



**PROFILE AND PROSPECTS OF OTHER METALS ASSOCIATED WITH LEAD IN
ENYIGBA LEAD-MINE, EBONYI STATE, NIGERIA**

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ABSTRACT

Composite soil samples were collected in June 2016 from top soil (0-30cm) and subsoil(60-90cm) depths in Enyigba Pb-Zn Mine in Ebonyi state, Nigeria. The soils were analyzed using X-ray fluorescence for Pb and other elements. Results show that total mean concentrations of the heavy metals decreased with depth which suggests that the source of the metals was anthropogenic in nature. Scandium in the topsoil and copper and gallium in the subsoil were not detected. Levels of metals such as K, Ca, Ti, Fe and Ga were in weight percentage (1000 x ppm) and in addition to Mn, Sr, Se, V, Cd and Zr were all significantly higher than Pb at $p < 0.05$ and their concentrations were above maximum allowable limit of heavy metals in the soil. High concentrations of these elements in the subsoil of Enyigba lead mines strongly indicates that more useful metals could be extracted from EnyigbaPb-Zn mine.

Keywords: Metals, XRF, top soil, subsoil, EnyigbaPb-Zn mine

INTRODUCTION

Metals generally are natural components of the Earth's crust and therefore are major constituents of soil. According to CODEX Alimentarius Commission (1995), theoretically for every 103 Kg of normal soil, there are at least 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium. Hence metals in the environment are either via activities of nature or anthropogenic (manmade) activities. 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. Natural processes such as flood, erosion, landslide, earthquake, hurricane, volcanic eruption and weathering of the parent rock are known to transfer metals from one place to another. However, the soil being the supports base for almost all the man-made activities, it serves as a repository for anthropogenic wastes. Anthropogenic source of metal in soil include metalliferous mining and smelting; agricultural and horticultural materials; fossil fuel combustion; chemical and other manufacturing industries and waste disposal. 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. Additional inputs from agricultural, mining and quarry activities, emissions from air fallouts, 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). Contamination of the environment by heavy metals due to certain industrial activities has been on the rise in recent times and the level of heavy metal pollution of soil and the environment has been correlated to the extent of industrialization notwithstanding mitigation measures. Toxicity of elements especially metals have been reported extensively (Galadima and Garba, 2012). This study examines the levels of lead and other elements (metals and metalloids) in the soils anthropogenically active areas of Enyigba Pb-Zn Mine. The objective was to obtain current data on the metal load using X-ray Fluorescence (XRF) rather than Atomic absorption Spectrophotometer (AAS) used by many researchers. The major disadvantage of AAS is that its application is limited to samples in solution phase and it cannot detect non-metals

(Bernard and Micheal, 1998). Moreover, analytes such as Hg and As at low concentrations (nanometer levels) cannot be determined by simple AAS except with ICP-AES (Leonardis *et al.*, 2000). Since AAS involves digestion of solid samples, accuracy of the results often depends on expertise of the person who digested the sample because AAS cannot give a reliable result in contaminated samples due to its high sensitivity. This is unlike XRF whose advantages include non-destructive of sample; multi-elements analyses; relatively simple spectra line void of much interference; speed and high accuracy with precision (Swift 1995; Spittler, 1995). The simultaneous quantification of a large number of elements in a sample makes XRF an important analytical tool for use in diverse toxicological studies unlike AAS which uses special lamp for every element to be analyzed. This paper, therefore, reports all the XRF-detectable elements in the soil samples collected from Enyigba Pb-Zn mine as a result of mining activities within the area.

MATERIALS AND METHODS

Sampling: Composite samples of soil were collected using pre-treated plastic spoon from 0-30cm and 60-90cm representing the top and sub soils. The samples were labelled appropriately and stored in treated polythene bag. The samples were ground,

sieved and air dried for 6 days so as to remove the moisture present and to avoid interference during analysis. The grounded samples were sieved using a 2.0 mesh size sieve in order to remove large fragments of the sample and to separate the coarse grains from the metal rich fine grained soil samples

Sample Pre-treatment and X-Ray Fluorescence (XRF) Analysis

Sample preparation was done by pulverizing the samples to fine powdery form using an agate mortar and a pellet of the sample was formed using a CARVER model manual pelletizing machine at a pressure of 6-8 torr. The XRF equipment used for this analysis was a portable AMPTEK^(R) Energy Dispersive X-ray Fluorescence (EDXRF) technique. The EDXRF instrumentation includes the X-ray source, Sample Holder, Detector, Current and Voltage Amplifier and Read out computer. The equipment model is PX 2CR Power Supply and Amplifier for XR-100CR Si-pin Detector. The pelletized samples were inserted into the sample holder of the XRF system and was bombarded by X-ray fluorescence spectrometer with a silver (Ag) anode at a voltage of 25 kV and current of 50 μ A for 1000 counts or approximately 18 minutes in an external chamber setup. Characteristic x-ray of the sample was detected by the solid state Si-

pin detector system and spectrum acquisition was done using ADMCA^R software. The spectrum analysis was done using the ADMCA plus Fundamental Parameter (FP-CROSS) Software which translates the peak areas into concentration values.

RESULTS

Table 1 and 2 present the mean concentrations of different elements in the soil samples and some of the maximum allowable limit of some of the investigated elements in some countries respectively.

Table 1: XRF Result: Mean Concentration of Elements in Enyigba Top and sub soils

Elements	Topsoil Mean Conc	Unit	Subsoil Mean Conc	Unit
K	3.0147±0.0725	wt.%*	0.3635±0.0103	wt.%
Ca	0.4358±0.0278	wt.%	798.01±54	ppm
Ti	1.3833±0.0317	wt.%	1958.02±55	ppm
Mn	2912.00±73	ppm	2156.00±38	ppm
Fe	13.6836±0.0587	wt.%	25.3051±0.0578	wt.%
Ni	149.01±11	ppm	54.03±6	ppm
Cu	18.01±2	ppm	ND	ppm
Zn	362.00±22	ppm	161.01±15	ppm
Ga	0.0276±0.0018	wt.%	ND	ppm
Pb	496.04±14	ppm	34.01±4	ppm
Rb	103.02±9	ppm	71.03±8	ppm
Sr	519.03±54	ppm	253.04±39	ppm
Se	672.01±8	ppm	45.00±7	ppm
Nb	41.02±7	ppm	26.01±6	ppm
V	1185.00±71	ppm	238.08±15	ppm
Sc	ND	ppm	42.02±10	ppm
Cd	412.00±02	ppm	40.00±42	ppm
Zr	1974.00±36	ppm	107.03±27	ppm

*wt % = 1000 ppm, ND= Not detectable, PI = Pollution Index

Table 2: Maximum Allowable Limits (M. A. L.) for Some Metals in Soil (mg/kg) used in Different Countries (adapted from Olubunmi and Olorunsola, 2010; Lacatusu, 2000)

Chemical Elements	Austria	Canada	Poland	Japan	Great Britain	Germany	USEPA (1993)
Cd	5	8	3	-	3	2	85
Cu	100	100	100	125	100	50	4300
Ni	100	100	100	100	50	100	75
Pb	300	400	300	250	300	300	420
Zn	300	400	300	250	300	300	7500
Se	-						100

DISCUSSION

Concentrations of metals in topsoil were found to be higher than those in the subsoil which is a strong indication that the sources of these metals were anthropogenic in origin (Table 1). Most metals such as Cd, Ni, Pb and Zn exceeded the maximum allowable limit in the investigated soil (Table 2). In this work, the concentrations of metals such as K, Ca, Ti, Fe and Ga

(measured in weight % = 1000 times ppm) were far higher than Pb which is the principal metal in the mine. Traditionally Enyigba mine focuses on lead and zinc. However metals such as Cu, Cd, Cr, Ni and As have been known to associated with Pb – Zn mineralisation. Zinc and cadmium are often found together in natural deposits in association with Mn (Ezeh and Anike, 2009). Scadium was not detected in the top

soil sample but was significantly present in the subsoil. The concentration of Se and Sr were comparable with Pb concentration in the topsoil. The values of the concentrations of V and Zr were four and two times higher than Pb. Copper and gallium were not detected in the subsoil. Metals in the subsoil such as K, Ca, Ti, Mn, Fe, Ni, Zn, Rb, Sr, Se V, Sc and Zr were higher than Pb. High concentrations of other metals aside Pb suggests that Enyigba mines soil has potential to supply.

Prospects of Other Metals in Everyday Life

Many of the metals present in Enyigba soil if found in commercial quantity will be useful in mobile phones and accessories whose many metal components include Cd, Pb, Mn, Zn and Cu. Tungsten-light filaments, Titanium-steel, paint, Sodium-grease, Calcium-oils and greases. Nickel is alloyed with are iron, copper, chromium, and zinc. Most nickel is used to make stainless steel (Derek and Kerfoot, 2005). In addition, special batteries utilizes some of the identified metals including Pb-acid, Ni-Cd, Ni-metal hydride, Zn-carbon, Zn-chloride, Alkaline/manganese, Zn-air, Ni-Oxyhydroxide, Zn-bromine and Vanadium redox. Zinc is mixed with other chemicals to form alloys such as brass and bronze (Prasad, 2003). Zinc can combine with other chemicals to form salts. Most

zinc ore found naturally in the environment is found as zinc sulphide and zinc oxide and they are used to make white paints, ceramics and several other products (Hambidge and Krebs, 2007). Zinc oxide is also used in producing rubber. Zinc salts, such as zinc acetate, zinc chloride and zinc sulphate are used in preserving wood and manufacturing and dyeing fabrics. Lead and tin are used for the solder to connect the electronic parts to the PC (printed circuit) board. Copper is used for electronic parts, PC board traces and wires. Many metals used in the components of cars include Mn-steel alloy, Niobium-high strength, low-alloy steel, Lead-battery, Chromium-plating, Cadmium-also plating, Nickel-plating, stainless steel, Copper-electrical wiring, radiator, Zinc-anti-corrosion plating, Gallium-also diodes, Vanadium-steel, Cobalt-also steel, Strontium-steel.

Cadmium is used in Ni-Cd batteries up to three-fourths of the total Cd produced worldwide, while the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission (Cotton, 1999). According to Roosenset *al.*,

2003, Cd always occurs in combination with zinc as it prefers oxidation state +2 in most of its (Kirk-Othmer, 1994). The rest of the cadmium is released through human activities, such as mining and manufacturing (Michael, 2010). Copper is a ductile metal with very high thermal and electrical conductivity used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys. Its compounds are commonly encountered as copper (II) salts, which often impart blue or green colours to minerals such as turquoise and have been widely used historically as pigments. Decorative art prominently features copper, both by itself and as part of pigments (Casarett and Doulls, 2004). Manganese is an alloying agent in stainless steels. Manganese phosphating is used as a treatment for rust and corrosion prevention on steel. Manganese ions have various colours and are used industrially as pigments. The permanganates of alkali and alkaline earth metals are powerful oxidizers. Manganese dioxide is used as the cathode (electron acceptor) material in standard and alkaline disposable dry cells and batteries (Sayre and Smith, 1961).

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