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Soil Contamination in *Fadama* Area in Zaria, Nigeria, Using X-ray Fluorescence Technique

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Abstract

In this paper, the contamination level of thirteen elements (Si, Ca, K, V, Ti, Fe, Co. Zn, Rb, Sr, Y, Zr and Nb) from soil samples of the Fadama areas in Zaria, Nigeria were investigated with Energy Dispersive X-ray Fluorescence Technique (EDXRF) method. Generally, EDXRF is one of the reliable tools for determining the concentration of trace elements and heavy metals. In this study, the soil contamination level of all heavy metals and trace elements was compared to the range, mean, and median values of the World soil as well as with other studies. The concentrations of Si (30.2%), K (1.98%), Ti (0.49%), V (242 ppm), Zn (149 ppm), Y (50.6 ppm), Zr (884 ppm) and Nb (33.1ppm) are relatively higher than those of the World mean values. Furthermore, comparison to world range values for soil revealed that high concentration ranges are also observed for Zn (56.23-664.53ppm) and Y (32.73-94.37ppm). However, contamination level of all elements was not evenly distributed in the studied area. For instance, the pollution levels of V, Zn, Zr and Nb were higher in the study area. The contamination level of potassium is everywhere lower than the average world value. The level of contamination is determined with help of enrichment factors which gave high values for K, Zn, Rb, Y, Zr, and Nb.

Keywords: Soil contamination, heavy metals, EDXRF, enrichment factor

1.0 Introduction

The soil, a main part of the terrestrial ecosystem, is a heterogeneous mixture of different organisms and minerals, organic and organo-mineral substances present in three phases: solid, liquid and gas [1]. The *Fadama* soil is one of the most endangered components of Zaria environment open to potential contamination by a variety of different pollutants arising from human activities such as industrial, agricultural, etc. [2]. Although the trace elements in soil are very important for the quality of soil and environment, excessive level of trace elements can cause pollution of water, toxicity in plants, foods and ultimately in animals and humans that feed upon them [3-4]. As a result, the limits of metal deposition rates to soils should take into account the general ecotoxicity, phytotoxicity, transfer to animals, and risk to the human health. The trace metal concentrations in soils may be affected by the deposition of wastes released from various industries, and other related establishments. The erosive weathering, lead-base paints from the outer walls of buildings, land treatment of sewage sludge and natural sources of trace elements, e.g., windblown dust, forest wildfires, sea salt emission and vegetation may also contribute to the soil trace metal elevation [5]. Uncontrolled development of industry, agriculture and urbanization accelerates the input of heavy metals into the Fadama environment in particular and the world in general [1]. Heavy metals have been the subject of particular attention because of their long-standing toxicity, mobility in the ecosystems and transfer into the food chains when specific thresholds have been exceeded [6]. An important background for this kind of work requires the knowledge of geochemical baseline concentrations of elements in the study area. The trace element pollution depends on geochemical and biochemical properties of a given element .The need of measuring the back ground levels of inorganic material in soils increases with time due to the increasing of man's activities susceptible of contaminating the environment.

The geochemical baseline concentrations of metals in soil for the *Fadama* area are not available. The aim of the present work is to assess the contamination level of the soil samples taken at different points around the study area. The risk assessment of the present study is based on the comparison between the levels of contamination in the studied areas and the established guidelines or screening values [7]. In addition, level of contamination in the soil samples was estimated by comparing with the world average levels and the other specified guidelines for the element in soils. It is more likely that the high content of some elements in the soils is a result of human activities around the area.

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2. Materials and Methods

In order to study the validity of EDXRF, samples were prepared from four reference materials namelyUSGS-AGV-1(Analyzed Andasite), USGS-G2 (Granite), NIST-278(Obsidian Rock) and NIST-688(Basalt Rock).The samples were analyzed using the EDXRF facility of CERT, A.B.U Zaria, Nigeria. Standard reference materials powders were used for preparation of pellets for EDXRF analysis. Pellets of 20 mm diameter and constant thickness of 5 cm were obtained from standard samples.

The spectrometer consists of a Si(Li) detector, a preamplifier, amplifier and a 4096 multi-channel analyzer(Fig 1).In the XRF spectrometer, the primary excitation results in the emission of the characteristic X-Rays photons of various energies. These photons enter the depletion volume of the Si(Li) detector and loose energies in photoelectric encounters. The resulting photoelectrons ionize the detector material, producing electron –holes pair whose number is proportional to the energy of the absorbed photon. The generated charge, collected by high voltage bias across the detector is converted to voltage pulses and amplified by charge sensitive Field Effect Transistor (FET), a preamplifier and a linear amplifier. The amplitude of each pulse is proportional to the energy of the initial X-Rays that produces the pulse. The process of generation of a pulse by a photon and collection is accomplished in less than one micro second. The repetition of identical events in a measure of specific radiation, relates to the concentration of an element in the sample which can be determined quantitatively.

In this work, X – Rays emanating from two sources ($^{109}C_d$, $^{55}F_e$) were used for the excitation of the characteristics K – lines of the analytes. The qualitative X-Ray Analysis System (QXAS) Software was used for the acquisition of spectra, fitting of photo-peaks and calculation of final concentration. A smooth-filter background model was used for fitting the spectrum of the energy region of interest using the non- linear least square fitting programme called AXIL, contained in the QXAS package.

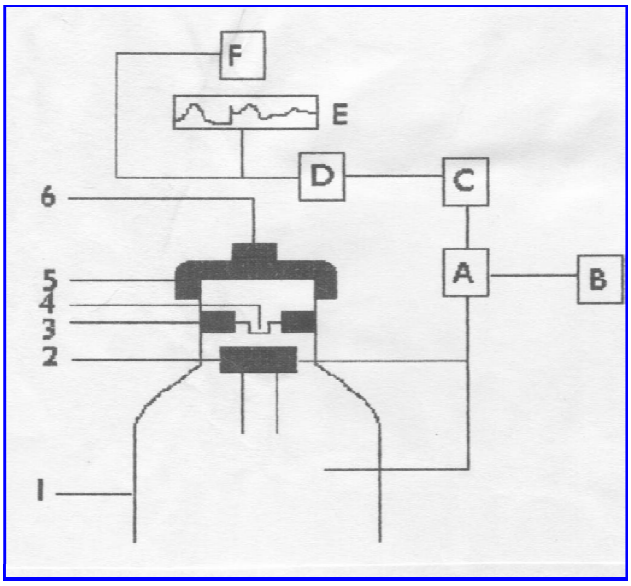

Fig. 1: Detection System for the EDXRF Technique

1. Dewar	A. Pre-amplifier
2. Si (Li) Detector	B. High Voltage Supply
3. Annular Source	C. Amplifier
4. Be Detector Window	D.Multi-channel analyser
5. Sample Holder	E. Computer
6. Sample	F. Printer

3. Results and Discussions

The measured concentrations of Si, Ca, K, Ti, V, Fe, Co, Zn, Rb, Sr, Y, Zr and Nb. in the soil samples with the absolute standard deviations and the World median values of the elements estimated by Bowen [8] are presented in Table 5. In order to evaluate the accuracy of this method, the concentration of the following elements: Si, Ca, K, Ti, V, Fe, Co, Zn, Rb, Sr, Y, Zr and Nb were reinvestigated and the values compared with literature values of Reference Materials. The quality assurance results (Table 1, 2, 3 and 4) shows that the determinations for most of the elements were in good agreement with the Standard

Reference Materials literature values. The values of the relative errors ranged from 1 to 30% for most of the elements and this is within the permissible limits [9].Only few elements showed a very high deviation from their literature values. This might be from the uncertainty in literature values because the concentrations of the elements showing large deviation were measured accurately in other standard reference materials. For Co, with exception of the value obtained for NIST- 688 our results were far from the recommended values of IAEA[2]. The relative errors for Co were 83% for UGSG – AGV -1, 73% for NIST-278 and 133% for USGS – G – 2, but they were within the values obtained by other researchers [9].

In Table 5 the mean concentrations, medians and the ranges of concentrations in the *Fadama* soils were compared with that of the world soils. In almost all the samples, the lowest concentration is found except for V, Zn, Zr and Nb which are above the corresponding range of the world.

Table 1: Determination of elemental content of NIST – 278 SRM (Values in %, otherwise in ppm).

Element	Literature value	This work	Relative error %
Si%	34	33.15	3
K%	3.44	3.49	1.5
Ca%	0.70	0.82	17
Ti%	0.15	<0.17	-
V%	15.0	ND	-
Fe%	1.05	1.06	1
Co%	1.5	2.6	73
Zn%	55.0	<73.4	-
Rb	127	127.4	0.3
Sr	63.5	63.8	0.5
Y	41.0	41.3	0.7
Zr	295	295	0
Nb	ND	16.8	-

Table 2: Determination of elemental content of USGS – AGV-1 SRM (Values in %, otherwise in ppm).

Element	Literature value[2]	This work	Relative error %
Si%	27.4	25.1	8
K%	2.41	2.50	4
Ca%	3.53	3.71	5
Ti%	0.63	0.68	8
V%	121	140	16
Fe%	1.60	1.60	0
Co%	15.3	28.0	83
Zn%	88.0	86.7	1
Rb	67.3	51.1	24
Sr	662	651	2
Y	20.0	15.4	23
Zr	227	227	0
Nb	15.0	<25.5	-

Table 3: Determination of elemental content of USGS – G-2 SRM (Values in %, otherwise in ppm).

Element	Literature value[2]	This work	Relative error %
Si%	32.2	32.0	1
K%	3.71	3.58	4
Ca%	1.40	1.28	9
Ti%	0.28	0.20	29
V%	36.0	36.5	1
Fe%	1.60	1.11	31
Co%	4.60	10.7	133
Zn%	86.0	86.0	0
Rb	170	170	0
Sr	470	495	4
Y	11.0	12.2	11
Zr	309	309	0
Nb	12.0	12.0	0

Table 4: Determination of elemental content of NIST - 688 SRM (Values in % otherwise in ppm).

Element	Literature value[2]	This work	Relative error %
Si%	22.5	26.5	18
K%	0.16	0.05	69
Ca%	8.68	8.35	4
Ti%	0.70	0.67	4
V%	250	223	11
Fe%	5.93	2.23	62
Co%	49.7	49.7	0
Zn%	58.0	79.6	37
Rb	1.91	ND	-
Sr	169	162.5	4
Y	17.0	15.4	9
Zr	60.6	60.6	0
Nb	ND	13.0	-

The application of EDXRF technique in this work has been successful in the determination of elements from the *Fadama* soil. Most of the elements identified are heavy metals of environmental concern. The elements determined were: Si, Ca, K, Ti, V, Fe, Co, Zn, Rb, Sr, Y, Zr and Nb. Only V, Fe, Co and Zn fell within the plants toxic limits as reported by Bowen [8]. However, the maximum values of most the elements except V, Zr and Zn are found to be below the given world range. The mean value of K is lower than that of the world. In most cases the median values of the present experiment show close agreement with that of the world median [7]. On the other hand, median values of measured elements except V, Zn and Zr are below to the World median [8]. The concentrations of major elements (major nutrients) such as K are in the range of 1.26-2.62%. On the regional scale, these soils are relatively rich in several heavy metals such as potassium, vanadium and yttrium. Vanadium is toxic to humans and other animals [8]. The concentration of V varies between 10.75- 124.94 ppm which is within the world mean range.

Table 5 Range, mean and median value for Fadama soils and world soils. All values are in % otherwise in ppm.

Soil from Fadama area (n=10)					World[1]		
Element	Range	Mean	$\pm$ SD	Median	Range Mean	Mea n	Median
Si%	28.52-37.74	33.74	3.23	32.45	NA	7.13	7.
K%	1.92-2.62	2.36	0.22	2.46	NA	1.4	1.4
Ca%	0.29- 0.52	0.38	0.08	0.35	NA	1.37	1.5
Ti (%)	0.38-0.52	0.45	0.04	0.45	0.1-0.9	0.46	0.5
V	10.77-124.94	27.14	49.07	67.86	3-500	100	90
Fe (%)	1.03-1.53	1.16	0.08	1.14	NA	0.63	4
Co	8.20-22.70	12.89	3.75	12.61	NA	850	8
Zn	57.36-201.82	107.17	55.93	80.24	NA	0.63	90
Rb	97.42-129.16	117.17	12.69	113.67	NA	7	150
Sr	54.89-76.38	66.13	8.28	63.05	NA	NA	250
Y	32.2-85.60	52.34	17.63	42.92	NA	NA	NA
Zr	821.68-1018.01	712.64	268.02	882.90	NA	NA	NA
Nb	25.78-34.32	28.15	6.95	29.65	NA	NA	NA

NA=NOT AVAILABLE

The lowest and highest concentrations of Ti are 0.38% and 0.52% which is within the limiting values of world soil (0.1-0.9 %).

Table 6 Elemental Enrichment Factors

Eement	Range	Mean	$\pm$ SD	Median
K	0.95-1.12	1.042	0.057	1.03
Ca	0.05-0.54	0.166	0.188	0.07
Ti	0.45-0.72	0.592	0.101	0.6
V	0.06-0.66	0.144	0.259	0.36
Fe	0.12-0.19	0.152	0.023	0.15
Co	0.2-0.72	0.444	0.182	0.44
Zn	0.56-2.19	1.176	0.663	0.76
Rb	0.93-1.43	1.228	0.175	1.38
Sr	0.11-0.18	0.138	0.027	0.12
Y	0.78-2.0	1.364	0.389	1.3
Zr	2.0-5.15	3.886	1.233	4.24
Nb	0.57-1.54	1.162	0.336	1.18

The enrichment factors shown in Table6 are the determined elements are calculated with the help of the following equation:

$$EF_{Crustal} = \frac{[X]_S / [S_i]_s}{[X]_C / [S_i]_C}$$

where $[X]_S$ is the concentration of element in the sample, $[X]_C$ is the concentration of the element in the earth crust, $[S_i]_S$ concentration of silicon in the sample and $[S_i]_C$ concentration of silicon in the earth crust.

The values of the enrichment factors are shown in Table 5. Elements that show enrichment are K, Zn, Rb, Y, Zr, and Nb. The other elements are depleted. A four class grouping of trace in soils according to their toxicity was reported by Wood [10]. Based on this classification, the enrichments of the element determined from the *Fadama* soils were plotted to show the extent of soil enrichments (Fig2).

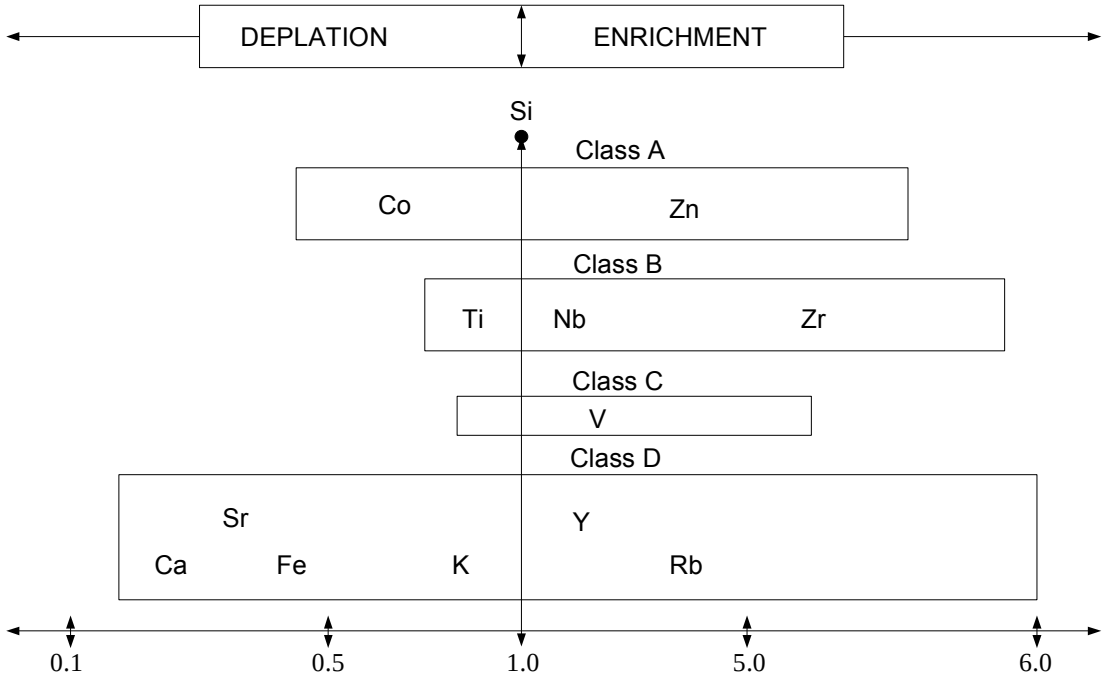

Fig. 2: A schematic representation of the Fadama Soil enrichments.

4. Conclusion

The study clearly showed that in certain location, the soil samples have higher values of concentration (mean, median and range) compared to that of the world which indicating that the soils of these sites have been contaminated by the activities carried out around the study area. The measured results show that surface soils in this region are polluted to a certain extent with several metals, for example the concentration of Si, K , Ti V, Y, Zr and Nb. The contamination level is relatively high for V. However, there are no available scientific studies that indicate the harmful effects of these pollutants on the human population or other biological species. Still, large amounts of vegetables and fruits are harvested in the gardens and farmlands by the people of the surrounding area. It is therefore, necessary to determine the levels of heavy metals and other trace elements in soils, and uptake by vegetations and other biological species and take appropriate steps to protect the people from the health hazard of the excessive levels of metals. The degree of soil pollution around the *Fadama* area poses a risk to human health, because it may pollute the fresh water sources that supply drinking water to the Zaria inhabitants and the nearby areas. Further studies should be carried out to understand the full-phase level of contamination in the water and vegetation of the nearby areas of the *Fadama* area.

The degree of soil pollution around the *Fadama* area may indicate a risk for human health also in connection with pollution of water sources supplying the city with drinking water. Further studies should be carried out in all areas where excessive levels are shown in the surface soils, even if the reason is a high natural content, in order to see to what extent growing of agricultural crops on these soils affects the concentration of the heavy metals naturally present in the *Fadama* soils.

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