Geochemical Characterization and Source Apportionment of Heavy Metals in Mining-Impacted Soils: Environmetric Analysis of Pb-Zn Mining Districts in Southeastern Nigeria

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ABSTRACT

The paper employed environmetric analysis to determine the distribution and source apportionment of heavy metals in soils affected by mining activities in the lower Benue trough area of Nigeria. Soil samples from mining areas in Enyigba, Ameri, Ameka, and Ishiagu were collected and analyzed for their heavy metal concentrations using Atomic Absorption Spectrophotometry. The results showed that Pb-Zn-Cu-Cd formed a distinct cluster indicating their common source from mining activities. On the other hand, Cr and Ni formed another distinct cluster indicating their source from geogenic activities. The results also showed a strong positive correlation between Pb-Zn (r = 0.85), Pb-Cd (r = 0.78), and Cu-Zn (r = 0.72) indicating their common source from mining activities. The results have demonstrated that environmetric analysis can be used to differentiate between geogenic and anthropogenic sources of heavy metals in mining areas.

Keywords: *geochemistry, source apportionment, cluster analysis, heavy metals, Pb-Zn mining, environmetrics, Nigeria*

I. INTRODUCTION

The identification and understanding of the sources and distribution patterns of heavy metals in mining areas are crucial for effective strategies to be developed for remediating the affected areas. Heavy metals have both geogenic and anthropogenic sources. Mining activities have been identified as one of the major sources of heavy metals in the environment (Alloway, 1995). The identification of the sources of heavy metals in mining areas requires advanced analysis that goes beyond mere concentration analysis.

Environmetric methods, which involve the application of multivariate statistical analysis, have come to the fore as a potentially valuable tool for source apportionment in environmental research. Cluster analysis, principal component analysis, and correlation matrices have the potential to elucidate the associations between the elements which indicate common sources or similar geochemical behavior as proposed by Krzanowski (1988). Environmetric methods have already been successfully employed in various mining environments across the globe to differentiate between lithogenic and anthropogenic metal contributions.

The Pb-Zn mining district of the Lower Benue Trough in Nigeria is an optimum environment for the application of these methods. The geological setting of the area is dominated by Cretaceous shales with associated sulfide mineralization. This has provided a natural setting for the concentration of metals. Several decades of mining activities have introduced significant anthropogenic contributions to the system. This has created a complex geochemical setting where sophisticated methods of analysis are warranted for source apportionment.

Objectives of the Study is to: (i) characterize the geochemical setting of the heavy metals in the mining-impacted soils; (ii) employ multivariate statistical analysis to establish associations between the heavy metals; (iii) differentiate between the anthropogenic and geogenic contributions of the heavy metals; and (iv) establish a framework for targeted interventions in the environment.

II. MATERIALS AND METHODS

2.1 Study Area Geology

The research was conducted in the Lower Benue Trough, which is a sedimentary basin filled with Cretaceous rocks of the Asu River Group. The dominant rock type is dark carbonaceous shale with associated limestone, siltstone, and volcanic intrusive rocks. Pb-Zn mineralization is present in the form of veins and lodes

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hosted in the shales. The major ore minerals are sphalerite (ZnS), galena (PbS), and associated pyrite (FeS2). The mineralization is of the Mississippi Valley-type and is the result of low-temperature hydrothermal activity during the Santonian orogenic event.

Figure 1 Ebonyi State maps

2.2 Sampling and Analysis

Soil samples were collected from abandoned mine areas (Abakaliki, Ikwo, Izzi Local Government Areas) and quarry sites (Ezza South, Ezza North, Ivo Local Government Areas) at depths of 0-15 cm and 15-30 cm. The samples were air-dried, sieved to 2mm, and ground into fine powder. The samples were digested in aqua regia (HNO3: HCl, 1:3) and analyzed for the concentration of heavy metals by Atomic Absorption Spectrophotometer (Unicam model) for Pb, Zn, Cu, Cd, Cr, Ni, Fe, Mn, and As.

2.3 Statistical Analysis

The results were subjected to multivariate analysis by SPSS software. Cluster analysis by Ward's method at Euclidean distance was used to determine element clusters. Pearson correlation was used to determine the relationship between the metals. Statistical significance was set at $p < 0.05$.

III. RESULTS AND DISCUSSION

3.1 Metal Distribution Patterns

The distribution patterns of heavy metals were distinct and indicated both geological background and mining effects. The range for lead was 16.63 to 127 ppm (mean 61.4 ppm), which was significantly higher than the crustal background value of 15 ppm. Zinc was the most enriched element, ranging from 21.14 to 120 ppm (mean 76.9 ppm). Copper (15 to 35 ppm), cadmium (0.4 to 4.2 ppm), and chromium (0.2 to 2.5 ppm) were moderately enriched.

Table 1: Statistical Summary of Heavy Metal Concentrations (ppm)

Metal	Minimum	Maximum	Mean	Std. Dev	Crustal Avg.
Pb	16.63	127	61.4	28.5	15
Zn	21.14	120	76.9	25.2	70
Cu	15	35	21.8	5.6	50
Cd	0.4	4.2	1.9	0.95	0.2
Cr	0.2	2.5	0.95	0.65	100
Ni	0.5	3.2	1.5	0.75	80

3.2 Correlation Analysis

The results from the Pearson correlation analysis indicated significant correlations between metals. These results provided valuable insights into the common sources for the metals. Strong positive correlations were observed between Pb-Zn (r=0.85, p<0.01), Pb-Cd (r=0.78, p<0.01), and Cu-Zn (r=0.72, p<0.01). The results for Cr and Ni indicated weak correlations with Pb, Zn, Cu, and Cd. These results indicated that the sources for Cr and Ni were likely to be different from those for the other metals. The results also indicated that Cr and Ni have a common source since there was a significant positive correlation between the two elements (r = 0.68, p < 0.05). This suggested that both Cr and Ni have a common geogenic source from the weathering of mafic minerals from the parent rocks. Iron was found to have moderate correlations with most of the metals. This was likely due to the fact that iron was part of the sulfide minerals as well as a major component of soil oxides.

Table 2: Correlation Matrix for Heavy Metals in Soil Samples

	Pb	Zn	Cu	Cd	Cr
Pb	1.00	0.85**	0.68**	0.78**	0.12
Zn	-	1.00	0.72**	0.65**	0.18
Cu	-	-	1.00	0.58**	0.22
Cd	-	-	-	1.00	0.08
Cr	-	-	-	-	1.00

*Note: ** Correlation significant at $p < 0.01$ level*

3.3 Cluster Analysis

The results from the cluster analysis indicated that there were two distinct clusters for the elements. Cluster 1 included Pb, Zn, Cu, and Cd. These results indicated that the anthropogenic source was from the processing of sulfide ores. The close association between the four elements was also consistent with the fact that they were found together in the Pb-Zn deposits and were released together during mining activities. Cluster 2 included Cr and Ni. These results indicated that the geogenic source was from the weathering of parent rock materials.

The results from the environmetric classification also indicated that there were two distinct clusters for the elements. Cluster 1 included Pb, Zn, Cu, and Cd. Cluster 2 included Cr and Ni. These results indicated that the sources for the elements were from the processing of sulfide ores and from the weathering of parent rock materials.

3.4 Source Apportionment Implications

The differences between anthropogenic and geogenic sources of metal contamination have profound implications in the management of the environment. Anthropogenic metals, which include Pb, Zn, Cu, and Cd, show the highest concentrations in areas closer to mining activities and gradually decrease as distance increases. These findings indicate the areas where remediation strategies are required. Acidic conditions, which are a result of sulphide oxidation, require pH adjustments as part of the remediation process. In contrast, geogenic metals, which include Cr and Ni, are background levels of metal contamination and do not require any remediation strategies. These findings have profound implications in the management of the environment, as the differentiation of metal sources will ensure effective allocation of resources in areas of significance.

IV. CONCLUSIONS

The purpose of the study has been fulfilled, and the significance of the use of environmetric techniques in the source apportionment of heavy metal contamination in mining areas has been demonstrated. Some of the findings include the following: Pb, Zn, Cu, and Cd are part of the anthropogenic cluster, which is a result of sulphide ore processing; Cr and Ni are separate clusters, which are a result of geogenic sources of contamination; Pb, Zn, Cu, and Cd are strongly correlated, which is a result of mineralogical association in the ore bodies; and environmetric techniques are a robust framework in differentiating between natural and anthropogenic sources of contamination. These findings have profound implications in the management of the environment in mining areas. Remediation strategies will be required in areas where anthropogenic sources of contamination are the most significant, which include Pb, Zn, Cu, and Cd. These findings will be useful in similar mining environments globally.

REFERENCES

[1]. Alloway, B. J. (1995). Heavy Metals in Soils (2nd ed.). Blackie Academic and Professional, London.
[2]. Kabata-Pendias, A., &Pendias, H. (2001). Trace Elements in Soils and Plants (3rd ed.). CRC Press.
[3]. Krzanowski, W. J. (1988). Principles of Multivariate Analysis. Clarendon Press, Oxford.
[4]. Nwachukwu, S. O. (1972). The tectonic evolution of the southern portion of the Benue Trough, Nigeria. Geological Magazine, 109, 411-419.
[5]. Orajaka, S. O. (1965). The geology of Enyigba, Ameri and Ameka lead-zinc lodes, Abakaliki Division, Eastern Nigeria. Journal of Mining and Geology, 2, 65-70.