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Evaluation of Heavy Metals in Stream Sediments from Abakaliki Pb – Zn Ore Mining Areas of Ebonyi State, Nigeria

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ABSTRACT: This research is an assessment of toxic metals in stream sediments from the Abakaliki Pb-Zn mine area of Ebonyi state. Heavy metals in stream sediment samples were analysed using Atomic Absorption Spectrometer (AAS). Physicochemical parameters were determined show that pH is generally low (3.65) resulting from the dissolution of the sulphide Ore. The heavy metal mean trend indicates that Fe > Zn >Pb> Cr >Cu > Ni > AS > Cd in the stream sediment samples. Fe, Zn, Cu, Pb and Cr were observed to be high. The variations for the heavy metals suggest that mining operation is responsible for the distribution and redistribution of chemical elements. The values of contamination factor for the stream sediment indicate moderate contamination for Cd, As and Ni while Fe, Zn, Pb, Cu and Cr show very high contamination. The result of enrichment factor (EF) using Fe concentration as normalizing value show that Ni, Cd, Cr, As, and Cu have depletion to mineral enrichment while Pb and Zn show moderate enrichment. The result of the Correlation analysis and principal component analysis (R- Mode and Q-mode) applied to the data analysis show that Zn, Pb, Cd, Cu, and Cr heavy metals originated from similar sources but may have been influenced by mining operation while Ni and As are attributed to a geogenic source. Proper sewage disposal practice and soil remediation are recommended.

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Soils constitute part of vital environmental, ecological and agricultural resource that has to be protected. The determination of elemental status of cultivated lands is necessary to identify yield limiting deficiencies of essential micronutrients and polluted soils (Alloway, 1990). This is especially important in Enyigba, Ameri and Ameka because the inhabitants are essentially farmers, and large quantities of yams, rice and okra are produced both for local consumption and also for food supplies to other parts of the world. Mining has also become important because of the existence of Pb-Zn lodes in the area. The study focuses on the heavy metals Pb, Zn, Cu, Cd, Ni, Cr and As. The potential for these heavy metals to constitute pollutants in the area is high. Availability of these metals and the presence of factors capable of mobilizing, distributing and storing them in pedologic system are critical. These metals are thus components of the existing rocks in the study area. Some may have been absorbed from the ancient depositional environments (Obiora and Umeji, 1995). Thus, Ni/Zn, Cu/Cd, Cd/Zn and Cu/Zn present a more hazardous effect than the individual metals (Down and Stocks, 1977). The Pb – Zn and pH concentrations of Enyigba top and bottom soils in Abakaliki and concluded that the soil recorded a pH mean value of 7.0 ± 0.02, and that the lead is relatively unavailable to plants when the soil pH is above 6.5, while availability of zinc decreases with increasing soil pH due to increased adsorptive capacity (Oti-Wilberforce et al. 2012). The aim of this study is to employ statistical tools and ecological factors to evaluate heavy metals in stream sediments from Pb-Zn mining areas.

MATERIALS AND METHODS

Description of the Study Area: The study area falls within Pb-Zn Ore mine area of Enyigba, Ameri and Ameka in Abakaliki district, Ebonyi State, Nigeria. It lies between latitudes 6^o8^l- 6^o24^l N and longitude 8^o4^l-8^o16^l E. Enyigba, Ameri, Ameka and its surrounding villages is about 14km South East of Abakaliki town. The area is accessible through Ndufu-Alike Ikwo/Federal University Ndufu-Alike Ikwo road. The Enyigba, Ameka and Ameri region is marked by undulating range of shale outcrops, which serve as the host for Pb - Zn mineral deposits (Figure 1).

Fig.1. Location Map of Enyigba, Ameri and Ameka at Abakaliki, Ebonyi State

The area forms part of the "Abakaliki antichrionium" and generally underlain by the Abakaliki shales of the Asu River Group. The Abakaliki shale of lower Cretaceous age is exposed in the area. The sedimentary rocks are predominantly black calcareous (calcite-cemented) shale with occasional intercalation of siltstone. The Asu River Group which consists of alternating sequence of shale, mudstone and siltstone with some occurrence of sandstone and limestone lenses in some places and attains an estimated thickness of 1500 meters (Farrington, 1952). Kogbe (1979) described the sediments as consisting of rather poorly-bedded sandy limestone lenses. Extensive weathering and ferrogenization have generally converted the black shales to a bleached pale grey colour with mottles of red, yellow, pink and blue (Ukpong and Olade, 1979). The rocks are extensively fractured folded and faulted. The lead-zinc Ore is found in the Albian carbonaceous shale of the Asu River Group. The mineralization is structurally controlled and localized in fissures, fault zones and gently dipping veins. The veins are steeply dipping and have been proven to over 150m depth. They vary in width from less than a meter to 20m and in length from 30m to 120m. The dominant Ores in the area are observed from the fissures which contain lodes of sphalerite (ZnS), and /or galena (PbS) in association with smaller quantities of copper (Onyeobi and Imeokparia, 2011). The deposits have been mined on and off for several decades. In the Enyigba, Ameri and Ameka areas near Abakaliki, there is incontrovertible evidence of post-mineralization deformation that the lodes were developed at the end of Santonian folding (Wright, 1968; Nwachukwu, 1972). Pb – Zn Ore mine area of Abakaliki district have been implicated in various disease conditions (Adaikpoh et al., 2005; Onyeobi and Imeokparia, 2011). As, Cd, Co,Cu, Fe, Mn, Ni, Pb, Zn) as well as the pH of soils in the active areas of Enyigba Pb – Zn Mine were determined , and results show that total mean concentrations of the heavy metals decreased with depth in the order of Fe > Pb > Zn > Cu > Cd > Co > Ni > As.

Samples Collection: A total of eight (8) stream sediment samples were collected from Pb-Zn mine of Enyigba, Ameri and Ameka area in dry and wet seasons respectively, of which two (2) samples were taken from areas (3 kilometers) away from the Pb-Zn mines as background values. Coordinate and elevation readings were taken with the aid of Global Positioning System (GPS) at the various sample collection points.

Stream Sediment Digestion and Analysis: The stream sediments samples were air – dried and any clods and crumbs were removed. The dried stream sediment was passed through a 2mm sieve to remove coarse particles; the stream sediment were then sub-sampled and ground to fine powder in a mortar in preparation for chemical analysis. A sample of 1.250g of air – dried ground soil was digested in aqua regia, a mixture of 25% of HNO3 and 75% of HCl (Fisher Scientific, UK). The resulting solution were analyzed for total Fe, As, Cu, Pb, Cd, Ni, Cr and Zn using flame Atomic Absorption Spectrophotometer (AAS). The extraction and analytical efficiency of the AAS was validated using a standard reference material.

pH was determined in a soil suspension of 10g in 25ml of deionised water using a pH-meter (Aqualytica Model pH 17). Other physico – chemical parameters were determined by titrimetric methods.

Statistical Analysis: This is a powerful tool in monitoring soil properties and assists in the interpretation of environmental data (Tuncer et. al. 1993; Einax and Soldy, 1999). A multivariate statistical analysis of the data results was made with the SPSS package, in order to quantify relationships between variables under simultaneous consideration of their interactions (Krzanowski, 1988). Specifically, it involved correlation and factor analysis of Q-Mode and R-Mode. Heavy metal contamination was carried out using the method proposed by Hakanson (1980) based on integrating data for a series of each specific heavy metals. This method is based on the calculation for each contaminant through a contamination factor (CF) and enrichment factor (EF).

The contamination factor (CF) is the ratio obtained by dividing the mean concentration of each metal in the soil (C^io – 1) by the baseline or background value (concentration in uncontaminated soil (C^in).

$$C_f^i = \frac{C_o^i - 1}{C_o^i}$$

C_f is defined according to four categories as follow; $C_f < 1$ low contamination factor, $1 \geq C_f \geq 3$ moderate contamination factor, $3 < C_f < 6$ considerable contamination factor, $C_f > 6$ very high contamination factor.

$$EF = \frac{\left({C_m}/{C_{Fe}}\right)_{sample}}{\left({C_m}/{C_{Fe}}\right)_{background}}$$

Where (C_m/C_{Fe}) sample is the ratio of concentration of heavy metal (Cm) to that of Fe/CFe) in the soil sample and (C_m/C_{Fe}) control value is the reference ratio in the control value.

RESULTS AND DISCUSSION

Stream Sediment Sample in the Wet Season: Stream sediment pH in the wet season varies between 3.99 and 6.30 with the mean value of 5.40. Calcium and magnesium values range from 114.00-159.00 mg/kg and 80.04-153.00 mg/kg with their mean values of 138.33 mg/kg and 119.35 mg/kg respectively. Anion varies in the study area with SO_4 (65.00-82.99 mg/kg), NO_3 (89.21-101.30 mg/kg) and PO_4 (63.00-81.00 mg/kg) with their mean values of 79.66 mg/kg, 95.20 mg/kg and 71.00 mg/kg respectively. Heavy metal varies in the river water of the area and ranges from Fe(109.49-148.00 mg/kg) with the mean value of 129.20 mg/kg; Pb (2.31-3.01 mg/kg) with the mean value of 2.62 mg/kg; Zn(7.00-28.04 mg/kg) with the mean value of 14.56 mg/kg; Cd(0.5 mg/kg) with the mean value of 0.33 mg/kg; Cu(2.41-3.01 mg/kg) with the mean value of 1.81 mg/kg; As(1.20 mg/kg) with the mean value of 0.40 mg/kg; Ni(1.00-1.44 mg/kg) with the mean value of 4.07 mg/kg and Cr(1.00-1.44 mg/kg) with the mean value of 19.26 mg/kg (Table 1).

Correlation Analysis of Stream Sediments Sample for Wet Season: In the stream sediment sample in the wet season correlation matrix; As, Cd, Cu, Ni and Cr are significantly correlated and weakly correlated with Fe, Zn and Pb is negatively correlated. pH has no defined relationship with any element (Table 2).

Principal Component Analysis: Two components were considered in the factor analysis. The first component explains 68.52 % of the total variance with high positive loading on Fe, Zn and pH and weak loading on Pb, Cd, Cu and Cr. The second component explains 31.48 % of the total variance with strong and high positive loading on Pb, AS, Cd, Cu, Ni and Cr and weak loading on Zn and Fe (Table 3).

Cluster Analysis: The cluster analysis identified two main cluster groups. The 1st cluster contains Cd, Ni, Cu, Pb, As and Cu. Loosely bonded to this cluster at Euclidean distance are Zn and Cr. The last cluster group order is made up of Fe and pH (Figure 33). First, second and third order degree of similarities were observed between Pb, Ni; Cu, As; Cd' Ni and Cr, Zn respectively. The cluster one and two are association to factor 1 and 2. (Table 3 and figure 2).

Table 1: Stream Sediments Samples in the Wet Season (mg/kg)

Sample Location	Mg	Ca	As	Pb	Cd	Cu	Ni	Cr	Zn	Fe	SO_4	NO_3	PO_4	pH
OSU/1/EN	153.00	114.00	BDL	2.31	BDL	BDL	1.00	BDL	28.04	148.00	82.99	95.10	81.00	6.30
OSU/2/AMR	125.00	159.00	1.20	2.55	0.50	3.01	1.44	11.21	7.00	130.11	82.00	101.3	69.00	5.90
OSU/3/AM	80.04	142.00	BDL	3.01	0.50	2.41	1.00	1.00	8.65	109.49	65.00	89.21	63.00	3.65
MEAN	119.35	138.33	0.40	2.62	0.33	1.81	4.07	19.26	14.56	129.20	76.66	95.20	71.00	5.40
CP	55.40	98.00	2.00	3.94	0.40	3.20	1.52	1.52	9.55	81.51	81.51	144.00	81.11	7.00

=EN=Enyigba, AM=Ameka AMR=Ameri, CP=Control point and BDL= below detection limit

Table 2: Correlation Matrix of Stream Sediments Sample for Wet Season

	As	Pb	Cd	Cu	Ni	Cr	Zn	Fe	pH
As	1.000								
Pb	-.179	1.000							
Cd	.500	.763	1.000						
Cu	.654	.627	.982	1.000					
Ni	1.000	-.179	.500	.654	1.000				
Cr	.759	.505	.943	.989	.759	1.000			
Zn	-.560	-.715	-.998	-.993	-.560	-.964	1.000		
Fe	.042	-.991	-.844	-.728	.042	-.618	.804	1.000	
pH	.353	-.984	-.634	-.477	.353	-.341	.578	.950	1.000

Table 3: Principal Component Analysis with Varimax Rotated Matrix

	Component	
	1	2
As	.276	.961
Pb	-.995	.100
Cd	-.694	.720
Cu	-.546	.838
Ni	.276	.961
Cr	-.415	.910
Zn	.642	-.767
Fe	.972	-.236
pH	.997	.081
Cum. %	68.52	100.00
Var. %	68.52	31.48

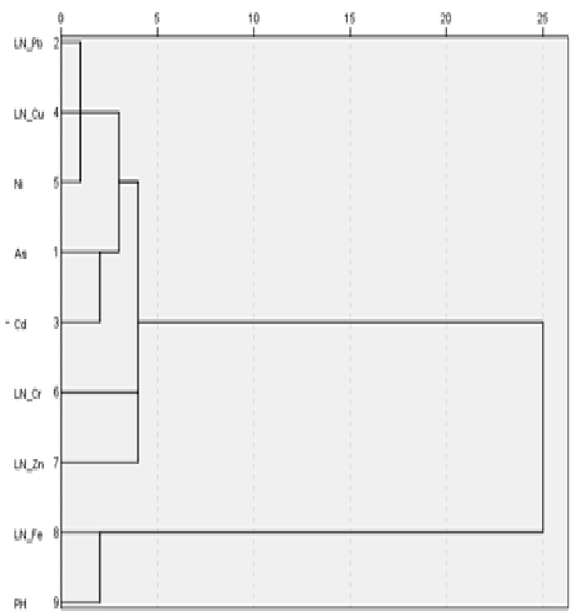

Fig 2: Hierarchical Cluster Analysis Dendrogram using Ward Linkage (Between Groups) (Rescaled Distance Cluster Combine)

Stream Sediment Sample in the Dry Season: Stream sediment pH in the dry season varies between 4.17 and 6.10 with the mean value of 5.32. Calcium and magnesium values range from 110.20-160.20 mg/kg and 94.40-154.20 mg/kg with their mean values of 137.80 mg/kg and 123.20 mg/kg respectively. Anion varies in the study area with SO_4 (61.34-79.88 mg/kg), NO_3 (14.40-130.20 mg/kg) and PO_4 (65.00-79.89 mg/kg) with their mean values of 73.32 mg/kg, 77.28 mg/kg and 74.56 mg/kg respectively. Heavy metal varies in the river water of the area and ranges from Fe(114.00-145.83 mg/kg) with the mean value of 131.05 mg/kg; Pb(3.00-4.00 mg/kg) with the mean value of 3.33 mg/kg; Zn(8.58-29.17 mg/kg) with the mean value of 16.47 mg/kg; Cd(0.9-2.71 mg/kg) with the mean value of 1.80 mg/kg; Cu(3.33-10.00 mg/kg) with the mean value of 5.83 mg/kg; As(1.50 mg/kg) with the mean value of 0.50 mg/kg; Ni(0.83-3.33 mg/kg) with the mean value of 2.09 mg/kg and Cr(1.81-15.15 mg/kg) with the mean value of 7.84 mg/kg (Table 4).

Correlation Analysis of Stream Sediment Samples in the Dry Season: In the stream sediment sample in the dry season correlation matrix; As and Pb are significantly correlated, and weakly correlated with Ni, Fe and Cr, Cd, Cu and Zn are negatively correlated. pH has no defined relationship with any element (Table 5).

Principal Component Analysis: Three components were considered in the factor analysis. The first component explains 41.47 % of the total variance with strong and high positive loading on Pb, Cr, Ni and pH and weak loading on Fe. The second component explains 34.65 % of the total variance with high loading on Cu, Zn, and Fe reflecting Ore association in the area. The third component explain 23.88 % of the total variance with high loading on AS, Pb and Fe, which also, reflecting Ore association in the area (Table 6)

Cluster Analysis: The cluster analysis identified two main cluster groups. The 1st cluster contains Ni, Cr, Cd, Pb, pH, As, Zn and Cu. Loosely bonded to this cluster at further Euclidean distance is Fe only (Figure 32). First and second order degree of similarities were observed between Fe, Cr, Cu, As; Cd' Ni, Pb and Cr, Zn respectively. The cluster one contains Ni, Cr, Cd, Pb, pH, As, Zn and Cu is close association of factor 1, 2 and 3, while loosely bonded to this cluster at Euclidean distance is Fe, which is similar to factor 2 and 3 (Table 6 and figure 3).

Table 4: Stream Sediments Samples in the Dry Season (mg/kg)

Sample Location	Mg	Ca	As	Pb	Cd	Cu	Ni	Cr	Zn	Fe	SO_4	NO_3	PO_4	pH
OSU/1/EN	154.20	110.20	BDL	4.00	1.80	10.00	2.10	1.81	29.17	145.83	78.75	14.40	78.80	5.70
OSU/2/AMR	121.00	160.20	1.50	3.00	0.90	3.33	0.83	15.15	8.58	133.33	79.88	130.20	79.89	4.17
OSU/3/AM	94.40	143.00	BDL	3.00	2.71	4.15	3.33	6.55	11.67	114.00	61.34	87.24	65.00	6.10
MEAN	123.20	137.80	0.50	3.33	1.80	5.83	2.09	7.84	16.47	131.05	73.32	77.28	74.56	5.32
CP	81.40	101.20	5.00	5.00	0.90	5.00	3.33	1.20	11.50	137.50	87.50	109.11	66.01	6.80

EN=Enyigba, AM=Ameka,AMR= Ameri and CP=Control point

Table 5: Correlation Matrix of Stream Sediment Samples in the Dry Season

	As	Pb	Cd	Cu	Ni	Cr	Zn	Fe	Ph
As	1.000								
Pb	.757	1.000							
Cd	-.719	-.455	1.000						
Cu	-.308	.365	.164	1.000					
Ni	.273	.457	.457	.031	1.000				
Cr	.320	.424	.425	-.084	.993	1.000			
Zn	-.430	.240	.250	.991	-.015	-.132	1.000		
Fe	.264	.590	-.626	.664	-.369	-.436	.598	1.000	
pH	.413	.696	.258	.223	.952	.927	.148	-.070	1.000

Table 6: Principal Component Analysis with Varimax Rotated Matrix

	Component		
	1	2	3
As	.322	-.357	.877
Pb	.551	.295	.781
Cd	.392	.132	-.910
Cu	.112	.994	.012
Ni	.993	-.080	-.086
Cr	.978	-.195	-.074
Zn	.055	.993	-.106
Fe	-.258	.689	.677
Ph	.981	.112	.156
Cum. %	41.47	76.13	100.00
Var. %	41.47	34.65	23.88

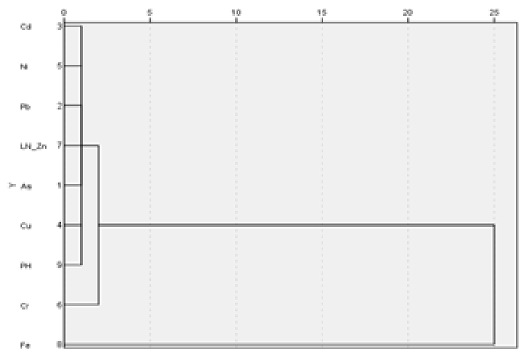

Fig 3: Hierarchical Cluster Analysis Dendrogram using Ward Linkage (Between Groups) (Rescaled Distance Cluster Combine)

Table 7: Contamination Factors of Sediment Samples

Element	Ameka Sediment (SSWS)	Ameri Sediment (SSDS)	Enyigba Sediment (SSDS)
Pb	0.67	0.67	2.15
Zn	1.53	1.43	6.22
Cu	0.56	1.17	3.95
Fe	0.93	0.95	78.29
Cd	0.83	2.00	30.00
Cr	6.90	6.53	21.4
As	0.20	0.10	0.75
Ni	0.75	0.63	5.8

SSWS = Stream sediment in the wet season; SSDS = Stream sediment in the dry season; KEY: Contamination Factor Classification

***KEY**: Enrichment Factor classification*

Cf< 1	1 ≥ Cf ≥ 3	3 < Cf < 6	Cf > 6
Low Contamination Factor	Moderate Contamination Factor	Considerable Contamination Factor	Very High Contamination Factor

Table 8: Enrichment Factor of Stream Sediment Samples

Elements	Enyigba Sediment (SSWS)	Ameka Sediment (SSDS)	Ameri Sediment (SSDS)
As	0.107	0.074	0.000
Pb	0.024	2.163	0.083
Cd	0.000	0.368	0.000
Cr	0.431	1.704	0.243
Cu	0.138	0.153	0.125
Ni	0.000	0.000	0.000
Zn	0.010	2.566	0.095
Fe	1.757	24.451	17.930

SSWS = Stream sediment in the wet season; SSDS = Stream sediment in the dry season

KEY: Enrichment Factor classification

EF<1	EF1-2	EF2-5	EF5-20	EF20-40	EF >40
Background of enrichment	Depletion enrichment	Moderate enrichment	Significant enrichment	Very high enrichment	Extremely high enrichment

Contamination Factor: The result of contamination factor indicate that Ni and Cu show considerable contamination especially in the soils collected at Enyigba and Ameka, while Cd and As show moderate contamination at Enyigba, Ameri and Ameka area Pb, Zn and Cr have CF > 6 indicating very high contamination, while Fe has CF > 6 in multiple fold indicating very high contamination, reflecting the sulphide mineralization in the area. Abakaliki soil is generally lateritic resulting in high Fe content of the environment (Table 7).

Enrichment Factor of Soil and Stream Sediment Samples: The results obtained from soil show that there was substantial evidence of mineralization in the area indicating background of enrichment to moderate enrichment. Thus, Pb, Zn, Cr and Fe elemental content indicate that galena; sphalerite, cerussite and pyrite are the main sulphide minerals in the study area. Thus, the strong association of elements such as Pb, Zn, it and Cu in most of the soil samples suggest a similar source (Onyeobi and Imeokparia (2011). However, the results of enrichment factor for Pb, Zn, Cr (and Cu) indicate that these metals may have been influenced by anthropogenic activities (Table 8).

Conclusion: This study has shown that the soils in Abakaliki areas of Pb – Zn mines are contaminated due to many years of random dumping of waste from the mining and processing of Ores of zinc and lead. The results of enrichment factor for Zn, Cd, Pb (and Cu) indicate that these metals are influenced by anthropogenic activities. The results of factor analysis show that Ni and Cr behave differently in the soils and possibly reflect contribution by geogenic sources only.The toxicological effect of heavy metals (Pb, As, Cd, Cr and Hg) includes hypertension, inhibition of haemoglobin formation, miscarriage, growth retardation and mental retardation to mention but a few. There is a need for soil remediation in the studied area.

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