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Analysis of Heavy Metals in Soils of Enyigba and Abakaliki Using Proton Induced X-Ray Emission (Pixe) Spectroscopy

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Abstract

Composite soil samples were collected about 200 m^2 apart at 0-30 cm (top soil) and 60-90 cm (subsoil) depths from Enyigba Pb-Zn Mine and Abakaliki Urban during the dry season in December, 2010. The soils were analyzed for pH and total contents of As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn using Proton Induced X-Ray Emission (PIXE) Technique. Results show that total mean concentrations of the heavy metals decreased with depth. Whereas the mean concentrations of the metals in the top and sub soil of Enyigba Mine decreased respectively in the order, Fe > Pb > Zn > Cu > Mn > Cd > Co > Ni > As and Fe > Zn > Cu > Mn > Pb > Co/Ni > Cd > As in the subsoil, the top and subsoil of Abakaliki Urban showed similar trend in the order, Fe > Mn > Pb> Zn > Co/Cu > Ni > Cd > As. The total mean concentrations of the metals in the top and sub soils of Enyigba Mine were found to be higher than those of Abakaliki Urban. Elevated concentrations of Pb > Ni > Cd above the US-EPA Regulatory Limits in that order was observed only in the Enyigba Mine top soil, while variations in the heavy metal levels were generally observed between and within groups. The mean soil pH obtained in Enyigba Mine and Abakaliki Urban was 6.5 and 6.8 respectively.

Keywords: heavy metals, pH, top soil, subsoil, Enyigba and Abakaliki

1. Introduction

Heavy metals such as lead (Pb), cadmium (Cd), iron (Fe) and manganese (Mn) are always part of life due to nature and human activities. Metals generally are natural components of the Earth's crust and therefore are major constituents of soil. Every 10^3 Kg of normal soil contains at least 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium theoretically (CODEX Alimentarius Commission, 1994). Therefore it may not be easy to assign a definite cause for an increase in metal content of a soil sample without recourse to the background level of the metal.

The soil is the supports base for almost all natural and man-made activities and as a result it is one of the repositories for anthropogenic wastes. Increasing industrialization has been accompanied throughout the World by the extraction and distribution of mineral substances from their natural deposits (Singh, 2001). The by-products and tailings resulting from such activities usually deposit or leach into the soil. Metals occur in different forms in their ores and their relative abundance in a given location may be exacerbated depending on the soil pH. Additional inputs from agricultural, mining and quarry activities, emissions from air fallouts, weathering of the parent rocks as well as transportation of accumulated pollutants into soil and water also increase metal load in an environment. Heavy metal load in soil is greatly influenced by metalliferous mining/smelting activities, burning of fossil fuel, waste disposal and industrialization (Reilly, 1980)

Heavy metal pollution is not only toxic to plants and deteriorates soil optimal bioproductivity but is a severe threat to human health especially at elevated level. Some of them such as Pb, Hg, As are known carcinogens and causes a long term damaging effect on the central nervous system. They are non-biodegradable and they have the tendency to bioaccumulate and biomagnify from one trophic level to another (Clark, 1992). Plants growing in polluted environment are likely to accumulate toxic metals more than others grown outside such an environment. Studies have shown that vegetables grown in metal contaminated soils accumulate heavy metals at higher level than ones grown on uncontaminated soils (Vousta et al., 1996). The heavy metal load in soil and plants from the

derelict Enyigba Mine and its environs have been reported (Chukwuma, 1994) and their prevalence in ground and surface water supplies in Ebonyi State have also been assayed (Afiukwa et al., 2009).

This study examines the levels of arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) as well as the pH of soils in the anthropogenically active areas of Enyigba Pb-Zn Mine and Abakaliki Urban. The objective was to obtain current data on the metal load using PIXE rather than AAS used by previous researchers and to make comparison on their distribution between the areas. The major disadvantage of AAS is that its application is limited to samples in solution phase and it cannot give a reliable result in contaminated samples due to its high sensitivity. Besides analytes such as Hg and As are present at very low concentrations (nanometer levels) cannot be determined by simple AAS but with ICP-AES (Leonardis et al., 2000). PIXE is a powerful yet non-destructive elemental analysis technique now used routinely by Scientist. The availability of high-energy accelerators has made PIXE an attractive alternative to other conventional, multi-elemental analytical methods. The simultaneous quantification of a large number of elements in a sample makes PIXE an important analytical tool for use in diverse toxicological studies. More importantly PIXE sample preparation method is simple and easy (Johansson & Campbell, 1988). Although this present work focused on heavy metals in the soil, it was necessary to determine the physical and chemical properties of soil which govern both availability and relative toxicity of metal contaminants such as soil pH, percentage of sand, silt, clay and organic matter and the nutritional status (Dickinson et al., 1988).

2. Materials and Method

2.1 The study Area

Abakaliki is the Capital City of Ebonyi State of Nigeria located at latitudes $6^{o}19'$N, $6^{o}21'$N and longitudes $8^{o}05'$E, $8^{o}07'$E (Microsoft Encarta, 2007). The City is in the mid of the South Eastern Nigeria and lies within the mineralized zone of lead - zinc deposits of the River Benue trough, which stretches for hundreds of kilometers north-easterly from Zurak (Olade, 1976). The Benue trough is one of the known major areas with Pb-Zn deposit in West Africa. Abakaliki, especially the Enyigba area which is about 14 Km south of Abakaliki urban, is overlain with tropical rocks which constitute gneisses, granites, shales, sphalerite and crustal rocks (Chukwuma, 1993). The prevailing climate is laden with high rainfall, high temperature, high atmospheric humidity and precipitation usually exceeding evapotranspiration for more than half the year. The Enyigba Pb-Zn Mine was intermittently mined for lead from 1925. Mining operations ceased due to low economic returns as well as the 1967-1970 Nigerian Civil War that badly affected the industry.

2.2 Reagents

All reagents were of analytical reagent grade and were used without further purification. Distilled mineralized water was used where necessary (Nweke et al., 1997; Chukwuma, 1993).

Instrumentation: Proton Induced X-ray Emission (PIXE) spectrometer, component of 1.7 MV NEC model Tandem Nuclear Accelerator at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria was used for metal analysis and determination.

2.3 Sample Collection and Preparation

Soil samples were collected at random 20m apart at 0-30 cm and 60-90 cm depth from four different points and pulled together composite samples (n=4). The former represents topsoil while the later represents subsoil samples. The samples were air-dried, ground mechanically and sieved to obtain < 2 mm fraction. 30 g sub-sample was drawn from the bulk (< 2 mm fraction) and reground to obtain < 200 μm fraction using laboratory mortar and pestle. The sample was further dry ashed in an open inert vessel in a muffle furnace at temperature between 450-550 ^{o}C so as to destroy organic combustibles in the sample and cooled in a desiccator.

2.4 Analysis of Soil Samples

The ashed samples were analyzed for heavy metal contents using similar procedure by Olabanji et al. (1995). The target soil sample was irradiated in PIXE spectrometer for 3 minutes in a vacuum chamber with 3 MeV protons (beam currents of 10-70 nA and beam diameter of 4 mm). The X- rays generated from the target were measured with two Si/Li detectors and the corresponding metal concentrations were recorded from a digital direct read-out computer device with a least square fitting program. Other physical and chemical properties of the soil such as pH, percentage of sand, silt, clay and organic matter were also analyzed (Dickinson et al., 1988).

3. Results and Discussion

The results of the pH values and the total mean heavy metal concentrations in two different soil types are presented in Table 1 and 2 respectively. The soil properties from both locations are presented in Table 3 while Table 4 indicates the P- values (ie *probability value*) of non-parametric analysis of variance for the analyzed metals. Figures 1 to 9 represent the distributions of arsenic, cadmium, cobalt, copper, iron, manganese, nickel, lead and zinc respectively in the top and sub soil of Abakaliki and Enyigba.

The total mean concentrations of heavy metals in Abakaliki Urban and the Rural Enyigba areas as well as data for the top and subsoil in both areas were compared. From Table 2 and figures 1 to 9, the total mean concentrations of each heavy metal in the soil samples decrease with depth which suggests anthropogenic source of contamination. The concentrations of the heavy metals in the Enyigba Mine show higher value than those obtained in Abakaliki Urban. Although this trend is general for all the metals, the ANOVA result (Table 4) shows that only Fe, Pb and Zn in the Enyigba samples were significantly higher than those of Abakaliki Urban.

Table 1. The pH values for top and sub soils of Enyigba and Abakaliki samples

pH	Sampling Point 1	Sampling Point 2	Sampling Point 3	Sampling Point 4	Mean pH
Abakaliki Topsoil	6.8	6.9	6.9	7.0	
Abakaliki Subsoil	6.7	6.6	6.7	6.8	6.8 ± 0.38
Enyigba Topsoil	6.5	6.6	6.6	6.7	
Enyigba Subsoil	6.5	6.5	6.4	6.5	6.5 ± 0.29

Table 2. Mean concentrations (mg/Kg) of heavy metals in soil of Enyigba Mine and Abakaliki Urban and their pollution indices

	Enyigba				Abakaliki				
Metal	Topsoil	PI	Subsoil	PI	Topsoil	PI	Subsoil	PI	US-EPA
As	4.8 ± 1.8	0.06	2.12 ± 1.6	0.03	2.84 ± 1.4	0.4	nd	–	75
Cd	126.0 ± 42	1.5	28.8 ± 6.2	0.34	3.4 ± 1.2	0.04	0.18 ± 0.2	–	85
Co	86.4 ± 38.8	–	34.8 ± 12.4	–	54.4 ± 14.6	–	16 ± 4.6	–	$0.3 - 200$ *
Cu	812.2 ± 141.2	0.19	322.2 ± 12.2	0.07	54.2 ± 18.6	0.01	16 ± 8.4	–	4300
Fe	24868 ± 661	–	18422.0 ± 412	–	12143 ± 248	–	422.8 ± 52.4	–	–
Mn	424.0 ± 50.4	–	120.0 ± 44.0	–	216.0 ± 42.1	–	88.6 ± 49.4	–	$1 - 18300$ *
Ni	82.6 ± 22.0	1.1	34.8 ± 8.2	0.46	34.6 ± 8.6	0.46	10.2 ± 4.8	–	75
Pb	1116.8 ± 43.2	2.7	91.7 ± 16.7	0.22	122.2 ± 22.2	0.30	0.21 ± 0.1	–	420
Zn	995.2 ± 82.4	0.13	322.0 ± 62.4	–	69.8 ± 22.2	0.01	42.4 ± 16.1	–	7500

* *Values refer to metal concentration in typical soils (Miroslav & Vladimir, 1999), PI = Pollution index.*

Table 3. Properties of Soil from Enyigba Mine and Abakaliki Urban

Properties	Enyigba Mine	Abakaliki Urban
Sand (%)	61.28 ± 5.2	53.96 ± 4. 6
Silt (%)	7.12 ± 0.8	16.44 ± 1.2
Clay (%)	31.60 ± 2.6	29.60 ± 2.2
Organic Matter (%)	1.34 ± 0.5	1.92 ± 0.7

Table 4. P-values of the non-parametric analysis of Variance for the heavy metal contents in soils with area as a grouping factor

	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Topsoil	0.481	0.100	0.521	0.034	0.003	0.087	0.179	0.002	0.008
SubSoil	0.316	0.044	0.291	0.002	0.001	0.682	0.122	0.032	0.49

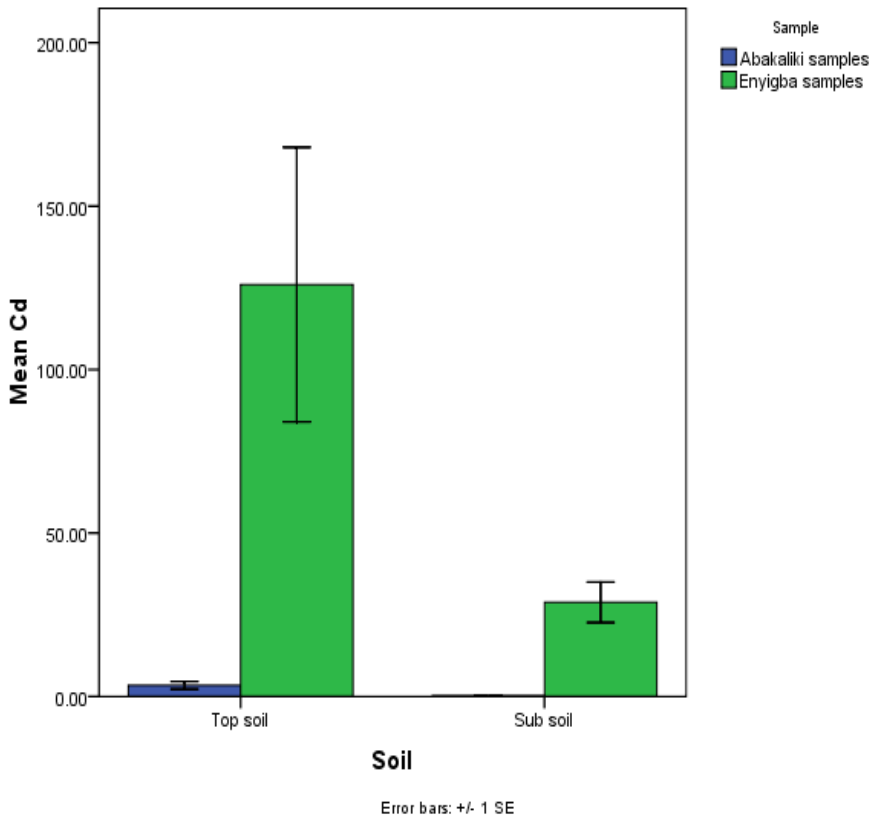

Figure 1. Arsenic distribution in Abakaliki and Enyigba soil

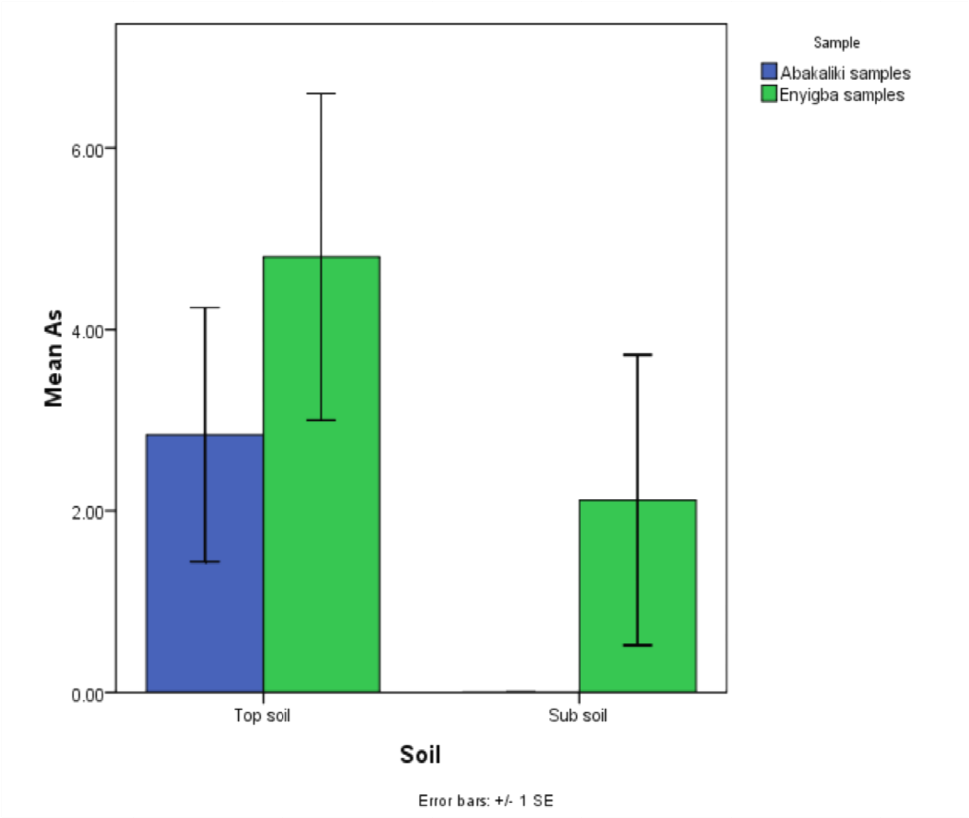

Figure 2. Cadmium distribution in Abakaliki and Enyigba soil

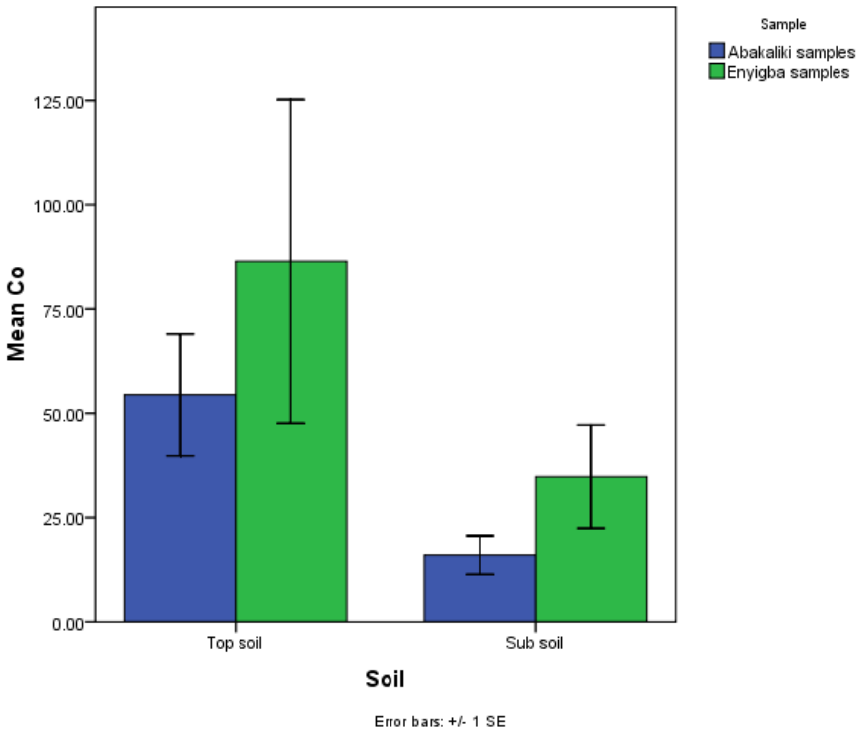

Figure 3. Cobalt distribution in Abakaliki and Enyigba soil

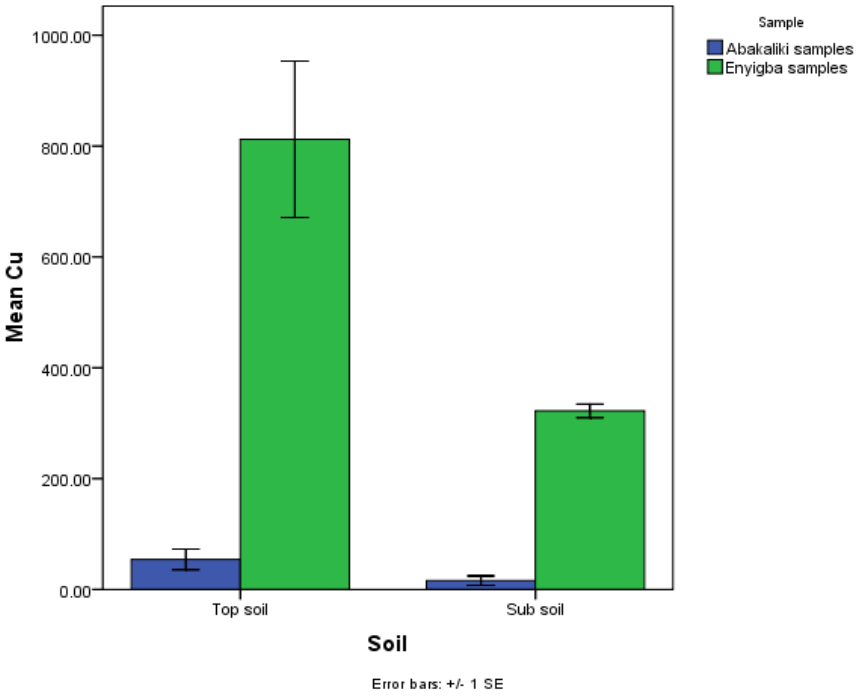

Figure 4. Copper distribution in Abakaliki and Enyigba soil

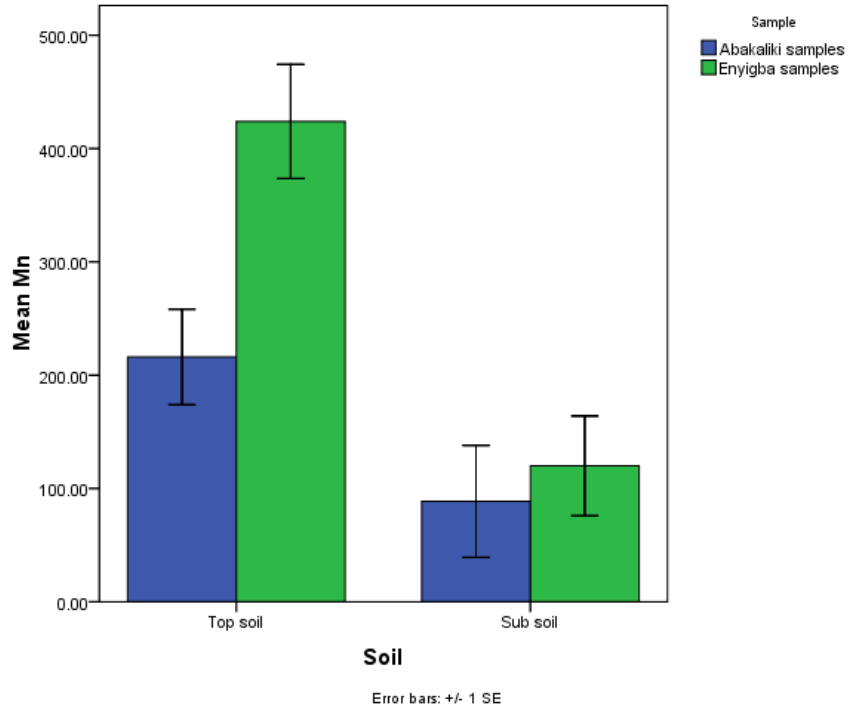

Figure 5. Iron distribution in Abakaliki and Enyigba soil

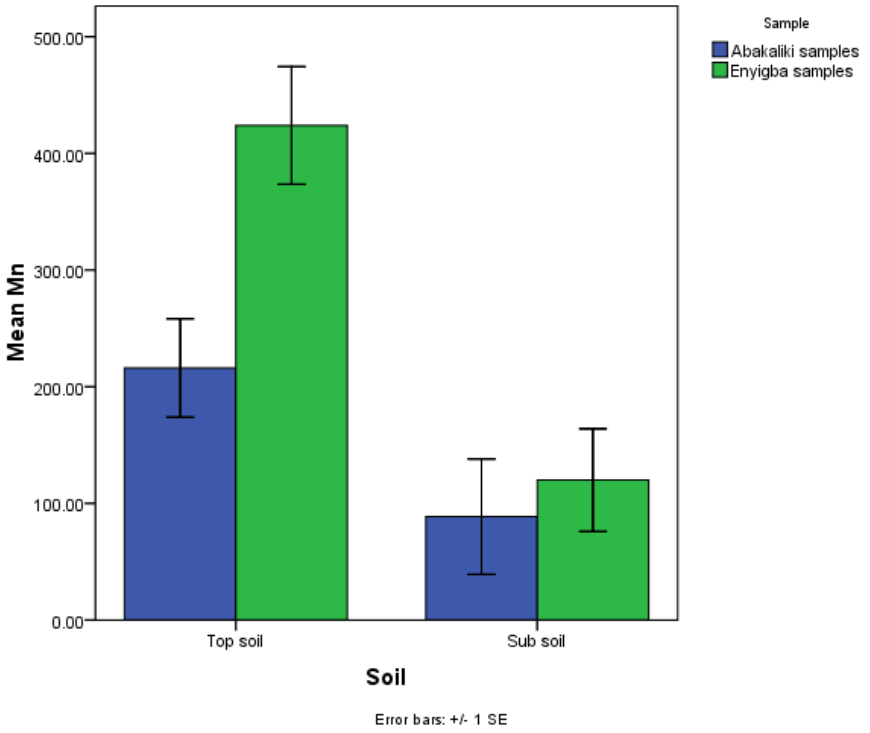

Figure 6. Manganese distribution in Abakaliki and Enyigba soil

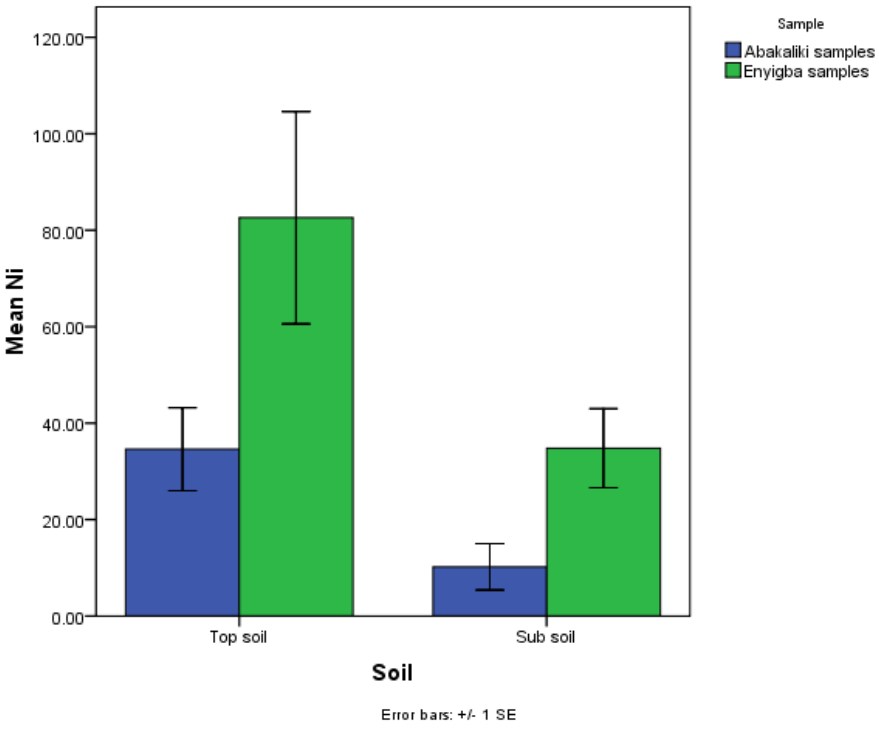

Figure 7. Nickel distribution in Abakaliki and Enyigba soil

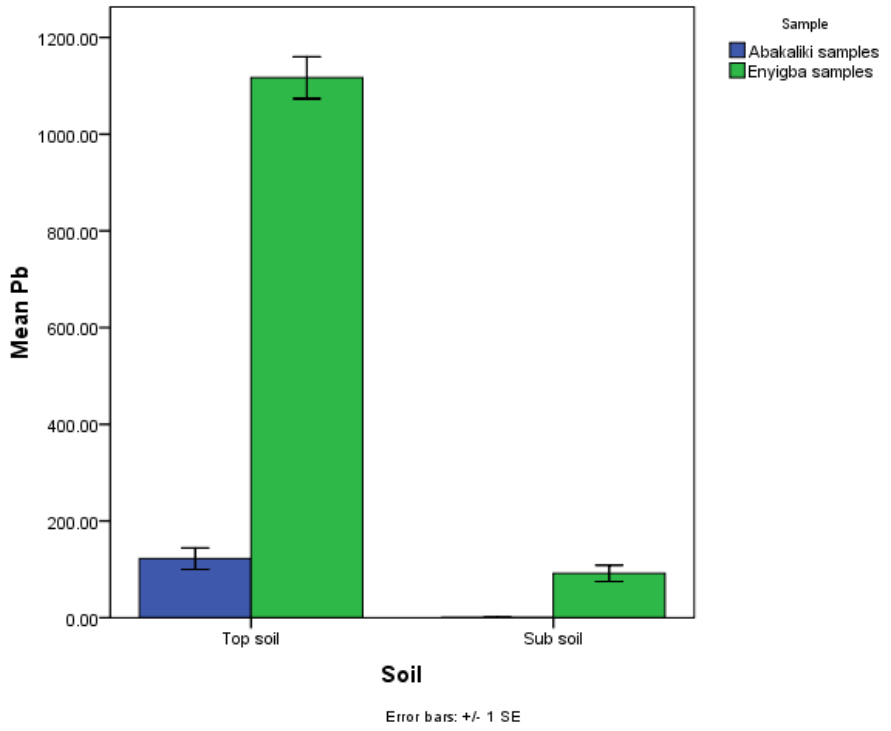

Figure 8. Lead distribution in Abakaliki and Enyigba soil

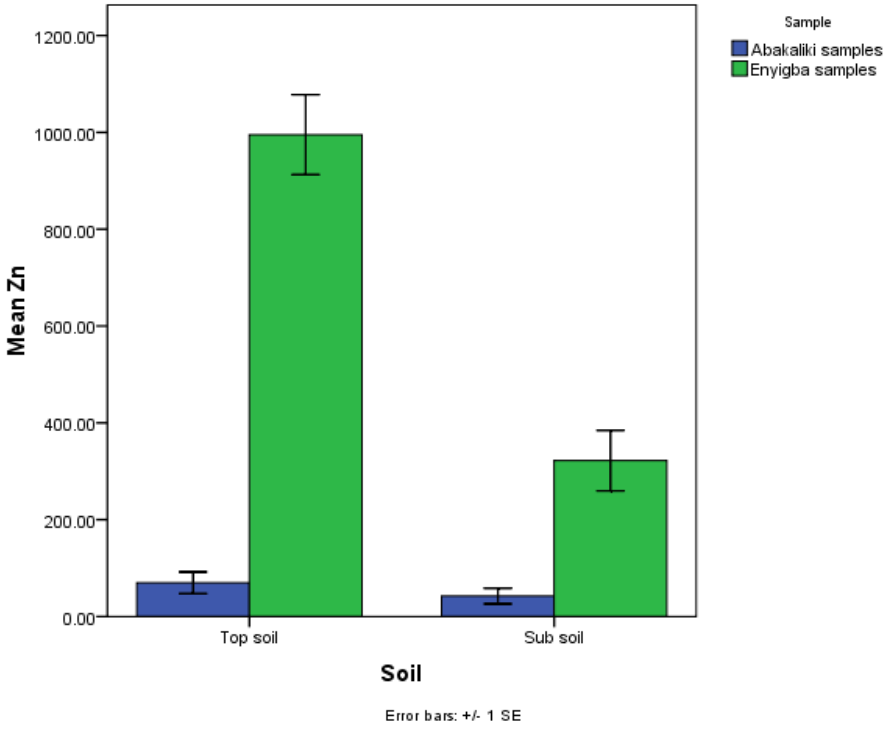

Figure 9. Zinc distribution in Abakaliki and Enyigba soil

In general, Table 2 and Figures 1 to 9 show that the heavy metal levels in the Enyigba Mine decrease in the order Fe > Pb > Zn > Cu > Mn > Cd > Co > Ni > As in topsoil and Fe > Zn > Cu > Mn > Pb > Co/Ni > Cd > As in the subsoil. The soil types in Abakaliki Urban show the same order as Fe > Mn > Pb > Zn > Co/Cu > Ni > Cd > As. These results are at variance both in trend and values obtained for each metal with the earlier results of previous investigation shown as Zn > Pb > Mn > Cu > Ni > Cd in the Enyigba Mine soil and Mn > Zn > Pb > Ni > Cu > Cd in Abakaliki (Chukwuma, 1994). The difference may be attributed to the analytical methods used or the fact that environmental dependent parameters are never static due to changes in temperature, pH and volume/nature of human perturbation on the natural ecosystem. While the present study is with PIXE technique, the previous study used less sensitive AAS technique which gave lower value of metal concentrations.

Table 2 also shows a comparison of the concentrations of the metals with the US-EPA Regulatory Limits (US-EPA, 1993). Only Pb, Ni and Cd from the Enyigba top soil exceeded the limits with their pollution index indicated in the order, Pb (2.7) > Cd (1.5) > Ni (1.1). Table 1 shows pH values for top and sub soils from four different sampling points. The observed variation in the trend of the metal levels between top and sub soils can be explained in terms of pH. The pH values in this study decreased with depth. Some metals such as Pb have low solubility at pH range of 5.5-7.5 which is normal for most mineral soils (Miroslav & Vladimir, 1999). Leaching of such metals at this pH range is also slow but is usually enhanced at pH < 5.0. The lead level in topsoil is therefore higher than in subsoil depending on soil pH. The average soil pH of the Enyigba Mine and Abakaliki Urban was 6.5 and 6.8 respectively (Table 1). Soils with pH around 7.0 have higher availability of nutrient elements such as Mg, Ca, K, N and S, while metals such as Pb, Cu, Mn and Zn are less soluble and therefore less available at about this pH.

Table 3 shows the soil characteristics by their organic matter, sand, silt and clay contents. The mean organic matter content is 1.34 % in Enyigba Mine and 1.92% for Abakaliki Urban soil. These values are in agreement with the observed pH and the heavy metal contents of the soils. Organic matter and pH values have been reported to independently and associatively influence the concentrations of heavy metals in soils (Chukwuma, 1994). The extent of soil pollution with heavy metals and subsequent uptake by crops depend on organic matter content among other factors (Adhikari et al., 2004). Usually, organic matter content increases with decrease in pH and an increase in metal concentrations. The organic matter content serves as reservoir of nutrients (N, P and S) and is often used as an index for soil fertility. It can also act as complexing agent for heavy metals. Therefore, soils with high organic matter content may also be high in heavy metal contents. Silt and sandy soils are generally dominated by quartz, calcite and in limestone base soils, dolomite ($CaMg(CO_3)_2$) may predominate. The clay fraction is composed of clay minerals, humic substances and oxides of Fe and Al. They are hydro-silicates which may also contain Mg and other metal ions. Due to their ability to hold sufficient water, they also hold vital plant nutrients. The results in Table 3 therefore indicate that the soils from the study areas of both Enyigba Mines and Abakaliki Urban can support agricultural activities efficiently.

Heavy Metal Impact: Although some metals such as Cu, Co, Fe, Mn and Zn are essential micronutrients, they can become harmful especially to humans at excessive levels. Iron at toxic level has been implicated in such diseases as vomiting, abdominal pains, diarrhea, convulsion and shock as a result of it's over deposition in the liver (Punnonen et al., 1994 and Zhao et al., 2005). It is generally known that iron is the major component of most soils. Trace metals also possess phytotoxic potentials which can inhibit biomass production (Pierzynski & Schwab, 1993). In solution, some group of metals exhibit synergism. Thus Ni/Zn, Cu/Cd, Cd/Zn and Cu/Zn present a more hazardous effect than the individual metals (Down & Stocks, 1977). Heavy metal pollution of terrestrial ecosystems is of environmental concern for a number of reasons. Metal pollutants in the soil maybe absorbed through the plants roots with soil water that dissolved the pollutants and may either cause harm to the plants or pass through the food chain to harm humans when these plants are eaten. Unlike organic pollutants which are biodegradable, metals are not. They can persist in the soil unless it is leached out into surface or ground water resources where more harm is done to human health. Heavy metal pollution also reduces biomass production through the deterioration of soil fertility. For instance, Cadmium was found to be toxic to plants at low pH and relatively low concentration in plants. Non-essential elements such lead, arsenic, mercury, nickel and cadmium has less toxicity to flora but has adverse effect on livestock, which may graze these plants. Human beings who occupy a higher level of the food chain are therefore at serious health risk due to bioaccumulation of the ingested metal toxin. The toxicological effect of heavy metals, especially Pb, As, Cd, Cr and Hg has been documented and they include gastro-enteritis, inhibition of haemoglobin formation, sterility, miscarriage, growth retardation, central nervous system disorder, kidney dysfunction, hypertension and mental retardation to mention but a few (Amdur, 1991; Ming-HO, 2001; Meharg, 2005).

4. Conclusion

The concentrations of heavy metals in topsoil of Enyigba Mine have been found to be higher than their levels in the subsoil and the levels of elemental contents of soil from Enyigba Mine indicate pollution while those of Abakaliki Urban indicate that the studied site are unpolluted. The pH and organic matter levels appear to have influenced the availability and concentrations of heavy metals observed in this study areas. Of all the heavy metals studied only Pb, Ni and Cd were found at elevated concentrations above the US-EPA guideline limits. It is therefore recommended the need to regularly monitor heavy metal loads in our environment particularly within and around mining /quarry and industrial sites of developing States like Ebonyi to be able to provide quick intervention in the event of emerging negative environmental impact.

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