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Elemental Composition in Soil Profiles around an Aluminum Smelting Industry-Alscon in Ikot Abasi, Nigeria, Using XRF Technique

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Abstract

Accumulation of trace elements in soil is a major concern globally due to the effects on the ecosystem and in particular, the carcinogenic and mutagenic health risks to humans. Soil samples taken randomly from two soil profiles (depths 0-15 cm and 15-30 cm) around an aluminium smelting plant (ALSCON) in Ibekwe, in Ikot Abasi Local Government Area of Akwa Ibom State, Nigeria were analysed for trace elements. X-ray fluorescence spectrometer-SPECTRO X-LAB 2000 analyser was used to determine the elements in the soil. The abundance of elements in soil followed the order: Zr>Ce>La>Zn>Y>Pb>Th>Hf>U>Sb>Mo>As>Bi in the topsoil and Zr>Ce>La>Zn>Pb>Y>Th>Hf>U>Sb>As>Mo>Bi in subsoil. Elements in soil profiles, except for Zr, Sb,Bi and U were within the earth's crust's mean/range values hence pose no risk to human, animal and plant lives. Significant correlations were found between Zn/Ce, As/Hf, Y/Pb,Th,Bi, Zr/Hf, La/Pb,Th, Pb/Bi,Th and Bi/U in both profiles, and Sb/Bi,U in the top soil. Dendrograms using Ward's method with Euclidean distance grouped locations HAB, CA and NE into the same cluster for both profiles while the elements appeared in five clusters. Five principal components extracted from the topsoil were explained by 99.92% of total variations and four from the subsoil explained by 96.86% of total variations.

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Three indices of pollution were used to determine the soil status; there is moderate contamination of top and subsoil with Bi and U, and very high contamination with Sb, suggesting anthropogenic input. Bi, U and especially Sb are of immediate concern. Monitoring of this environment is therefore required to determine any health risk to the community from possible metals contamination of food plants, surface and ground water.

Keywords: Elements; aluminium smelter; Soil contamination; X-ray fluorescence (XRF)

1. Introduction

In recent years, significant attention has been paid to problems of environmental contamination by wide variety of chemical pollutants including heavy metals [1, 2, 3, 4]. These metals enter the environment from both natural and anthropogenic sources causing water, air and soil pollution [5, 6, 7]. The distribution of metal between soils, invertebrates and vegetation is reported to be a key issue in assessing environmental effects of metals [6, 8]. The soil serves as sink to dispose of undesirable materials, and a transmitter of many pollutants to surface water, ground water, atmosphere and food [9, 7]. It also constitutes the medium on which plants grow, and the platform on which industrialization takes place. Increasing level of industrialization and urbanization however, is causing environmental pollution the world over [10, 5, 11, 12, 13].

Industries discharge pollutants containing heavy metals such as zinc, copper, manganese, cadmium, nickel, mercury, lead, chromium, iron and cobalt in excess of natural levels into the environment [2, 11, 12, 4]. Mining, smelting, manufacturing, and the use of synthetic products (e.g. pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge) are industrial processes that are implicated in heavy metal contamination of urban and agricultural soils [14, 15, 16,17].

Soil pollution therefore, may threaten human health through its effects on hygiene quality of food and drinking water. Preventing soil pollution and the harmful effects demands knowledge of the soil composition; hence this study aims at determining the levels of some essential, trace and rare earth elements in the top and subsoils around an aluminum smelting industry (ALSCON) in Ikot Abasi local government area, Nigeria; Identifying the possible sources of elements in soil using multivariate analyses [Pearson's correlation matrix, cluster analysis (CA) and principal component analysis (PCA)]; assessing the pollution status of top and subsoils in the study area using pollution indices- contamination factor (CD), degree of contamination (DC) and geoaccumulation index (I_{geo}); and evaluating the influence of human activities on element accumulation in the soil profiles using enrichment factor (EF).

2. Materials and Methods

Ikot Abasi Local Government Area is an industrial area of Akwa Ibom State. It is located in the South West corner of Akwa Ibom on latitude 40` 32` to 40^{o} N and longitude 70` 25` to 70^{o} 45`E, and bounded by Oruk nam Local Government in the North, Mkpat Enin and Eastern Obolo Local Government Areas in the West and the Atlantic Ocean in the South. The Imo River forms a natural boundary in the East separating it from Rivers State (Figure 1). Fishing, trading and subsistence farming are the major occupation of the people.

Samples were collected from two soil profiles-depths of 0-15 cm and 15-30 cm randomly, from five locations around the industry. Each location was made of a composite of five soil samples. The samples collected per location were thoroughly mixed and stored in polythene bags.

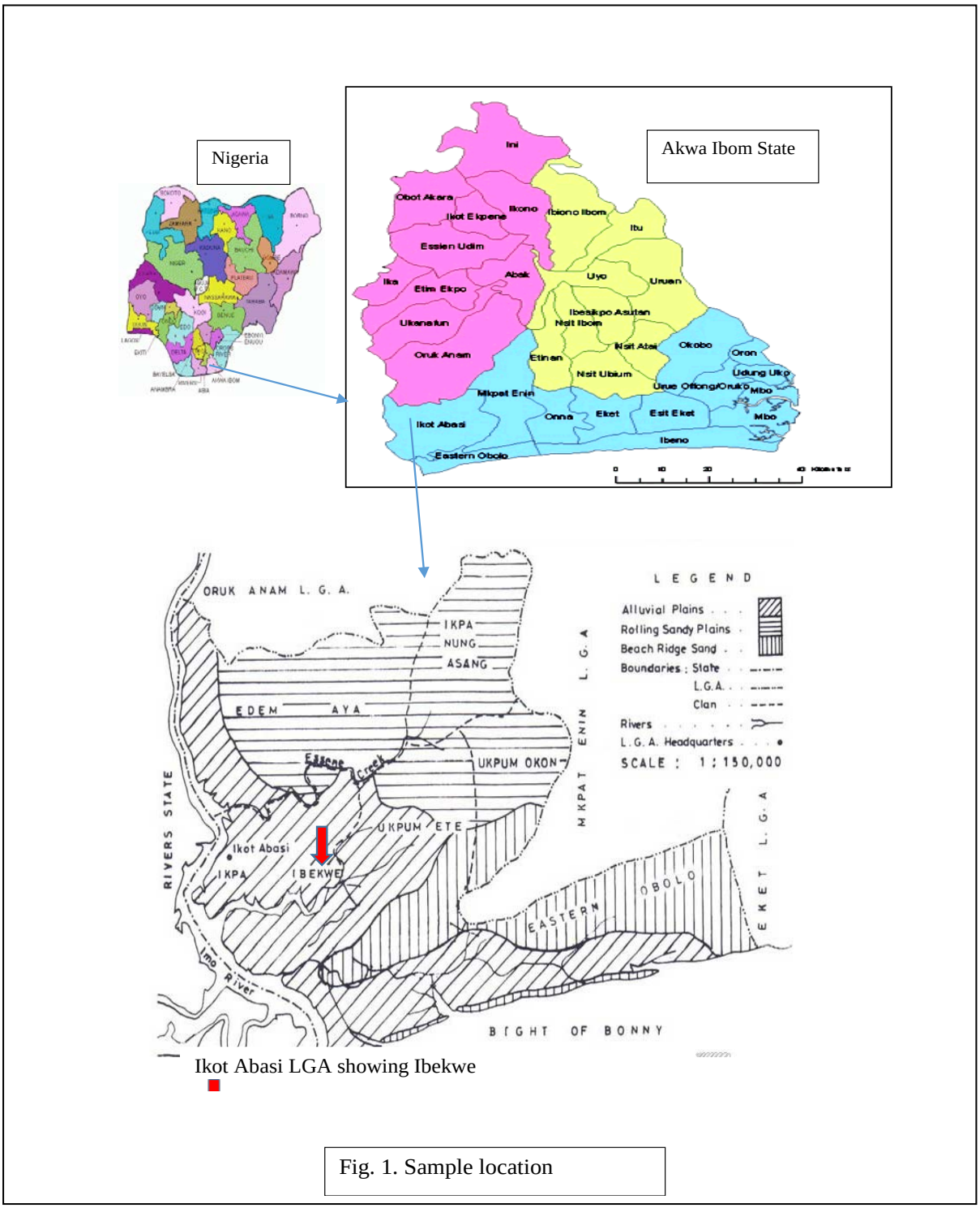


Fig. 1. Sample location

In the Laboratory, the samples were air-dried, ground and passed through 2 mm sieve and stored in labelled Ziploc bags. The elemental composition (Zn, As, Y, Zr, Mo, Sb, La, Ce, Hf, Pb, Bi, Th and U) in the sample were analysed in Ghana using X-ray fluorescence (XRF) spectrometer (SPECTRO-X-Lab 2000). Before

commencing the analysis, pellets from the samples were prepared. About 4-8 grams of the soil sample and 0.9-1.8 gm of the licowax powder were weighed into a metallic dish and allowed to mix for about 3 minutes to a homogenous state. Acetone was added to the mixture and stirred; after evaporation of the acetone, the mixture was then placed in the die and pressed with the press pellet machine (pressure of 10 to 15 tons). With the press pellet set, it was then inserted into the XRF machine for analysis.

Soil contamination was assessed using contamination factor (CF), degree of contamination (DC), enrichment factor (EF) and geoaccumulaton index (Igeo); with their calculations based on the modified formula suggested by Hankanson [10], Chester and Stoner [18], Hernandez et al. [19], and using the background values given by Kabate-Pendias [6] and Müller [20], in addition to multivariate analysis.

$$CF = \frac{C_n}{B_n} \quad - \quad - \quad - \quad - \quad (1)$$

$$CD = \sum CF \quad - \quad - \quad - \quad - \quad (2)$$

$$EF = \left[\frac{C_n / X_{n(ref)}}{C_r / X_{r(ref)}} \right] \quad - \quad - \quad - \quad - \quad (3)$$

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right] \quad - \quad - \quad (4)$$

Where C_n is the concentration of the element in the soil sample, B_n is the background concentration of soil in the earth crust [6], $X_{n\,(ref)}$ is the concentration of the reference element in the soil sample use for normalization, C_r is the concentration of the element in the earth crust, and X_r (ref) is the concentration of reference element used for normalization in the crust. For this study, Zr is used as the reference element (X).

- Four categories have been defined for contamination factor (CF, Eqn. 1)- <1 low contamination, ≥1 to <3 moderate contamination, ≥3 to <6 considerable contamination, and ≥6 very high contamination; and four for degree of contamination (DC, Eqn. 2)- <8 low degree of contamination, ≥8 to <16 moderate degree of contamination, ≥16 to <32 considerable degree of contamination and ≥32 very high contamination.
- Enrichment factor (EF, Eqn. 3) is classified into five contamination categories- <2 deficiency to minimal enrichment, ≥2 to <5 moderate enrichment, ≥5 to <20 significant enrichment, ≥20 to <40 very high enrichment, and ≥40 extremely high enrichment.

- Geoaccumulation index (I_{geo}, Eqn. 4) is divided into seven classes as by Müller: $I_{geo} \leq 0$ -Class 0, unpolluted; $0 < I_{geo} \leq 1$ -Class 1, unpolluted to moderately polluted; $1 < I_{geo} \leq 2$ -Class 2, moderately polluted; $2 < I_{geo} \leq 3$ -Class 3, moderately polluted to strongly polluted; $3 < I_{geo} \leq 4$ -Class 4, strongly polluted; $4 < I_{geo} \leq 5$ -Class 5, strongly polluted to extremely polluted; and $I_{geo} > 5$ -Class 6, extremely polluted.
- Multivariate statistical analyses using Principal Component Analysis (PCA), Cluster Analysis (CA) and Pearson's correlation coefficients are conducted to identify relationships between elements in soil.

Analytical quality control and quality assurance are obtained using triplicate measurements and reagent blanks. International Centre for Diffraction Data (ICDD) certified reference soil GSR-02 (Andesite) is used for the validation of analytical techniques and the recovery ranges from 78%-120%. Statistical analyses were performed using SPSS version 11, Statgraphics IX and Microsoft Excel.

3. Results and Discussion

Elemental compositions in two soil profiles-topsoil (0-15 cm) and subsoil (15-30 cm) at different locations around a moribund aluminum smelting company (ALSCON) in Akwa Ibom State, and the descriptive statistics are presented in Tables 1 and 2, respectively and Pearson's correlation coefficients in Tables 3 and 4, respectively for top and subsoils.

3.1. Essential elements (Zn and Mo)

The levels (mg/kg) of Zn range 11.60-19.40 in the topsoil and 10.60-14.90 in the subsoil, with mean 14.0±3.65 and 12.9±1.78, respectively for top and subsoils. Zinc level in the study did not exceed levels in the continental crust (Table 3); and comparatively lower than values reported in soils in Lagos-Nigeria (25.87-198.32), Ethiopia (140.9-302.8) and U.S.A. (12.60-183.0) [21, 22, 23]. Zinc correlated positively with Ce in both the top and subsoils. In the topsoil, Zn correlated positively with La and Pb, and negatively with As; while in the subsoil, it correlated positively with Y and negatively with Zr and Hf (Tables 3 and 4). The metal is used in many industries for the production of plastics, lubricants, pesticides, pigments and rubber. The anthropogenic sources of Zn in soils include industry and agricultural practices [6].

Molybdenum (Mo) level in the top and subsoils is the same (1 mg/kg) in all the sample locations, and is higher than the value reported in U.S.A. (0.17 mg/kg), but lower than in Ethiopia (1.23 mg/kg) [22, 23]. Negative correlation was found between Mo and Sb, Bi and U in the topsoil (Tables 3 and 4). Molybdenum is considered an essential trace element in animals, plants and humans. It is very vital in human nutrition for the processing of amino acids. Molybdenum, though essential in human health, can be toxic in large amounts. Industrial pollution from smelting, processing of metals, and oil refining could result in elevated levels of Mo in soil [6].

3.2. Toxic elements (As, Pb, Sb, Th, U)

The arsenic (As) range (mg/kg) is 0.6-1.3 (topsoil) and 0.5-2.40 (subsoil), with mean values of 0.95±0.35 (topsoil) and 1.28±0.80 (subsoil).

Table 1: Metals content in two soil profiles around a smelting industry in Ikot Abasi, Nigeria

		Metals (mg kg^{-1})												
Soil profile	Location	Zn	As	Y	Zr	Mo	Sb	La	Ce	Hf	Pb	Bi	Th	U
0-15 cm	HAB1	19.40a	0.70d	7.00bc	296.9dc	1.00a	1.50a	27.90a	36.53a	1.70d	8.00a	0.50a	5.67b	2.00a
	CA1	13.00b	0.60e	6.90c	310.6c	1.00a	1.50a	14.10c	3.00d	1.30e	6.50d	0.50a	6.10a	2.00a
	NE1	12.00c	1.20c	7.50ba	282.6d	1.00a	1.50a	2.00e	31.33b	1.80c	6.70c	0.50a	4.50c	2.00a
	BC1	11.60d	1.30b	7.70a	608.9a	1.00a	1.50a	18.70b	31.20b	5.20a	7.80b	0.50a	6.40a	2.00a
	Control	9.50e	1.40a	4.60d	408.8b	1.00a	1.50a	11.20d	11.90c	2.10b	5.10e	0.57a	3.50d	2.00a
	LSD	0.328	0.041	0.581	14.85	0.089	0.163	0.269	3.702	0.081	0.199	0.094	0.308	0.163
15-30 cm	HAB2	10.60d	2.40a	4.73d	393.6a	1.00a	1.50a	20.40c	26.40c	2.30a	6.90c	0.50b	4.20d	2.00a
	CA2	14.90a	0.50a	6.80b	287.7c	1.00a	1.50a	22.00b	34.40a	1.50b	7.30b	0.50b	5.00b	2.00a
	NE2	12.80c	1.20a	5.40c	343.2b	1.00a	1.50a	15.00d	28.80b	2.30a	6.60d	0.50b	4.40c	2.00a
	BC2	13.30b	1.00a	7.70a	408.3a	1.00a	1.50a	24.80a	28.40b	2.30a	7.70a	0.60a	7.10a	2.00a
	Control	13.30b	1.00a	7.70a	408.3a	1.00a	1.50a	24.80a	28.40b	2.30a	7.70a	0.60a	7.10a	2.00a
	LSD	0.453	2.537	0.124	15.4	0.00	0.00	0.810	0.763	0.00	0.081	0.00	0.199	0.00

Means with the same letters are not significantly different at α=0.05, n=15, LSD (Least significant difference)

Table2: Descriptive statistics of elements distribution in soils from the study area compared to other levels (mg/kg)

	0-15 cm		15-30 cm		Continental crust values		*World median	Turkey
Element	Median	Mean ± sd (Range)	Median	Mean± sd (Range)	[25]	[25, 26]		mean (Range)
Zn	12.0	14.0±3.65 (11.6-19.4)	13.3	12.9±1.78 (10.6-14.9)	52.0	71.8	*90.0 #70.0 a,b	45.0 (6.0-165)
As	1.20	0.95±0.35 (0.60-1.30)	1.00	1.28±0.80 (0.50-2.40)	2.00	1.50	*6.00 #1.80b	8.00 (1.90-51.0)
Y	7.00	7.28±0.39 (6.90-7.70)	6.80	6.16±1.34 (4.73-7.70)	20.7	22.0	- #12.0a	- -
Zr	310.6	374.8±156.5 (301.6-608.9)	393.6	358.2±54.6 (282.7-408.3)	237.0	190.0	- #100-200 (305)b	- -
Mo	1.00	1.00±0.00 (0.00)	1.00	1.00±0.00 (0.00)	1.40	1.50	*1.20 #1.1b	0.60 (0.08-4.60)
Sb	1.50	1.50±0.00 (0.00)	1.50	1.50±0.00 (0.00)	-	-	*1.00 #0.2-0.9 (0.2)b	0.90 (0.20-6.70)
La	14.1	15.68±10.8 (2.00-27.9)	22.0	20.55±4.12 (15.0-24.8)	32.3	30.0	*40.0 #30.0b	26.0 (11.5-59.7)
Ce	31.2	25.52±15.2 (3.00-36.53)	28.4	29.5±3.43 (26.6-34.4)	-	-	*50.0 #60.0b	69.0 (30.0-150)
Hf	1.80	2.50±1.81 (1.30-5.20)	2.30	2.10±0.4 (1.50-3.30)	-	-	*6.00 #3.00-4.90 (6.4)b	5.50 (2.20-10.0)
Pb	6.70	7.12±0.94) (6.50-8.00)	7.30	7.12±0.48 (6.60-7.70)	17.0	20.0	*35.0 #15.0b	33.0 (4.80-968)
Bi	0.50	0.50±0.00 (0.00)	0.50	0.52±0.05 (0.50-0.60)	-	-	- #0.20b	- -
Th	5.67	5.67±0.83 (4.50-6.40)	5.00	5.18±1.33 (4.20-7.10)	10.3	10.7	*9.00 #3.60-9.60b	9.00 (4.00-240)
U	2.00	2.00±0.00 (0.00)	2.00	2.00±0.00 (0.00)	2.50	2.80	*2.00 #0.90-1.70b	2.60 (1.30-5.50)

* [2], # [6], aWorldwide mean and bEarth crust (mean or range) [6].

It is lower than the levels recorded in the earth's crust, Lagos State (7.08) and Ethiopia (12.06) (Table 2, [21, 22]). Kabata-Pendias [6] reported elevated As level, up to 732 mg/kg for Slovakian soils in some locations (400-folds higher than in the present study), and 0.9-3.4 mg/kg in soils of Poland-with the highest levels in soils from shales. There was positive correlation between the following: As/Zr and Hf (topsoil) and As/Hf (subsoil); and negative correlation between As/Th and Zn (topsoil) (Tables 3 and 4). Arsenic is released into the atmosphere

from both natural (volcanic, absent in Nigeria) and anthropogenic sources such as smelting of metals, industrial wastes, manufacture of pesticides and Pb-acid batteries [6]. Arsenic in soil can be bioavailable for plant uptake, thus posing significant health risk.

Lead (Pb) levels in the soil samples range (mean±sd) mg/kg6.50-8.00 (7.12±0.94) and 6.60-7.70 (7.12±0.48) in top and subsoils, respectively. The value of Pb (8 mg/kg) in the present study is lower than values reported in Lagos State (69.20 mg/kg), Ethiopia (235.5 mg/kg) and U.S.A. (55.4 mg/kg) [21, 22, 23].

Lead correlated positively positively with Zn, Y, La, Ce and Th, and negatively with Bi in the topsoil; and positively with Y, La, Bi and Th in the subsoil (Tables 3 and 4). In soils, lead is bioavailable for plant uptake and storage. The effects of acute lead poisoning include kidney damage, brain damage, miscarriage, behavioral disruptions in children, high blood pressure and disruptions of the nervous system [27].

Table 3: Pearson's correlation coefficients for metals in 0-15 cm soil profile

	Zn	As	Y	Zr	Mo	Sb	La	Ce	Hf	Pb	Bi	Th	U
Zn	1	**-.722****	.366	-.420	-.016	.016	**.725****	**.537***	-.285	**.702****	-.385	.435	.016
As		1	-.312	**.566***	-.056	.056	-.465	.126	**.541***	-.381	.445	**-.538***	.056
Y			1	.077	.224	-.224	.106	.505	.306	**.818****	**-.843****	**.707****	-.224
Zr				1	.018	-.018	.191	.094	**.955****	.173	.070	.286	-.018
Mo					1	**-1.000****	.013	.005	-.026	.070	**-.674****	-.084	**-1.000****
Sb						1	-.013	-.005	.026	-.070	**.674****	.084	**1.000****
La							1	.327	.187	**.611***	-.164	**.542***	-.013
Ce								1	.333	**.727****	-.314	.165	-.005
Hf									1	.385	-.066	.388	.026
Pb										1	**-.654****	**.777****	-.070
Bi											1	**-.531***	**.674****
Th												1	.084
U													1

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed). N=15

The level of antimony (Sb) is the same (1.50 mg/kg) at all the locations and soil profiles (Table 1). The level is higher than the world's median, the mean value from Turkey (Table 3) and the mean value from the earth's crust [28]. Antimony correlated positively with Bi and U and negatively with Mo in the topsoil (Tables 3 and 4). Recently, Sb and its compounds have been considered by USEPA and the EU to be serious pollutants hence listed in the priority list of hazardous substances [29]. It is used as an alloying element for Pb-acid batteries and, also, in the manufacturing of flame-retardants synthetic fibers [6]. Thorium (Th) range (mean±sd) mg/kg is 4.50-6.40 (5.67±0.83) in topsoil and 4.20-7.10 (5.18±1.33) in the subsoil. The topsoil contained more thorium than the subsoil, but the values were below the world's median (Table 2). Thorium (mg/kg) in uncontaminated soils worldwide range 8.1-11, and in the earth's crust 3.6-9.6.

Table 4: Pearson's correlation coefficients for metals in 15-30 cm soil profile

	Zn	As	Y	Zr	Mo	Sb	La	Ce	Hf	Pb	Bi	Th	U
Zn	1	-.024	**.670****	**-.551***	.^{c}	.^{c}	.259	**.858****	**-.686****	.429	.187	.377	.^{c}
As		1	.188	.400	.^{c}	.^{c}	-.245	-.417	**.678****	-.038	.431	.347	.^{c}
Y			1	.199	.^{c}	.^{c}	**.789****	.298	-.135	**.923****	**.837****	**.928****	.^{c}
Zr				1	.^{c}	.^{c}	.419	**-.835****	**.850****	.385	**.691****	**.537***	.^{c}
Mo					.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}
Sb						.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}
La							1	.066	-.083	**.961****	**.764****	**.810****	.^{c}
Ce								1	**-.943****	.136	-.265	-.059	.^{c}
Hf									1	-.069	.408	.217	.^{c}
Pb										1	**.858****	**.918****	.^{c}
Bi											1	**.976****	.^{c}
Th												1	.^{c}
U													.^{c}

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed) c. Cannot be computed because at least one of the variables is constant. N=15

Soils from other countries have been reported to contain 0.21-53.2 (Europe), 6.1-7.6 (US), 4.0-240 (Turkey) (Table 2, [6]). Positive correlation is observed between Th and Y, La and Pb, negative with As and Bi (topsoil); and positive with Y, Zr, La, Pb and Bi (subsoil) (Tables 3 and 4). Thorium is used as coating material for optical lenses and some metallic wires, and as an addition to metallic alloys [6].

Uranium (U) level in the study area is 2.0 mg/kg at all locations and in the soil profiles. It is within the world's median value, and lower than in Turkey (Table 3) and the earth's crust 0.9-1.7. Uranium in uncontaminated soil worldwide may vary within 1.9-4.4 mg/kg. Kabata-Pendias [6] reported range (mg/kg) in soil of 0.8-11.0 in Europe and 2.3-3.7 in the US, both higher than in the present study. Uranium correlated positively with Sb and Bi, and negatively with Mo in the topsoil (Tables 3 and 4). Compounds of U are used in photography for toning, for special lamps, and in leather, ceramic and wood industries, for strains and dyes. Fertilizers are sources of actinides; in particular U, which is associated with superphosphates fertilizers [6].

3.3. Toxic elements (As, Pb, Sb, Th, U)

Zirconium (Zr) is the most abundant element in the soil profiles. The range (mean±sd) mg/kg is 301.6-608.9 (374.8±156.5) in the topsoil and 282.7-408.3 (358.2±54.6) in the subsoil; it is higher in topsoil than subsoil [30]. The mean values though within the crustal abundance range (20-500 mg/kg) [31], are much higher than those reported by Wedepohl [24] and Taylor and Mclennan [25, 26] (Table 2); and values obtained in Lagos state (0.23-18.5 mg/kg) [21]. Kabata-Pendias [6] and Hutton [32] found average of about 350 mg/kg Zr for Australian soils, which is similar to the mean values obtained in the present study. Zirconium correlated positively with Hf and As in the topsoil; in the subsoil, there was positive correlation with Hf, Bi and Th, and negative with Zn and Ce (Tables 3 and 4). Sources of Zr include anthropogenic emissions into the environment from nuclear fallout, ceramic dusts, heavy metal mining, improper waste dumping, abandoned industrial activity sites, incidental release (e.g., leakage, corrosion) and atmospheric fallout [31, 33]). Although Zr plays no biological role in humans and, generally, not considered as a soil pollutant, high exposure could cause serious illnesses, like cancer, because of its radioactive nature [34].

Hafnium (Hf) content is in the range (mean±sd) mg/kg of 1.30-5.20 (2.50±1.81) in the topsoil, and 1.50-2.30 (2.1±0.4) in subsoil. The mean values are lower than the worldwide mean of 6.4 (range 2.5-12.7) ([6], Table 2). Levels in soils in other countries are reported to range/average (in mg/kg): Bulgaria [35], 1.8-18.7; Canada [36], 1.8-10; EU Russia [37] average 20.8; and Sweden [38], average 7.6. Hafnium correlated positively with As and Zr in both topsoil and subsoil, and negatively with Zn and Ce in subsoil (Tables 3 and 4). Hf occurs mainly in minerals of Zr, such as Zircon (Zr, Hf)SiO_4 and baddeyite, (Zr, Hf, Ti, Fe, Th)O_2, and may also associate with other metals such as biotite and pyroxenes. Hf is used mainly (up to 90% of its production) in the nuclear industry to make super alloys, especially for reactor control rod and coatings for cutting tools. It is applied in photographic flashes. Biometals, also contain Hf due to its good biocompatibility and osteoconductivity [39].

The Yttrium (Y) content range (mean±sd) mg/kg 6.90-7.70 (7.28±0.39) in topsoil and 4.73-7.70 (6.16±1.34) in the subsoil; both lower than the worldwide soil average (range, 7-60) and the world's median ([6], Table 2). Higher values for Y in soils are reported by Ure and Bacon [40] for Great Britain (22 mg/kg) and Duddy [41] for Australia (17 mg/kg). Yttrium correlates positively with Pb and Th, and negatively with Bi in the topsoil;

while the relationship was positive with Zn, La, Pb, Bi and Th in the subsoil (Tables 3 and 4). The metal is used in ceramic, glass and plastic industries and high-temperature bricks. It is also contained in nitrogen fertilizers in a range 2-4 mg/kg [6].

Lanthanum (La) in the study area range (mean±sd) mg/kg is 2.00-27.90 (15.68±10.80) in topsoil and 15.00-24.80 (20.55±4.12) in the subsoil. The highest value of La is lower than the world's median, and the level in the earth's crust (Table 2, [6]). The mean/range values (mg/kg) of La in some countries topsoils are: 33.00 (Sweden), 5.50-33.20 (Swedish forest samples), 15.38 (Australia) and 8-31.40 (Japan) [6]. Lanthanum correlated positively with Zn, Pb and Th (topsoil) and Y, Pb, Bi and Th (subsoil) (Tables 4 and 5).

Cerium (Ce) range (mean±sd) mg/kg of 3.00-36.53 (25.52±15.20) in the topsoil and 26.60-34.40 (29.50±3.43) in the subsoil was lower than the values reported for the earth's crust and world's median (Table 3, [6]). The mean value was higher in the topsoil than in the subsoil; the mean/range values (mg/kg) of Ce in other countries topsoil are: 60.00 (Sweden), 11.00-68.00 (Swedish forest samples), 60.49 (Australia) and 15.80-64.40 (Japan) [6]. Positive correlation was obtained for Cerium with Zn and Pb in the topsoil. Cerium correlated positively with Zn and negatively with Zr and Hf in the subsoil (Tables 3 and 4). Cerium is added to diesel fuel for lowering soot ignition temperature and is slightly trapped by filters [42].

Bismuth (Bi) level in topsoil is 0.50 mg/kg. It has range of 0.50-0.60 mg/kg with a mean of 0.52±0.05 mg/kg in the subsoil. Bi levels in this study are higher than the mean/range values reported for the earth's crust 0.20 (0.13-0.20 mg/kg) [6]. Reported values [6] for different soils - arable Scottish soils derived from different rocks 0.25 mg/kg (range, 0.13-0.42), garden soil of Canada 1.33-1.52 mg/kg and the reference soil of China range 0.04-1.20 mg/kg are all lower than the values in the study. Positive correlation exists between Bi/Sb and U and negative correlation with Y, Mo, Pb and Th in the topsoil; in the subsoil, it correlates positively with Y, Zr, La, Pb and Th (Tables 3 and 4). Bismuth accumulates in coals and in granite shales and is reported to average about 5.00 mg/kg. Sewage sludge, and fertilizers-phosphate in particular, are often significant sources of Bi in soil. It is used in fuses, sprinklers, glass, and ceramics production, as a catalyst in rubber production, and in some metallurgical industries as well as electronic devices. A non-toxic replacement for Pb, Bi is used in several food-processing equipment and recently in pellets [6]. Due to its versatile properties, it is used in pharmaceutical and cosmetic production, dentistry and medicine.

3.4. Cluster analysis

The cluster analysis in this study is based on Ward's method, and the distance metric is the Euclidean. The cluster is used to classify sample locations around ALSCON for two soil profiles, the topsoil (0-15 cm) and the subsoil (15-30 cm) (Fig 2). The dendrogram is interpreted at a similar level (distance coefficient 5), and it identifies 3 clusters and 2 clusters for 0-15 cm and 15-30 cm soil profiles, respectively. Cluster 1 for both profiles is represented by soil samples from locations HAB, CA and NE which show similarity of the top and subsoils in terms of elemental composition, and different from CB1 and the control location (CB2). Cluster 2 is made of soil samples from locations BC1 (for topsoil) and BC2, CB2 (for subsoil). In the subsoil, BC2 is similar to the control location (CB2). Cluster 3 for the topsoil is comprised of sample from the control location (CB1).

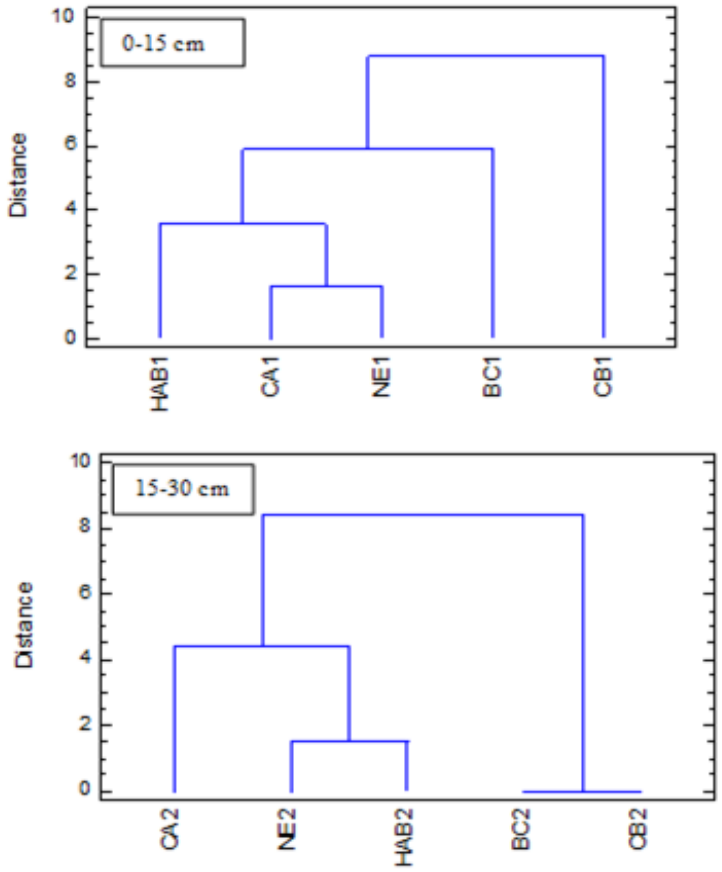


Figure 2: Dendrograms for clusters of sample locations in two soil profiles (0-15 and 15-30) cm around ALSCON using Ward's method.

Cluster analysis is also applied to the samples to enable their classification by the elemental characteristics. The dendrogram derived using the elements (13) as variables is interpreted at a similar level (distance coefficient 3.6) for both profiles; and 6 clusters each are found to exist for both the top and subsoils (Fig.3). Cluster 1 consists of As (arsenic) only for both the top and subsoils. Cluster 2 includes one variable (Bi) in the topsoil, and two variables (Hf and Zr) for the subsoil. Cluster 3 includes two variables (Hf and Zr) in the topsoil, and three variables (Bi, Th and Y) in subsoil. Cluster 4 in topsoil consists of three variables-Ce, Zn and La, while in the subsoil it has two variables- La and Pb. Cluster 5 has three variables in the topsoil (Pb, Th, and Y) and two variables in the subsoil (Ce and Zn). Lastly, Cluster 6 included three variables which were the same Mo, Sb and U in both the top and subsoils. There is similarity in elements in clusters 1 and 6 for both soil profiles; the other clusters are different.

3.5. Factor analysis (Principal component analysis- PCA)

Data from two soil profiles, topsoil (0-15 cm) and subsoil (15-30 cm) from four locations (HAB, CA, NE and BC) are examined for 13 variables. The results of analyses suggest 5 principal components (PCs) for the topsoil and 4 PCs for the subsoil; and are explained by 99.921% and 96.857% of the cumulative variance, respectively (Table 5).

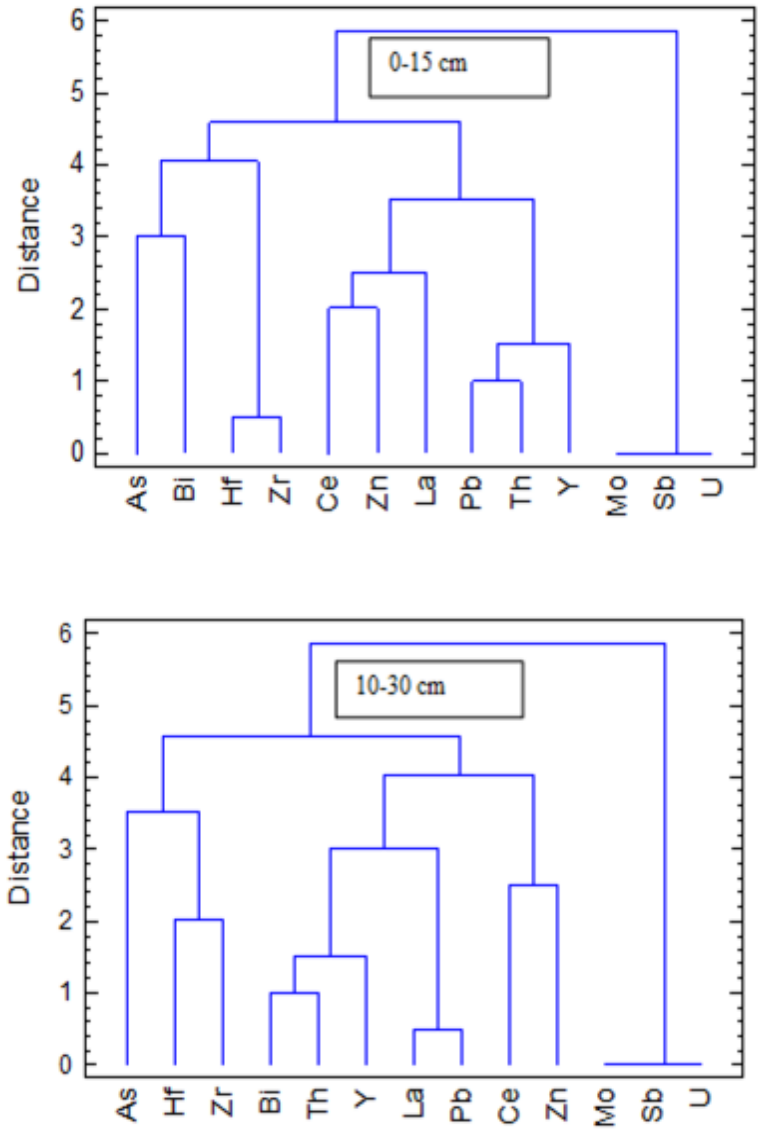


Figure 3: Dendrograms for clusters of elements in two soil profiles (0-15 and 15-30) cm around ALSCON using Ward's method.

Principal Component 1 accounts for 26.511% (topsoil) and 37.433% (subsoil) of total variance. In the topsoil, it shows high positive loadings to Sb and U, moderate positive loading to Bi and high negative loading to Mo. This could come from anthropogenic input related to the activities of the company, poor waste disposal and from agriculture (Mo, Sb, and U are components of fertilizers) [6]. In the subsoil, there is high positive loading to Y, La, Pb, Bi, Th and U, indicating lithogenic source (Y, La and Th occur together in rock minerals), and other anthropogenic sources like fossil fuel combustion and waste Pb-acid batteries disposal (Fig. 4) [2, 6].

Principal Component 2 accounts for 23.536% (topsoil) and 28.505% (subsoil) of the total variance. The positively associated components of PC2 are Y, Th and Pb, Bi the negative, for the topsoil; while in the subsoil,

Zr, Hf and U components associate positively, and Zn and Ce negatively (Fig. 4). The source could be

lithogenic from the rock minerals, and anthropogenic- from the combustion of fossil fuel power plant located in the area [6].

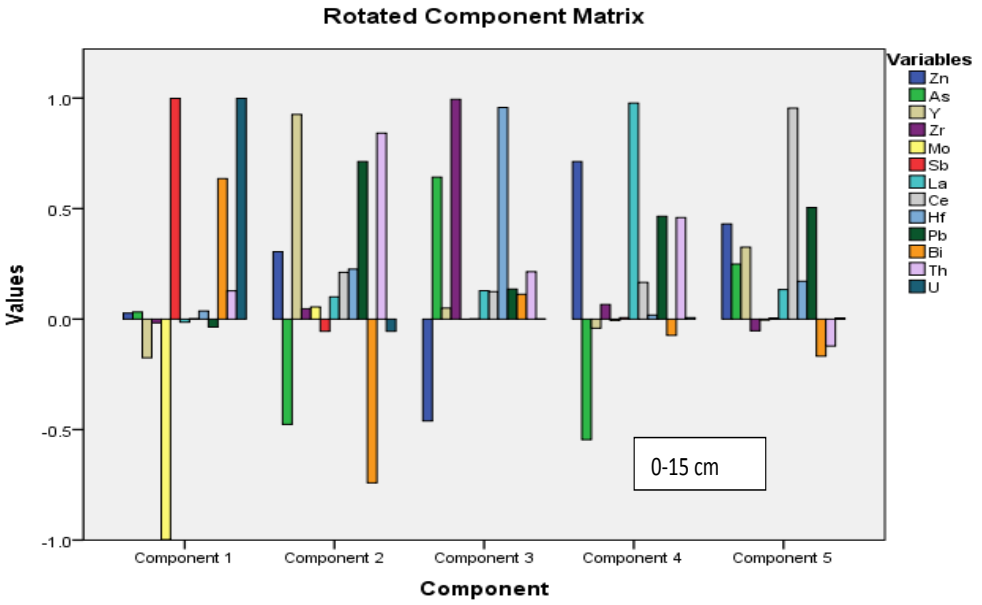
Principal Component 3 accounts for 20.334% (topsoil) and 18.847% (subsoil) of total variance, and is dominated by high positive loading to As, Zr and Hf. Zirconium and hafnium usually are from the same source rock, therefore of lithogenic origin. It may also be the impact of pesticide applications prior to suspension of production at the industrial site [6]. The high positive loadings to Mo and high negative to Sb in the subsoil could be as a result of anthropogenic input from the industry and poor disposal of wastes (Fig. 4, [6]).

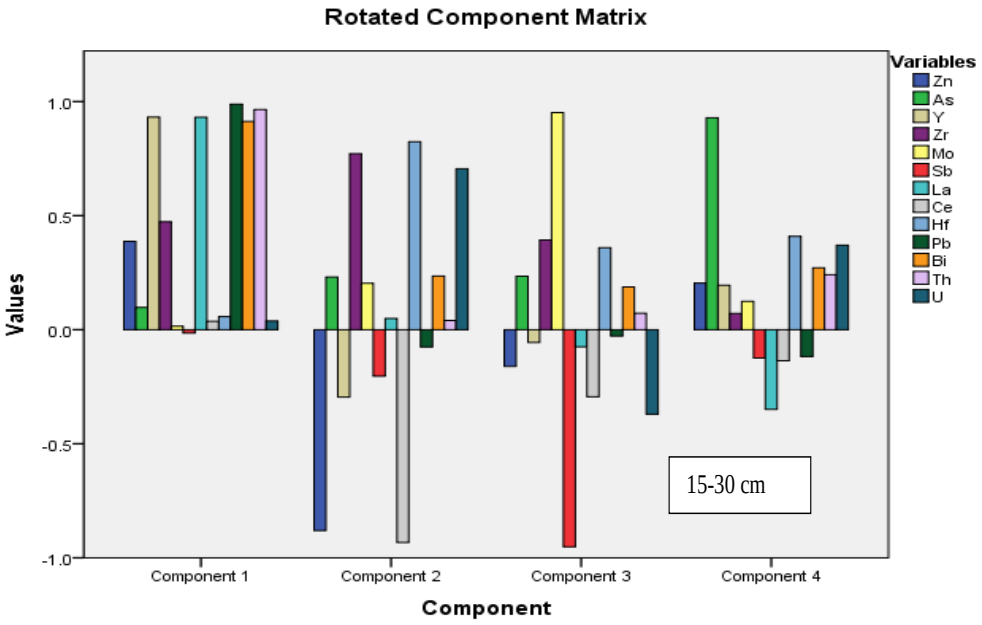
Principal Component 4 accounts for 17.132% (topsoil) and 12.072% (subsoil) of total variance. It shows high positive loading to La and moderate to Zn; while in the subsoil it is high positive loading to As (Fig. 4). This is explained by input from industrial and agricultural sources [6]. Principal Component 5 accounts for 12.408% (topsoil) of total variance, and shows high positive loading to Ce (Fig. 4). This could be natural background levels or from poor waste disposal [2, 6].

Table 5: Total variance explained by principal component analysis for elements in soil profiles

0-15 cm							
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		Rotation Sums of Squared Loadings	
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.780	36.770	36.770	4.780	36.770	36.770	3.446	26.511	26.511
2	3.263	25.102	61.872	3.263	25.102	61.872	3.060	23.536	50.047
3	2.747	21.133	83.005	2.747	21.133	83.005	2.643	20.334	70.381
4	1.116	8.586	91.591	1.116	8.586	91.591	2.227	17.132	87.514
5	1.083	8.330	99.921	1.083	8.330	99.921	1.613	12.408	99.921
15-30 cm							
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		Rotation Sums of Squared Loadings	
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.180	39.843	39.843	5.180	39.843	39.843	4.866	37.433	37.433
2	4.563	35.102	74.945	4.563	35.102	74.945	3.706	28.505	65.938
3	1.660	12.770	87.714	1.660	12.770	87.714	2.450	18.847	84.785
4	1.189	9.143	96.857	1.189	9.143	96.857	1.569	12.072	96.857

Extraction Method: Principal Component Analysis.





Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 5 iterations.

Fig. 4: Rotated component matrices of elements in two soil profiles around ALSCON, Nigeria

3.6. Assessment of soil contamination by elements

The indices of contamination used for assessment in this study are: contamination factor (CF), degree of contamination (DC), enrichment factor (EF) and geoaccumulation index (I_{geo}).

Soil contamination based on CF and DC are presented in Table 6. The mean of CF range is from 0.185 (low contamination) to 7.50 (very high contamination) for the top and subsoils of the study area. Zinc (Zn), As, Y, Mo, La, Ce, Hf, Pb and Th show low contamination in the soil, Bi and U moderate contamination, and Sb very high contamination. The CF value of Zn (moderate contamination) and Pb (very high contamination) reported in auto mechanic workshops in Gboko and Makurdi (central Nigeria) are higher than in the present study [13].

The values for Pb, Zn, Mo, As, and Sb are much lower than in soils of the Bassa industrial zone; while Mo and Sb in the study are higher than in the administrative area soils of Bananjo and Joss in Cameroon [15]. The average of all the locations indicates moderate contamination in the topsoil, and considerable contamination in the subsoil. Locations CA, NE, CD (topsoil) and CA and NE (subsoil) show moderate degree of contamination; and considerable degree of contamination for locations HAB and BC (topsoil) and HAB, BC and CD (subsoil).

The result of enrichment factor (EF) for 12 elements calculated in this study is presented in Fig. 5a and b. The mean values of EF range from 0.282 (Hf) to 5.596 (Sb) in the topsoil, and 0.139 (Zn) to 5.602 (Sb) in the subsoil. The mean values of EF for elements in the topsoil are 0.140 (Zn), 0.431 (As), 0.419 (Y), 0.678 (Mo), 5.596 (Sb), 0.368 (La), 0.283 (Ce), 0.282 (Hf), 0.339 (Pb), 1.917 (Bi), 0.407 (Th) and 0.878 (U), and subsoil 0.139 (Zn), 0.506 (As), 0.403 (Y), 0.679 (Mo), 5.602 (Sb), 0.533 (La), 0.365 (Ce), 0.250 (Hf), 0.361 (Pb), 2.017 (Bi), 0.433 (Th) and 0.879 (U). Zinc (Zn), As Y, Mo, La, Ce, Hf, Pb, Th and U in both topsoil and subsoil and, Bi in topsoil have EF<2 indicating deficiency to minimal enrichment in the soil. In the subsoil however, Bi shows moderate enrichment 2 >EF<5. Antimony (Sb) with the highest value, is significantly enriched in both top and subsoils 5>EF<20. The deficiency to minimal enrichment of Zn, Pb and Y in soils in the present study is as reported in the Ghana river basin [4, 12].

Geoaccumulation index values in the study area are represented in Figure 5c and d. The range and (mean value) are as follows: -2.40 to -1.69 (-2.11) for Zn, -1.50 to -0.66(-1.01) for As, -1.36 to -0.85(-0.99) for Y, -3.11to -0.48(-1.40) for La, -3.40to-0.90 (-1.69) for Ce, -.1.99 to -0.61(-1.51) for Hf, -1.48 to -1.03 (-1.21) for Pb, 0.51 to 0.64 (0.54) for Bi, -1.41 to – 0.81 (-1.04) for Th in the topsoil; and-2.29 to -1.95 (2.09) for Zn, -1.69 to -1.12 (-0.92) for As, -1.34 to – 0.85 (- 1.04) for Y, -1.09 to -0.59 (-0.76) for La, -1.23 to -0.96 (-1.13) for Ce, -1.86 to -

1.43 (-1.51) for Hf, -1.23 to -1.07 (-1.14) for Pb, 0.51 to 0.69 (0.58) for Bi, -1.23 to -0.71 (-0.98) for Th in the subsoil. The same value of I_{geo} was obtained for Mo (-0.50), Sb (1.61), U (-0.24) in both soil profiles.

The study area is moderately polluted with Sb (class 2), unpolluted to moderately polluted to Bi (class 1) and unpolluted to Zn, As, Y, Mo, La, Ce, Hf, Pb, Th and U (in class 0). I_{geo} values show the soil profiles in the industrial area are not polluted with Pb and Zn; the finding is similar to those reported around a cement factory [43] and in a mining area [4].

Table 6: Contamination Factor (CF)

Location	Soil profile	Zn	As	Y	Mo	Sb	La	Ce	Hf	Pb	Bi	Th	U	**DC***
HAB	0-15 cm	0.277	0.389	0.583	0.909	7.500	0.930	0.609	0.266	0.533	2.500	0.591	1.176	16.263 (**C**)
CA	0-15 cm	0.186	0.333	0.575	0.909	7.500	0.470	0.050	0.203	0.433	2.500	0.635	1.176	14.971 (**M**)
NE	0-15 cm	0.171	0.667	0.625	0.909	7.500	0.067	0.522	0.281	0.447	2.500	0.469	1.176	15.334 (**M**)
BC	0-15 cm	0.166	0.722	0.642	0.909	7.500	0.623	0.520	0.813	0.520	2.500	0.667	1.176	16.758 (**C**)
CD	0-15 cm	0.136	0.778	0.383	0.909	7.500	0.373	0.198	0.328	0.340	2.850	0.365	1.176	15.337 (**M**)
	Min	0.136	0.333	0.383	0.909	7.500	0.067	0.050	0.203	0.340	2.500	0.365	1.176	
	Max	0.277	0.778	0.642	0.909	7.500	0.930	0.609	0.813	0.533	2.850	0.667	1.176	
	Mean	**0.187**	**0.578**	**0.562**	**0.909**	**7.500**	**0.493**	**0.380**	**0.378**	**0.455**	**2.570**	**0.545**	**1.176**	15.733 (**M**)
		L	**L**	**L**	**L**	**VH**	**L**	**L**	**L**	**L**	**M**	**L**	**M**	
HAB	15-30 cm	0.151	1.333	0.394	0.909	7.500	0.680	0.440	0.359	0.460	2.500	0.438	1.176	16.341 (**C**)
CA	15-30 cm	0.213	0.278	0.567	0.909	7.500	0.733	0.573	0.234	0.487	2.500	0.521	1.176	15.691 (**M**)
NE	15-30 cm	0.183	0.667	0.450	0.909	7.500	0.500	0.480	0.359	0.440	2.500	0.458	1.176	15.623 (**M**)
BC	15-30 cm	0.190	0.556	0.642	0.909	7.500	0.827	0.473	0.359	0.513	3.000	0.740	1.176	16.885 (**C**)
CD	15-30 cm	0.190	0.556	0.642	0.909	7.500	0.827	0.473	0.359	0.513	3.000	0.740	1.176	16.885 (**C**)
	Min	0.151	0.278	0.394	0.909	7.500	0.500	0.440	0.234	0.440	2.500	0.438	1.176	
	Max	0.213	1.333	0.642	0.909	7.500	0.827	0.573	0.359	0.513	3.000	0.740	1.176	
	Mean	**0.185**	**0.678**	**0.539**	**0.909**	**7.500**	**0.713**	**0.488**	**0.334**	**0.483**	**2.700**	**0.579**	**1.176**	16.285 (**C**)
		L	**L**	**L**	**L**	**VH**	**L**	**L**	**L**	**L**	**M**	**L**	**M**	

L, M and V means low, moderate and very high contamination * **(M)** and **(C)** for moderate and considerable degree of contamination **(DC)**

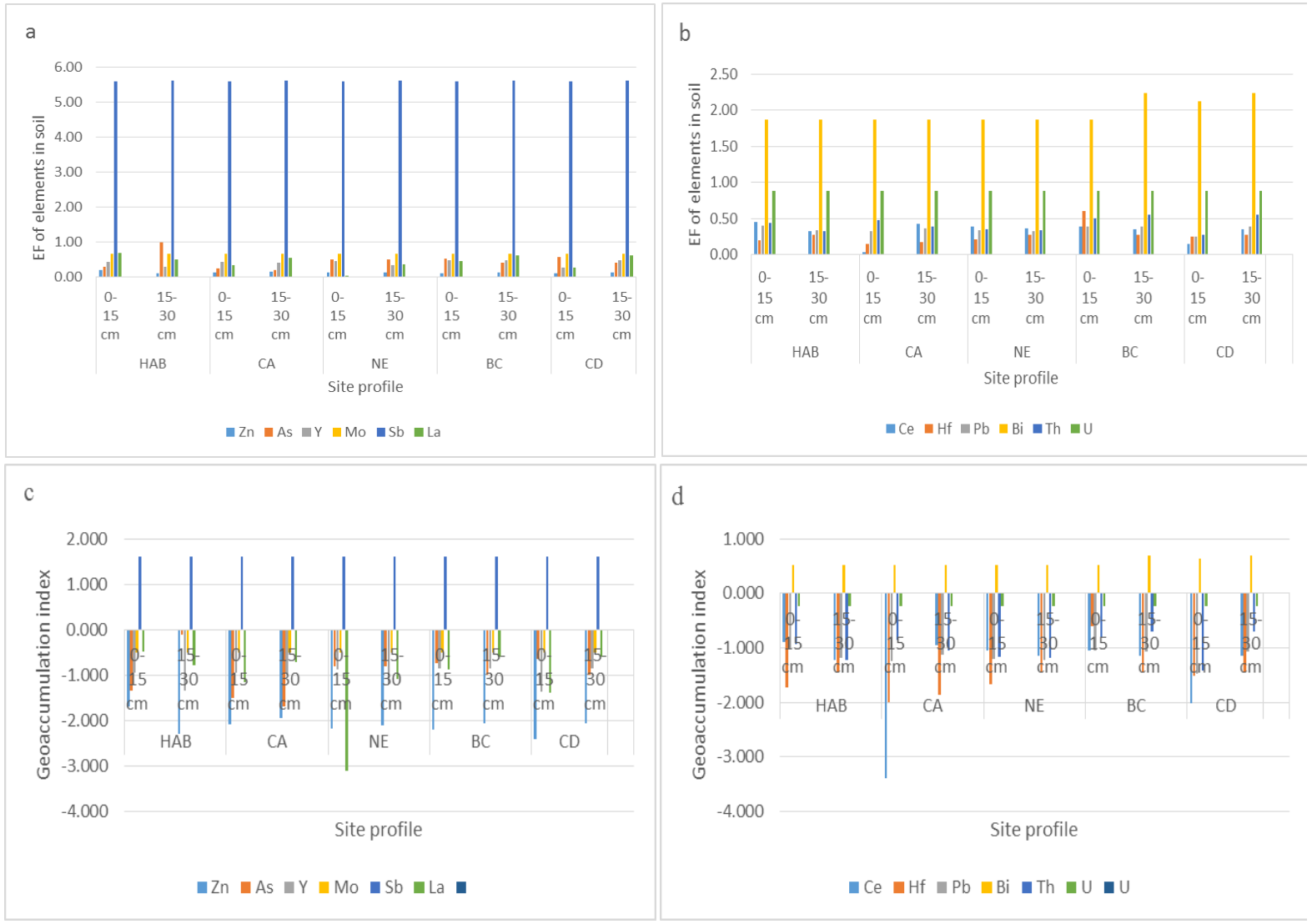


Fig. 5: Enrichment factor (EF) and geoaccumulation index of elements in two soil profiles around ALSCON, Nigeria

4. Conclusion

Assessment of elemental composition in the top and subsoils around a moribund aluminum smelting industry in Ikot Abasi Local Government Area of Akwa Ibom State, Nigeria has shown that the levels of toxic elements in the area are within the range in the earth's crust, except for Zr, Sb, Bi and U. The relative abundance of elements in soil followed the Pattern: Zr>Ce>La>Zn>Y>Pb>Th>Hf>U>Sb>Mo>As>Bi in the top-soil and Zr>Ce>La>Zn>Pb>Y>Th>Hf>U>Sb>As>Mo>Bi. Significant correlations were observed between Zn/Ce, As/Hf, Y/Pb,Th,Bi, Zr/Hf, La/Pb,Th, Pb/Bi,Th and Bi/U in both soil profiles.

The degree of contamination of the locations range from moderate to considerable; locations HAB and BC indicate considerable degree of contamination in both soil profiles. Bismuth (Bi) and uranium (U) have moderate contamination factor; Sb however, has very high level of contamination with significant enrichment in the soil profiles, suggesting contaminating sources as anthropogenic in origin. Geoaccumulation index, classifies the soil as moderately polluted with Sb, and unpolluted to moderately polluted with Bi.

Bi, U and especially Sb are of immediate concern. A study to assess the impact of the metals in food plants, surface and ground water should determine if the community is exposed to any health risk.

Acknowledgment

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