DETERMINATION OF HEAVY METAL CONTENTS IN SOILS FROM PARTS OF CROSS RIVER STATE NIGERIA, USING ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY.

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ABSTRACT

Surface (0 – 15cm) soil samples obtained from randomly selected sites were analyzed with a portable XRF Spectrometer. Fifteen elements potassium, K, calcium, Ca, titanium, Ti, vanadium, V, chromium, Cr, manganese, Mn, iron, Fe, nickel, Ni, zinc, Zn, germanium, Ge, gallium, Ga, strontium, Sr, rubidium, Rb, zirconium, Zr and lead Pb were detected. In Obudu 2, Unical, Unicem and Calabar South, Fe recorded the highest concentration values of 52700.00 ppm, 41130.00 ppm, 200390.00 ppm, and 16900.00 ppm respectively. Ga recorded the least value in Obudu 2 and Unical, while Ni recorded the least value of 39.32 ppm in Unicem. Lead, a carcinogenic element was not detected in Obudu 1 and 2, but was highest in Bakassi 2 and Unicem. Concentrations of Vanadium above the threshold value were recorded in Itigidi, Obudu, Unicem and Calabar South. Elements with high concentrations suggest that there may be high level of anthropogenic activities going on in such locations. Pearson's Correlation analysis revealed that K had strong positive correlation values of 0.91, 0.88 and 0.76 with Mn, Fe and Sr respectively, while Mn had positive correlation coefficients (0.88 and 0.69) with Fe and Sr, respectively. Fe was found to be positively correlated (0.79) with Sr. Strong positive correlation suggests strong affinity among the elements and may indicate possible common source and origin. The cluster analysis shows three cluster groups with each group showing elements that may have a common source and origin. From the result of the study, it is recommended that human activities which release elements which are harmful to soil dwelling organisms and man should be regulated and closely monitored by government agencies and institutions.

INTRODUCTION

Soil is a key component of the terrestrial ecosystem, vital for the growth of plants. It is a complex heterogeneous medium comprising minerals and organic solids, aqueous and gaseous components (Ramola *et al*, 2008). The problem of contamination of agricultural products by toxic/heavy elements in the soil makes it necessary to determine the presence and concentration of some contaminants, so as to monitor their tolerance levels in soil. Elemental analyses of environmental samples by atomic techniques have been known since 1930s. Since then many analytical techniques has been in use for the determination of elements present in soil samples. These include the use of the Energy dispersive X-ray Fluorescence (EDXRF) spectroscopy (Inyang, 2009). Using the EDXRF method, this study sought to determine the elemental compositions of soils in selected locations in Cross River State, Nigeria, with particular attention on heavy metal contaminants.

MATERIALS AND METHOD

Eight soil samples were collected for analyses. The samples were taken from different locations namely: Bakassi 1 & 2, Calabar Municipality (University of Calabar), Calabar South, Akampka (United Cement Company, Unicem), Itigidi and Obudu 1 & 2, all in Cross River State, Nigeria. A soil auger was used to remove a core of about 1kg of top soil (0-15cm in depth). As a precaution, stones and plants were discarded. The samples were dried under the sun to remove water and grinded with mortar and pestle to form a homogenous powder and sieved to discard pebbles and coarse sand (Ramola *et al* 2008). This follows the method adopted by Scott and Allen (1971) and Obiajuwa *et al* (2006). Twenty percent ultrapure carbon was added to each of the samples to aid pelletizing. These mixtures of carbon and samples were re-homogenized and was pelletized using a Carver Model Manual Pelletizing Machine at a pressure of 6-8 Torr (Eze *et al*, 2012; Uwah, 1992). Pelletizing was done at the Centre for Energy Research & Development (CERD), Obafemi, Awolowo University, Ile-Ife, Nigeria. A Portable Amptek (PXZCR) Model Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer linked with a Multi-Channel Analyzer (MCA) was used for the work.

The pelletized samples were inserted into the sample-holder of the X-ray system and were bombarded by beams of X-rays produced from the X-ray tube source at a voltage of 25kV and current of 50µA for 1000 counts for approximately 18 minutes (Eze *et al*, 2012).

The choice of using XRF is due to its low detection limit, high speed, convenience, low cost, reliability, and ultra-sensitivity and for routine multi-elemental analyses. Besides, it is non-destructive and does not contaminate elements, (Ikamaise, 2009).

RESULTS

The results of the elemental concentrations of the soils analyzed are shown in Table 1. Fifteen elements were detected, namely: Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Ga, Ge. Rb, Zr, Pb and Sr. Titanium (Ti) recorded the highest concentration value of 15279 ppm in Obudu 2, while gallium (Ga) had the least concentration value of 25 ppm in Itigidi and Obudu 1. In Bakassi 1 & 2, Itigidi, Obudu 1 & 2, Unical, Unicem and Calabar South, iron (Fe) recorded the highest concentration with values of 2759.20 ppm, 5616.9 ppm, 43280 ppm, 46760 ppm, 52700 ppm, 41130 ppm, 200390 ppm and 16900 ppm respectively. Calcium (Ca) recorded the highest concentration value of 101710 ppm in Unicem and the lowest in Bakassi 1. In Unicem, nickel (Ni) recorded the least concentration of 39.32 ppm and the highest value of 571.17 ppm at Bakassi 1. Rubidium, (Rb), was not detected in Bakassi 1& 2, Itigidi, Obudu I & II and Unical. However, Rb, Pb and strontium (Sr) were not detected in Obudu I, II and Calabar South respectively.

The metal, manganese (Mn) displayed very strong positive correlation coefficients with K and Ca with values of 0.91 and 0.91 respectively. It was also observed that Fe had a strong positive correlation with K, Ca and Mn with values of 0.88, 0.88 and 0.88 respectively. Zinc (Zn) correlated fairly positive with Ti and excellently positively with Ni with correlation coefficients of 0.50 and 0.93 respectively. Ga correlated moderately with Ni and Zn with a correlation coefficient values 0.52 and 0.60 respectively. Germanium (Ge) had moderate positive correlation values of 0.67and 0.52 with Ni and Ga respectively, and a strongly positive correlation with Zn at a value of 0.81. Rubidium (Rb) had correlation values of 0.55 and 0.59 with chromium (Cr) and gallium Ga respectively. Zr recorded fair to good positive correlation of Ni (0.57), Zn (0.69) and Ge (0.79). Also, Pb was found to be strongly correlated with Ga at $r = 0.81$. Strontium (Sr) had strong positive correlation values of 0.76, 0.76, 0.69 and 0.79 with K, Ca, Mn and Fe respectively.

Results for cluster analysis are shown in Figure 1. The elements Ga, Ge, Zn, Rb, Cr, V, Ni, Sr, Mn and Zr appeared in cluster one, while, K, Ti and Ca appeared in the second cluster, with Fe in the third cluster. These support the results of the correlation analysis shown in Table 2.

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 C A S E          0         5         10        15         20       25
 Label      Num  +---------+---------+---------+---------+--------
Ga         10   -+
 Ger        11   -+
 Zn          9   -+
Pb         14   -+
Rb         12   -+
 Ni          8   -+
 V           4   -+
 Cr          5   -+
Sr         15   -+
Mn          6   -+
Zr         13   -+---------------------------------------------+
 K           1   -+
 Ti          3   -+
Ca          2   -+-------------------------+---------------------+
 Fe          7   -+--------------------------+
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Figure 1.A dendrogram showing the Cluster Analysis of Elemental Concentrations

Figure 2 shows a multiple bar chart of the various elemental concentration in the different sample sites. Fe concentrations seemed to be the highest with a value of 200390 ppm in Unicem. These confirm the high relative abundance of Fe in nature. While Ga recorded the least concentration values of 25 ppm respectively in Itigidi and Obudu 1.

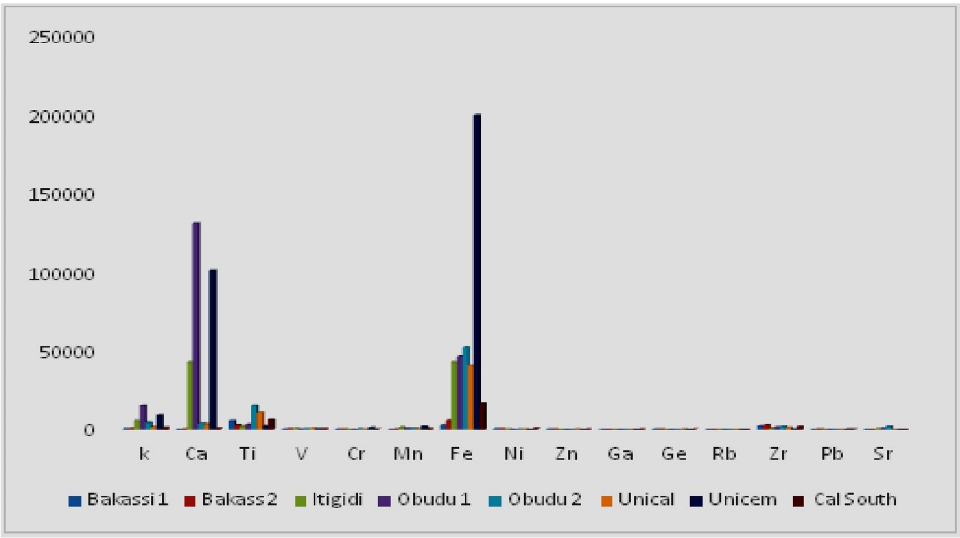

Figure 2: A multiple bar chart showing the elemental concentrations of the various elements present in the different sample locations.

Table 1: Elemental concentrations of samples

	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Zn	Ga	Ge	Rb	Zr	Pb	Sr
Bakassi 1	501.30	133.97	5502.06	280.98	151.64	317.86	2759.20	571.17	270.8	99.1	176.5	0.00	2218.6	198.16	0.000
Bakassi 2	852.70	195.98	3078.87	444.78	234.45	243.98	5616.96	541.73	218.4	124.1	163.4	0.00	2950.9	334.41	0.000
Itigidi	5484.40	43280	2245.36	728.27	0.000	1373.67	43280	295.20	104.5	25	53.7	0.00	980.0	62.37	527.32
Obudu1	15180	131610	3346.39	215.38	0.000	825.01	46760	126.25	101.2	25	95.7	0.00	1390.3	0.00	737.05
Obudu 2	4357.16	3704.75	15279	531.43	400.07	703.92	52700	185.50	107.5	39.1	74.45	0.00	2113.3	0.00	2113.32
Unical	1779.69	3372.31	10680	708.74	350.66	487.66	41130	262.72	133.3	63.6	136.6	0.00	1306.7	108.61	0.000
Unicem	9250	101710	2161.86 S	445.78	1156.93	1895.65	200390	39.32	73.3	109.9	67.46	97.5	297.83	249.91	69.288
Cal south	1175.69	645.71	6344.85	585.56	300.56	452.14	16900	682.56	276.2	170.6	148.0	88.4	1650.4	180.71	0.000

Table 2: Pearson's Correlation Table

	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Zn	Ga	Ge	Rb	Zr	Pb	Sr
K	1.00														
Ca	1.00	1.00													
Ti	-0.33	-0.33	1.00												
V	0.02	0.02	0.14	1.00											
Cr	0.00	0.00	0.24	0.20	1.00										
Mn	**0.91**	**0.91**	-0.41	0.24	0.13	1.00									
Fe	**0.88**	**0.88**	-0.17	0.12	0.42	**0.88**	1.00								
Ni	-0.83	-0.83	0.24	0.17	-0.32	-0.76	-0.88	1.00							
Zn	-0.91	-0.91	**0.50**	0.07	-0.08	-0.88	-0.86	**0.93**	1.00						
Ga	-0.62	-0.62	-0.05	0.02	0.44	-0.52	-0.43	**0.52**	**0.60**	1.00					
Ge	-0.83	-0.83	0.33	-0.45	-0.13	-0.93	-0.86	**0.67**	**0.81**	**0.52**	1.00				
Rb	0.19	0.19	-0.33	0.09	**0.55**	0.33	0.33	-0.11	-0.11	**0.59**	-0.19	1.00			
Zr	-0.74	-0.74	0.41	-0.45	-0.17	-0.88	-0.67	**0.57**	**0.69**	0.31	**0.79**	-0.44	1.00		
Pb	-0.54	-0.54	-0.46	-0.17	0.25	-0.42	-0.44	0.32	0.31	**0.81**	0.47	0.41	0.22	1.00	
Sr	**0.76**	**0.76**	-0.01	-0.05	-0.04	**0.69**	**0.79**	-0.67	-0.71	-0.74	-0.74	-0.16	-0.29	-0.74	1.00

$n=\alpha=0.0$, $r \geq 0.754$ at 95 (Confidence Interval level, positively high correlated metals are presented in bold type)

DISCUSSION

The results of the analysis of the elemental concentrations of elements presented in Table 1; showed that Fe had a concentration of 200390 ppm in Unicem. This value is above the natural threshold value range of 10,000-100,000ppm (Brady and Weil, 1996) (Table 3). However, in other locations like Bakassi 1&2, Itigidi, Obudu 1&2, Unical and Calabar South, the range of Fe is within the value of 2759.20 ppm-16900 ppm which is within the natural level of 10,000 ppm-100,000 ppm for mineral soils of the humid region (Brady and Weil, 1996) as seen in Table 3. The high concentration of iron tends to contribute excessively towards soil acidity by hydrolysis with the release of hydrogen ions (H^+), fixation of phosphorous and toxicity to crop plants. Other effects of a high concentration of iron in soils include the pollution of the quality of drinking and irrigation waters (Landon, 1991).

Table 3: Threshold values of heavy metals in mineral soil

Heavy metals	Range in mineral soils ($mgkg^{-1}$)
Iron	10,000 – 100,000
Manganese	200 – 2000
Nickel	10 – 1000
Zinc	10 – 300
Chromium	5 – 1000
Lead	2 – 200
Copper	2 – 100
Vanadium	20 – 500
Boron	2 – 100
Cobalt	1 – 70
Molybdenum	0.2 – 5
Mercury	0.02 – 02
Cadmium	0.01-7

Manganese (Mn) levels in the soil samples varied from 243.98 ppm in Bakassi 2 to a value of 1895.65 ppm in Unicem. This range of Mn values is within the natural level of 200-2000 ppm for mineral soils of the humid region (Brady and Weil, 1996) (Table 3). Mn in the soil activates enzymes and is involved in the biochemistry of glycoproteins (Bowen, 1979). It is present in Metalloenzymes such as Arginase and Pyruvate Carboxylase. Mn is also involved in fatty acid synthesis and bone development in poultry (Leach, 2000).

The levels of Zn in the soil samples varied from 73.3 ppm in Unicem to 276.2 ppm in Calabar South (Table 1). When compared with natural level of 10-300 ppm in soil (Bohn *et. al*., 1985) as seen in Table 3, it indicates that all the locations under investigation have normal concentration range for Zinc. Although Zn constitutes an essential element (micronutrient), it is toxic to crop plants especially at the level of about 400 ppm in soil (Abreu *et. al*., 1998), and to animals if the Zinc content of the diet exceeds 1000 ppm (Harrison, 1993). Since excess Zn in soil can be toxic to plants and animals, it is expected that toxicity will be prevented by the control of Zn-laden waste indiscriminate discharge into the environment.

Chronium (Cr) content in the soil samples showed that Bakassi 1&2, Obudu 2, Unical and Calabar South had normal concentrations of 151.64 ppm, 234.45 ppm, 400.07 ppm, 350.66 ppm and 300.56 ppm respectively as compared with natural level of 5-1000 ppm. Unicem concentration of 1156.93 ppm showed a very high concentration value when compared with the natural level of 5-1000 ppm (Bohn *et. al*., 1985) as seen in Table 3. These show that Unicem, an industrial site is polluted with Cr. However, zero concentration values of Cr were recorded in Itigidi, and Obudu 1 respectively.

In all the samples collected from the eight locations, Nickel Ni was detected within a range of 39.12 ppm in Unicem to 682.56 ppm in Calabar South. When compared with the natural level of 10-1000 ppm (Table 3). Nickel appeared to be within the normal concentration range in these sites. However, Odiete (1999) reports that Ni is toxic, especially if associated with crude petroleum. It is highly toxic to plant and can cause cancer in humans (Harrision, 1993).

The levels of Pb accumulated in Bakassi 1, Itigidi, Unical and Calabar South showed values of 198.16 ppm, 62.37 ppm, 108.61 ppm and 180.00 ppm respectively, compared with the natural level of 2-200 ppm. Pb appeared to be within the normal concentration range. Hence, these sites may not be said to be polluted with Pb. However, in Bakassi 2 and Unicem, there are higher concentrations valued at 334.41 ppm and 249.91 ppm respectively. These values were far above the natural level of 2-200 ppm. This suggests high level of Pb pollutions inBakassi 2 and Unicem. Pb is associated with petrol and cement as is the case in Bakassi 2 and Unicem. Most Pb however enter the environment through combustion of petrol by vehicle. Eating and drinking Pb-contaminated food and water results in anaemia, damaged kidney, liver and brain cell. Other effects include abdominal pains, irritability, nausea, tiredness, diarrhea and constipation, loss of appetite, headache and dizziness (Akpan, 2006).

The level of Vanadium V in Bakassi 1&2, Obudu1, Unicem were 280.98 ppm, 444.78 ppm, 215.38 ppm and 445.78 ppm respectively. Compared with natural level of 20-500 ppm, as seen in Table 3 vanadium V concentration appeared to be low. However, in Itigidi, Obudu 2, Unical and Calabar South, the concentrations were 728.27 ppm, 531.43 ppm, 708.74 ppm and 585.56 ppm respectively. These values were high in comparison with the natural level of Vanadium in mineral soils. V concentration may seem to be low but its toxicity can occur at concentration of 0.05-1.00 ppm for some plant species and at 5 ppm for man and animals (Harrison, 1993). V-laden waste therefore should not be discharged into any environment.

CONCLUSION AND RECOMMENDATION

Apart from Bakassi 2 and Unicem which recorded high concentrations of Pb due to the presence of petroleum and a cement factory respectively, most of the elements have their concentration levels below the threshold values in mineral soils. The study therefore has been able to re-define the content, occurrences and locations of heavy metals in some parts of Cross River State of Nigeria. The foregoing establishes a baseline data on heavy metals concentrations in some areas of Cross River State. Therefore EDXRF has proved a successful analytical technique in the determination of heavy metal concentration values in soils from some selected locations in Cross River State, Nigeria. We wish to recommend that human activities which release element which are injuries to soil dwelling organism and man should be regulated and closely monitored by government agencies and institutions.

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