Geochemical Effects Of Mineralization In Arufu Area NE Nigeria: Implication On Human Health

Ekeleme I. Aquila
Petroleum Trust And Development Fund, Chair, Department Of Geology And Mining, University Of Jos, Nigeria
Uzoegbu M. Uche
Geology Programme, Abubakar Tafawa Balewa University, Bauchi, Nigeria
Olorunyomi A. Enoch
Petroleum Trust And Development Fund, Chair, Department Of Geology And Mining, University Of Jos, Nigeria

Abstract:
The sulphide mineralization in Arufu and environs, northeastern Nigeria was investigated with the view of determining the concentrations of selected trace elements in soils, to examine the mineralization potential and their possible health implications. The stratigraphy of the study area shows a dominance of altered carbonates of the Asu River Group which also hosts the mineralization and some outcrops of gneisses. Fifty soil and stream samples were analysed using the Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) technique. The values for the concentrations of some selected elements ranges from; As(0 - 97.19ppm), Cd(0 - 4.653ppm), Co(0 - 503.2ppm), Cr(4.401 - 6020ppm), Cu(0 - 74.77ppm), Ni(0 - 24560ppm), Pb(3.357 - 59660ppm), S(0 - 4469ppm). Multiple correlation and regression analysis of the geochemical data showed a relationship between Pb and As and significant regression of Pb on As and Cd. The results of the Index of geoaccumulation (Igeo), Contamination Factor (CF) and Degree of Contamination (Cdeg) indicate moderate to high Pb and As contamination. The values obtained indicates As, Pb and Cd have concentrations above the maximum permitted levels of 0.01ppm, 0.01ppm and 0.003ppm respectively in water for human consumption, and above the threshold of contamination of 15ppm and 20ppm for As and Pb respectively. This suggests that more people will be at risk of pollutants as lead – zinc exploitation proceeds. The frequency distribution plots of the elements generally show unimodal distribution indicating that most of the elements belong to a common parent material.

Key words: Mineralization, geochemistry, threshold, contamination, lead-zinc, water.

1. Introduction

The studied area is situated in the northwestern part of Wukari Local Government Area of Taraba State. It lies between Latitudes $7^0 47$'N and $7^0 52$'N and Longitudes $9^0 13$'E and $9^0 17$'E (Fig. 1). The geology of the entire area reveals that the northern parts of Arufu have few outcrops of gneiss in-laws which form a part of the Pan-African basement. The dominant rock type around Arufu are sedimentary rocks of the Asu River Group formation with a few indications of the Keana Formation characterized by coarse-grained sandstone and bands of shale in the area east of Arufu. Further down in the southern and southeastern parts of the area reveals more exposures of gneisses. However, extensive superficial cover and poor exposures of the carbonate rocks made it difficult to establish the contact relationship pattern between the basement rocks and the Asu River Group.

Offodile (1976) work in the Upper, Middle and Lower Benue Trough reported that the area consists of sediments of the Cretaceous age (136 ± 25 Ma) and surrounded by the Pan African Precambrian Basement Complex (600 ± 150 Ma). He also observed that the region has three stratigraphical correlations; an upper or northeastern region; middle Benue region or the Lafia-Muri area and the lower or southwestern part of Makurdi (Fig. 2). He discussed the stratigraphic sequence of the Middle Benue trough under two sections of the Cretaceous Age.

- Lower Cretaceous (which is represented by the Asu River Group and consists of dark shales, siltstones and fine grained sandstones) passing upwards into shales and limestones of the Upper Albian substage.
- Upper Cretaceous; which shows that the Asu River Group is immediately overlain by the Keana Sandstones which consists mainly of poorly sorted felspathic, coarse grained, gritty, commonly arkosic, pebbly sandstones.
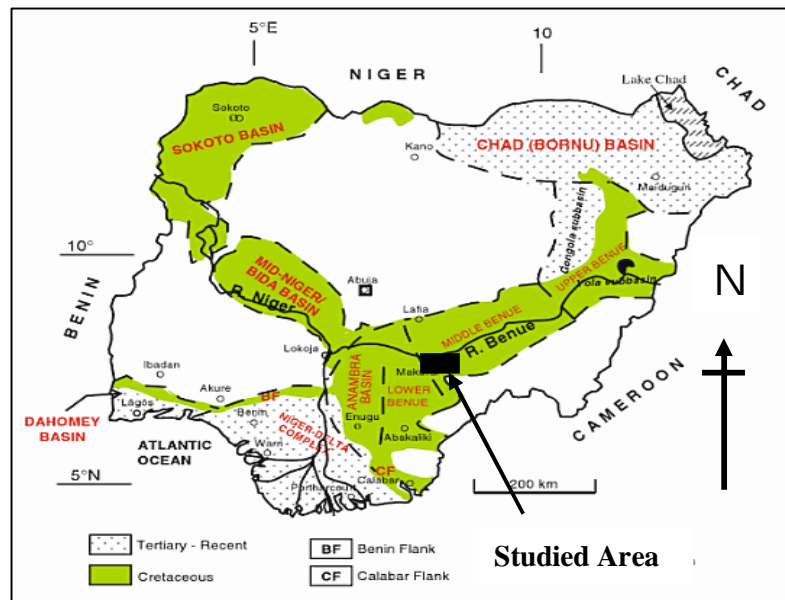
Figure 1: Geological Map Of Nigeria Showing The Studied Location (Modified From Obaje, 2009)
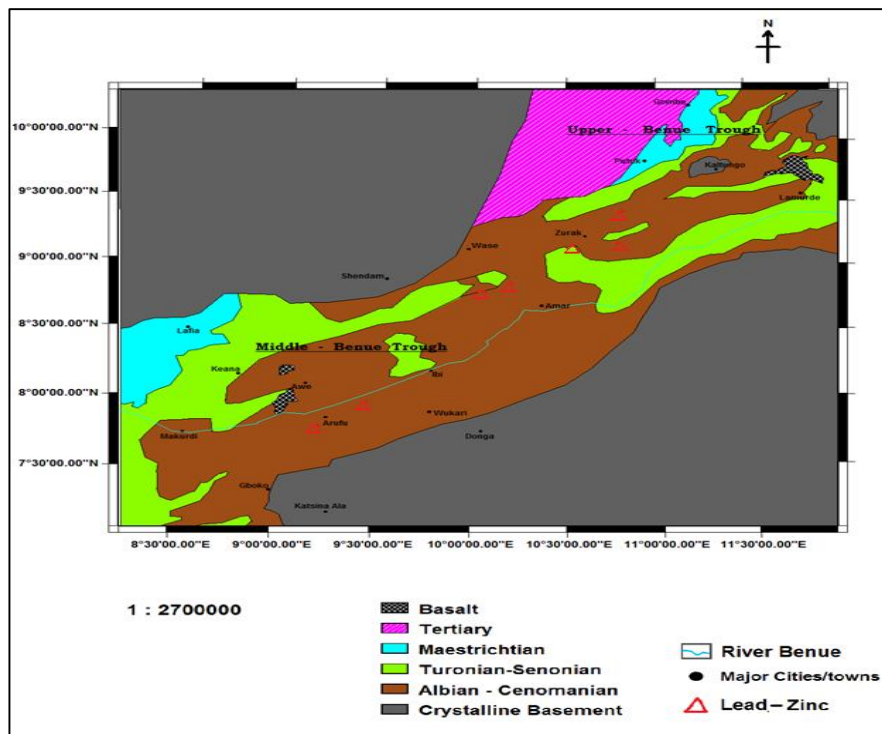

Figure 2: Geological Map Of The Benue Trough, Showing The Units Of The Middle Benue And Upper Benue Subdivisions And Lead-Zinc Occurrences. (Modified From Cratchley And Jones, 1965 & Whiteman, 1982)

The Middle Benue valley is subdivided into two parts which are: An Upper or northern part, which covers Bashar, Amar, Muri and Zurak areas and a Lower or Southern part which covers Lafia, Keana, Awe and Arufu area (Cratchey and Jones, 1965). They suggested the stratigraphic sequence in the Middle Benue valley given in Fig. 3.

GEOLOGICAL STAGES		MIDDLE BENUE	
		KEANA-AWE-ARUFU AREA	BASHAR-MURI-AMAR AREA
Maastrichtian		?	Gombe sandstone
		Lafia Sandstone	?
Senonian	Campanian	?	Kumberi Formation
	Santonian	Marine Deposits	
	Coniacian		
Turonian	Upper		
	Lower		
Cenomanian		Transition Deposit	"Passage beds"
Albian		Keana sandstone	Muri sandstone
		Asu River Group	Marine deposits
Palaeozoic and Pre-Cambrian		Crystalline Basement	

Figure 3: Stratigraphic Sequence In The Middle Benue Valley (After Cratchley And Jones, 1965)

They also recognized a transitional zone (beds) overlying the Keana sandstone. These transitional beds are overlain by an unnamed marine formation consisting of shales, clays, siltstones and shelly limestones with some coals. Farrington (1952) described the lead-zinc mineralization of the Abakaliki fold belt pointing to its close association with the dioritic intrusive and albitized dolerites. He stated that the lead-zinc deposits are mainly fracture filling veins which form parts of fractured or sheeted zones. Farrington (1952) summarized ore genesis as follows for both Abakaliki and Benue areas:

- Early intrusives are un-mineralized by sulphides (except for pyrite) but dolerites and porphyries are cut by ore bearing veins.
- Dolerites are albitized suggesting that emanations were active shortly after emplacement.
- Mineralization and intrusion both favour anticlinical structures.
- Dioritic intrusions are commonly associated with lead-zinc veins.
- Mineralization west of Ishiagu is less than 4 miles from and at the same elevation as the base of mineralized and unintruded sediments of Coniacian age.

He believed in a magmatic hydrothermal origin but Whiteman (1982) suggests the more likely sources were hot brines which leached metals from sediments and Basement Complex. Some brine springs are known in the Abakaliki area and in the Benue Trough to the northeast. Whiteman (1982) suggests that the igneous bodies, because presumably they were warmer than the country rocks acted as sources of heat aiding movements of hot brine mineralizing fluids, and eventually became the loci for mineralization. Olade (1976) thinks that the ore solutions started as connate brines mobilized by geothermal heat from mantle plume activity during Cretaceous rifting. These solutions were able to leach chlorides from the sediments and evaporites, as well as base metals from clays and feldspars which combined with sulphur to form ores along permeable zones. Olade (1976) suggested also that the age of the mineralization is pre-Turonian. He thinks that the lead-zinc ores occur mainly in Albian sediments. Akande (1989) suggested a model which interpretes the Nigerian deposits in the Abakaliki, Ishiagu, Arufu–Akwana, Gombe and Zurak districts as distinct epigenetic ore bodies controlled by fractures which were formed about ninety (90) million years ago. The model suggests that the primary ore target should be the Asu River Group sediments in which the metal ore bodies are stratabound. Adikwu-Brown and Ogezi (1991) reported the adverse effects of lead mining in the Upper Benue Trough. They observed that lead mines pollute water sources in the area with cadmium. Lar and Sallau (2005) analysed the trace elements in water and stream sediments from the Keana brines field, middle Benue Trough. They indicated that high concentrations of elements such as As, Pb, Ni and Cr were discovered in refined salt, while the concentration of Cd in well water was above WHO (World Health Organization) admissible limits. Ntekim (2008) carried out statistical analysis of trace

elements concentrations in shale and carbonate sediments in Guyuk, North-eastern Nigeria. They observed that there are strong associations between trace elements such as Cu, Cr, Ni and Co and the process of mineralization in the area. They also observed that the trace elements have potential for use as mineralization indicators. This paper deals with determining the concentration of base metals (Pb, Ni, Cu,) in the soils and stream sediments within the locality, highlighting the possible toxicity effects on man, animals and crops of the area and to examine the mineralization potential of the area based on elemental analysis using ICP-OES.

2.Regional Geologic Setting

The Benue Trough of Nigeria is a rift basin in central West Africa that extends NNE – SSW for about 800 Km in length and 150 Km in width. The southern limit is the northern boundary of the Niger Delta, while the northern limit is the southern boundary of the Chad Basin (Fig. 4).
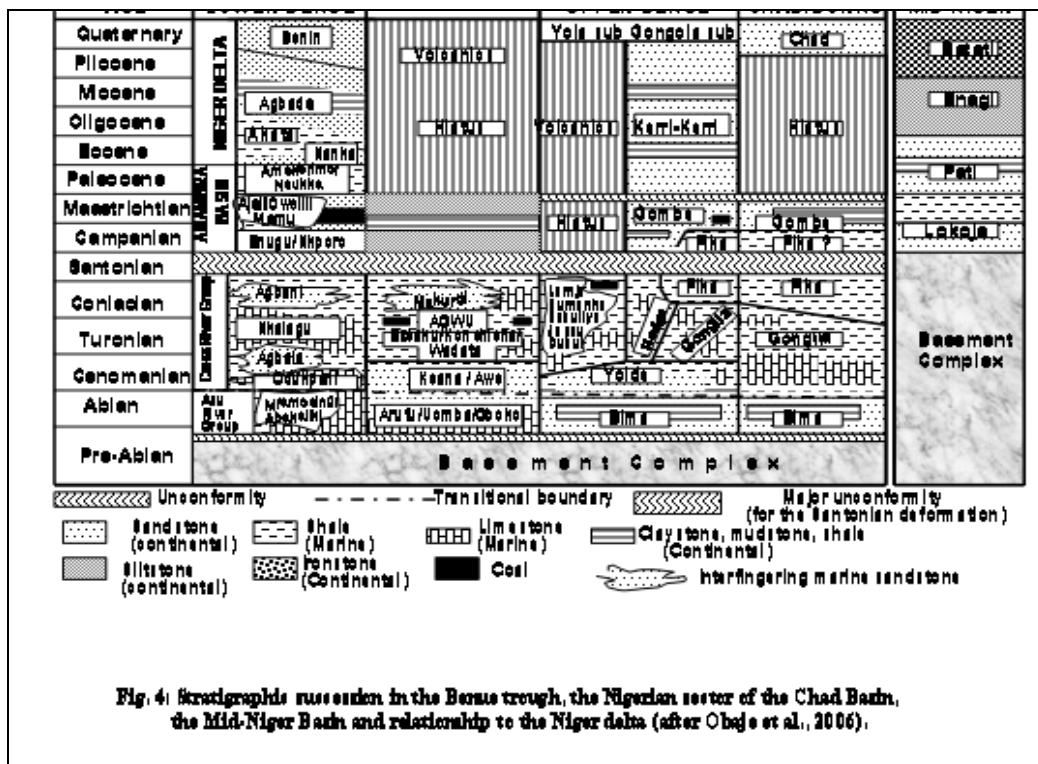

Fig. 4: Stratigraphic succession in the Benue trough, the Nigerian sector of the Chad Basin, the Mid-Niger Basin and relationship to the Niger delta (after Obaje et al., 2006).

Figure 4

The trough contains up to 6000m of Cretaceous – Tertiary sediments of which those predating the mid-Santonian have been compressionally folded, faulted, and uplifted in several places. Compressional folding during the mid-Santonian tectonic episode affected the whole of the Benue Trough and was quite intense, producing over 100 anticlines and synclines (Benkhelil, 1989).The Benue Trough is arbitrarily subdivided into a Lower, Middle and Upper portions (Fig. 1). No concrete line of subdivision can be drawn to demarcate the individual portions, but major localities (towns/settlements) that constitute the depocentres of the different portions have been well documented (Obaje, 2009). The depocentres of the Lower Benue Trough comprised mainly the areas around Nkalagu and Abakaliki, while those of the Anambra Basin centre are around Enugu, Awka and Okigwe. The Middle Benue Trough comprises the areas from Makurdi through Yandev, Lafia, Obi, Jangwa to Wukari. In the Upper Benue Trough, the depocentres comprise Pindiga, Gombe, Nafada, Ashaka (in the Gongola arm) and Bambam, Tula, Jessu, Dukul, Numanha (in the Yola arm), (Obaje, 2009).

In the Middle Benue Trough, around the Obi/Lafia area, six Upper Cretaceous lithogenic formations comprise the stratigraphic succession (Fig. 5). This succession is made up of Albian Arufu, Uomba and Gboko Formations, generally referred to as the Asu River Group (Offodile, 1976; Nwajide, 1990). These are overlain by the Cenomanian –Turonian Keana and Awe Formations and the Cenomanain –Turonian Ezeaku Formation. The Ezeaku Formation is coterminous with the Konshisha River Group and the Wadata Limestone in the Makurdi area. The Late Turonian-Early Santonian coal-bearing Awgu Formation lies conformably on the Ezeaku Formation. In the Makurdi area, the Makurdi Sandstone interfingers with the Awgu Formation. The mid-Santonain was a period of folding throughout the Benue Trough. The post-folding Campano-Maastrichtian Lafia Formation ended the sedimentation in the Middle Benue Trough, after which widespread volcanic activities took over in the Tertiary.
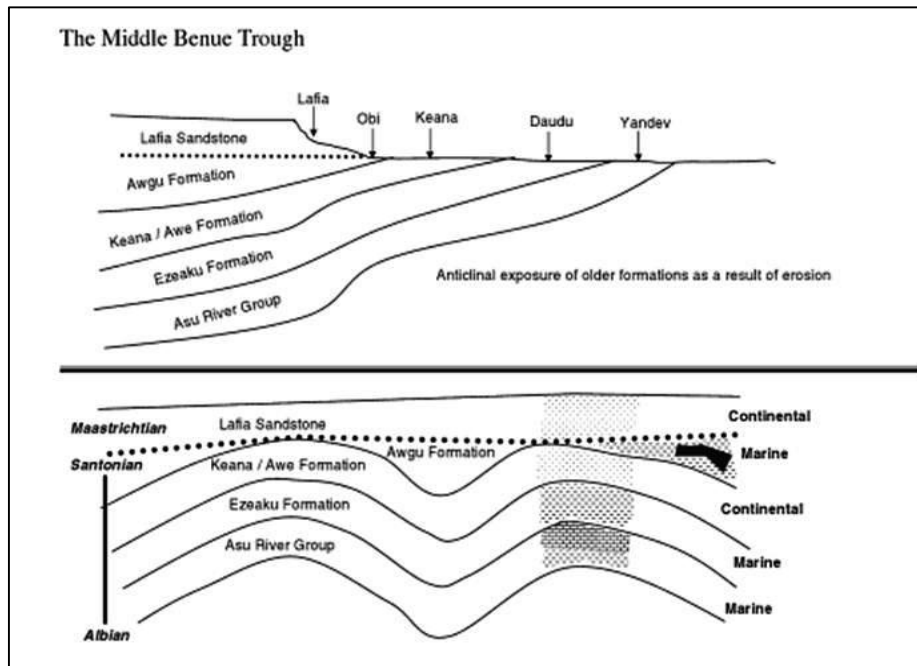
The Middle Benue Trough

Lafia
Obi   Keana   Daudu   Yandev

Lafia Sandstone

Awgu Formation

Keana / Awe Formation

Ezeaku Formation

Asu River Group

Anticlinal exposure of older formations as a result of erosion

Maastrichtian   Lafia Sandstone   Continental

Awgu Formation   Marine

Santonian   Keana / Awe Formation

Ezeaku Formation   Continental

Asu River Group   Marine

Marine

Albian

Figure 5: Stratigraphic Successions In The Middle Benue Trough (After Obaje, 2009)

The entire area reveals that the northern parts of Arufu have few outcrops of gneiss inliers which form a part of the Pan-African basement. The dominant rock type around Arufu are sedimentary rocks of the Asu River Group formation with a few indications of the Keana Formation characterized by coarse-grained sandstone and bands of shale in the area east of Arufu. However, further down in the southern and south-eastern parts of the study area reveals more exposures of Gneisses (Fig. 6).
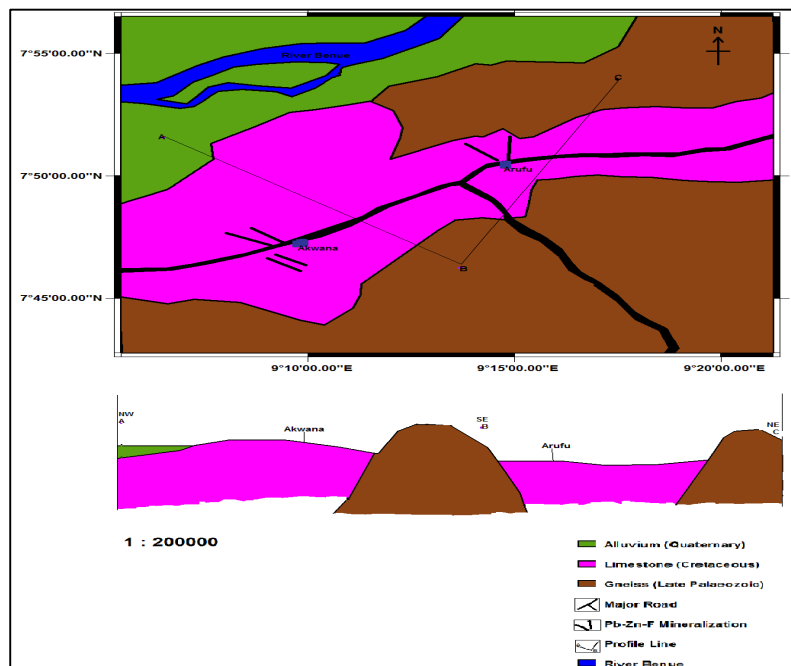
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Alluvium (Quaternary)
Limestone (Cretaceous)
Gneiss (Late Palaeozoic)
Major Road
Pb-Zn-F Mineralization
Profile Line
River Benue

Figure 6: Local Geology In The Arufu And Akwana Areas (After Akande, 1988)

However, extensive superficial cover and poor exposures of the carbonate rocks made it difficult to establish the contact relationship pattern between the basement rocks and the Asu River Group.

3.Materials And Methods

The sampling intensity varied; at least three samples were obtained from most of the sample locations at intervals of 2m to 6m and five samples around mineralized veins or mine sites at intervals of 50cm, 1m, 4m, 20m and 75m respectively. The stream sediment samples were taken at the base of dried stream and at about 30cm to 50cm from the edge of the streams.

Precautions were taken to minimize contamination of samples during collection, preparation and analysis. Photographs of features as well as structural measurements were taken and all the observations and data obtained is recorded. The structural elements measured are mineralized veins and joints in altered carbonates, foliations and quartz veins in the gneisses. The collected samples were dried in the oven easy disintegrated to allow for homogenization. The samples were disintegrated using mortar and pestle which were properly cleaned with distilled water, methylated spirits and tissue paper in between each sample to prevent contamination. The fine powdery products were packed in labelled airtight sample bags for easy identification. The collected and prepared samples were forwarded to the Geochemistry Laboratory of the Department of Geology and Mining, University of Jos for analyses. A total of 50 soil samples was analysed for Lead, Nickel, Copper, Arsenic, Cadmium, Cobalt, Chromium and Sulphur use the ICP-OES machine. The disintegrated samples were decomposed using aqua regia. The conventional aqua regia digestion procedure consists of digesting soil samples on a hotplate with a 3:1 mixture of HCl and HNO_3. The nitric acid reacts with concentrated HCl to form aqua regia (nitrosyl chloride and chlorine): HNO_3 (aq) + 3 HCl (aq) → NOCl (g) + Cl_2 (g) + 2 H_2O (l). The digested samples were then analysed using the Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) machine. With the ICP-OES multi-element capabilities were detected.

4.Results And Discussion

On the 50 soil samples analysed 8 elements were obtained (Table 1). The concentrations of the selected elements ranges with As (0 - 97.19p.m.), Cd (0 - 4.653ppm), Co (0 - 503.2ppm), Cr (4.401 - 6020ppm), Cu (0 - 74.77p.m.), Ni (0 - 24560ppm), Pb (3.357 - 59660ppm), S (0 - 4469ppm). The mean values are 9.072, 0.227, 6.766, 26.06, 3.070, 6.541, 3656.7 and 1082.8ppm respectively. The multiple correlation and regression analysis in Figs. 7 and 8 are used to show the relationships between concentrations of the different elements in the samples as well as detect the variation in their concentration with respect to that of lead (Pb). Regression of lead against seven elements arsenic, cadmium, cobalt, chromium, copper, nickel and sulphur reveals significant regression of lead on arsenic and cadmium as 0.0000 and 0.0149 values respectively. Other elements show values higher than the acceptable 0.05 significant levels (Fig. 8). The correlation of lead against other elements is generally low with the exception of arsenic. This may indicate some sorts of geochemical restrictions on distribution and concentrations of the elements. It is also significant considering that the elements associated with lead – zinc mineralization are arsenic, silver, gold, iron, copper, antimony and selenium in sulphide and base-metal deposits (Fig. 7). A significant correlation exists between cobalt, chromium, copper and nickel.

The frequency distribution plots of the elements except lead generally show unimodal distribution indicating that most of the elements belong to a common parent material (Fig. 9).

Sample Name	As (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	S (ppm)
Ar1 (0.5m)	0.0	0.0	3.5	86.9	6.5	5.3	802.8	0.0
Ar1 (3m)	0.0	4.7	2.7	37.4	3.5	6.7	797.4	1544.0
Ar1 (6m)	15.9	1.7	1.6	35.8	0.6	4.4	1774.0	712.1
Ar2 (S3)	0.0	1.4	3.5	22.6	0.5	3.4	274.4	599.8
Ar2 (S2)	0.0	1.8	2.7	19.1	0.0	2.7	109.0	245.8
Ar3	0.0	0.0	3.3	41.1	1.2	3.3	124.2	312.8
Ar4 (S1)	0.0	0.0	58.4	106.7	33.3	33.8	66.3	376.3
Ar4 (S3)	18.9	0.0	4.7	27.8	0.0	3.1	57.6	883.4
Ar6	0.0	0.0	27.9	44.1	16.0	31.2	41.4	1028.0
Ar8 (3m)	74.7	0.0	7.3	32.8	6.2	11.0	47790.0	3197.0
Ar8 (5m)	70.1	0.2	13.8	34.1	5.6	14.1	59660.0	4461.0
Ar8 (0.5m)	62.2	0.6	17.7	55.4	5.1	31.0	44480.0	4469.0
Ar9	1.7	0.0	5.0	28.0	0.0	2.8	79.2	668.1
Ar10 (1m)	0.0	0.0	16.1	26.4	0.2	16.4	256.6	866.2
Ar10 (4m)	0.0	0.0	6.6	15.5	0.0	4.2	150.1	760.3
Ar10 (6m)	0.0	0.0	6.2	18.3	2.0	7.5	234.3	898.9

Ar11 (S1)	0.0	0.0	20.8	35.1	0.3	5.8	218.5	604.3
Ar11 (S2)	0.0	0.0	15.0	25.2	0.0	3.2	133.3	551.5
Ar12 (0.5m)	0.0	0.0	3.3	16.7	0.0	2.5	359.9	166.1
Ar12 (2m)	0.0	0.0	2.6	19.3	0.0	3.4	290.7	481.8
Ar12 (5m)	22.8	0.0	2.5	16.9	0.0	2.8	227.5	358.9
Ar13 (0.5m)	97.2	0.0	3.4	25.7	0.0	14.6	19790.0	745.6
Ar13 (5m)	29.0	0.0	2.4	30.8	0.0	0.4	3130.0	1229.0
Ar13 (10m)	0.0	0.0	2.8	75.4	1.0	3.4	120.6	1634.0
Ar14 (5m)	14.0	0.0	6.7	38.3	0.0	0.0	94.2	614.7

Ar14 (10m)	0.0	0.0	1.3	31.2	0.0	0.0	15.6	581.6
Ar14 (0.5m)	0.0	0.0	3.2	43.3	0.0	6.1	30.7	962.5
Ar15	0.0	0.0	12.1	19.4	13.0	27.2	140.3	505.4
Ar16	0.0	0.0	7.7	16.3	22.9	14.0	77.1	1088.0
Ay1	2.2	0.0	0.1	6.3	0.0	0.0	65.1	549.0
Ay2	0.0	0.0	1.0	9.7	0.0	0.4	38.4	588.4
Ay3	0.0	0.0	3.3	16.8	0.0	1.5	132.6	1337.0
Ay4 (S1)	0.0	0.0	1.6	10.4	0.0	0.0	94.9	948.4
Ay4 (S2)	0.0	0.0	1.9	15.8	0.0	3.6	127.0	1659.0
Ak1 (S1)	0.0	0.1	4.6	7.8	0.0	1.3	87.8	1621.0
Ak1 (S2)	0.0	0.3	2.1	7.0	0.0	0.2	294.1	1470.0
Ak2	0.0	0.0	0.8	4.4	0.0	0.3	70.9	1054.0
Aj1	0.0	0.0	42.1	52.2	25.1	31.8	18.3	918.2
An1	0.0	0.0	1.8	9.6	2.0	0.0	31.4	827.2
An2	0.0	0.0	1.2	15.7	0.0	2.4	9.5	568.8
Gb1 (S1)	8.1	0.3	1.3	22.4	4.7	2.7	36.6	1839.0
Gb1 (S3)	0.0	0.0	2.0	14.9	0.0	10.0	20.4	975.1
Ny1 (S1)	0.0	0.1	0.0	8.7	0.0	0.0	3.4	1234.0
Ny1 (S2)	0.8	0.0	1.1	10.1	0.0	1.9	13.1	807.7
Sa1 (S3)	7.3	0.0	1.2	7.7	0.0	0.2	74.6	649.5
Sa1 (S2)	0.0	0.2	0.3	4.9	0.0	0.0	48.9	745.4
Sa2	28.8	0.0	0.2	5.4	0.0	0.0	59.5	1037.0
Ty1	0.0	0.0	0.0	13.7	0.8	0.0	32.1	1300.0
Ts2	0.0	0.0	0.0	7.9	0.0	0.0	129.7	584.1
Ts1	0.0	0.0	503.2	6020.0	74.8	24560.0	121.6	2882.0

Table 1: Result Of The Analysis Of 50 Soil Samples From The Study Area

The plots are generally skewed right and indicated only a few outliers not belonging to the population. The calculated Igeo values of the elements in samples are As (5.43), Cd (1.63), Co (3.07), Cr (2.00), Ni (5.03) and Pb (7.64). The mean values of Igeo decrease in the order As>Pb>Cd>Co>Cu>Cr>Ni (2.74, -1.00, -1.92, -4.00, -5.40, -6.08, -7.26) indicating that arsenic and lead have significant concentrations. This is buttressed by the Contamination Factor (CF) which shows mean values decrease in the order Pb>As>Ni>Co>Cr>Cd>Cu (298, 65, 49, 13, 6, 5, 1). The mean values also decreases in the same order as 18.29>6.05>1.00>0.42>0.23>0.15>-0.05. The degree of contamination (Cdeg) ranges from 0.086 to 345.7 with mean value of 26.16

indicating a low to moderate degree of contamination. However, high degree of contamination is observed in the immediate vicinity of the Arufu village with peak values greater than 200 Cdeg.

Statistical analyses which involve histogram and cumulative frequency plots, correlation and regression analysis were carried out on the result obtained from the laboratory. Further quantification of contamination indices such as contamination factor (CF) and Index of geoaccumulation (Igeo) were used to determine the relationships in the concentrations and distribution patterns of the elements analyzed which will help in the interpretation of results obtained.
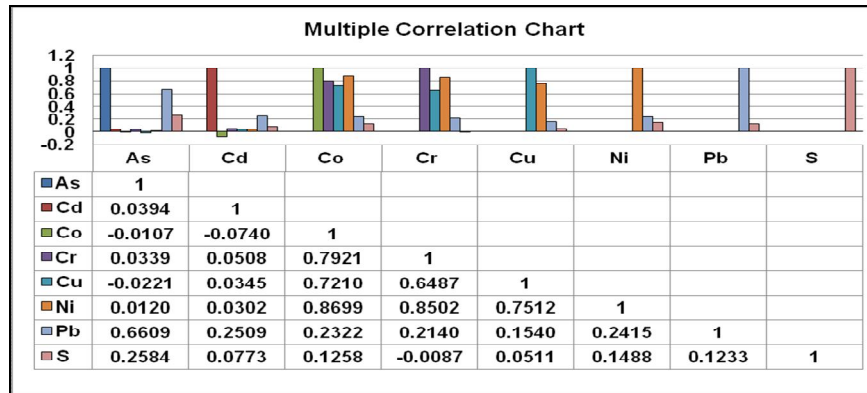
Figure 7: Chart Reflecting The Effect Of Coefficient Of Correlation Indicating The Relationship Between Various Elements Across The Area
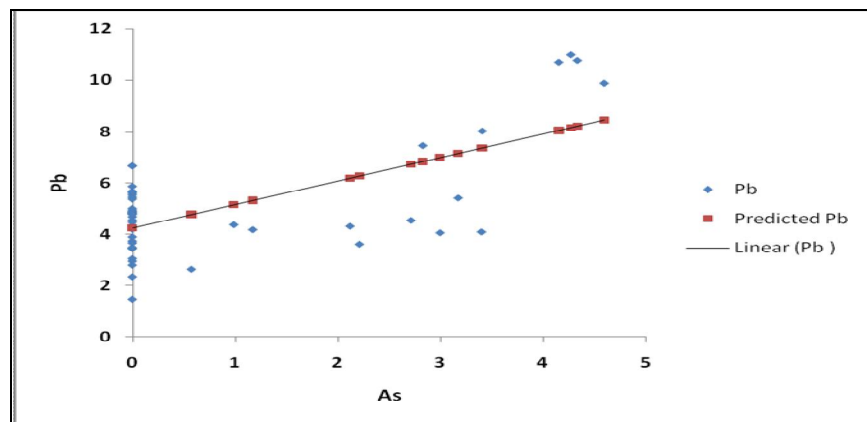
Figure 8: Chart Reflecting The Result Of Regression Analysis Indicating The Relationship Between As And Pb Across The Area
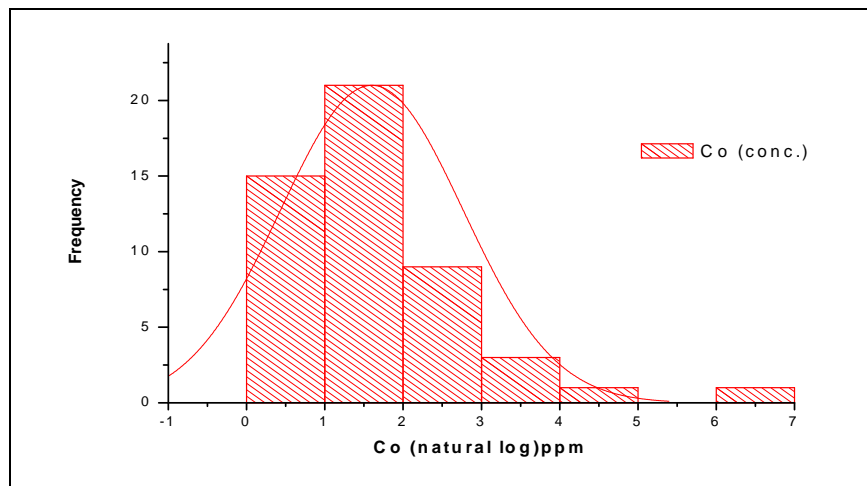
Figure 9: Frequency Distribution Of Base Metal Values

Geochemical maps for the studied area are presented below in form of contours. The purpose is to indicate the distribution and concentrations of each of the elements analyzed in the area (Fig. 10).
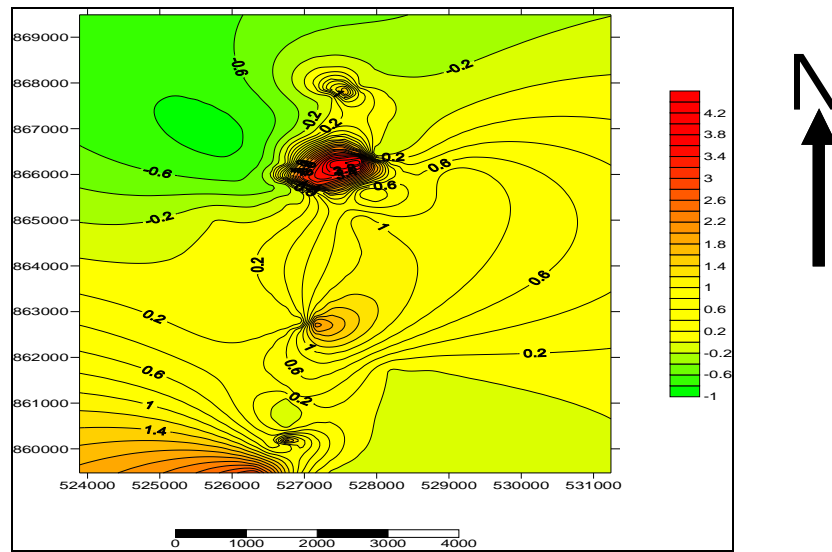

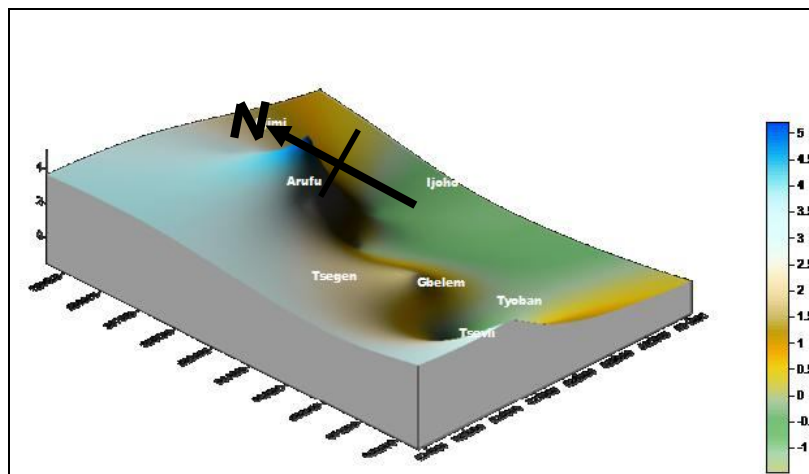*Figure 10: The Distribution And Concentration Of Elements In The Area*

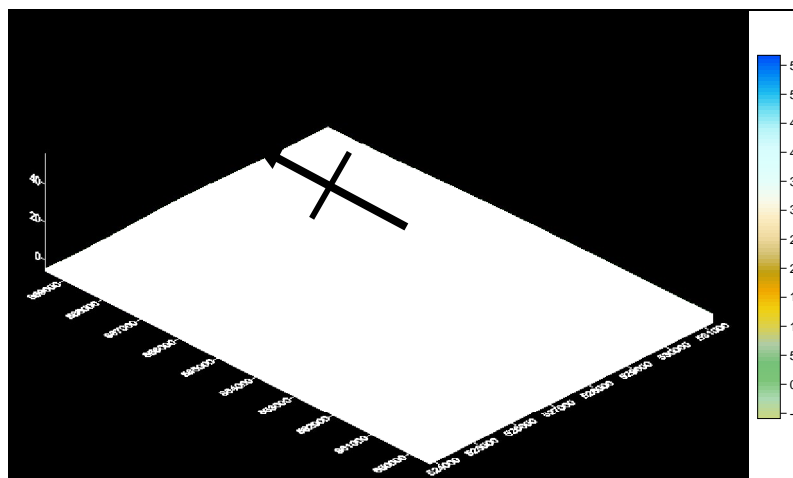*Figure 11: The Contamination Map For IGEOI Values*

Figure 12: The Contamination Map For CF Values

- **Arsenic**

Arsenic concentrations within the study area (Table 1) range from 0 to 97.19ppm with a mean value of 9.072ppm. Forty (40) of the samples (representing 80%) have values within the range of 0 and 10ppm. Samples with greater than average arsenic content were those around mine pits.

There was a positive correlation between the concentration of Arsenic and Lead. The Correlation Coefficient was 0.6609 (Fig. 7). The bivariate scatter plot (Fig. 8) also predicts that with increasing concentration of arsenic in the study area, more lead will be discovered. The value of the Igeo (5.43) showed moderate to high contaminations of arsenic in soils around areas where active mining is going on or have been done over the years. This is also supported by the result obtained from the calculation of the contamination factor (6.05) which shows very high contamination factor (Figs. 11 and 12). Most environmental arsenic problems are the result of mobilization under natural conditions. However, man through mining activity has added more arsenic problem to the area. Mining-related arsenic problems in water and the environment have been identified in many parts of the world, including Ghana, Greece, Thailand and the USA (Smedley and Kinniburgh, 2002). Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides and oxides. The greatest concentrations of these minerals occur in mineralized areas. As the chemistry of arsenic follows closely that of sulphur, the greatest concentrations of the element tend to occur in sulphide minerals of which pyrite is the most abundant (Smedley and Kinniburgh, 2002). Arsenic is present in the crystal structure of many sulphide minerals as a substitute for Sulphur. Arsenic can also substitute for Si^{4+}, Al^{3+}, Fe^{3+} and Ti^{4+} in many mineral structures and is present in other rock-forming minerals at much lower concentrations. Carbonate minerals usually contain less than 10ppm arsenic. Arsenic concentrations in igneous rocks are generally low. Ure and Berrow (1982) quoted an average value of 1.5ppm for all igneous rock types (undistinguished). Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most contain around 5ppm or less. Pelitic rocks (slates, phyllites) typically have the highest concentrations with an average value of 18ppm. The concentration of arsenic in sedimentary rocks is typically in the range 5-10 ppm (Wester, 1999). The background level in top-soils is typically low, but generally higher than that of the parent material (Norrish, 1975) and occasionally exceeds the threshold of contamination of 15 ppm as given by the NRCC (National Research Council of Canada) (NRCC, 1978b). Arsenic minerals and compounds are soluble, but there is limited movement of arsenic in soil because it is absorbed by hydroxides, clays and organic matter (Kabata-Pendias and Pendias, 1992), and retained by iron oxides (Norrish, 1975). Therefore, its mobility is highest in sandy soils and lowest in fine textured soils and those high in iron (NRCC, 1978)

Arsenic concentrations much higher than baseline values have been found in sediments and soils contaminated by the products of mining activity, including mine tailings and effluent. Concentrations in tailings piles and tailings-contaminated soils can reach up to several thousand ppm. Humans can be exposed to arsenic through ingestion of arsenic-containing water, food, and drugs (such as Fowler's solution containing 1% of potassium arsenite used to treat psoriasis and arsenic trioxide used to treat leukemia). Airborne arsenic can be absorbed into the bloodstream in workers involved in the processing of copper, gold, and lead ores; in the production and use of arsenic-containing pesticides. Water contamination is the most common source of arsenic exposure (Weinstein et. al, 1997). Of concern today are the skin lesions and cancers observed among the millions of people drinking arsenic-rich well water, especially in West Bengal and Bangladesh. Chronic arsenic poisoning may affect many organ systems. For example, in affected populations in Taiwan and India, ingestion of drinking water high in arsenic has been associated with a variety of skin lesions, which include increased or decreased pigmentation and keratosis. Gangrene has also been reported (blackfoot disease). The carcinogenic role of arsenic has been suggested in a range of studies: exposure increases the risk of cancer of the skin, lung, liver, bladder, and kidneys (Weinstein, 1997). In recent years, long-term exposure to arsenic from drinking water has also been found to be highly associated with hypertension and diabetes mellitus (Tseng, 1999). The maximum permitted concentration of arsenic in drinking water is 0.01 mg/L ($\approx$ 0.01 ppm). Arsenic is not a requirement for animals or humans. It can be toxic to plants in leaf concentrations of 5-20 ppm (dry weight basis) with symptoms including wilting, reduced growth and root discolouration (Kabata-Pendias and Pendias, 1992). It is unlikely that phytotoxic arsenic levels will result in the poisoning of consumers because plants will cease to grow if roots have absorbed too much arsenic, and fruits and seeds will not have elevated levels (NRCC, 1978).

- **Cadmium**

Cadmium concentrations within the study area (Table 1) range from 0 to 4.653ppm with a mean value of 0.227ppm. There is no significant correlation between the concentration of Cadmium and Lead. The Correlation Coefficient was 0.2509 (Fig. 7). This is also reflected by the bivariate scatter plot (Fig. 8). The value of the Igeo (1.63) showed that the soils have low to moderate levels of contamination. This is also supported by the result obtained from the calculation of the contamination factor (5.00) which indicated low to moderate contamination factor (Figs 11 and 12). The samples from locations Ar1 and Ar2 in particular, indicate moderate levels of contamination. This raises health concerns about the inhabitants of the area considering that the maximum level of Cadmium permitted in water for human consumption is 0.003 mg/L ($\approx$0.003 ppm). Cadmium is present mainly in organic-rich shales (0.22-0.30 ppm), and in igneous rocks. It is highest in mafic units (0.13-0.22 ppm) (Kabata-Pendias and Pendias, 1992). Cadmium can be found primarily in sulphide minerals such as sphalerite and pyrite. Upon weathering, these minerals will release Cd^{2+} into solution. It is in this form that Cadmium is taken up by plants, although content in solution will be low, as Cd^{2+} will form complex ions and organic chelates in soil. Its mobility will then be controlled primarily by pH and redox potential (Kabata-Pendias and Pendias, 1992). Cadmium is most mobile at pH 4.5-5.5 (Kabata-Pendias and Pendias, 1992). With no known biological functions, the main concern regarding cadmium is its role as a toxicant. It can rapidly accumulate in livestock and other animals, particularly in kidneys and other organs, creating a potential hazard for human consumption (CCREM, 1995). Cadmium is phytotoxic at leaf levels of 5- 30 ppm

(Kabata-Pendias and Pendias, 1992) but it can accumulate within edible portions of the plant to sub-toxic levels without resulting in any plant distress (Alloway, 1990). Cadmium can be taken up by plants through leaves or roots but soluble soil Cd is readily available (Kabata-Pendias and Pendias, 1992) and it is thought that this is the main source of plant Cd (FAO, 1992). Actual phytotoxicity can occur on polluted soils, but it is rare (Alloway, 1990), and Cadmium is generally not harmful to plants (FAO, 1992). Accumulation of Cadmium in animals can cause disease if it replaces Zinc in enzymes; symptoms of toxicity include renal degradation, emphysema, intestinal dysfunctions and anaemia (Lagerwerff, 1972). Cadmium is known to be more toxic to an animal if dietary calcium is low (CCREM, 1995).

- **Cobalt**

Cobalt concentrations within the area (Table 1) range from 0 to 58.43ppm (exempting suspect value of 503.2ppm) with a mean value of 6.766ppm. There is no correlation between the concentration of Cobalt and Lead. The Correlation Coefficient was 0.2322 (Fig. 7). This is also indicated by the bivariate scatter plot (Fig. 8). The value of the Igeo (3.07) showed the area is uncontaminated with Cobalt. This is also supported by the result obtained from the calculation of the contamination factor (0.42) which shows low contamination factor Figs. 11 and 12). The largest amounts of Cobalt are present in ultramafic (100-200 ppm) and mafic rocks (35-50 ppm) with a substantial amount present in organic-rich shales (14-20 ppm). It is present in soil as Co^{2+} and Co^{3+} and possibly as $Co(OH)^{3-}$ (Kabata-Pendias and Pendias, 1992). Manganese oxide minerals are the most important factor governing cobalt distribution and availability in the soil (Kabata-Pendias and Pendias, 1992; McKenzie, 1975). Crystalline Manganese oxide minerals can retain almost all soil cobalt, even that applied to soil as fertilizer (Tisdale et al., 1985) and Cobalt held in such a way is unavailable to plants. Iron oxides, clay minerals and organic matter may also adsorb Cobalt, and the availability is affected by the type of clay minerals and organic matter on which it is adsorbed (Kabata-Pendias and Pendias, 1992).

Cobalt is mobile in oxidizing, acid environments; and soils with low Cobalt levels tend to be either;

(i) alkaline and calcareous,(ii) high in organic matter content,(iii) acidic and highly leached, or (iv) high in Iron and Manganese (Kabata-Pendias and Pendias,1992).

Cobalt is essential for blue-green algae and N_2 -fixing rhizobia but its essentiality for higher plants is not proven although it has been shown to be beneficial to plant growth. In ruminants, it is the precursor to vitamin B12 for which the sole natural source is plant Cobalt (Kabata-Pendias and Pendias, 1992; Tisdale, 1985). Deficiencies lead to inhibition of N_2 fixation in legumes, but this does not generally occur as the requirements of the rhizobia are low (Kabata-Pendias and Pendias, 1992). It is widely accepted that soil Cobalt levels below 5 ppm (Kubota, 1964) will lead to deficiency problems in ruminants which include emaciation, muscular atrophy and anaemia (Tisdale, 1985). Under natural conditions, toxicity to either plants or animals is unlikely, but cobalt toxicity can be a problem in areas with high natural Cobalt levels and particularly in areas that are Cobalt contaminated (Kabata-Pendias and Pendias, 1992).

- **Chromium**

Chromium concentrations within the area (Table 1) range from 4.401 to 106.7ppm with a mean value of 26.06ppm. There was no correlation between the concentration of Chromium and Lead. The Correlation Coefficient was 0.2140 (Fig. 7). The bivariate scatter plot (Fig. 8) also reflects this. However there are positive correlations between the concentrations of Chromium, Copper and Nickel (Fig. 7). The value of the Igeo (2.00) showed the samples are uncontaminated; hence the concentrations of Chromium in the area are not significant. This is also supported by the value obtained from the calculation of the contamination factor (0.23) on the map (Fig.11 and 12). There extremely high amounts of Chromium in ultramafic rocks (1600-3400 ppm), and lower amounts in felsic (4-25 ppm) and sedimentary rocks (5-120 ppm). Chromium is present in chromite ($FeCr_2O_4$), in other spinel structured minerals (Kabata-Pendias and Pendias, 1992), and ferromagnesian minerals (Garrett, 1998). The naturally occurring forms in soil are chromite (Cr^{3+}) and chromate (CrO_4^{2}). Chromite (Cr^{3+}) is resistant to weathering but may oxidize to chromate (Cr^{6+}). Cr^{3+} is only slightly mobile under very acid conditions, and it is almost completely precipitated at pH 5.5 (Kabata-Pendias and Pendias, 1992). While the presence of organic matter promotes reduction of Cr^{6+} to Cr^{3+}, which may lead to low plant availability, the presence of Manganese oxides encourages oxidation of Cr^{3+} to Cr^{6+}, which is very toxic and more readily available (McBride, 1994). Sandy soils and organic soils are low in Cr (Kabata-Pendias and Pendias, 1992) but Cr^{3+} may be more available in sandy soils due to the lower cation exchange capacity (NRCC, 1976).

There is no evidence that chromium is essential for plants but there are some reports of growth stimulation by Cr^{3+} (Kabata-Pendias and Pendias, 1992; McGrath and Smith, 1990). Cr^{3+} is required for removal of excess glucose in mammals (Scott, 1972) and deficiencies have been found to occur in humans and animals (NRCC, 1976). Cr^{6+} is toxic to both plants and animals. Phytotoxicity occurs at leaf levels of 5-30 ppm (dry weight basis) and there is some evidence of toxicity to livestock grazing on plants high in Cr (Kabata-Pendias and Pendias, 1992), but most Cr taken up by plants remains in the roots (McGrath and Smith, 1990). The maximum permitted levels of Cr^{6+} for water used for human consumption have been set at 0.05 mg/L ($\approx$ 0.05ppm).

- **Copper**

Copper concentrations within the area (Table 1) range from 0 to 33.26ppm with a mean value of 3.07ppm. It is interesting to note that thirty-two (32) of the samples (representing 64%) have values less than 1ppm. Oral reports from on-site miners suggest that the sulphide veins around Arufu are low in Copper whereas those around Akwana (some 11km west of Arufu village) have higher contents. There was no correlation between the concentrations of Copper and Lead. The correlation coefficient was 0.1540 (Fig. 7),

this is also indicated in the bivariate scatter plot (Fig. 8). However, a positive correlation exists between the concentrations of Copper and Nickel, with a correlation coefficient of 0.7512 (Fig. 7).

The mean value of the Igeo (-5.40) showed the samples are uncontaminated with copper. This is corroborated by the result obtained from the calculation of the contamination factor (1.00) which shows low contamination factor (Figs. 11 and 12). Copper is found in relatively high levels in mafic rocks (60-120 ppm) and argillaceous sediments (40-60 ppm), and in much lower levels in limestones (2-10 ppm). Mean copper contents for uncontaminated soils world wide range from 13-24 ppm, but the overall range for world soils is higher (1-140 ppm) depending on the nature of the soil parent materials (Kabata-Pendias and Pendias, 1992). Copper in soil can be fixed by adsorption, precipitation, organic chelation, as well as microbial fixation, and is basically immobile in soils. It can precipitate with sulphides, carbonates and hydroxides and is tightly held on organic and inorganic exchange sites, with the bulk of copper adsorption occurring on Iron and Manganese oxides (Kabata-Pendias and Pendias, 1992), which is a non-exchangeable form (Tisdale, 1985). The main form of copper in solution is that of soluble organic chelates, but solubility of all forms of copper decreases at pH 7-8 (Kabata-Pendias and Pendias, 1992). Acid leached sandy soils and calcareous sandy soils may be low in soluble copper (Tisdale, 1985) and mobility of copper is low in reduced and neutral soils (McBride, 1994). Copper mobility may be higher under high pH because of Cu^{2+} complex formation which may increase overall Cu solubility (McBride, 1994). Copper functions in oxidation, photosynthesis, and metabolism; consequently, it is essential in plants (Kabata-Pendias and Pendias, 1992). As well, it is necessary in animal nutrition where it plays a role in oxidase functions (Kubota and Alloway, 1972). In particular, ruminant health requires that a dietary balance of a two parts Copper to one part Molybdenum (Cu:Mo ratio of 2:1) be maintained (CCREM, 1995). Deficiencies can occur in plants at dry weight levels of 2-5 ppm. Levels toxic to plants are 20-100 ppm (dry weight basis) (Kabata-Pendias and Pendias, 1992) but 15ppm in feed is generally toxic to animals (CCREM, 1995). Copper accumulates in the organs of animals which can lead to problems for human consumption (CCREM, 1995). The maximum concentration of copper permitted in drinking water is 1.0 mg/L ($\approx$1.0 ppm).

- **Nickel**

Nickel concentrations within the study area (Table 1) range from 0 to 33.78ppm with a mean value of 6.541ppm. There was no correlation between the concentrations of Nickel and Lead. The correlation coefficient was 0.2415 (Fig. 7), this is also indicated in the bivariate scatter plot (Fig. 8). The value of the Igeo (5.03) suggests the samples are uncontaminated with Nickel. This is corroborated by the result obtained from the calculation of the contamination factor (1.00) which shows low contamination factor (Figs. 11 and 12). However, considering that the maximum permitted levels of Nickel in drinking water is 0.02 mg/L ($\approx$ 0.02 ppm). It advisable to further examine the implications of having higher concentrations of Nickel in water sources around the area (possibly carcinogenic).

Nickels are extremely high in ultramafic rocks (1400-2000 ppm) and lower in mafic rocks (130-160ppm). Of the sedimentary rocks, it is highest in the organic rich shales (40-90 ppm) (Kabata-Pendias and Pendias, 1992). The most important nickel mineral is pentlandite, and nickel occurs as a constituent of pyrrhotite and ferromagnesian minerals (Garrett, 1998). While there are several oxidation states of Ni, only Ni^{2+} is stable in the soil environment (McGrath and Smith, 1990). Nickel minerals will release Ni^{2+} upon weathering, which may precipitate with Fe and Mn oxides, or be adsorbed onto clay and organic fractions (Kabata-Pendias and Pendias, 1992). Nickel bioavailability decreases as soil pH increases, and mobility will also be lower in soils with high cation exchange capacity (NRCC, 1981). Nickel in solution exists primarily as Ni^{2+} which is readily mobile and available to plants (NRCC, 1981). It has not been established that Nickel is essential for plant growth, although it may be active in hydrogenase and translocation of nitrogen, and is known to be present in urease. It is easily translocated within plants and accumulates in leaves and seeds (Kabata-Pendias and Pendias, 1992). Nickel is required for animals, and some instances of deficiency have been established (NRCC, 1981). It may also be essential for human health (McGrath and Smith, 1990). Deficiencies of Nickel are unlikely to occur in plants or animals under natural conditions. If there is a nickel requirement for plants, it is thought to be very small and well met under natural conditions, while Nickel intake levels in the animal diet are generally higher than levels shown to cause deficiencies (McGrath and Smith, 1990). Plants show symptoms of toxicosis at leaf levels of 10-100 ppm Ni (dry weight basis) and may exhibit chlorosis, gray-green leaves and stunted root and plant growth (Kabata-Pendias and Pendias, 1992).

- **Lead**

Lead concentrations within the study area (Table 1) range from 3.357 to 59660ppm with a mean value of 3656.7ppm. Arsenic concentrations show a strong correlation with the concentrations of Lead. The correlation coefficient was 0.6609 (Fig. 7), this is also indicated in the bivariate scatter plot (Fig. 8). The values of the Igeo (7.64) for samples around mining sites show a range from moderate to extreme lead contamination. This is corroborated by the result obtained from the calculation of the contamination factor (18.29) which shows moderate to very high contamination factor (Figs. 11 and 12). Those used as control samples obtained from other locations around shows they are largely uncontaminated.

Lead occurs as a sulphide in rocks and replaces K, Ba, Sr and Ca in minerals (Norrish, 1975). The largest presence of lead occurs in argillaceous sediments (20-40 ppm) and shales (18-25 ppm), but amounts are also high in felsic rocks (15-24 ppm). The overall range of lead in world soils is 3-189 ppm with a range in means of 10-67 ppm and an overall average level of 32 ppm (Kabata-Pendias and Pendias, 1992). A threshold of contamination of 20 ppm has been suggested based on the low lead levels found in Alaskan soils (range of means: 22-28 ppm) (Kabata- Pendias and Pendias, 1992).

Least mobile of the heavy metals, lead accumulates in the surface horizons of soils and is not usually leached (Davies, 1990). Its concentration in solution is low, and this limited amount is available for plant uptake (Davies, 1990). It exists in soil solution mainly

as Pb^{2+}, but it may also occur in the Pb^{4+} oxidation state. Soil is mainly associated with organic matter, clay minerals and oxides of Manganese, Iron and Aluminum (Kabata-Pendias and Pendias, 1992). Lead is most available under acid conditions (particularly in sandy soil) (NRCC, 1978a) and precipitates as hydroxides, phosphates and carbonates as pH increases (Lagerwerff, 1972). In association with Manganese oxides, the solubility of lead decreases as Pb^{2+} is oxidized to Pb^{4+} (McBride, 1994).

Lead is a non essential element for plants, animals and humans. It is toxic to plants at leaf levels of 30-300 ppm (dry weight basis), at which point plants exhibit dark green leaves, wilting, and stunted foliage and roots (Kabata-Pendias and Pendias, 1992). Although lead can be absorbed through roots and foliage (Lagerwerff, 1972) phytotoxicities are rarely observed under field conditions. Lead is highly toxic to animals at a level of 30ppm in diet on a dry weight basis (FAO, 1992) and leads to efficiency problems in red blood cell synthesis (NRCC, 1978a). Translocation of lead within plants is low (McBride, 1994; Kabata-Pendias and Pendias, 1992), so the main health concern for humans and animals is ingestion of soil with plants (McBride, 1994), although elevated Lead levels in root crops may be a problem. The guideline established for Lead in water for human consumption is 0.01 mg/L ($\approx$ 0.01 ppm).

The wide range in concentration of total trace elements investigated in this area reflects the interaction of at least two factors:

- The varied nature of the physical and chemical composition of soil parent materials, and
- The source of the mineralogic contribution to the soil parent material.

Lead and arsenic were found to be present in some soil samples in amounts exceeding the higher limits of the levels found in soils and are potentially highly toxic to biological systems and therefore of environmental concern. The analysis showed these elements have concentrations above maximum permitted levels of 0.01ppm, 0.01ppm and 0.003ppm respectively in water for human consumption and above the threshold of contamination of 15ppm and 20ppm for As and Pb respectively. This is buttressed by the values of the Index of Geoaccumulation (Igeo), Contamination Factor (CF) and Degree of Contamination (Cdeg) which indicates moderate to high lead and arsenic contamination of the soils. The most important ores of several base metals such as lead, zinc, and copper are sulphide minerals. The sulphide ore minerals represent the most serious threat of environmental contamination, because they are fairly easily oxidized in the presence of air to considerably more soluble sulphates. As a result, soils, surface and groundwater in the vicinity of the weathering sulphide minerals can be severely contaminated. Although tailings left after exploitation of the minerals are sources of environmental contamination it is the subsequent processing of the ores that results in the greatest environmental problems.

5.Conclusion

The study of the distributions and concentrations of arsenic, cadmium, cobalt, chromium, copper, nickel and lead in the soil samples identified the potential risks associated with lead-zinc mineralization and mining due to enrichment in the surface soils and continuous exposures of human beings and animals to these risks. The concentrations of arsenic and lead are higher than permissible levels and pose a threat to the health of the communities where mining activities are ongoing or were carried out. The observed significant regression and correlations of lead and arsenic reveals a close association between the elements during the process of mineralization.

Although there are likely to be significant natural enrichments of several elements in the vicinity of mineral deposits, mining and extraction of the deposit will add greatly to these enrichments. The mining and subsequent beneficiation of minerals and the separation and refining of their various components is one of the most serious sources of contamination of soils, waters, and the biosphere. This study generally concludes that statistical methods are strong tools for monitoring current environmental quality of soils in terms of enrichment of toxic elements and predicting future soil contamination.

6.Acknowledgements

7.References

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