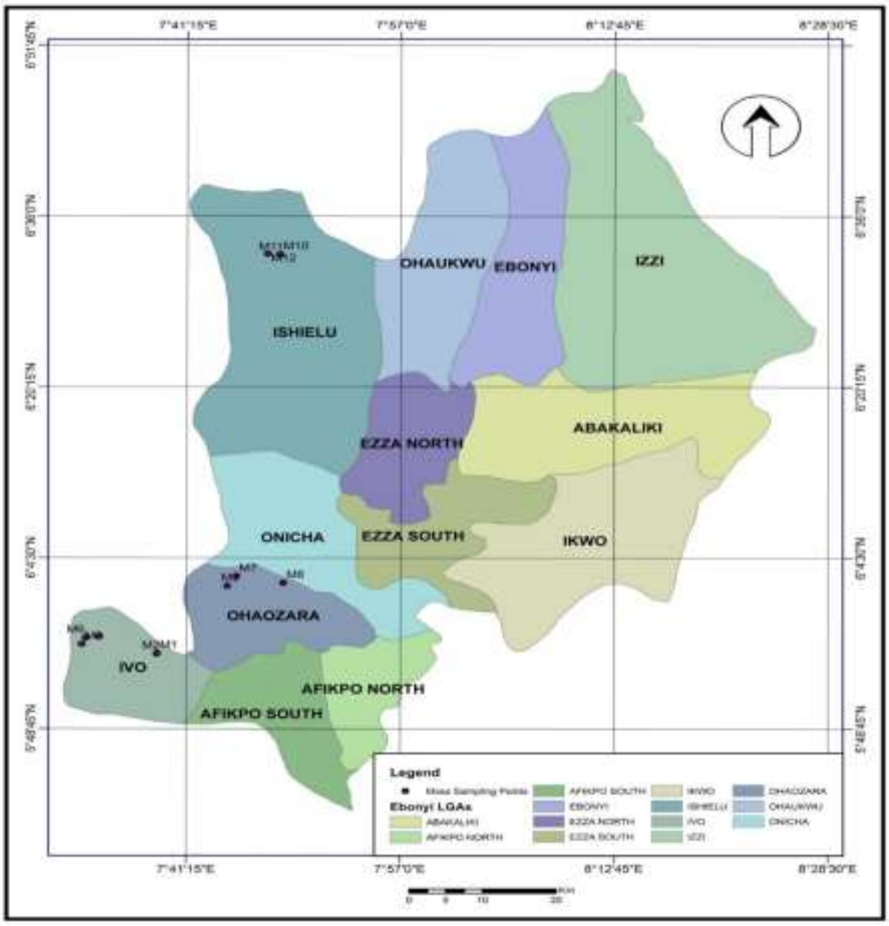


Figure 3: Map of Ebonyi State Showing the Moss Sampling Points
Source: Researcher's Field Data Analysis

Preparation, Digestion and Determination of Heavy Metals

Collected samples of moss were thoroughly segregated and cleaned (from particles of soil, needles, leaves, and bark) (Ziadat *et al.*, 2015; Jiang *et al*., 2018). Cleaned samples were placed on a filter paper and dried in the air and in a dryer at 100°C to a constant mass. Next, samples of moss were pulverized for homogenization in agate mill for 10 minutes (Macedo-Miranda *et al.*, 2016). Obtained powder was weighed on an analytical balance with accuracy of 0.0001g. For establishing the optimum time of grinding periods 10, 15, 20 and 25 min.

were tested. To achieve full homogenization and good analytical results for 0.lg sample 10 min. of grinding is sufficient. 0.1 g of pulverised samples of moss, weighed with the accuracy of 0.0001g were placed in Teflon vessels suitable for mineralization under pressure in a microwave oven. Then to each vessel 4 ml of concentrated HNO_3 and 1 ml of H_2O_2 were introduced (Barandovski *et al,* 2013; Hristosova *et al.,* 2014; Macede-Miranda *et al*., 2016).
The following were performed for the standard program I of the oven:
(1) 2 min., 252 W; (2) 2 min., without heating,
(3) 6 in., 250 W, (4) 5 min., 400 W,
(5) 5 min., 650 W; (6) 10 min., ventilation.

After mineralization the samples were transferred quantitatively to the 25 ml measuring flasks and filled to the mark with distilled water. Obtained solutions were clear light yellow solutions. Digestion was carried out in solution containing 4 ml HNO_3 and 2 ml H_2O_2 (Macedo-Miranda *et al*., 2016).

The concentration of Al, Ca, Cd, Cu, Fe, K, Mg, Na, Pb, Zn, As, Mn and Hg in the solutions were determined by means of a Perkin Elmer 3110 Atomic Absorption Spectrophotometer (Hristova *et al.,* 2014; Macede-Miranda *et al*., 2016). The detection of metals were performed at specific wavelengths for each element, using monoelemental hollow-cathode lamps. The accuracy and reproducibility of the results were tested by means of duplicate samples analysis (Ziadat *et al*., 2015).

The data obtained from the laboratory analysis of the moss samples were descriptively analysed using ranges, means and standard deviation, presented in tables and graphs and described accordingly.

Results and Discussion

Table 1 and 2 shows the descriptive data (mean, range, standard deviation) from the analyses of the moss samples across the different mining areas of Ebonyi State.

Mean Concentration of Heavy Metals across Mining Sites

From the results in Table 1 and 2, the moss samples were able to accumulate heavy metals. These metals are deposited on the surface of mosses as wet and dry atmospheric deposition of particulate matter and dissolved materials (Cortis *et al*., 2016; De Agostini *et al*., 2020). They are retained by adsorption and physico-chemical processes such as ion exchange or passive-active intracellular uptake. It has been suggested that this latter mechanism is the dominant process in the bryophytes (Chakraborty and Paratkar, 2006; Cortis *et al*., 2016). The results in Table 1 and 2 also shows that the moss samples exhibited variation in the mean levels of the heavy metals with locations. The order of the heavy metals in terms of their mean concentration at the Ihietutu Pb/Zn mining area was Al>K>Ca>Fe>Mg>Pb>Zn>Na>Cu>Mn>As>Cd>Hg; while the order for the Amaokwe stone quarry area was Al>Ca>Mg>Fe>K>Cu>Na>Zn>Pb>Mn>Cd>As>Hg. The order of the mean heavy metal concentration at the Uburu/Okposi salt mining area was Na>Mg>Ca>K>Al>Fe>Zn>Cu>Pb>Hg>Mn>Cd>As and this varied from the order at the Nkalagu limestone mining area which was Ca>Mg>Al>Fe>K>Zn>Cu>Pb>Na>Mn>Hg>As>Cd.

These variations in ambient levels of atmospheric pollutants across the different mining areas suggest that it is dependent on the strength and amount of anthropogenic activities carried out at the sources (Aroh *et al*., 2007). Large amounts of particulates matter were generated during mining activities at the Ihietutu Pb/Zn mining area and at the Amaokwe stone quarry site due to the type of activities involved (Aloh *et al.*, 2016). Minimal amount of particulates (dusts) are however, generated at the Uburu/Okposi salt mining area due to the minimal activities that are carried out during salt mining (Makwe, 2019; Makwe, 2020). The dusts generated at the Nkalagu limestone mining area are mainly due to the action of wind on the heaps of mining wastes, which are a common feature in the area, since limestone mining activities has been suspended in the area for over a decade (Eyankware *et al.*, 2018).

Other factors that may influence the variation in concentration of the heavy metals in the moss samples across the mining locations may include efficiency of particulate matter (dust) dispersion, meteorological conditions, morphological and physiological properties of the immediate environment, age of the moss and the metal supply in the environment (WHO, 2001; Chakrabortty *et al*., 2006). This result is in agreement with that obtained by Hristozova *et al.* (2014) in their biomonitoring study of the atmospheric heavy metal deposition in the lead-zinc plant area of Kardzhali.

Table 1: Dry Season Mean Concentration of Heavy Metals in Moss Samples across Mining Areas in Ebonyi State (SD=Standard Deviation)

Metal (mg/kg)	Ihietutu Pb/Zn Mining Area		Amaokwe Stone Quarry Area		Uburu/Okposi Salt Mining Area		Nkalagu Limestone Mining Area	
	Range	**Mean±SD**	**Range**	**Mean±SD**	**Range**	**Mean±SD**	**Range**	**Mean±SD**
Fe	1061.3-1577.1	1319.2 ± 364.7	1644.7-1976.5	1810.6 ± 234.6	512.2-622.5	567.35 ± 77.9	756.3-1132.2	944.25 ± 265.8
Pb	89.5-456.3	272.9 ± 259.4	61.0-64.1	62.55 ± 2.2	28.2-37.3	32.75 ± 6.4	30.6-46.1	38.35 ± 10.9
Zn	82.6-460.7	271.65 ± 267.4	77.5-103.2	90.35 ± 18.2	46.4-58.4	52.4 ± 8.5	58.5-74.2	66.35 ± 11.1
Cu	84.5-146.2	115.35 ± 43.6	92.7-104.2	98.45 ± 8.1	40.2-47.1	43.65 ± 4.9	42.0-48.5	45.25 ± 4.6
Cd	3.5-3.7	3.6 ± 0.1	3.2-4.01	3.605 ± 0.6	1.20-1.30	1.25 ± 0.1	1.04-1.35	1.195 ± 0.2
Mg	847.2-1489.5	1168.35 ± 454.2	1850.4-2281.0	2065.7 ± 304.5	848.3-968.0	908.15 ± 84.6	2205.6-2415.7	2310.65 ± 148.6
Ca	1433.1-1976.6	1704.85 ± 384.3	2004.9-2541.6	2273.25 ± 379.5	682.7-840.0	761.35 ± 111.2	2889.7-3009.5	2949.6 ± 84.7
Na	113.7-158.9	136.3 ± 31.9	93.5-103.2	98.35 ± 6.9	1978.6-2396.3	2187.45 ± 295.4	26.1-42.3	34.2 ± 11.5
Al	1759.4-2317.0	2038.2 ± 394.3	2005.3-2738.1	2371.7 ± 518.2	589.9-720.5	655.2 ± 92.3	870.2-1101.4	985.8 ± 163.5
K	1647.5-2106.2	1876.85 ± 324.3	946.9-1173.0	1059.95 ± 159.9	655.7-863.5	759.6 ± 146.9	312.0-452.1	382.05 ± 99.1
Mn	41.8-80.4	61.1 ± 27.3	13.2-15.8	14.5 ± 1.8	1.8-2.1	1.95 ± 0.2	2.8-4.3	3.55 ± 1.1
Hg	0.08-1.01	0.545 ± 0.7	1.80-2.08	1.94 ± 0.2	2.7-3.8	3.25 ± 0.8	2.3-3.8	3.05 ± 1.1
As	4.5-6.6	5.55 ± 1.5	2.7-3.5	3.1 ± 0.6	0.9-1.2	1.05 ± 0.2	2.3-2.5	2.4 ± 0.1

Table 2: Wet Season Mean Concentration of Heavy Metals in Moss Samples across Mining Areas in Ebonyi State (SD=Standard Deviation)

Metal (mg/kg)	Ihietutu Pb/Zn Mining Area		Amaokwe Stone Quarry Area		Uburu/Okposi Salt Mining Area		Nkalagu Limestone Mining Area	
	Range	**Mean±SD**	**Range**	**Mean±SD**	**Range**	**Mean±SD**	**Range**	**Mean±SD**
Fe	1121.0-1322.3	1221.65 ± 142.3	1211.2-1811.5	1511.35 ± 424.5	436.5-588.3	512.4 ± 107.3	572.5-822.6	697.55 ± 176.8
Pb	66.9-416.0	241.45 ± 246.9	47.3-51.7	49.5 ± 3.1	24.6-31.6	28.1 ± 4.9	29.2-33.3	31.25 ± 2.9
Zn	71.1-409.5	240.3 ± 239.3	74.3-86.1	80.2 ± 8.3	34.4-51.4	42.9 ± 12.0	45.4-56.4	50.9 ± 7.8
Cu	82.4-112.9	97.65 ± 21.6	73.3 -87.92	80.61 ± 10.3	31.6-37.7	34.65 ± 4.3	30.1-37.1	33.6 ± 4.9
Cd	2.3-2.9	2.6 ± 0.4	1.90-2.00	1.95 ± 0.1	0.89-1.00	0.945 ± 0.1	1.00-1.14	1.07 ± 0.1
Mg	810.0-1109.1	959.55 ± 211.5	1433.0-1988.4	1710.7 ± 392.7	639.0-748.7	693.85 ± 77.6	1966.7-2200.5	2083.6 ± 165.3
Ca	1080.3- 1325.5	1202.9 ± 173.4	1700.6-2109.2	1904.9 ± 288.9	487.8-632.0	559.9 ± 101.9	2483.2-2877.5	2680.35 ± 278.8
Na	92.6-121.8	107.2 ± 20.6	69.1-77.8	73.45 ± 6.2	1538.2-2100.0	1819.1 ± 397.3	18.6-22.3	20.45 ± 2.6
Al	1415.3-1879.3	1647.3 ± 328.1	1847.5-2108.7	1978.1 ± 184.7	466.5-580.0	523.25 ± 80.3	720.0-876.9	798.45 ± 110.9
K	1284.3-1719.1	1501.7 ± 307.5	816.3-874.8	845.55 ± 41.4	658.2-758.6	708.4 ± 70.9	280.0-463.8	371.9 ± 129.9
Mn	38.0-68.1	53.05 ± 21.3	6.6-8.9	7.75 ± 1.6	1.4-1.6	1.5 ± 0.1	2.1-2.9	2.5 ± 0.6
Hg	0.05-0.86	0.455 ± 0.6	1.10-1.54	1.32 ± 0.3	2.2-3.1	2.65 ± 0.6	1.8-3.2	2.5 ± 0.9
As	3.9-4.2	4.05 ± 0.2	2.1-2.2	2.15 ± 0.1	0.6-0.7	0.65 ± 0.1	1.8-1.8	1.8 ± 0

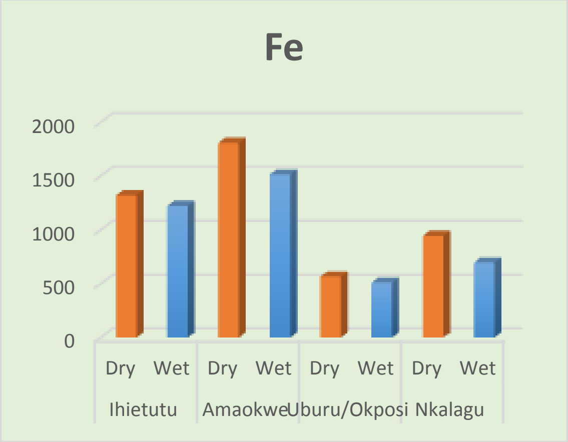
Seasonal Variation in Heavy Metal Concentration across Mining Sites

The mean concentration of all the analysed heavy metals (Al, Ca, Cd, Cu, Fe, K, Mg, Na, Pb, Zn, As, Mn and Hg) in the moss samples, for both dry and wet seasons across the different mining areas are as shown in Tables 1 and 2 and Figures 4-16.

Iron: The concentration of iron are higher in the dry season moss samples than the wet season samples across the different mining areas, with mean concentration of 1319.2 ±364.7mg/kg, 1810.6±234.6mg/kg, 567.35±77.9mg/kg and 944.25±265.8 mg/kg from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively compared to the wet season mean concentration of 1221.65±142.3mg/kg, 1511.35±424.5mg/kg, 512.4±107.3mg/kg and 697.55±176.8mg/kg in the same locations (Figure 4).

Lead: The mean concentration of Lead in the dry season moss samples from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu are 272.9±259.4mg/kg, 62.55±2.2mg/kg, 32.75±6.4mg/kg and 38.35±10.9mg/kg respectively. These values are higher than the mean concentration in the wet season samples which were 241.45±246.9mg/kg, 49.5±3.1mg/kg, 28.1±4.9mg/kg and 31.25±2.9mg/kg for same locations (Figure 5). Lead is usually found in ores with zinc, silver and copper and it is extracted together with these metals (MMSD, 2010). Mining and a lot of other human activities release lead into the atmosphere, from where they deposit to pollute soils and water

Zinc: The dry season moss samples have mean concentration of zinc as 271.65±267.4mg/kg, 90.35±18.2mg/kg, 52.4±8.5mg/kg and 66.35±11.1mg/kg at Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively. These values are higher than the mean concentration of the metal in the wet season samples which were 240.3±239.3mg/kg, 80.2±8.3mg/kg, 42.9±12.0mg/kg and 50.9±7.8mg/kg for same locations (Figure 6).



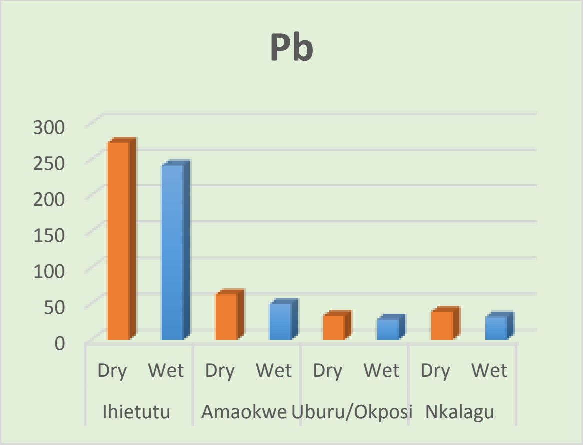
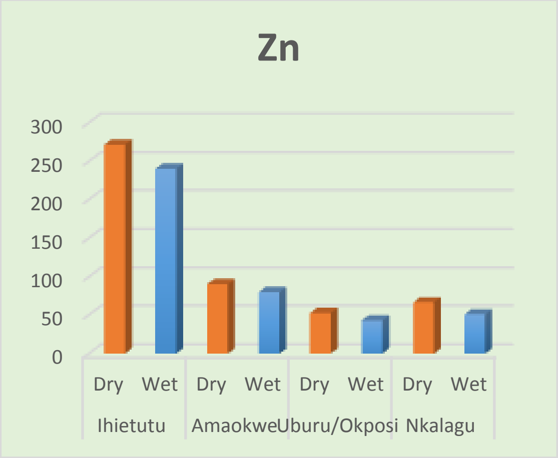


Fig. 4: Seasonal Variation in Concentration of Fe

Fig. 5: Seasonal Variation in Concentration of Pb



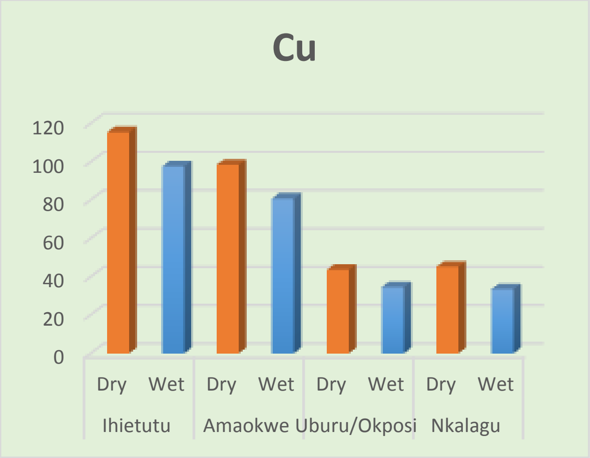
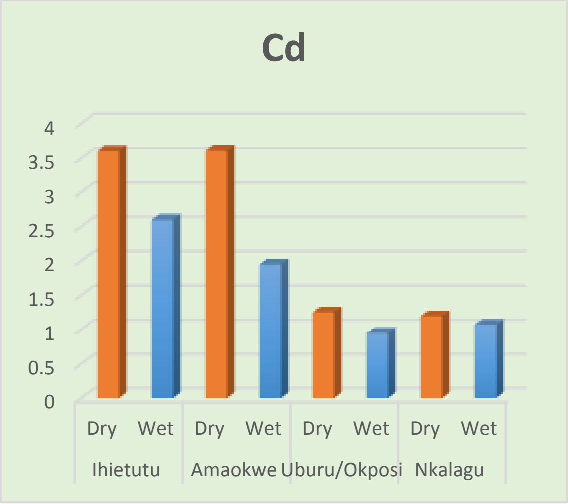


Fig. 6: Seasonal Variation in Concentration of Zn

Fig. 7: Seasonal Variation in Concentration of Cu



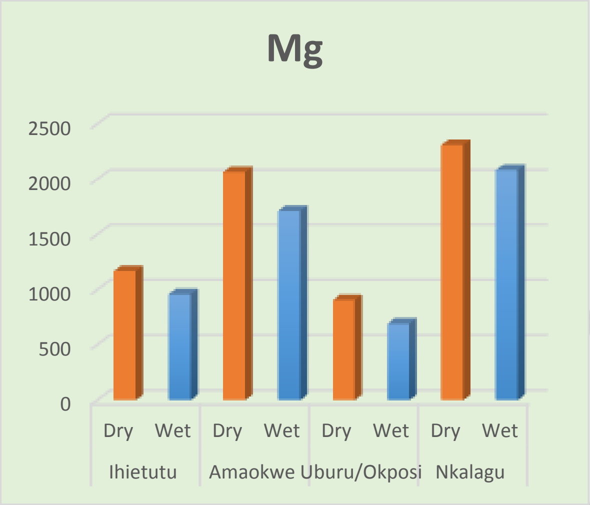


Fig. 8: Seasonal Variation in Concentration of Cd **Fig. 9: Seasonal Variation in Concentration of Mg**

Copper: Like iron, lead and zinc, copper also has higher mean concentration in the dry season moss samples from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu (115.35±43.6mg/kg, 98.45±8.1mg/kg, 43.65±4.9mg/kg and 45.25±4.6mg/kg). The wet season samples had lower mean concentration in same locations (97.65±21.6mg/kg, 80.61±10.3mg/kg, 34.65±4.3mg/kg and 33.6±4.9mg/kg) (Figure 7). Mining activities release copper into the environment (Fashola *et al.*, 2016) as mine dust and these are deposited into water and on soils.

Cadmium: The mean concentration of Cadmium were 3.6±0.1mg/kg, 3.605±0.6mg/kg, 1.25±0.1mg/kg and 1.195±0.2mg/kg in the dry season moss samples collected from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively (Figure 8). These values are higher than the wet season samples which had mean concentration of 2.6±0.4mg/kg, 1.95±0.1mg/kg, 0.945±0.1mg/kg and 1.07±0.1mg/kg. Cadmium always occurs in combination with zinc. It is also a by-product of zinc, lead and copper extraction.

Magnesium: The mean concentration of magnesium are higher in the dry season moss samples than those of the wet season samples across the different mining areas, with mean concentration of 1168.35±454.2mg/kg, 2065.7±304.5mg/kg, 908.15±84.6mg/kg and 2310.65±148.6mg/kg from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively compared to the wet season mean concentration of 959.55±211.5mg/kg, 1710.7±392.7mg/kg, 693.85±77.6mg/kg and 2083.6±165.3mg/kg (Figure 9).

Calcium: The dry season moss samples have mean concentration of calcium as 1704.85±384.3mg/kg, 2273.25±379.5mg/kg, 761.35±111.2 mg/kg and 2949.6±84.7mg/kg at Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively. These values are higher than the mean concentration in the wet season samples which were 1202.9±173.4mg/kg, 1904.9±288.9mg/kg, 559.9±101.9mg/kg and 2680.35±278.8mg/kg respectively (Figure 10).

Sodium: Like other metals that were analysed, sodium also has higher mean concentration in the dry season moss samples from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu (136.3±31.9mg/kg, 98.35±6.9mg/kg, 2187.45±295.4mg/kg and 34.2±11.5mg/kg) (Figure 11). The wet season samples had lower mean concentration (107.2±20.6mg/kg, 73.45±6.2mg/kg, 1819.1±397.3mg/kg and 20.45±2.6mg/kg).

Aluminium: Aluminium also has higher mean concentration in the dry season moss samples. These were 2038.2±394.3mg/kg, 2371.7±518.2mg/kg, 655.2±92.3mg/kg and 985.8±163.5mg/kg from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively. While the wet season mean concentration of the metal from the same location were 1647.3±328.1mg/kg, 1978.1±184.7mg/kg, 523.25±80.3mg/kg and 798.45±110.9mg/kg. These are lower than the dry season mean concentration of the metal (Figure 12).

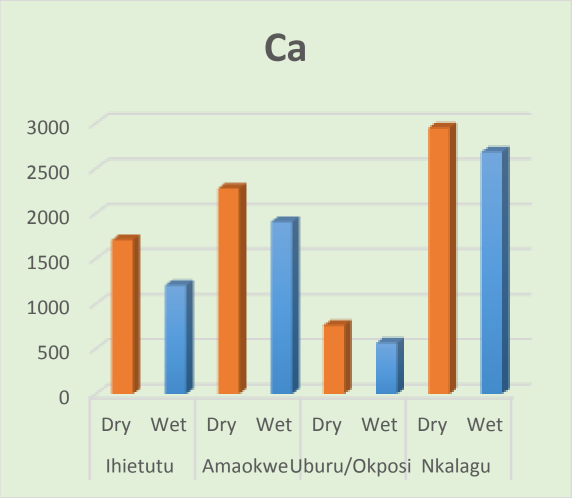


Fig. 10: Seasonal Variation in Concentration of Ca

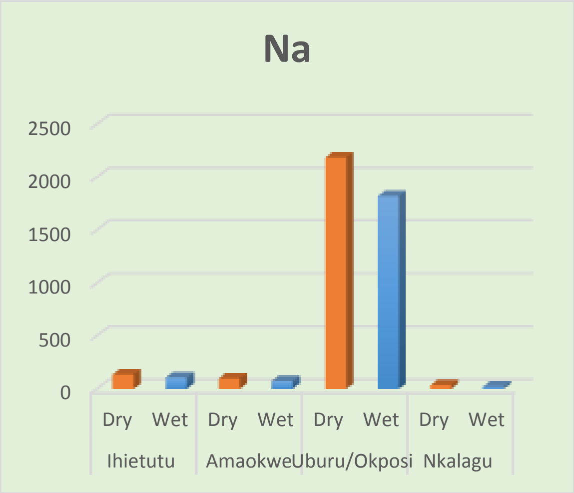
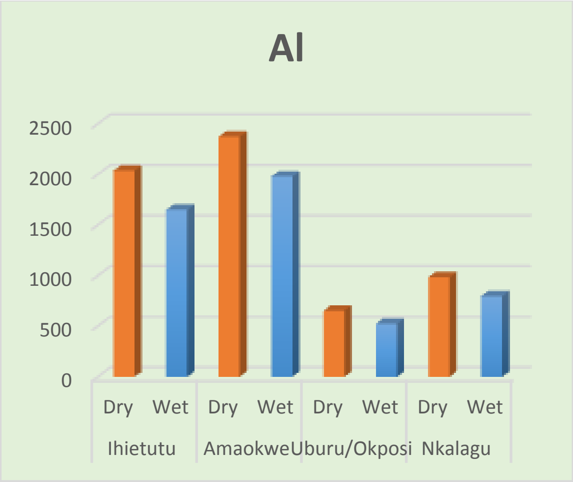


Fig. 11: Seasonal Variation in Concentration of Na



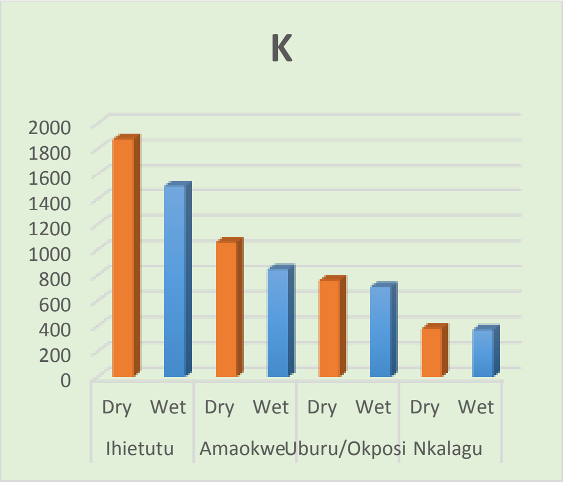
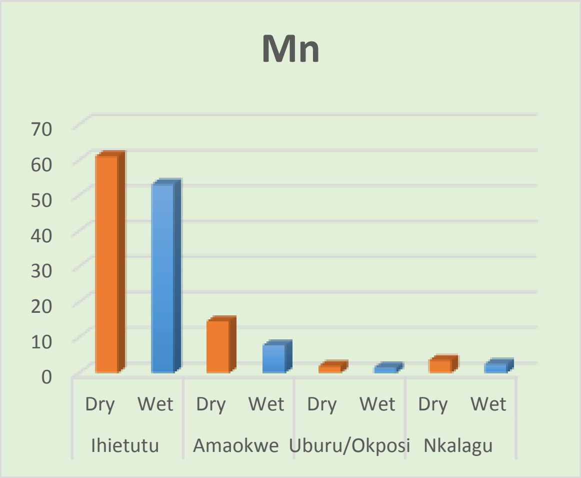


Fig. 12: Seasonal Variation in Concentration of Al

Fig. 13: Seasonal Variation in Concentration of K



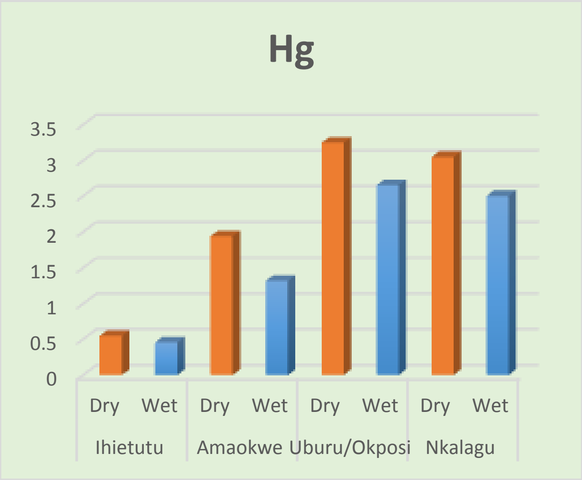


Fig. 14: Seasonal Variation in Concentration of Mn

Fig. 15: Seasonal Variation in Concentration of Hg

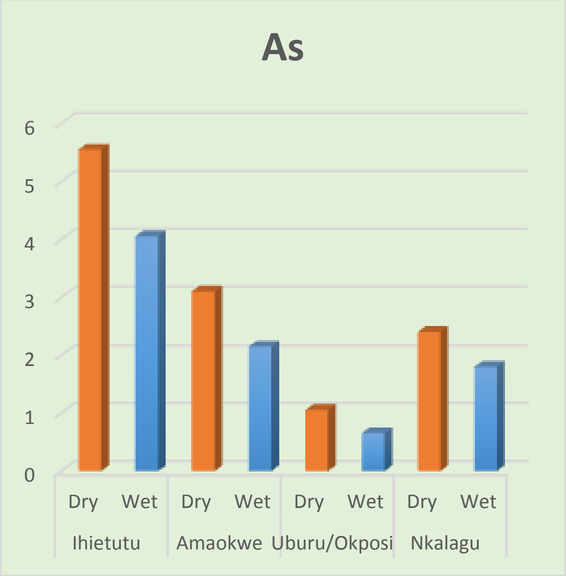


Fig. 16: Seasonal Variation in Concentration of As

Potassium: Potassium has higher mean concentration in the dry season moss samples than those of the wet season samples across the different mining areas, with mean concentration of 1876.85±324.3mg/kg, 1059.95±159.9 mg/kg, 759.6±146.9mg/kg and 382.05±99.1mg/kg from Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively compared to the lower wet season mean concentration of 1501.7±307.5mg/kg, 845.55±41.4mg/kg, 708.4±70.9mg/kg and 371.9±129.9mg/kg (Figure 13).

Manganese: Manganese does not occur naturally in its pure state but are most found as oxides, carbonates and silicates (Islam *et al.*, 2015). The dry season moss samples have mean concentration of manganese as 61.1±27.3mg/kg, 14.5±1.8mg/kg, 1.95±0.2mg/kg and 3.55±1.1mg/kg at Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively. These values are higher than the mean concentration of the metal in the wet season samples which were 53.05±21.3mg/kg, 7.75±1.6mg/kg, 1.5±0.1mg/kg and 2.5±0.6mg/kg for same locations (Figure 14). Manganese is one of the toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when the concentrations are higher than the recommended daily allowance.

Mercury: From the different mining areas at Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu, the mean concentration of Mercury in the dry season samples (0.545±0.7mg/kg, 1.94±0.2mg/kg, 3.25±0.8mg/kg and 3.05±1.1mg/kg respectively) are higher than the mean concentration of the wet season samples (0.455±0.6mg/kg, 1.32±0.3mg/kg, 2.65±0.6 mg/kg and 2.5±0.9mg/kg) (Figure 15). Mercury is released into air through mining activities and they are mostly deposited on soils and into water bodies.

Arsenic: Though arsenic occur in trace amounts in the environment, its mean concentration in the dry season moss samples are higher (5.55±1.5mg/kg, 3.1±0.6mg/kg, 1.05±0.2mg/kg and 2.4±0.1mg/kg) than those of the wet season samples (4.05±0.2mg/kg, 2.15±0.1mg/kg, 0.65±0.1mg/kg and 1.8±0mg/kg) from the different mining areas in Ihietutu, Amaokwe, Uburu/Okposi and Nkalagu respectively (Figure 16). Arsenic is mainly emitted during lead and zinc mining and production. It may enter air through wind-blown dust as particulates (Islam *et al.,* 2015).

The higher concentrations of heavy metals in the Dry season moss samples are most likely due to the exposure of the mosses to high levels of dusts with suspended particulate matter, replete with heavy metals (Fernández and Carballeira 2001; Onianwa 2001; Markert and Weckert 2008), which are a major characteristic feature of most of the mining areas during the dry season. The heaps of overburden and other waste materials at the mining locations become loose during the dry season. They are easily carried by wind and deposited on the surfaces of materials around the mining area. This therefore explains the higher concentration of the heavy metals in the dry season moss samples. In addition, the force of impacting rain may wash off the deposited particulates from the moss surfaces, hence reducing the metals available for absorption and adsorption.

Shahid *et al* (2016) argued that climatic conditions greatly alter the potential of metal uptake in mosses through their direct effect on the physico-chemical properties of the plant and the leaf surface. According to them, climatic conditions also influence the biological and metabolic processes inside the plant and in turn affects foliar transfer and compartmentation of metals. Relative humidity and rainfall are important climatic factors affecting foliar uptake of heavy metals. They influence the permeability potential of the moss surface due to hydration of cuticle, opening of stomata and penetration and accumulation of the hydrated metal (Lawson and Mason, 2001; Rai *et al*., 2014). In this study however, the results of the seasonal variation in the heavy metal concentration of the moss samples are in contrast with the arguments above. They are also in contrast with the results obtained by Macedo-Miranda *et al*, (2016) in their biomonitoring study of the accumulation of heavy metals in mosses in the metropolitan area of the Toluca Valley, Mexico. This is because in the current study, the bioavailability of metals for the moss uptake around the mining areas are mostly in the form of dry atmospheric deposition (dust), which are higher during the dry season due to dryness and the effects of wind. This in turn makes available more pollutants (including heavy metals) for absorption and adsorption by the bryophytes.

Excessive amounts of heavy metals in the atmosphere could have adverse environmental and human health implications particularly around the mining areas and on the members of the mining communities. Apart from their deposition on plants, the atmospheric heavy metals can deposit on soils and water. On soil, the heavy metals can accumulate and increase the metal loads of the soil thereby leading to changes in the productivity, diversity, population size and overall activity of the soil microbial communities (Ashraf and Ali 2007). At higher concentration, some of the metals such as As, Cd, Hg or Pb, may inhibit some vital plant processes like photosynthesis, mitosis and water absorption (Bhattacharyya *et al*., 2008; Najeeb *et al*., 2014).

On water bodies, the heavy metals reduces the water quality (Adesiyan *et al*., 2018) and this may affect aquatic plants, animals and human health. Human exposure to these heavy metals are through inhalation, dermal contact, drinking of polluted water and ingestion of heavy metal-contaminated plants. Short and long term human exposure to these metals can have several adverse health implications. The heavy metals can deplete some essential nutrients in the body and this may further decrease the immunological defences, leading to health complications such as headaches, stomach aches, dizziness, vomiting, diarrhoea, reproductive failure, gastrointestinal cancer, disruption of the biosynthesis of haemoglobin and anaemia, rise in blood pressure, kidney damage miscarriages and subtle abortions, disruption of nervous systems, brain damage, diminished learning abilities of children among others (Irfan *et al.,* 2013; Chakraborty *et al*., 2013; Jaishankar *et al.,* 2014; Engwa *et al.,* 2019)

Dust control is therefore very important in every aspect of the mines planning and operation. The activities in mines which require planned dust control system include construction, topsoil stripping, blasting, road transport, transfer systems, crushing and waste rock dumps. Surface wetting could provide a short term solution to dust emissions in mines, but a more permanent measure can take the form of a vegetative cover.

Conclusion and Recommendations

The detection of heavy metal concentrations in moss samples is a valuable method for monitoring the quality of the atmospheric environment. The concentration of thirteen metals: Al, Ca, Cd, Cu, Fe, K, Mg, Na, Pb, Zn, As, Mn and Hg were determined and they showed variation from location to location and from season to season. The spatial patterns of heavy metal concentrations in the mosses are metal specific, reflecting local variation in heavy metal deposition due to differences in the kind of mining activities in the area. Seasonal variation reveals higher concentration of the metals in the dry season moss samples, probably because the mosses were exposed to high amounts of metal-enriched dusts. The higher concentration levels of the heavy metals in the dry season moss samples from the current study differed from many biomonitoring studies in different parts of the world. In other to reduce the metal deposition around the mining areas, there is need for proper air quality management through the reduction of emissions and use of safer processes. Dust control should also be built into every aspect of the mines planning and operation system. This will not only reduce air pollution, but will also reduce the resultant environmental degradation and the potential effects on human health.

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