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Geobotanical and Biogeochemical Prospecting Method of Complex Sulphide Ore of Pb-Zn-Cu-Ba in Abuni-Adudu areas of the Middle Benue Trough, Nigeria

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Abstract

This research work focused on two plant species namely, the *Anogeissus leiocarpus (DC.)* and *Dichrostachys cinerea* for mineral prospecting. The two plants were sampled based on their occurrence, abundance and outlook. Twelve samples (six each of *Anogeissus leiocarpus (DC.)* and *Dichrostachys cinerea)* were collected around Abuni-Adudu mining communities in the Middle Benue Trough, Nigeria. In addition, bulk ore and twelve soil samples were also collected and analysed for correlation. Geologically, the study area is made up compacted shale, baked shale (hornfels), and sandstones of sedimentary origin, which are intruded by tertiary basalts of igneous origin. Samples were analysed for elemental composition, using inductively coupled plasma mass spectrometry method. Analysis revealed that the geobotanical method of prospecting for Pb-Zn-Cu-Ba mineralization in the area is promising as biogeochemical data indicated that the *Dichrostachys cinerea* are good indicator of Pb-Zn-Cu mineralization while the *Anogeissus leiocarpus* were indicative of Barium. Given the relatively low concentration of Barium in the ore (3.8 ppm) as against concentration in the soil samples, which ranges from 83 ppm (sample YS6) to 552 ppm (sample YS12), Barium has its source from the shale and sandstone or nearby Barite mineralization and not the ore.

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1. Introduction

Excess or deficiency in mineral content in addition to salt and water can be indicated by plants [1]. This deficiency or enrichment can in turn be used for prospecting or exploration. Where plants are so used, the method is termed geobotanical prospecting or exploration [2-6]. Thus, geobotanical methods of prospecting considers the distribution of vegetation (visual observation) based on the principle of limits of tolerance; the method assumes that only specialized species of plants, can withstand metal-contaminated soils [1, 5, 7-10]. Consequently, plants have been used with great success in exploring for ores globally. Commonest amidst many are *Haumaniasstrom Katangense* and *Becium homblei* for Copper exploration [11].

Biogeochemistry involves the chemical analysis of vegetation, to identify plants of anomalous elemental concentration [11, 12]. Application thus takes into account the fact that certain plant species accumulate specific types of metals in large amounts and apparently require same for healthy growth. Thus, identifying the plants aids in locating and mapping the presence of such metals [1, 12]. Therefore, both methods involve the traditional use of indicator plant species or assemblages to detect the possible presence of metal-rich deposits or anomalies [11-12]. Present research involves strategic study of the plant community, and the chemical analysis of the dominant plant species, soils and ore, sampled around mineralized areas of Abuni/Adudu mine site in the Middle Benue Trough, Central Nigeria. Investigation is aimed at delineating or identifying suitable plant species that can be used for complex sulphide ore (Pb-Zn-Cu-Ba) prospecting and possible exploration. This will entail relating certain assemblages to the presence of specific metals or elemental anomalous concentration. Thus, present work tends to explore the application of plants as sample media for complex sulphide (Pb-Zn-Cu-Ba) prospecting and exploration.

The Benue Trough of Nigeria is one of the major intra cratonic or rift basins in the world and it is divided geographically into the Upper, Middle and Lower Benue Troughs [13-15]. The study area is located within the Middle Benue Trough. The stratigraphic succession of the Middle Benue Trough from the oldest to the youngest formations include; the Asu River Group, Awe Formation, Keana Formation, Ezeaku Formation, Awgu Formation and the Lafia Formation [17, 18]. The intracontinental Benue Trough initiated during the Lower Cretaceous is characterized by two major compressional phases: in the Lower and Middle Benue (during the Santonian); and in the Upper Benue Trough (end of the Cretaceous). The existence of structural controlled mineralization along NW-SE, N-S and NE-SW fracture systems associated with these compressional episodes are well documented [19-22]. The Benue Trough of Nigeria is known for its important mineral resources such as barite, gypsum, calcite, limestone, coal, amongst others [16, 20, 22] and exploitation of these mineral resources which is ongoing have contributed immensely to the national wealth with associated socio-economic benefits in Nigeria.

2. Materials and Methods

Samples were collected around Abuni and Adudu mining communities in the Middle Benue Trough Central Nigeria.

Three different media (Ore, soils and plants) were sampled for geochemical analysis. The representative ore samples (as-mined) were collected from six active pits around Abuni-Adudu mining communities. The samples were homogenized into a single bulk sample, for representative bulk analysis

Twelve soil samples were collected from the Adudu-Abuni area, at an average depth of 30cm using plastic picks and trowels, with each sample packed in paper bags. At each location, about 100g of soil was collected and labeled, with coordinate of each sample noted (Figure 1).

The area was surveyed for the dominant plant species or type (in terms of occurrence and outlook). Two plants species *Anogeissus leiocarpus (DC.)* locally called "Marke" and *Dichrostachys cinerea,* also known as sickle bush and locally called "kaya", were observed to occur dominantly around the area with healthy outlook, hence the plants were selected and sampled for biogeochemical studies. According to Carlisle and Cleveland [23] and Brooks [11], the concentration of trace elements in plant organ can be arranged in decreasing order as leaves, twigs, cones, wood, roots and barks. Hence, in order to get better background concentration, the bark of each tree was sampled and analysed for their elemental composition and concentration. A total of twelve samples, six each of *Anogeissus leiocarpus (DC.)* and *Dichrostachys cinerea* were analysed. Plant bark were collected by peeling the plants using a bush knife. The collected samples were kept in paper bags, sealed and labelled

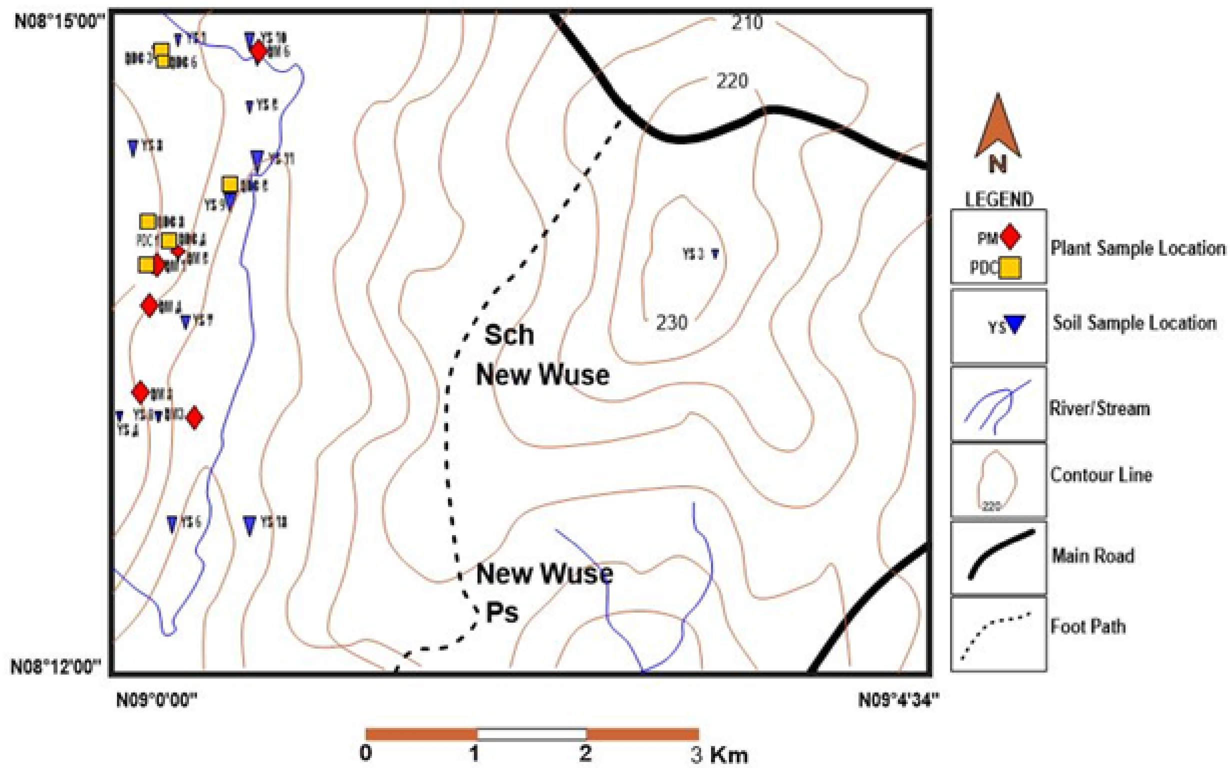

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Figure 1. Sample collection points

Geochemical analyses of the various samples (ores, soils and plants), were carried out at Activation Laboratory (ACTLAB) in Ontario Canada. Methods of analysis applied were sample dependent. Both soils and ore samples were analysed using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using the aqua regia "partial" digestion method which uses a combination of concentrated hydrochloric and nitric acids to leach sulphide, some oxides and silicates. The Plant samples were analysed using Ash Inductively Coupled Plasma Mass Spectrometry (Ash-ICP-MS). The samples were ashed at temperature of 480^0C and metals determined on the ash. This method is particularly advantageous for base metal exploration, but disadvantaged as when samples are ashed, there may be volatile loss of certain elements. This method uses first a proprietary acid digestion on the ash followed by ICP-MS, hence extending the list of available elements (www.actlabs.com).

3. Results and Discussion

3.1. Geology

The study area is underlain by four (4) different rock types, three of sedimentary origin (compacted shale, baked shale (hornfels) and sandstones) and one of igneous origin (basalt). The sandstone, also known as the Lafia Sandstone is the youngest formation in the Middle Benue Trough. In the study area, the sandstones are found in the Northwestern part (Figure 2). The sandstones are reddish in color and range between medium – fine grain sizes, with evidence of jointing system on the surface of the exposures.

The baked shales (hornfels) are practically very fine-grained and fissile in nature. They are so weak that on mere trampling, they split along preferred weak planes. The baked shales host the mineralized Lead-Zinc veins in the area.

Highly compacted shales are greyish in color, occurring around the northeastern part of the study area. Basalts intruded the shale forming a hill of about 225m high, outcropping in the Northeastern part of the study area (Figure 2). These basalts are responsible for the baking of the shales [24].

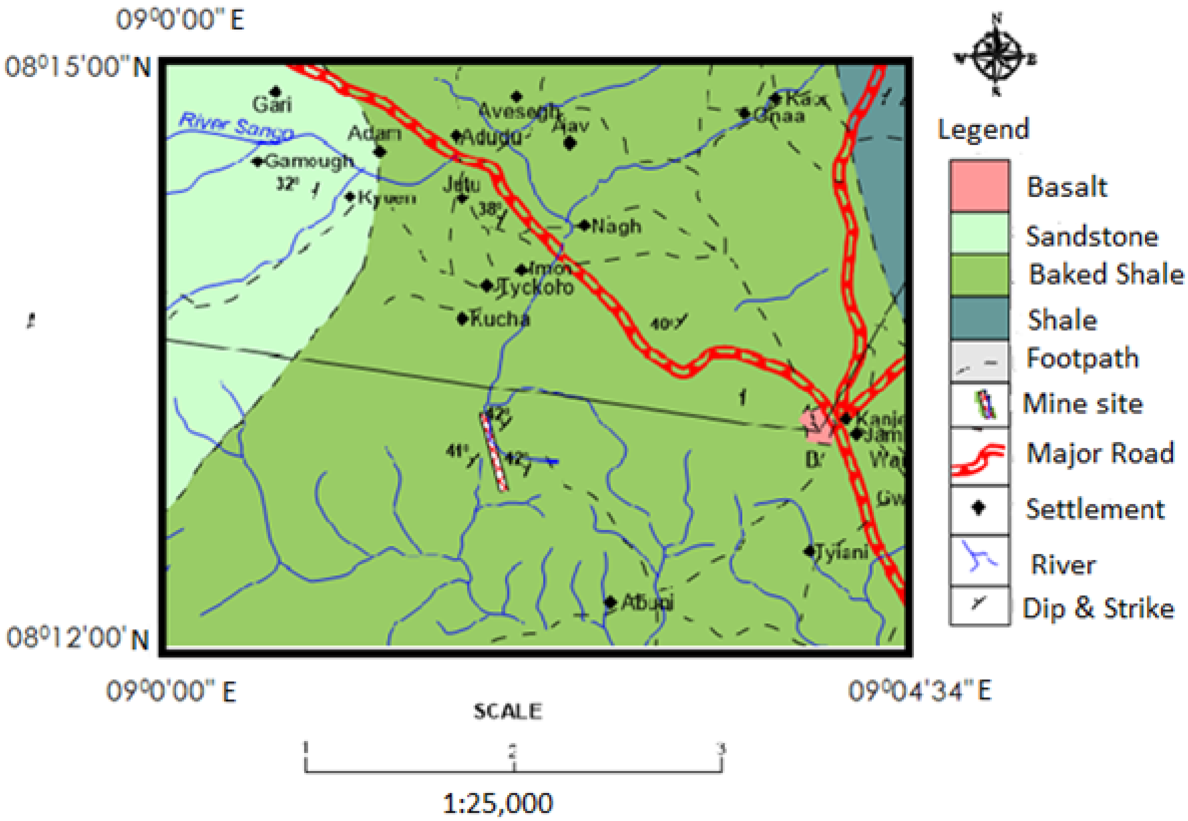

Figure 2. Geological map of the study area

Profiles along road cuts and streams reveal the compacted shale as the oldest formation in the study area. this is directly overlain by the Lafia sandstone. Basalt intrudes the Lafia sandstones and the shales, causing the formation of the baked shales.

3.2. *Geochemistry*

The elements analysed for in ore, soils and selected plant barks at Activation Laboratories (ACTLAB) Canada, comprised of major, trace and rare -earth-elements.

A selection of trace and rare earth elements associated with typical Pb-Zn-Cu ore deposits are interpreted in this work. Elements selected are

1. Trace elements: Pb, Zn, Cu, Co, Ba, Cd, Cs, Mo, Ni, As, Ag, Hg
2. Rare Earth Element: La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu

The trace elements selected are associated elements in a typical Pb-Zn-Cu deposit, be it Skarn type, Volcanic associated massive sulfide, Mississippi Valley type, Sandstone type or the Kupfercheifer (Copper Shale) type deposit [25 - 26]. Also, a majority of them are chalcophile elements, selected on the basis of the fact that Pb-Zn-Cu deposit is chalcophiliic (Sulphide) [27].

3.2.1. *Ore (as-mined)*

From Table 1 and Figure 3, it can be observed that the element with highest concentration is copper with concentration of 7830 ppm. This is followed by Pb and Zn which have concentration of 5000 ppm each. From the twelve

Table 1. Trace elements concentration in the homogenized ore (values in ppm)

Sample ID	Co	Cu	Zn	Mo	Cd	Cs	Pb	Ba	Ag	As	Ni	Hg
As-Mined	552	7830	5000	0.3	508	0.07	5000	3.8	100	52.7	10.1	10

Table 2. Rare earth element concentration in the homogenized ore (values in ppm)

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
As-Mined	1.2	2.83	0.4	1.84	0.6	0.2	0.6	0.1	0.6	0.1	0.3	0.1	0.3	0.1

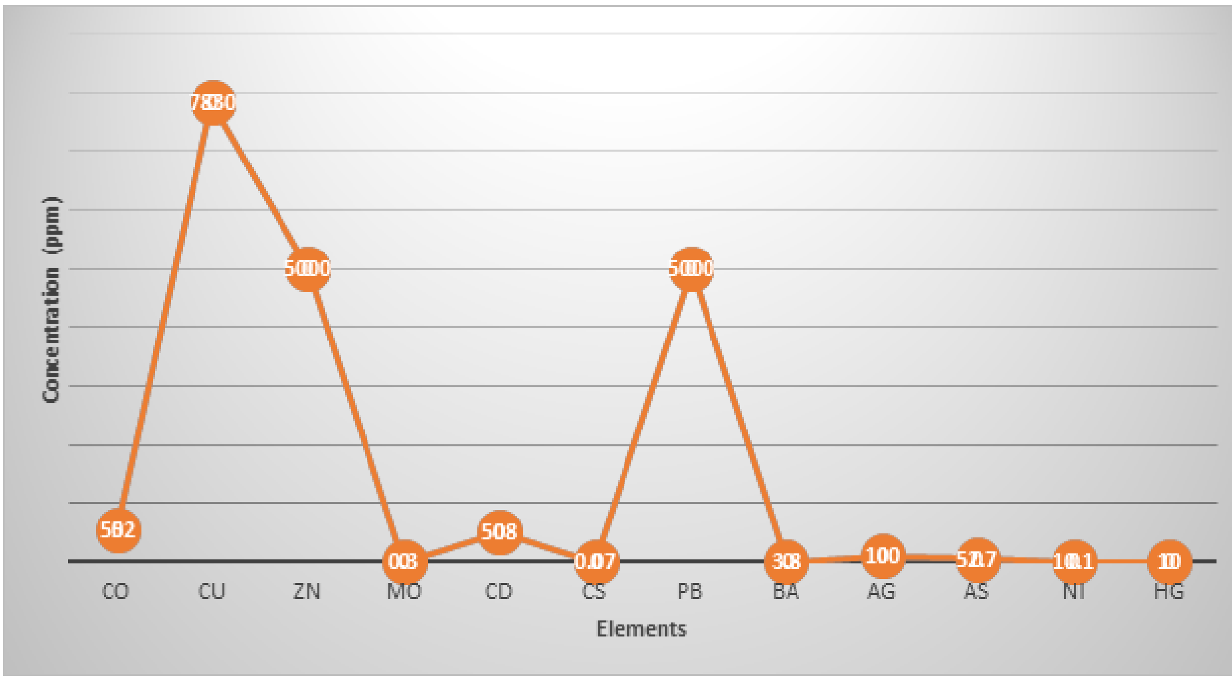

Figure 3. Trace elements concentration in as-mined

trace elements presented (Table 1), Cs has the least concentration of 0.07 ppm which is followed by Mo (0.3 ppm), with traces of Ag, as it shows Ag concentration of 100 ppm. Thus, from the analysis it can be concluded that the ore (as-mined) is dominantly a Pb-Zn-Cu deposit, confirming the material being mined in the area. The Pb-Zn-Cu deposit is a sulphide deposits [27]. The trend of the trace element enrichment in the ore can be summed or represented as Cu>Pb/Zn>Co>Ag>Cd>As>Ni>Hg>Ba>Mo>Cs (Table 1 and Figure 3).

According to Rollinson [28], rare earth elements can be grouped into three (Light, Middle and Heavy) on the basis of their atomic numbers. Thus, the Light Rare Earth Elements (LREE) include La, Ce, Pr and Nd. The Middle Rare Earth Elements (MREE) are Sm, Eu, Gd, Tb, Dy, and Ho. While the Heavy Rare Earths Elements (HREE) are Er, Tm, Yb and Lu.

The plot for rare earth elements in the ore (Figure 4) indicates that Ce (Cerium) has the highest concentration of 2.83 ppm. The ore is deficient in Tb, Ho, Tm and Lu which have concentration of 0.1 ppm. The trend of the rare earth element enrichment can be shown as Ce>Nd>La>Sm>Dy>Gd>Pr>Er>Yb>Eu>Tb>Ho>Tm>Lu (Table 2, and Figure 4).

Hence, from the summary of enrichment above it can be observed that the LREE (La, Ce, Pr and Nd) are more enriched in the ore. Only Sm, Dy, and Gd show concentration of 0.6 ppm, in the MREE group. There is a general depletion of HREE. Though, the relatively low concentration of the MREE in rocks could be chiefly influenced by hornblende, the negative Europium (Eu) anomaly is chiefly controlled by feldspars or effects of hydrothermal fluid [28]. Also, to a lesser extent negative Eu anomaly may be influenced, by depletion in sphene, clinopyroxenes,

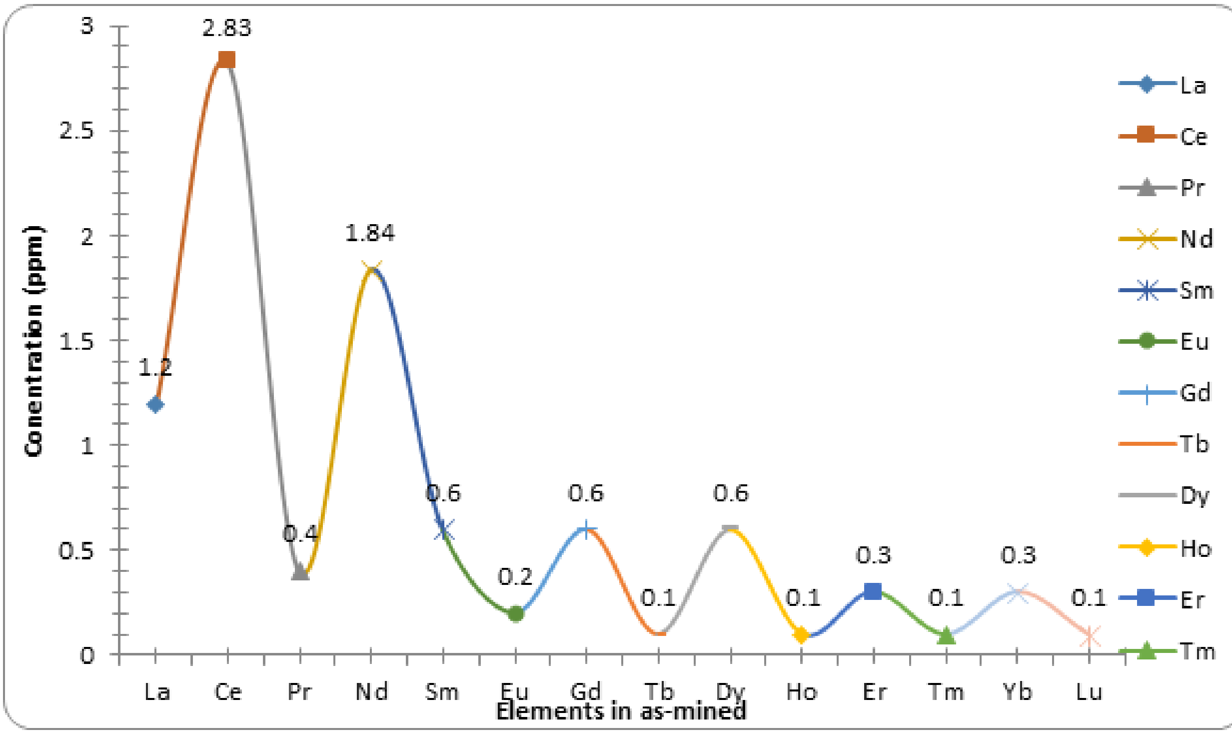

Figure 4. Rare earth elements in as mined

orthopyroxenes and garnet.

The presence of olivine, orthopyroxenes and clinopyroxenes leads to depletion of LREE relative to HREE [28]. The reverse is the case in the ore of Abuni-Adudu, where the HREE are depleted relative to the LREE. This could therefore, mean that the hydrothermal fluid that deposited the ore was deficient in high temperature minerals (olivine, orthopyroxene and clinopyroxenes).

3.2.2. Soils

Though Cu concentration was higher in as-mined relative to Pb and Zn, the soils show that Zn has higher concentration relative to Cu and Pb. This could mean Zn is less mobile relative to Pb and Cu, since Cu and Pb dissolve more rapidly.

Table 3 presents trace elements data of soils in the study area. Also, presented is local average abundance in the area. Both Hg and As, are below their instrumental detection limit of 1 ppm and 0.1 ppm respectively (Table 3). Ag, is low in concentration with values ranging from 0.002 to 0.043 ppm. Similarly, only three samples (YS2, YS6 and YS8) show Au concentration above detection limit. Sample YS 11 has the highest Co concentration (93.2 ppm) in the samples analyzed. Cu has a mean concentration of 26.93 ppm. Sample YS 12 has the highest Cu concentration in the sample analyzed relative to the mean value. Analyses indicate that samples YS7, YS8, YS10, YS 11, &YS 12 have copper concentrations above their mean. Five samples, YS3, YS5, YS6, YS 11, and YS 12 have higher Mo concentration above their local mean of 0.98 ppm. The remaining sample shows Mo concentration below average.

Only five samples (YS1, YS2, YS3, YS4, and YS7) have Pb concentration above the local mean of 18.42 ppm in soils, while the remaining samples show concentrations below average. Out of the twelve samples analyzed for Zn, only six samples (YS4, YS7, YS8, YS10, YS11 and YS12) show Zn concentration above the local mean of 69.49 ppm. Hence, both YS4 and YS7 show Pb and Zn above their average.

Three samples (YS8, YS10, & YS11) have higher Cd concentration above the local mean of 0.02 ppm. Among the twelve samples analyzed, only 6 samples have Cs concentration below average of 1.74 ppm.

Only four samples analyzed (YS8, YS10, YS11, and YS12) have higher concentration of Ba above their local

Table 3. Trace element concentration in soils of the study (values in ppm)

Sample ID	Co	Cu	Mo	Pb	Zn	Cd	Cs	Ba	Ag	As	Ni	Hg	Au
YS1	17.3	22.4	0.52	21.7	56.2	0.01	1.88	171	0.035	0	112	0	0
YS2	19.4	10.1	0.69	22.3	17.4	0.01	0.98	119	0.021	0	11.7	0	1.8
YS3	15.2	23.1	1.23	30.4	58.8	0.01	2.22	133	0.033	0	33.4	0	0
YS4	11.8	24.9	0.43	23.6	98.4	0.01	1.83	170	0.043	0	36.5	0	0
YS5	29.8	26.6	1.36	14	34.2	0.01	1.34	150	0	0	89	0	0
YS6	31.7	18.3	1.44	14.8	23.5	0.01	1.94	83	0.023	0	53.1	0	0.7
YS7	36.9	30.8	0.85	31	84	0.01	1.1	181	0.02	0	29.4	0	0
YS8	21.2	30	0.65	18	120	0.04	2.98	356	0.066	0	72.2	0	1.6
YS9	44.6	21.7	0.95	12	35.5	0.02	1.49	147	0.014	0	111	0	0
YS10	83.6	35.4	0.94	9.7	86.7	0.03	1.2	296	0	0	273	0	0
YS11	93.2	39.7	1.7	12.7	127	0.03	2.77	744	0.021	0	569	0	0
YS12	84.8	40.1	1	10.8	92.2	0.01	1.16	552	0	0	268	0	0
Total	**489.50**	**323.10**	**11.76**	**221.00**	**833.90**	**0.20**	**20.89**	**3102.00**	**0.28**	**0.00**	**1658.30**	**0.00**	**4.10**
Average	**40.79**	**26.93**	**0.98**	**18.42**	**69.49**	**0.02**	**1.74**	**258.50**	**0.02**	**0.00**	**138.19**	**0.00**	**0.34**

where YS represent the Soil Sample ID

Table 4. Rare earth element concentration in soils of the study (values in ppm)

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
YS1	65.1	80.8	14	61.1	10.7	2.3	8.3	1	5.1	0.9	2.1	0.3	1.7	0.2
YS2	28.8	89.3	5.6	23.5	3.6	0.5	2.7	0.3	1.5	0.2	0.6	0.1	0.5	0.1
YS3	76.1	141	16.6	70.8	10.3	1.7	7.8	0.8	4.3	0.7	1.5	0.2	1.1	0.1
YS4	82.1	159	18	74.6	10.8	1.8	8.5	0.9	4.2	0.6	1.4	0.2	1	0.1
YS5	56.8	107	9.4	36.6	5.2	1.2	4.1	0.4	2.4	0.4	0.9	0.1	0.6	0.1
YS6	31.4	113	6.4	27.3	4.2	0.9	3.8	0.4	2.3	0.4	0.9	0.1	0.8	0.1
YS7	45.3	153	12.2	55.4	10.6	1.6	7.2	0.8	3.7	0.6	1.3	0.2	1	0.1
YS8	98.2	169	22.5	96.8	16.9	2.8	13.1	1.5	8.1	1.3	3	0.4	2.2	0.2
YS9	30.9	86.8	7	31.2	4.9	1.4	4.9	0.6	3.4	0.6	1.5	0.2	1.4	0.1
YS10	61.5	155	11.3	49.9	7.7	2.1	7.1	0.8	4.6	0.8	2	0.3	1.7	0.2
YS11	121	237	23.8	103	17.6	4.5	14	1.6	9.1	1.6	3.7	0.5	3.1	0.3
YS12	75.6	148	16.3	71.2	13.6	3.2	10.4	1.2	6.5	1	2.5	0.3	2	0.2

where YS represent the Soil Sample ID

average of 258.5 ppm.

From the general analysis, it can be observed that Ba has the highest concentration per sample of soils. The trend of concentration in soils can be summarized as Ba>Ni>Zn>Co>Cu>Pb>Ag>Cs>Mo>Au>Cd>Hg>As (Table 3). This does not compare favorably with that of the ore, which is the primary source.

Given that Ba released through weathering is often not very mobile [29] and the Ba concentration in the ore (3.8 ppm) is relatively low compared to that in all the soil samples (Tables 1 and 3), the high Ba concentration in the soil does not owe it source to the ore, it is geology related. According to Mielke [30], shale display the highest concentration of Ba in sedimentary environment compared to carbonates and sandstones. Therefore, given the area is made up dominantly of shales and sandstone (Figure 2) the Ba concentration in the soils is derived from shales and sandstone. Also, given the known barite mineralization in the Middle Benue trough [31], the Ba concentration could also be indicative of $BaSo_4$ enrichment in the study area.

Table 4 indicates that Ce has the highest concentration in all of the samples compared to other elements. Ce has the lowest concentration of 80.8 ppm in sample YS1 and a high concentration of 237 ppm in sample YS11. Similar to that obtained in the ore (Table 2) the soil is deficient in Tb, Ho, Tm and Lu.

Table 5. Trace elements concentration in plants of the study area (values in ppm)

Sample ID	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Cs	Ba	Pb
PM1	0.33	0	3.6	9	0	0	0	0.16	0.055	191	3.2
PM2	0.07	0	1.3	2	0	0.1	0	0.02	0.014	65	0.4
PM3	0.09	0	1.6	5	0	0.7	0	0.06	0.039	103	0.5
PM4	0.28	0	3.1	5	0	0.1	0	0.05	0.014	238	1
PM5	0.24	0	3.3	9	0	0.2	0	0.02	0.048	334	0.5
PM6	0.19	0	2.3	7	0	0	0	0.01	0.014	784	0.6
PD1	0.27	0	3.5	8	0	0	0	0.02	0.068	142	4.9
PD2	0.08	0	2.8	12	0	0.9	0	0.03	0.061	32	3.8
PD3	0.09	0	5.9	12	0	6.2	0	0.01	0.075	79	0.8
PD4	0.07	6	3.7	19	0	2.4	0	0	0.061	25	1.7
PD5	0.15	0	1.9	2	0	0.2	0	0	0.009	279	0.6
PD6	0.15	0	2.1	7	0	0.3	0	0.02	0.014	254	3.9
Total	2.01	6	35.1	97	0	11.1	0	0.4	0.472	2526	21.9
Average	0.17	0.50	2.93	8.08	0.00	0.93	0.00	0.03	0.04	210.50	1.83

where: PM= *Anogeissus leiocarpus (DC.)* samples; PD= *Dichrostachys cinerea* samples

Thus, the general REE trend in soil conform with that obtained in the ore, where LREE (La, Ce, Pr and Nd) show higher concentrations than the MREE (Sm, Eu, Gd, Tb, Dy and Ho) and HREE (Er, Tm, Yb and Lu). The trend in soils can be represented as Ce>La>Nd>Pr>Sm>Gd>Dy>Eu>Er>Yb>Tb>Ho>Tm>Lu.

Therefore, like revealed in the ore sample, the enrichment above can be represented as LREE>MREE>HREE. Thus, showing the depletion of HREE in the soils of the area, which is indicative of deficiency of high temperature minerals [28]

3.2.3. Plants

Hg and Au were not detected. Ag, Ni, and As, were below the instrumental detection limits of 0.2, 5 and 1 ppm respectively. With only sample PD4 having Ni concentration of 6 ppm.

Ba concentration, though reflected in the Table 5, was not used for plotting in Figure 5. This is because of its high concentration across the plants samples. Plotting Ba alongside other elements led to suppressing of other values when attempted. Thus, from Table 5 it can be observed that Sample PD4 has the least concentration of Ba at 25 ppm while sample PM5 has the highest concentration of 334 ppm. Comparatively, *Anogeissus leiocarpus (DC.)* (PM samples) show more Ba concentration than the *Dichrostachys cinerea* samples (PD samples)

Thus, from the analyses of Figure 5, it can be observed that sample PD4 has the highest concentration of the ten elements plotted. The sample PD4 is the only sample that shows Ni (6 ppm) concentration. The remaining eleven samples have Ni below instrument detection limit. The elements with the highest concentration in the sample PD4 is Zn (19 ppm). From all the samples analysed, the *Dichrostachys cinerea* samples (PD) have more of Pb, Zn and Cu concentration compared to the *Anogeissus leiocarpus (DC.)* samples (PM). Samples PD1, PD3, and PD4 have 3.50, 5.90 and 3.70 ppm Cu concentration respectively, while samples PD2, PD3, and PD4 have 12 ppm, 12 ppm and 19 ppm concentration of Zn respectively (Table 5). Samples PD1, PD2 and PD6 have 4.90 ppm, 3.80 ppm and 3.90 ppm of Pb concentration respectively. The *Anogeissus leiocarpus (DC.)* samples (PM) with high Cu concentration is Sample PM1 which has concentration of 3.60 ppm. Only sample PM1, and PM5 have Zn concentration of 9 ppm and only sample PM1 has Pb of 3.20 ppm. Thus, only sample PM1 which was sampled close to an active mining pit shows relatively higher concentration of Pb-Zn-Cu amongst the *Anogeissus leiocarpus (DC.)* samples.

Interestingly, the *Anogeissus leiocarpus (DC.)* samples (PM) are rich in Ba compared to the *Dichrostachys cinerea* samples (PD). Sample PM6 has Ba concentration of 784 ppm which is the highest of all samples analyzed (Table 5). Same is true for samples PM5, PM4, PM1 and PM3. Only sample PM2 has Ba concentration below 100 ppm. For the *Dichrostachys cinerea* sample (PD), the highest Ba concentration is 279 ppm as shown by sample PD 5. Hence, it can be deduced that while the *Dichrostachys cinerea* (PD) samples are more indicative of Cu, Zn, and Pb, the *Anogeissus leiocarpus (DC.)* samples are indicative of Ba mineralization or enrichment.

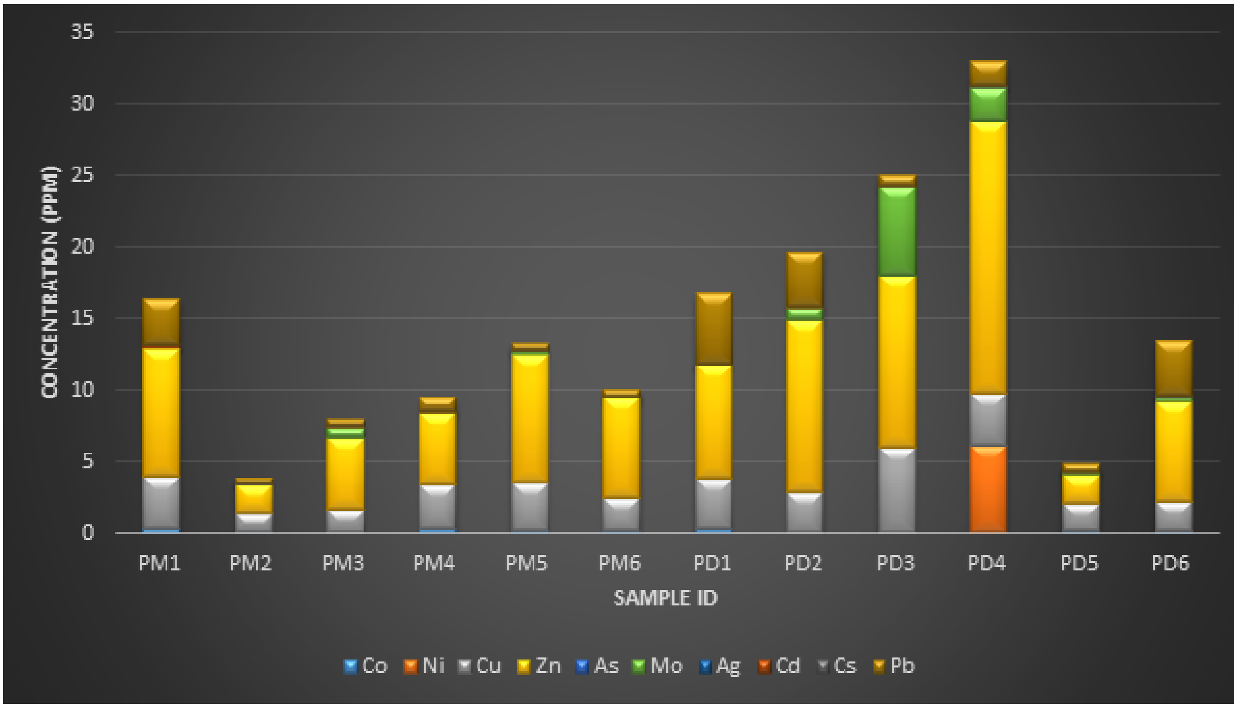

Figure 5. Modal concentration (ppm) of trace elements in plant samples

Sample PD3, PD4, PM1 and PM5 were taken close to an active mining pit (Figure 1). From the four samples, it can be observed that the two *Dichrostachys cinerea* samples (PD3 and PD 4) have higher Cu, Zn, Pb and Mo concentration compared to the *Anogeissus leiocarpus (DC.)* (PM3 and PM5). Only sample PM5 has Cu concentration of 3.30 ppm and the sample was taken closest to sample PD4 (Figure 1).

Samples PD5, PD6, PM2 and PM6 were taken far from the mining pits and far apart. Both samples PM6 and PD 6 have Cu above 2 ppm, Zn at 7 ppm with PD6 with high Pb (3.90 ppm) as against 0.60 ppm for PM6. Therefore, this further confirms that the *Dichrostachys cinerea* samples (PD) are more indicative of Pb, Zn, and Cu mineralization in the study area. From Table 5, the trend of elemental concentration in *Anogeissus leiocarpus (DC.)* samples can be summed as Ba>Zn>Cu>Pb>Co>Cd>Cs>Mo, while that of *Dichrostachys cinerea* can be summed as Ba>Zn>Cu>Pb>Co>Cd>Cs>Mo. Comparatively, though similar trend is observed, the concentration of Ba is higher for all samples species, while Zn, Cu, and Pb is higher in the *Dichrostachys cinerea* samples. Collectively it can be observed from the data that the plants in the area are rich with Ba, Zn, Pb and Cu mineralization.

Sample PD5 has the highest concentration of rare earth elements amongst the samples analyzed (Table 6 and Figure 6). The composition of rare earth elements is largely made up of La and Nd (both of which are LREE). Both elements of which are comparatively dominant in all the other sample media discussed. Both elements are followed by Ce in dominance. This is a reflection of Figure 4 and Tables 2 and 4, where the three elements (La, Nd and Ce) were observed to dominate the ore sample. The only difference is that unlike in the ore and soil where Ce had higher concentration relative to La and Nd, here La is more dominant. This also indicates the dominance of the LREE over the HREE and MREE. Thus, suggesting that the rare earth elements in plants may have their source from the ore.

Without soils, no plants can exist, thus analysis and correlation of these two media (plants and soils) often provide useful guide for correlation in prospecting and/or exploration, as plants can accumulate metals directly from soils rich in such metals [3, 10, 12]. Plants that do well in the vicinity of ore bodies and mineral outcrop are useful guide in geobotanical prospecting as they are direct indicators of the likelihood of occurrence, be it natural (primary site) or anthropogenic or technogenic sites where ores are processed (secondary site) [32].

For the metal contents of a sample of plant material to be useful in prospecting or exploration as the case may be, it should bear a fairly simple relationship to the metal content of the bedrock or ore material. This may not necessarily

Table 6. Rare earth elements concentration in plants of the study area (values in ppm)

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
PM1	0.263	0.37	0.044	0.187	0.033	0.01	0.03	0.003	0.016	0.003	0.007	0	0.004	0
PM2	0.283	0.26	0.03	0.112	0.016	0.004	0.01	0.001	0.005	0	0.002	0	0.001	0
PM3	0.052	0.07	0.007	0.031	0.006	0.002	0	0	0.003	0	0.001	0	0	0
PM4	0.455	0.15	0.064	0.237	0.033	0.008	0.03	0.002	0.01	0.001	0.003	0	0.002	0
PM5	0.36	0.34	0.049	0.187	0.031	0.01	0.02	0.003	0.013	0.002	0.005	0	0.003	0
PM6	0.177	0.11	0.02	0.078	0.012	0.008	0.01	0.001	0.005	0	0.002	0	0.001	0
PD1	0.412	0.67	0.075	0.309	0.058	0.015	0.05	0.006	0.031	0.005	0.013	0	0.009	0
PD2	0.074	0.13	0.013	0.054	0.01	0.003	0	0.001	0.006	0	0.002	0	0.002	0
PD3	0.268	0.24	0.028	0.11	0.019	0.005	0.02	0.002	0.011	0.002	0.004	0	0.002	0
PD4	0.075	0.12	0.013	0.054	0.01	0.003	0	0.001	0.006	0	0.002	0	0.002	0
PD5	1.08	0.31	0.202	0.846	0.141	0.039	0.13	0.013	0.055	0.008	0.017	0	0.007	0
PD6	0.354	0.28	0.041	0.166	0.027	0.009	0.02	0.003	0.014	0.002	0.006	0	0.004	0

where: PM= *Anogeissus leiocarpus (DC.)* samples; PD=*Dichrostachys cinerea* samples

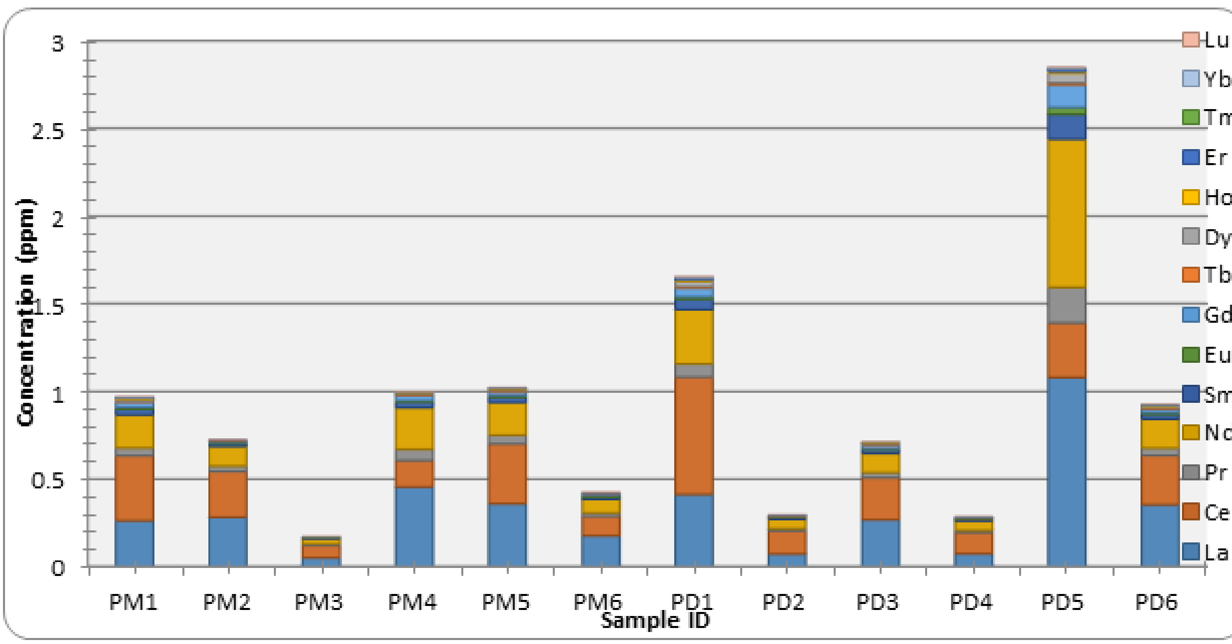

Figure 6. Modal concentration of rare earth elements in plant samples from the study area

be as simple as it appears. According to Rose et al., [25], other factors such as age of the plant or organ, depth of root system, health of plant and aspect (amount and direction of sunlight) among others may affect background and contrast of biogeochemical survey.

Elements often associated with sulphide mineralization were selected, statistically analyzed and interpreted. Interpretation was correlated for the different media. Result obtained indicate that the two plant samples can be good exploration guide for sulphide mineralization, while the *Anogeissus leiocarpus (DC.)* plants are good indicators for Barium and cobalt, the *Dichrostachys cinerea* showed better guide for lead, zinc, and copper mineralization (Table 5 and Figure 5).

4. Conclusion

In light of the geobotanical, geological and geochemical (paedogeochemistry, biogeochemistry) evidences obtained from this study, the following conclusions are hereby made,

The dominant Plant species in the study area in terms of occurrence, abundance and outlook are *Anogeisus leiocarpus* and *Dichrostachys cinerea*. The area is rich with Pb-Zn-Cu-Ba sulphide mineralization as analyzed from the three media (ore, soils and plants). Geobotanical method of prospecting for Pb-Zn-Cu-Ba mineralization is promising as geochemical data revealed that the *Dichrostachys cinerea* are good indicators of Pb-Zn-Cu mineralization while the *Anogeissus leiocarpus* are better indicators for Ba. Though indicated in the ore, with considerably high concentration, both plant samples showed no presence of silver, arsenic, gold, nickel or mercury. Singularly, the analysis of the ore indicates Pb-Zn-Cu mineralization with high values for Cu (7830 ppm), Pb (>5000 ppm) and Zn (>5000 ppm) with associated silver having concentration above 100 ppm, and gold with concentration of 53.5 ppm. Comparison of geochemical data of soil, plants and ore indicates the presence of Barium in high concentration in soil and plant, unlike it was measured in Ore (As mined). Also, Pb, Zn, and Cu concentration are relatively lower in soils and plant as against values measured in the ore. Thus, the trend of metal enrichment could be represented as ore>soil>plant. This is true as the ore is the primary source, while the soils is the medium from which the plants take up the elements as micronutrients.

From the forgoing, the two plants are promising good guide for complex Pb-Zn-Cu-Ba sulphide exploration.

In conclusion, geobotanical and biogeochemical prospecting approach is promising as application will be cost effective where similar plants occur.

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