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Petro Chemistry of Major and Trace Elements Concentrations in the Stream Sediments of Awo Area and its Environs, Southwestern Nigeria.

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ABSTRACT

Stream sediments are believed to record the environmental impact on fluvial system overtime and are often study to determine the overall pollution of an environment. This research work is aimed at mineralogical appraisal of various rock types through petro logical study, also to estimate the degree of enrichment of the element in the stream sediments and to determine if such enrichment has led to any form of pollution and also to produce a baseline geochemical data base for further geochemical investigation of the area under investigation.

Ten soil samples were collected randomly within the study area and were analyzed for major and trace elements concentration using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrumentation techniques, while five rock types were selected for petro graphic studies.

Thin section study shows that muscovite, biotite, microcline, and quartz are the main mineral assemblages present in the rocks of the study area. The result of the geochemical analysis were thereafter subjected to multivariate statistical analysis, the statistical plot from the result of major elements shows that Iron oxide (Fe_2O_3) range from 9.30% - 1.60 %, with a mean value of 4.6865%. Aluminum oxide (Al_2O_3) range from 2.63% - 0.55% with a mean value of 1.6802%, Fe_2O_3 and Al_2O_3 are dominant major oxides within the study area and they show moderate enrichment in the environment under investigation. From the result of the trace elements, Manganese [Mn] with mean value of 3996.00 ppm, Zinc [Zn] with mean value of 272.40 ppm, Copper [Cu] with mean value of 628.10 ppm, Lead [Pb] with a mean value of 61.22 ppm, Nickel [Ni] with a mean value of 109.40 ppm and Cobalt [Co] with mean value of 89.0 ppm have high concentration within the area of study, with Copper [Cu] having the highest degree of contamination factor 33%. The enrichment of Lead [Pb] in the study area has been linked to anthropogenic input of exhaust from motor bikes that ply the area, very strong positive correlation exist between V and Cr (0.737), Co and Ni (0.648) while a positive strong correlation exist between Co and Cr (0.550), Mo and Ga (0.535) indicating that they are from the same source.

The conclusion drawn from the box plot study show that V, Cr, Co, Ni, Zn, Mn, As, Rb, Pb, Mo, Ga and Cd have values that are greater than zero, while Sr and Zr have values that are less than zero. Copper [Cu] is the highest contaminating element within the study area, the presence of high amount of cupper in the study area may be probably due to geogenic factor, and in addition the weathering of the associated rocks and precipitation of same within the environment and it can also be attributed to the mining operations going on in the study area; from this it can therefore be deduced that the study area range in the category of practically contaminated to moderately contaminated.

Keywords: Sediment, Biotite, Enrichment, weathering, Geogenic

1. INTRODUCTION

Stream sediments are believed to record the environmental impact on fluvial systems over time and are often studied to determine the overall pollution in an area (Hillier *et al.*, 2001). However, information on the bulk concentration of a contaminant alone is not sufficient to assess the fate or potential mobility of contaminants and must be combined with other, more precise mineralogical or chemical technique. Mining and smelting constitute the principal sources of metals in the environment at a large number of sites (Hudson-Edwards *et al.*, 1996; Miller, 1997; Monna *et al.*, 2000; Hillier *et al.*, 2001; MacKenzie and Pulford, 2002; Ettler *et al.*, 2004, 2005). Mined watersheds provide an opportunity to investigate relationships between contaminated sediment patterns and the fluvial processes involved such as channel sediment transport and floodplain storage (Davies and Lewin 1974; Knighton 1989; Macklin 1985; Knox 1987; James 1989; Lecce and Pavlowsky 1997). Historical mining operations commonly introduce large volumes of mine wastes and associated metal contaminants to river systems of the world (Down and Stocks 1977). After release to the river system, contaminated mining sediment can be used as a geochemical tracer to identify input locations, monitor transport and storage, and date alluvial deposits (Bradley 1989; Graf 1996; Miller and Orbock-Miller 2007). The geochemical contrast between undisturbed river sediment and tailings inputs is typically high, so the mining signal can be detectable for relatively long distances below the source (Miller and Orbock-Miller 2007). Mining-contaminated sediment may also be stored in channel and floodplain deposits for periods ranging from months to centuries or longer depending on the timing for remobilization by mass-wasting, erosion, and/or weathering (Bradley 1989). Thus, mining sediment tracers are potentially useful to investigate fluvial processes across a range of watershed sizes and timescales (Ongley 1987). Geochemical monitoring of active channel sediment is often used to evaluate present-day risks posed by the re-introduction of contaminated legacy mining sediment back into the channel network in mined watersheds (Wolfenden and Lewin 1978; Bradley and Cox 1990; Graf 1996). Active channel deposits are composed of recently eroded and transported materials, reflect the influence of the present flood regime, and have the potentials to be remobilized by frequent flood events occurring several times annually (Wolfenden and Lewin 1978; Marcus 1987). Channel sediments can become contaminated from three mining-related sources which are differentiated according to mine history and input process: (i) direct discharge of tailings and effluents during mining operations; (ii) medium-term erosion and leaching of in-transit mining sediment as well as abandoned railings piles; and (iii) long-term erosion and weathering of previously contaminated alluvial deposits or legacy sediment . Where mining operations have been closed for several decades, onsite sources of contaminated tailings and mining sediment have usually been controlled or depleted. Hence, contemporary contamination trends are primarily controlled by the rates of contaminant remobilization by weathering and erosion from channel and floodplain storages (Bradley 1989; James 1989; Moore and Luoma 1990). Longitudinal variations in metal concentrations in channel sediments affected by mining inputs are strongly influenced by watershed factors such as upland erosion rates (Rose *et al*., 1970; Hawkes 1976). Contamination levels generally decrease exponentially downstream from mine waste sources (Wolfenden and Lewin 1978; Ongley 1987; Lecce and Pavlowsky 1997, 2001). In most rivers, the primary processes accounting for the downstream decrease in sediment-metal concentrations below a mining source at the watershed-scale are tributary dilution and mixing (Marcus 1987) and sedimentary deposition and storage (Bradley 1989). This research work is aimed at mineralogical appraisal of various rock types through petrological study, also to estimate the degree of enrichment of the major and trace element in the stream sediments samples of the study area with a view to determine if such enrichment has led to any form of pollution and in addition to produce a baseline geochemical data base for further geochemical investigation of the area under investigation. The study area lies approximately on latitude 4° 22’N and 4°25N and longitude 7°45’E and 7°48'E within the basement complex terrain of southwestern part of Nigeria. (Figure.1). The map of the study area is easily accessible with minor and major roads which includes Awo-Iragberi road , Awo-Iwo road as well as foot path linking one sampling point to the other. The climate is sub-humid tropical with average annual rainfall 1348.4mm. The area is well drained and the stream sediments samples for this study are collected from first order streams.

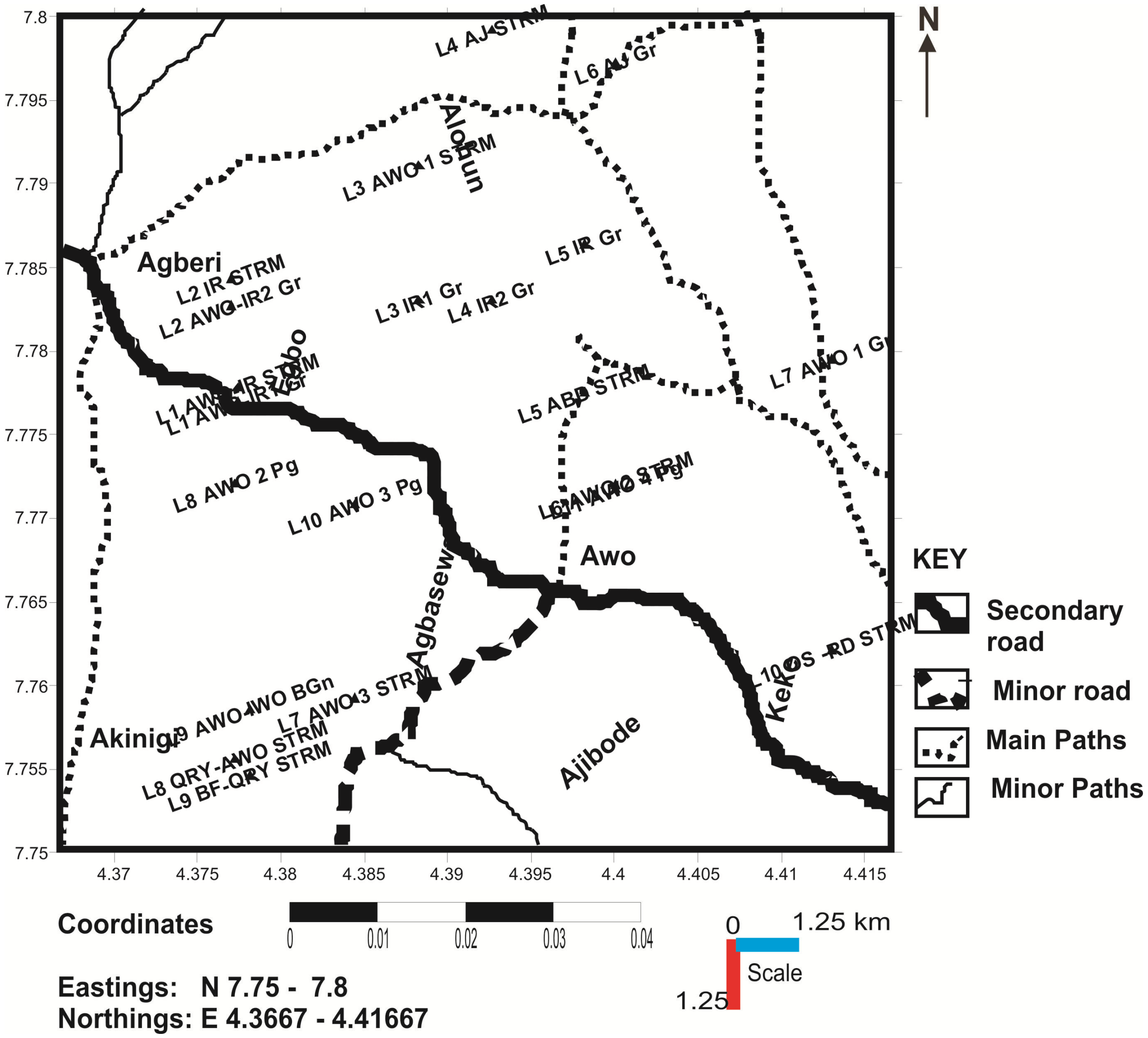


Figure1: Accessibility map of the study area

2. REGIONAL GEOLOGICAL SETTING

Rocks of the Precambrian basement complex of Nigeria underlie the project area. The Precambrian basement of African can be divided into three large cratons, these are the Kalahari craton, Congo and West African cratons, separated from each other by a number of mobile belts active in late Proterozoic times. The Nigerian basement complex lies north-east of the Congo Craton in a mobile belt affected by the Pan African Orogeny. These rocks outcrop in two large areas (viz the south-western and north-central parts of the country) and in smaller areas in the northeastern parts and the southeastern parts notably around the Oban massif and Obudu areas (Ekwueme, 2000). Three main lithologic groups are usually distinguished in the Nigerian basement. These are (i) a gneiss migmatite complex with evidences of polycyclic metamorphism mainly of amphibolites facies grade with Archean and Pan African ages (ii) A N-S trending schist belts of low grade sub crustal rocks with minor volcanic assemblages. They are concentrated in the western half of Nigeria although minor occurrences have been noted in the northern eastern and southern eastern parts (iii) Syn-late tectonic Pan African granite, which are collectively termed Older Granites and intrude the schist belts and the gneiss migmatite complex. They comprise mainly granites pegmatites, gabbros, charnockites, diorites and syenites. The schist belts, despite paucity of agreements in terms of their nomenclature, geographic delimitation and geodynamic setting are composed largely of metamorphosed pelitic and psammitic assemblages. Secondary lithologies such as ferrugineous rocks (Banded Iron Formation), carbonate, and metal ultramafic bodies are often used to discriminate them.

2.1. Lithological Association and Petrography

Three different rock lithologies were observed in the study area and they include Granite, Biotite-Gneiss and Pegmatites. The older lithologies of Granite were intruded by the Awo pegmatites.

Granite is the predominant rock type in the study area. Granite is an Igneous rock of visible crystalline formation and texture. The granite in the study area are mostly low lying, they are composed of quartz, biotite, muscovite and plagioclase mineralization. Granite occupy about 90% of the area mapped.

Pegmatite which is a variety of extremely coarse-grained igneous rock chemically similar to and closely associated with granite intrudes the older lithologies of Granitic rocks this pegmatite occupy small portion of the area mapped and they are coarse grain with felsic minerals and these minerals includes quartz, microcline feldspars biotite and muscovite mica, the dominant minerals within the pegmatite mapped is the mica, It has size and thickness that ranges in few meters and it is concentrated towards the south western corner of the study area where it intrudes the granite, based on field observation; the pegmatite is complex in nature with distinct textural and mineralogical variations.

Biotite Gneiss are metamorphic rocks in which biotite minerals predominates it is foliated and it is the oldest rock type found in the Awo study area with an average dip of 25^0E, this rocks occupy a small portion of the area mapped and it occurs in the lower portion within the southwestern part of the Awo study area. it is composed of minerals quartz, , muscovite, biotite and feldspar (Figure. 2a)

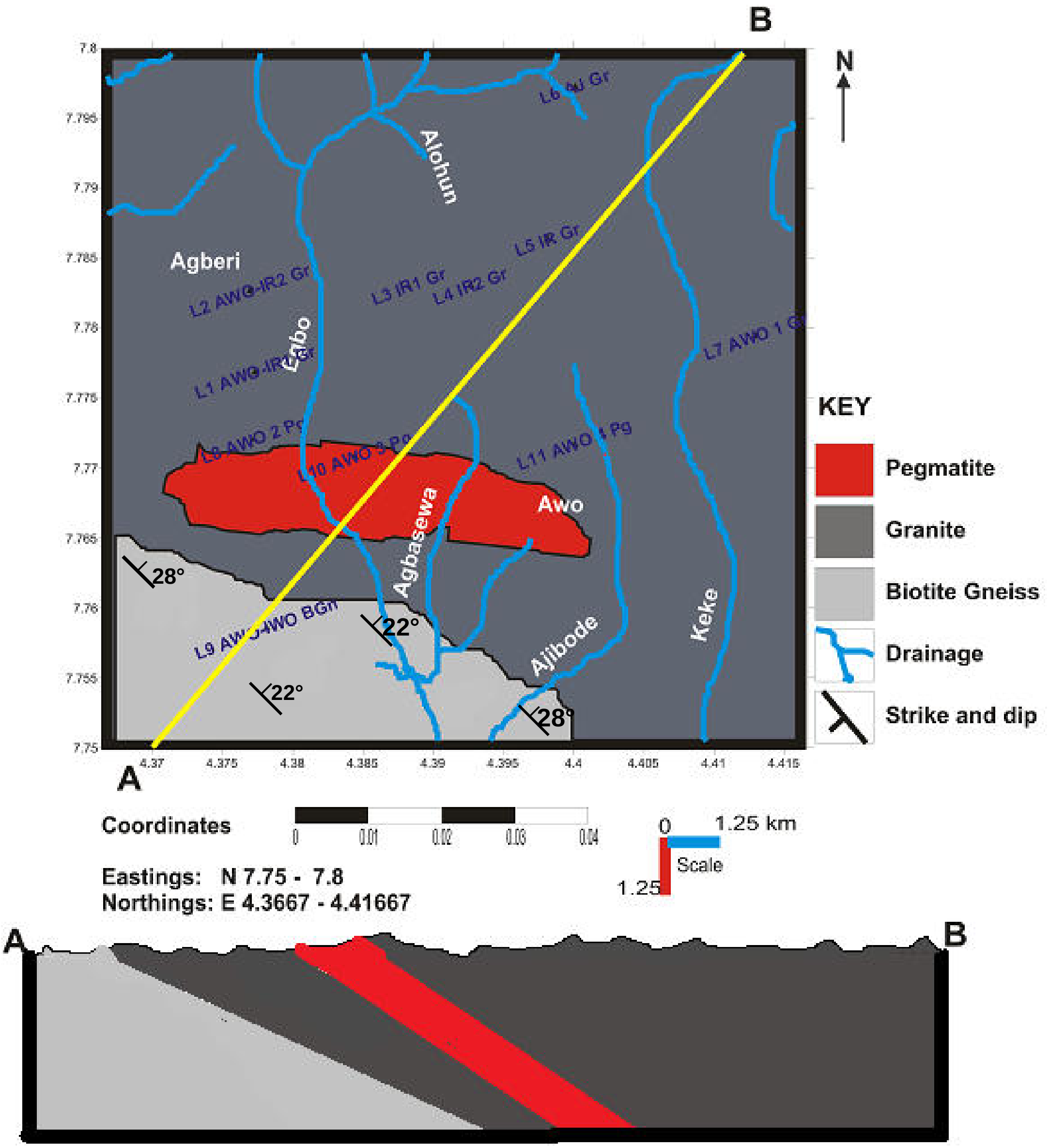
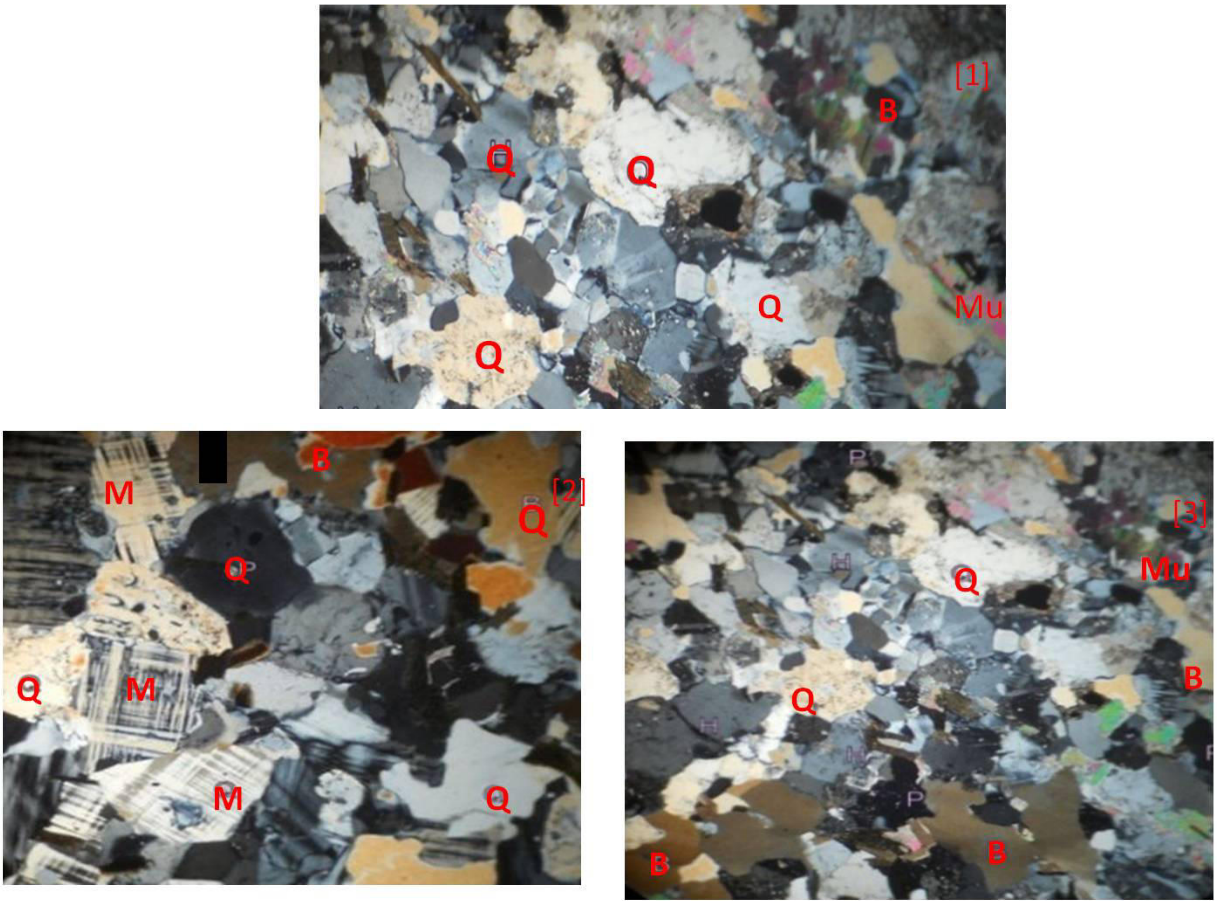


Figure 2a: Geological map of the study area



Bar scale = 20mm, Resolution: 150 dpi, Mag X40

Figure 2b. *[1]* Photomicrograph of Granite in transmitted light showing Quartz (Q), Muscovite (MU) and Biotite (B). *[2]* Photomicrograph of pegmatite in transmitted light showing Quartz (Q), Microcline (M) and Biotite (B). *[3]* Photomicrograph of Biotite gneiss in transmitted light showing Quartz(Q), Muscovite (Mu) and Biotite (B)

3. METHODOLOGY OF STUDY

Systematic geological mapping and stream sediment sampling of first order streams in other to represent weathered rocks in the drainage system was carried out followed by thin section Petrographic studies of fresh whole rock samples. Ten stream sediments samples were then analyzed for major and trace elements using inductively-coupled plasma atomic emission spectrophotometry (ICP-AES), at ACME Laboratory Vancouver Canada. The geochemical analytical procedure involves addition of 5ml of Perchloric acid (HClO4), Trioxonitrate (V) HN03 and 15ml Hydrofluoric acid (Hf) to 0.5gm of sample. The solution was stirred properly and allowed to evaporate to dryness after it was warmed at a low temperature for some hours. 4ml hydrochloric acid (HCl) was then added to the cooled solution and warmed to dissolve the salts. The solution was cooled; and then diluted to 50ml with distilled water. The solution is then introduced into the ICP torch as aqueous - aerosol. The emitted light by the ions in the ICP was converted to an electrical signal by a photo multiplier in the spectrometer, the intensity of the electrical signal produced by emitted light from the ions were compared to a standard (a previously measured intensity of a known concentration of the elements) and the concentration then computed.

4. RESULTS AND INTERPRETATION.

The analytical results of the major elements are presented in Tables 1 [a-b]. Table 1a, shows the major elements oxides composition of Awo study area in (Wt %) and Table 1b, shows the statistical summary of major elements oxides with respect to their average shale content respectively. From the analytical data and the various statistical plots figures 3 [a-c] shows the line diagrams of graphical illustration for major elements oxide composition in stream sediments of Awo study area. The analyses show that Iron oxide [Fe_2O_3] has the highest major element composition with value ranging from 1.41 % - 8.37% with an average value of 4.6865%. This highest concentration of Iron oxide was find in location *Awo-sed4* with a value of 8.37%. However when compared with its average shale content it shows a moderate enrichment level in the environment. It is likely that the parent rock from which materials are leached into the surrounding stream as sediments is highly ferruginized or contained Iron-bearing minerals. Calcium oxide [CaO] range from 0.04% - 0.34% with an average value of 0.16%, this value is higher than the average shale content for the study area, hence depicting that calcium enrichment in the area could be attributed to the presence of Ca-rich feldspar in the rocks that underlain the study area . The Magnesium oxide range from 0.03% - 0.30% with a mean value of 0.160%, this value is also higher than the average shale content for the study area and this could have resulted from the Magnesium-rich micas in the study area. Aluminum oxide [Al_2O_3] range from 0.55% -2.63% with an average value of 1.6802 %, It is next dominant oxide within the study area after Iron oxide, when compared with its average shale content it shows a higher concentration than its average shale this is an indication of prevalence of clay minerals in the stream sediments. Phosphorus oxide [P_2O_5] ranges from 0.03% - 0.18% with an average value of 0.879%, the highest concentration of phosphorus was found in location *Awo-sed7* while the lowest concentration was found in location *Awo sed2* . Sodium oxide [Na_2O] has values that range from 0.001-0.01% with an average mean value of 0.005% , on comparison with its average shale content it shows a higher concentration than its shale content which was observed in *Awo-sed2* indicating enrichment of sodium at this location, this might have occurred from the weathering of sodium-rich feldspar in the granite of the study area. The concentration of Potassium oxide [K_2O] in the stream sediments of Awo study area range from 0.02% - 0.14% with an average mean value of 0.088% on comparison with the average shale content, the average mean value is higher than its average shale content which indicate an enrichment of potassium in the study area, this might have occurred as a result of weathering of mica and from the pie chart diagram obtained for the major elements in the stream sediment of the study area (Figure 3d), it could be observed that [Fe_2O_3] has percentage composition of (65%) while [Al_2O_3] has percentage composition of (26%) indicating that iron oxide is the dominant major element in the study area followed by Aluminum oxide. (Figure. 3f) below shows the scatter diagram of major element in the stream sediments of Awo study area. A positive strong correlation exist between CaO and Fe_2O_5 (Table 1c), while a very strong positive correlation exist between P_2O_5 and Fe_2O_5; MgO and Fe_2O_5; and a positive moderate correlate correlation exist between TiO_2 and MgO; Al_2O_3 and TiO_2; K_2O and Na_2O_3. The strong positive, very strong positive and moderately positive correlation that exist between these elements shows they are from the same source.

The analytical results for trace element geochemistry of Awo study area is presented in Tables 2 [a-e]. Table 2a, shows the trace element concentrations of Awo study area in (ppm) and Table 2b, shows the statistical summary of trace elements with respect to their average shale content respectively. From these tables, Manganese [Mn] has the highest concentrations followed by chromium [Cr] with values ranging from 77.00ppm - 3996.00ppm and 44.25ppm - 630.33ppm with an average mean values of 1015.0000ppm and 250.8291ppm respectively. Manganese [Mn] has a significant enrichment values that is higher than that of the average shale content and the highest concentration value of this [Mn] was found in location *Awo-sed9bq*.Their is also a significant enrichment of Chromium [Cr] in the stream sediment of Awo study area, [Cr] was found to be the second trace element that has high concentration next to [Mn] within the study area. The average mean value of [Cr] is higher than its average shale content except at locations *Awo-sed2, Awo-sed3, Awo-sed8 and Awo-sed10,* at this locations the values of [Cr] are lower than that of its average shale content. Zinc [Zn] has concentration values ranging from 16.30ppm - 272.40 ppm with a mean value of 100.l500 ppm. while Copper [Cu)] has concentration ranging from 16.74ppm - 628.10 ppm with a mean value of 194.9310 ppm, the average mean concentration values of Zn and Cu are higher than their average shale content on comparison hence suggesting Zn and Cu to have significant enrichment in the stream sediments of the Awo study area. Asernic [As], Rubidium [Rb] and Strontium [Sr] has concentrations that ranges from 0.50ppm - 1.40ppm , 3.80ppm - 27.50 ppm and 3.90ppm -26.60ppm respectively with mean values of 0.8625ppm ,14.6800ppm and 14.5600 respectively. The mean values of [As], [Rb] and [Sr] is lower than their average shale content suggesting insignificant enrichment of these elements in the study area in the same vein, Cadmium [Cd] and Zirconium [Zr] with concentrations ranging from 0.03ppm - 0.22ppm and 0.70ppm - 1.80ppm with an average mean value of 0.800ppm and 1.2800 ppm respectively, has values lower than its average shale content suggesting an significant enrichment of [Cd] and [Zr] in the stream sediment of the study area. Lead [Pb] and Molybdenum [Mo] has concentrations ranging from 12.64ppm - 61.22ppm and 0.18ppm -2.87ppm with an average mean values of 26.2810ppm and 1.1.40ppm respectively, the mean values of [Pb] and [Mo] are higher than their average shale content suggesting significant enrichment of this elements in the area of study. The highest concentration of [Pb] and [Mo] were found in location *Awo sed4* and location *Awo sed9bq* respectively. Figures 4 [a-c] shows 2D and 3D geochemical maps of [Mn], [Cr], [Cu], [Zn], [As], [Rb], [Sr], [Cd] [Zr], [Pb], and [Mo] respectively within the Awo study area. A very strong positive correlation exist between V and Cr , Co and Ni, Ni and V, Ni and Cr, Cu and Ni, Zn and V, Zr and V. A positive strong correlation exist between Co and Cr, Mo and Ga while a positive moderate correlation exist between Mn and V, Pb and Mn, Zr and Cr. The very strong positive, strong positive and moderate positive correlation between these elements suggests they are derived from the same source (Table. 2c). The geo-accumulation index (Igeo) is an environmental parameter that enables the assessment of contamination by means of comparison. It is used in relation to bottom sediment (Muller,1969). It is computed using the formula: Igeo=Log2(Cn/1.5*Bn); Where Cn is the measured concentration of the elements. Bn is the normal or average shale content 1.5 is the correcting or matrix factor for geo-accumulation. The Igeo consist of seven grades (Table 2d) ranging from practically uncontaminated to extremely contaminated (Muller 1981). The geo-accumulation values of the trace elements in the stream sediment samples of Awo study area is shown in (Table. 2e). From the box plot (Figure. 5), it shows that V, Cr, Co, Ni, Zn, Mn, As, Rb, Pb, Mo, Ga and Cd have values that are greater than zero while Sr and Zr have values that are less than zero , Copper has a high contamination value within Awo study area and this contamination may be adduced to weathering activities of the associated rocks, leaching and concentration of metals due to mining operations within the study area, hence suggesting the area to be classified under the practically contaminated to moderately contaminated. From the pie chart diagram obtained for the degrees of contamination of trace elements in the stream sediment of Awo study area (Figure 6), it could also be observed that [Cu] has highest degree of contamination of about 33^0 degrees, followed in a decreasing order by [Co], [Pb], [Mn], [Zn] and [Mo] respectively.

TABLE 1a: MAJOR ELEMENT OXIDES COMPOSITION OF AWO STUDY AREA (Wt %)

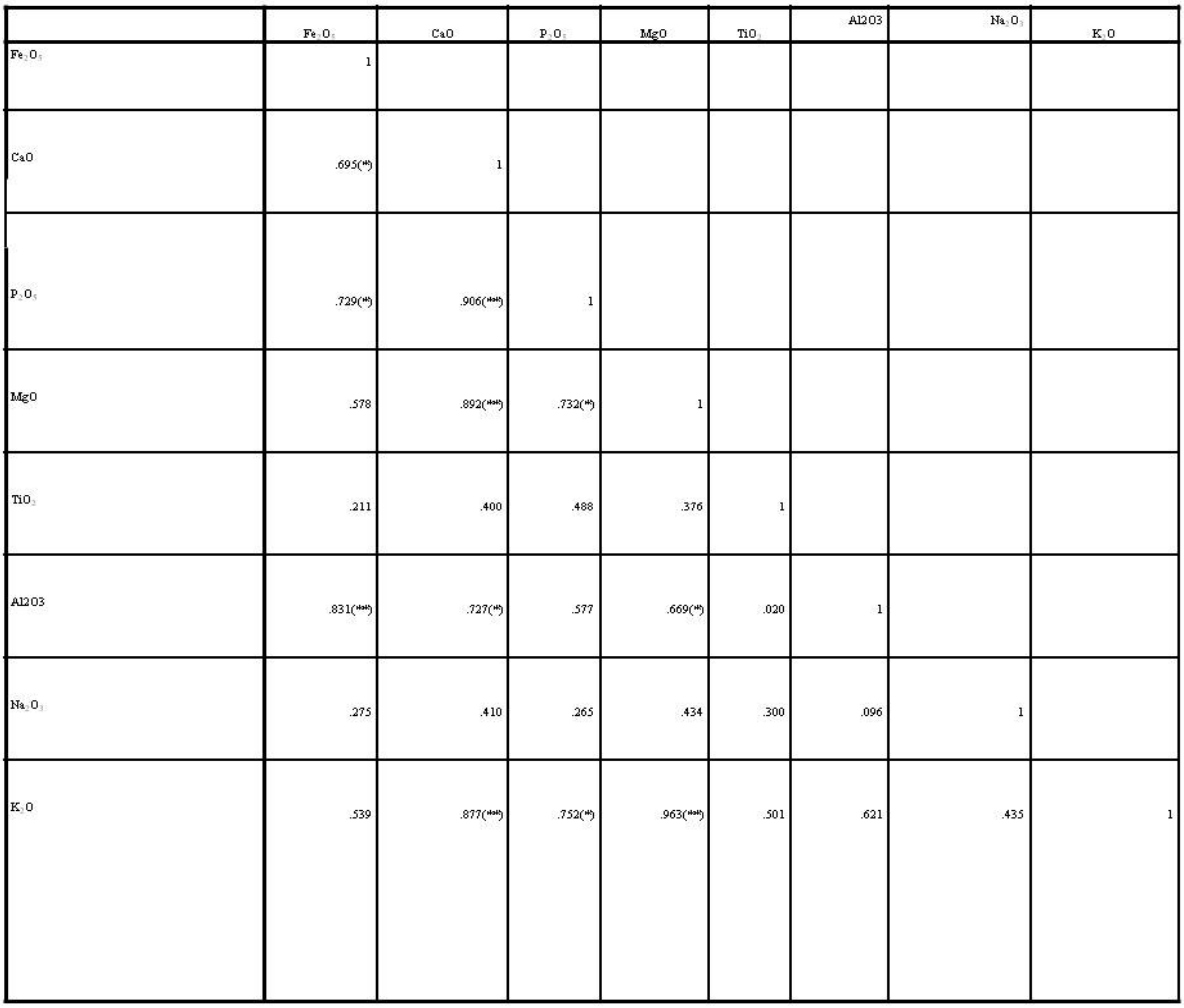
LOCATIONS	Fe_2O_3 %	CaO %	P_2O_5 %	MgO %	TiO_2 %	Al_2O_3 %	Na_2O %	K_2O %	SO_3%
AWO SED1	5.21	0.154	0.055	0.18	0.05	2.29	0.01	0.09	<0.05
AWO SED2	1.69	0.07	0.03	0.07	0.06	0.62	0.01	0.04	<0.05
AWO SED3	1.41	0.04	0.04	0.03	0.08	0.55	0.01	0.02	<0.05
AWO SED4	8.37	0.29	0.18	0.26	0.08	2.09	0.01	0.14	<0.05
AWO SED5	4.29	0.09	0.08	0.06	0.04	1.43	0.01	0.02	<0.05
AWO SED6	3.54	0.08	0.06	0.07	0.05	1.81	0.001	0.04	<0.05
AWO SED7	5.59	0.34	0.14	0.29	0.06	2.63	0.009	0.14	<0.05
AWO SED8	2.70	0.21	0.12	0.18	0.07	1.41	0.01	0.13	<0.05
AWOSED9BQ	6.73	0.18	0.09	0.18	0.07	2.53	0.006	0.11	<0.05
AWO SED10	2.57	0.15	0.07	0.26	0.07	1.42	0.006	0.13	<0.05

TABLE 1b :SUMMARY OF MAJOR ELEMENT IN THE STREAM SEDIMENT

Elements	N	Ranges	Mean	Std Deviation	*Average shale content
Fe_2O_3	10	8.37-1.41	4.69	2.51	0.047
CaO	10	0.34-0.04	0.16	0.09	0.025
P_2O_5	10	0.18-0.03	0.09	0.05	**
MgO	10	0.26-0.03	0.16	0.09	0.074
TiO_2	10	0.08-0.04	0.06	0.01	0.0045
Al_2O_3	10	2.63-0.55	1.68	0.73	0.02
Na_2O	10	0.01-0.001	0.007	0.005	0.009
K_2O	10	0.14-0.02	0.088	0.052	0.025

*The average shale content of the elements is a global standard while it is used as a reference to determine anomalous concentration of any element

TABLE 1c :CORRELATION CO-EFFICIENTS FOR MAJOR ELEMENT OXIDES



	Fe_2O_3	CaO	P_2O_5	MgO	TiO_2	Al2O3	Na_2O_3	K_2O
Fe_2O_3	1							
CaO	.695(*)	1						
P_2O_5	.729(*)	.906(**)	1					
MgO	.578	.892(**)	.732(*)	1				
TiO_2	.211	.400	.488	.376	1			
Al2O3	.831(**)	.727(*)	.577	.669(*)	.020	1		
Na_2O_3	.275	.410	.265	.434	.300	.096	1	
K_2O	.539	.877(**)	.752(*)	.963(**)	.501	.621	.435	1

TABLE 2a: SELECTED TRACE ELEMENTS AND RARE EARTH ELEMENTS (PPM) RESULTS FOR STREAM SEDIMENTS OF AWO STUDY AREA

LOCATION	Sb	Bi	V	La	Ba	B	W	Sc	Tl	Hg	Se	Te	Ga	Cs	Ge
AWO SED1	0.03	0.14	79	33.8	170	<20	<0.1	4.7	0.35	32	0.2	<0.02	5.8	1.53	<0.1
AWO SED2	0.03	0.1	26	25.2	107	<20	<0.1	1.5	0.08	14	<0.1	<0.02	2.1	0.49	<0.1
AWO SED3	0.04	0.55	37	37.8	26.4	<20	<0.1	3.1	0.03	10	<0.1	<0.02	2.8	0.6	<0.1
AWO SED4	0.2	0.17	125	38.8	169	<20	0.6	5.6	0.2	23	<0.1	<0.02	5.7	1.66	<0.1
AWO SED5	0.12	0.28	85	12.1	61.6	<20	<0.1	2.6	0.09	15	<0.1	<0.02	4.6	0.77	<0.1
AWO SED6	0.19	3.03	66	10.7	104	<20	<0.1	2.8	0.22	20	0.2	<0.02	6.1	1.58	<0.1
AWO SED7	0.07	0.42	66	27.6	159	<20	<0.1	4.2	0.23	47	0.3	<0.02	6.7	2.28	<0.1
AWO SED8	0.12	0.05	38	10.3	75.1	<20	0.3	1.5	0.15	<5	<0.1	<0.02	4.4	0.89	<0.1
AWO SED9BQ	0.08	0.55	122	20.2	326	<20	<0.1	3.7	0.66	22	0.3	<0.02	7.2	1.12	<0.1
AWO SED10	0.04	0.11	44	23.8	103	<20	<0.1	2.2	0.17	9	<0.1		4	1.98	<0.1

TABLE 2a: CONTINUED

LOCATION	Hl	Nb	Rb	Sn	Ta	Zr	Y	Ce	in	Re	Be	Li	Pd	Pt
AWO SED1	0.03	0.24	18.7	1	<0.05	1.4	12.94	137.4	0.02	<1	1.3	5.2	<10	<2
AWO SED2	<0.02	0.32	6.8	0.8	<0.05	0.8	7.16	64.1	<0.02	<1	0.5	2.2	<10	<2
AWO SED3	<0.02	0.47	3.8	0.8	<0.05	0.9	11.44	79.9	0.03	<1	0.8	3.3	<10	<2
AWO SED4	0.03	0.67	20.3	3.1	<0.05	1.6	16.89	98.9	0.05	<1	2.8	9.9	<10	<2
AWO SED5	0.02	0.41	7.1	2.4	<0.05	1	5.25	52.4	0.03	<1	1	3.5	<10	<2
AWO SED6	0.05	0.77	10.3	2	<0.05	1.7	4.28	61.2	0.03	<1	1	5.7	<10	<2
AWO SED7	0.05	1.3	27.5	2.2	<0.05	1.7	11.28	74.4	0.03	<1	1.7	11.7	<10	<2
AWO SED8	0.03	0.26	15	0.9	<0.05	1.2	3.29	59	<0.02	<1	0.4	10.2	<10	<2
AWO SED9BQ	0.03	0.43	15.8	1.9	<0.05	1.8	7.6	226.3	0.03	<1	1.5	8.1	<10	<2
AWO SED10	<0.02	0.39	21.5	1.6	<0.05	0.7	7.89	71.2	<0.02	<1	1.3	12.5	<10	<2

TABLE 2a: CONTINUED

LOCATION	Mo	Cu	Pb	Zn	Ag	Ni	Co	As	U	Au	Th	Sr	Cd
AWO SED1	0.68	67.2	34.5	45.9	16	19.5	45	0.6	2.9	0.8	10.7	15	0.03
AWO SED2	0.18	16.7	13.21	16.3	8	6.1	14.2	<0.1	2.3	1.5	23.1	7.9	<0.01
AWO SED3	0.35	67.5	12.64	24.3	5	8	2.6	<0.1	1.7	1.3	11.9	3.9	<0.01
AWO SED4	1.42	204	61.22	174.9	102	39.7	36	0.6	4.8	3.2	12.9	23	0.22
AWO SED5	2.65	563	15.78	230.1	58	94.8	17.7	1.1	3.4	2.6	5.5	10	<0.01
AWO SED6	0.69	94.2	17.77	45.4	14	18.8	29.3	0.8	3	1	3.6	14	<0.01
AWO SED7	1.16	228	22.54	125.2	38	52.6	24	1.4	3.5	1.8	6.5	27	0.03
AWO SED8	0.62	36.2	15.9	33.8	16	7.9	12.7	0.5	1.4	1	8.1	6.6	<0.01
AWO SED9BQ	2.87	628	55.98	272.4	50	109	89	1.4	3.1	1.7	8.4	15	0.04
AWO SED10	0.42	44.3	13.27	33.2	10	14.8	13.9	0.5	3.2	0.8	6.2	23	<0.01

TABLE 2a: CONTINUED

LOCATION	Mn	Cr
AWO SED1	1436	4.05
AWO SED2	848	1.31
AWO SED3	77	1.12
AWO SED4	1321	6.5
AWO SED5	587	3.34
AWO SED6	1100	2.75
AWO SED7	770	4.35
AWO SED8	495	2.1
AWO SED 9 BQ	3996	5.23
AWO SED10	673	2

TABLE 2b: SUMMARY OF SELECTED TRACE ELEMENTS CONCENTRATION OF STREAM SEDIMENT

Elements	N	Ranges	Averages	Std Deviation	*Average shale content
V	10	125.00-26.00	68.80	34.61	130
Cr	10	630.33-44.25	250.83	212.00	100
Co	10	89.0-2.60	28.44	24.64	20
Ni	10	109.40-6.10	37.16	37.43	80
Cu	10	628.10-16.74	194.93	222.75	50
Zn	10	272.40-16.30	100.15	94.50	90
Ga	10	7.20-2.10	4.94	1.66	25
Mn	10	3996.00-77.00	1015.00	1124.38	850
As	10	1.40-0.50	0.86	0.39	10
Rb	10	27.50-3.80	14.68	7.58	50
Sr	10	26.60-3.90	14.56	7.77	400
Pb	10	61.22-12.64	26.28	18.26	20
Mo	10	2.87-0.18	1.10	0.95	2
Cd	10	0.22-0.03	0.08	0.09	0.3
Zr	10	1.80-0.70	1.28	0.41	180

*The average shale content of the elements is a global standard while it is used as a reference to determine anomalous concentration of any element .

TABLE 2c: CORRELATION CO-EFFICIENT FOR TRACE ELEMENT

	V	Cr	Co	Ni	Cu	Zn	Ga	Mn	As	Rb	Sr	Pb	Mo	Cd	Zr
V	1														
Cr	.737(*)	1													
Co	.772(**)	.550	1												
Ni	.726(*)	.951(**)	.648(*)	1											
Cu	.702(*)	.962(**)	.618	.992(**)	1										
Zn	.839(**)	.935(**)	.654(*)	.965(**)	.959(**)	1									
Ga	.750(*)	.550	.738(*)	.579	.510	.591	1								
Mn	.476	.475	.906(**)	.607	.591	.520	.549	1							
As	.390	.736(*)	.477	.817(*)	.769(*)	.709(*)	.691	.548	1						
Rb	.328	-.051	.290	.104	-.012	.152	.613	.111	.049	1					
Sr	.449	.150	.276	.221	.112	.283	.584	.068	.168	.886(**)	1				
Pb	.902(**)	.434	.793(**)	.485	.456	.643(*)	.630	.488	.177	.394	.425	1			
Mo	.775(**)	.959(**)	.644(*)	.982(**)	.987(**)	.978(**)	.572	.564	.712(*)	.055	.156	.535	1		
Cd	.640	.016	-.248	-.224	-.167	.189	-.567	-.530	-.556	-.072	.359	.683	-.030	1	
Zr	.695(*)	.444	.696(*)	.433	.381	.488	.909(**)	.486	.509	.442	.410	.666(*)	.440	-.063	1

TABLE 2d: GEO-ACCUMULATION INDEX CLASSES(MULLER 1981)

Igeo class	Values	Sediment quality
0	Igeo<o	Practically uncontaminated
1	0<Igeo<1	Uncontaminated to moderately contaminate
2	1<Igeo<2	Moderately contaminated
3	2<Igeo<3	Moderately to heavily contaminated
4	3<Igeo<4	Heavily contaminated
5	4<Igeo<5	Heavily to extremely contaminated
6	5<Igeo<6	Extremely contaminated

TABLE 2e: GEO ACCUMULATION INDEX FOR TRACE ELEMENT IN THE STREAM SEDIMENT

samples	V	Cr	Co	Ni	Cu	Zn	Ga	Mn	As	Rb	Sr	Pb	Mo	Cd	Zr
1	0.12	0.10	0.45	0.05	0.27	0.10	0.05	0.34	0.01	0.07	-0.07	0.14	0.07	0.02	-0.02
2	0.04	0.04	0.14	0.01	0.07	0.06	0.02	0.21	***	0.03	0.03	0.05	0.02	***	-0.01
3	0.06	0.12	0.03	0.02	0.27	0.05	0.02	0.06	***	0.005	-0.02	0.05	0.03	***	-0.01
4	0.19	0.29	0.36	0.09	0.82	0.39	0.04	0.31	0.01	0.08	0.01	0.24	0.14	0.15	-0.02
5	0.13	0.59	0.18	0.24	2.26	0.51	0.04	0.14	0.02	0.03	-0.05	0.06	0.26	***	-0.01
6	0.34	0.26	0.29	0.05	0.38	0.10	0.05	0.26	0.02	0.04	-0.07	0.07	0.09	***	-0.02
7	0.34	0.26	0.24	0.13	0.91	0.28	0.05	0.18	0.03	0.11	0.01	0.09	0.12	0.02	-0.02
8	0.06	0.05	0.13	0.02	0.14	0.07	0.03	0.12	0.01	0.06	-0.03	0.063	0.062	***	-0.01
9	0.19	0.55	0.89	0.27	2.52	0.61	0.06	0.92	0.03	0.06	-0.07	0.224	0.287	0.03	-0.02
10	0.07	0.08	0.14	0.04	0.18	0.07	0.03	0.16	0.1	0.09	0.01	0.05	0.04	***	-0.01

*** Below detection limit <0.01,0.02

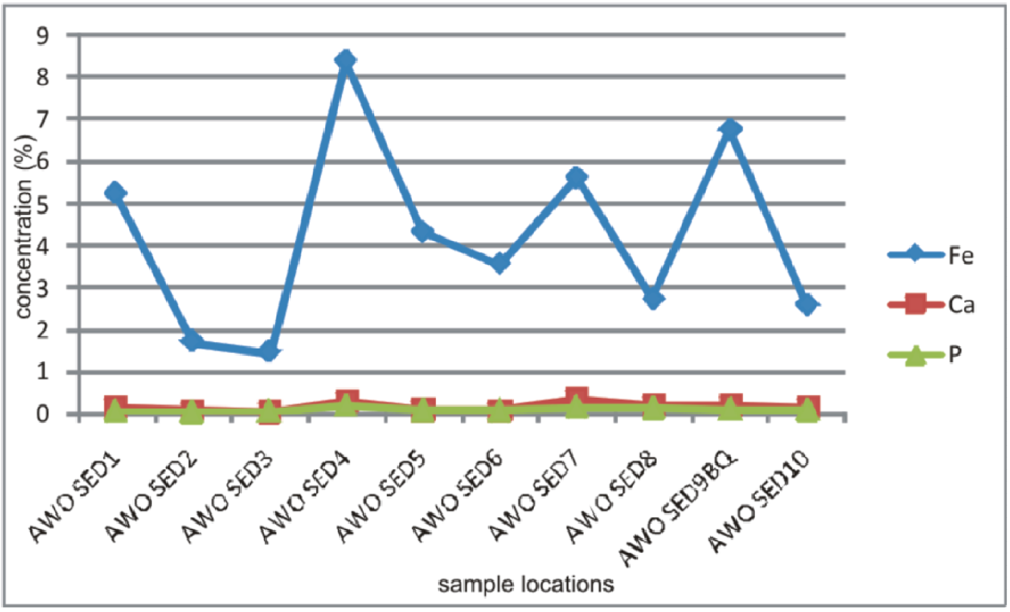


Figure 3a: showing the line diagram of Fe, Ca and P

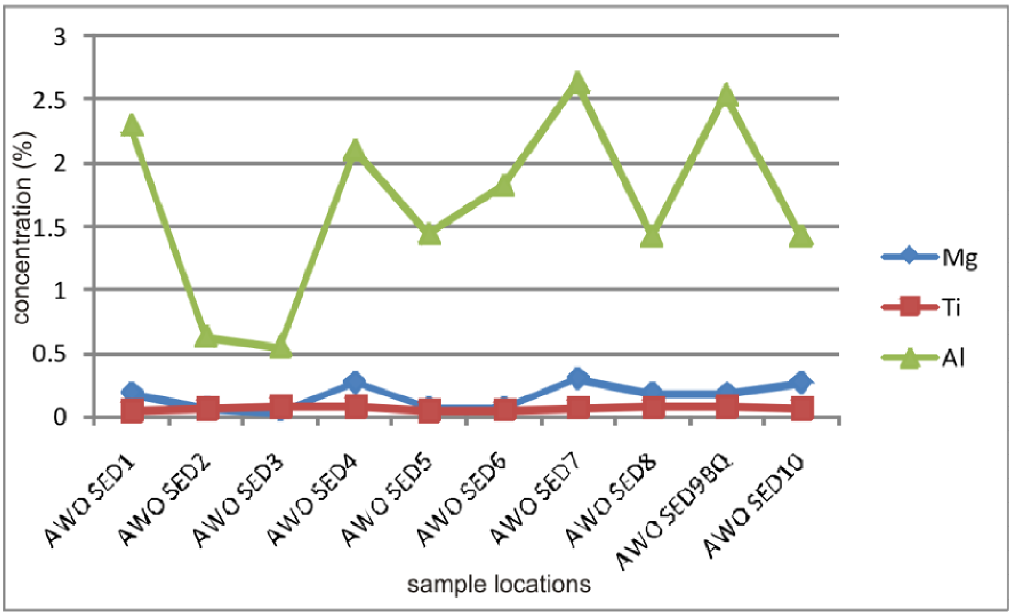


Figure 3b: showing the line diagram of Mg, Ti, and Al

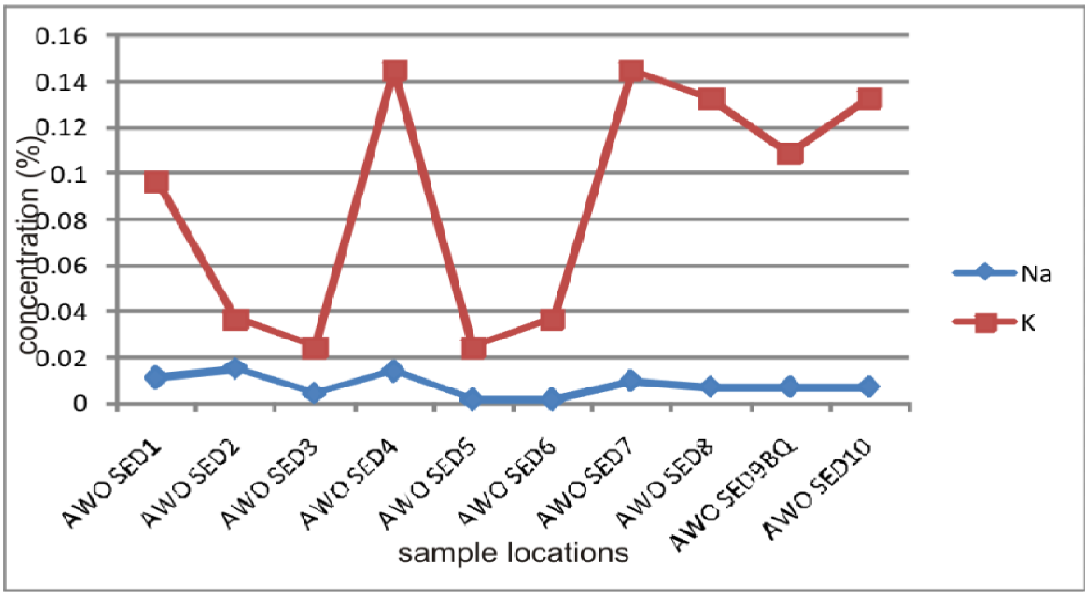


Figure 3c: showing the line diagram of Na and K.

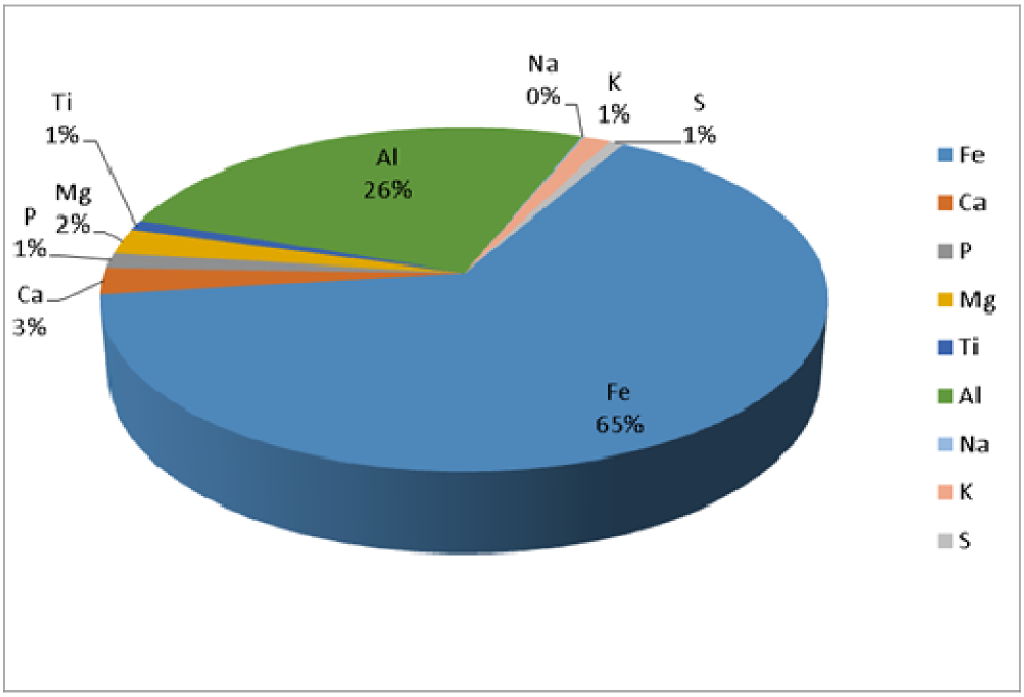


Figure 3d: Pie chart representing the mean distribution of major oxides in the study area

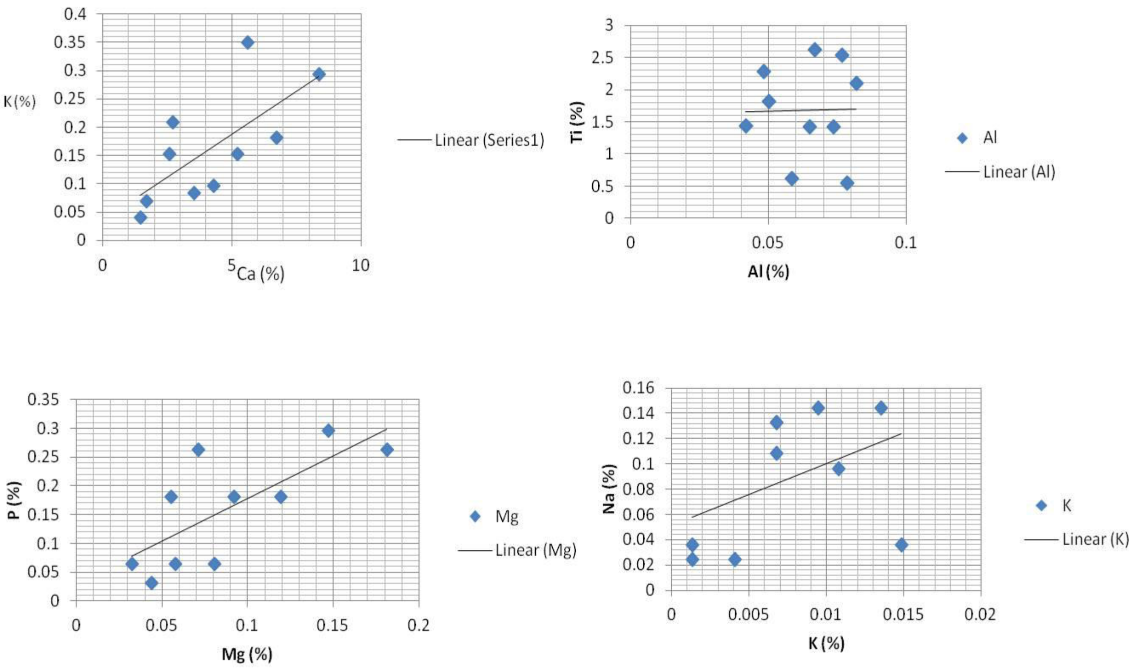


Figure 3f: Scatter diagram for Fe against Ca ; P against Mg; Ti against Al; Na against K

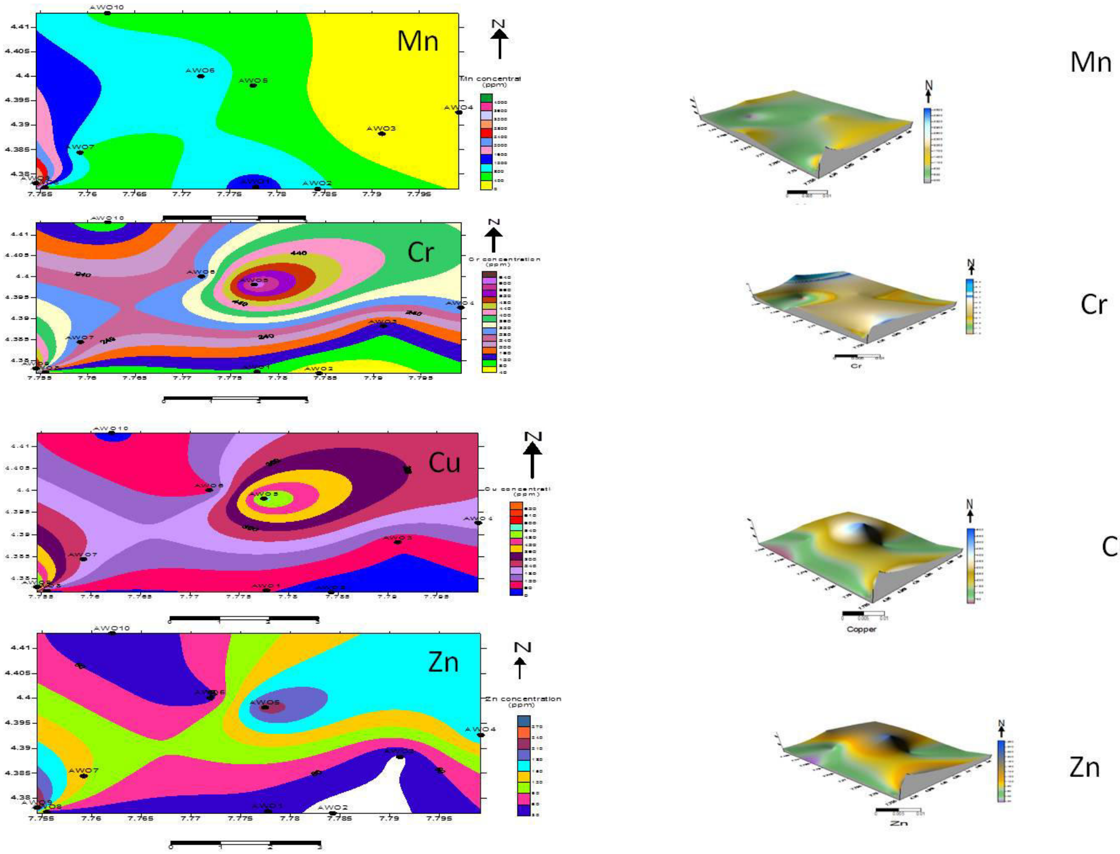


Figure 4a: showing 2D and 3D geochemical maps of [Mn], [Cr], [Cu] and [Zn] respectively.

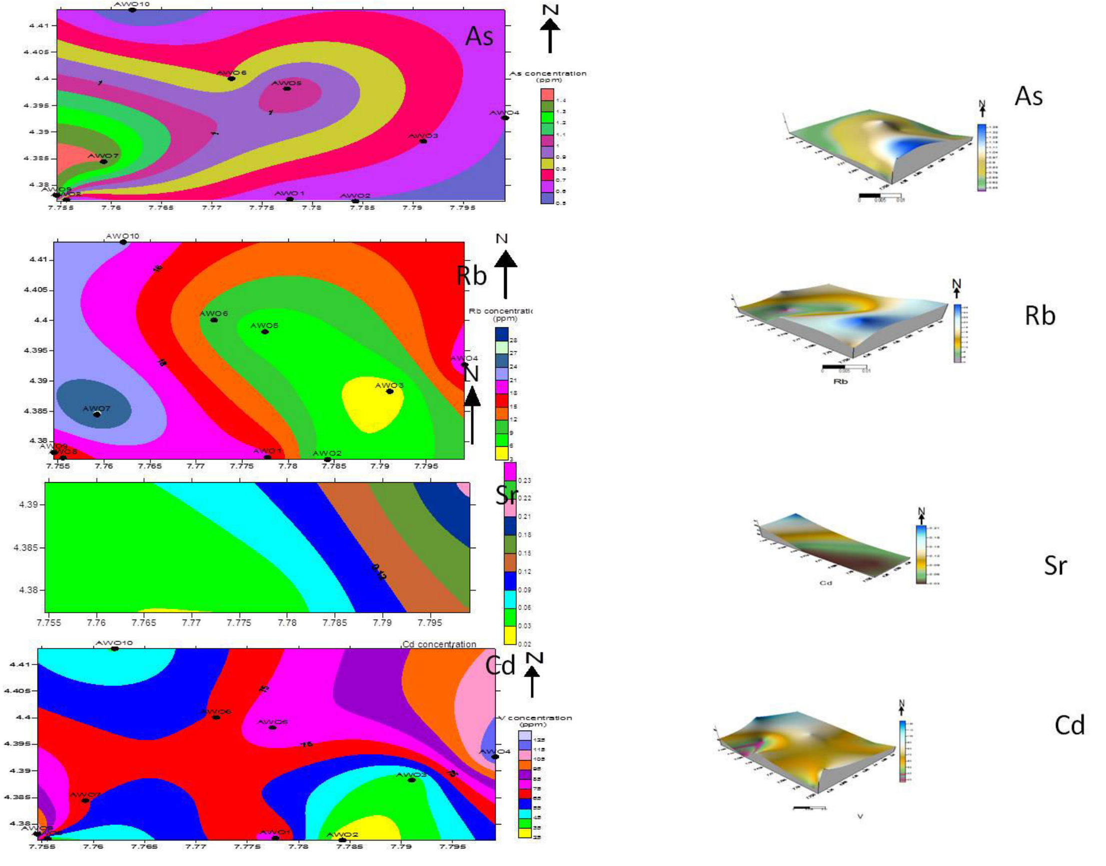


Figure 4b: showing 2D and 3D geochemical maps of [As], [Rb], [Sr] and [Cd] respectively.

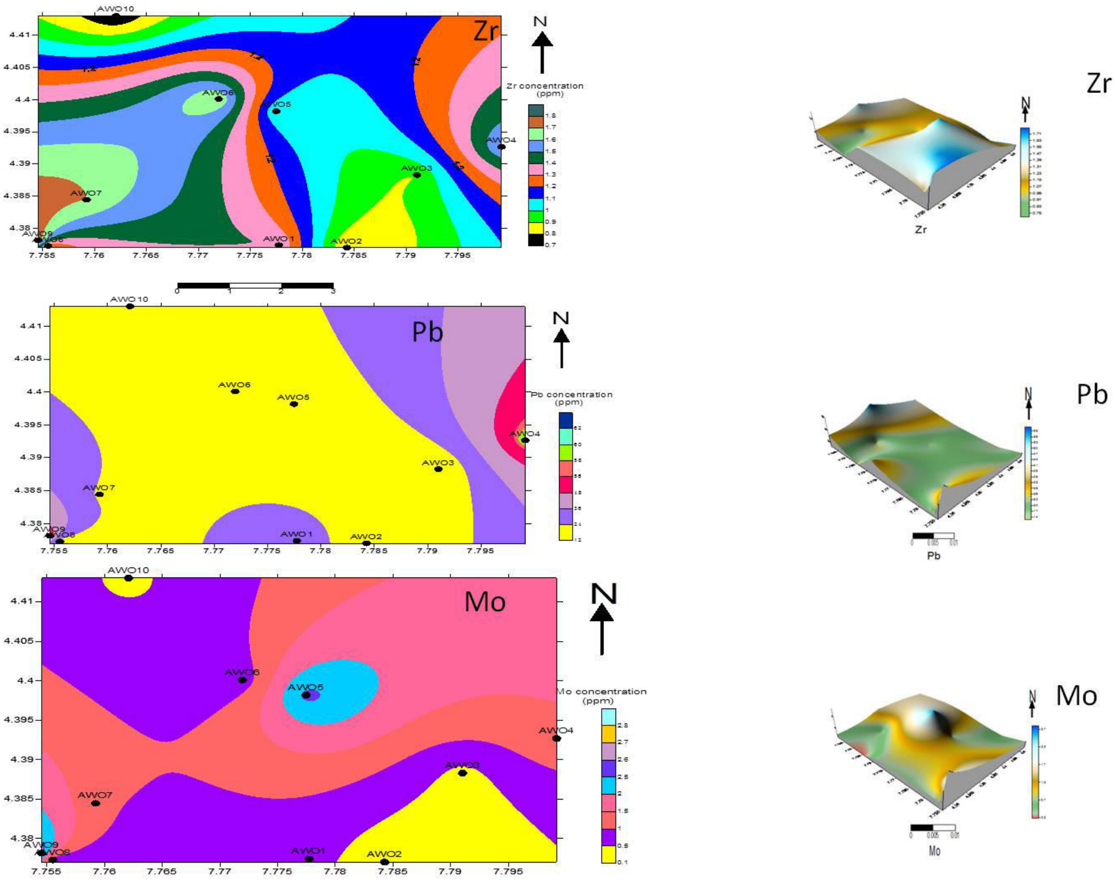


Figure 4c: showing 2D and 3D geochemical maps of [Zr], [Pb], and [Mo] respectively.

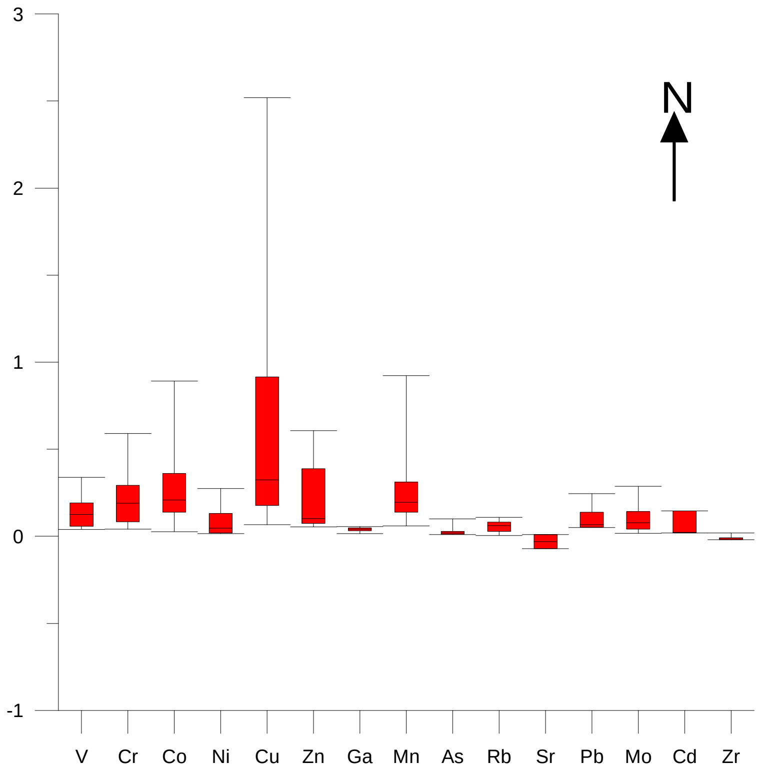


Figure 5 : Box plot showing the geo-accumulation index of each element

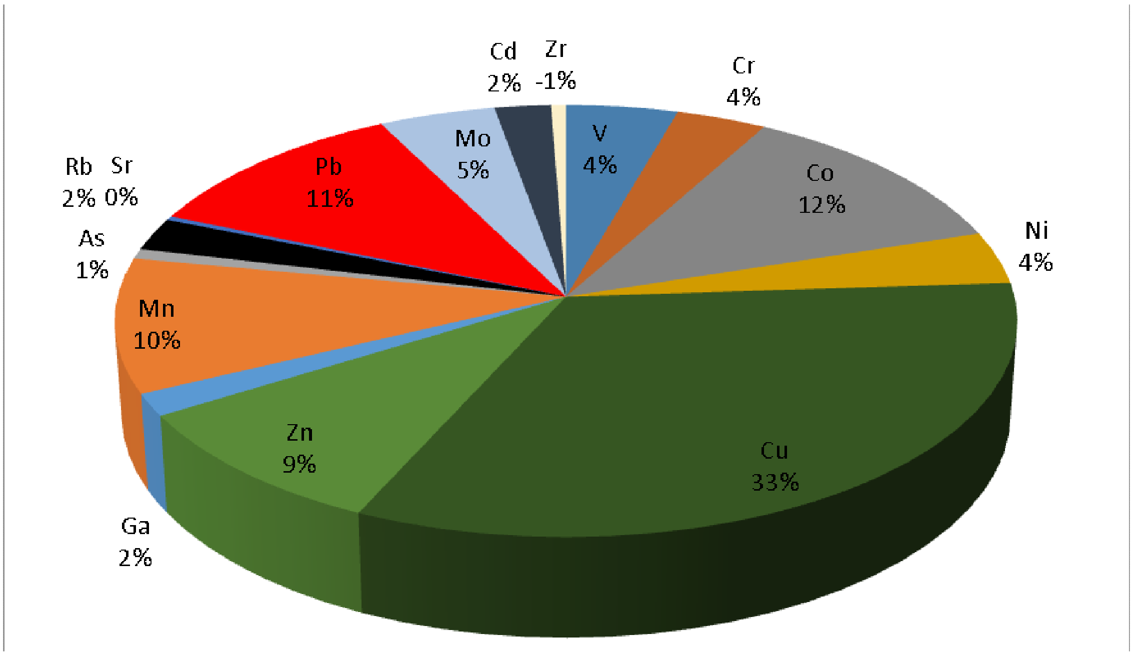


Figure 6: Pie chart showing the Degree of contamination of trace element

5. CONCLUSION

The result of geochemical investigation carried out on the stream sediments of Awo and its environs shows that Iron oxide [Fe_2O_3] has the highest major oxide composition. It is likely that the parent rock from which iron materials are leached into the surrounding stream as sediments is highly ferruginized or contained Iron-bearing minerals and next in abundance is Aluminum oxide [Al_2O_3] and when compared with its average shale content it shows a higher concentration than its average shale this is an indication of prevalence of clay minerals in the stream sediments. A very strong positive correlation exist between P_2O_5 and Fe_2O_5; MgO and Fe_2O_5; and a positive moderate correlation exist between TiO_2 and MgO; Al_2O_3 and TiO_2; K_2O and Na_2O_3. The strong positive, very strong positive and moderately positive correlation that exist between these elements shows they are from the same source. The analytical results for trace element geochemistry of Awo study area shows that Manganese [Mn] has high concentrations as well as chromium [Cr] and these elements [Mn] and [Cr] has significant enrichment values that is higher than that of the average shale content, Zinc [Zn], Lead [Pb] and Cobalt [Co] also has significant enrichment because their values are higher than that of the average shale contents. Copper [Cu)] has the highest concentration value and a significant enrichment. Asernic [As], Rubidium [Rb] Cadmium [Cd], Zirconium [Zr] and Strontium [Sr] has concentrations that is lower than their average shale content suggesting insignificant enrichment of these elements in the study area. From the box plot and geo-accumulation values of the trace elements in the stream sediment samples of Awo study area, it shows that V, Cr, Co, Ni, Zn, Mn, As, Rb, Pb, Mo, Ga and Cd have values that are greater than zero while Sr and Zr have values that are less than zero , Copper has a high contamination value within the study area and this contamination may be adduced to weathering activities of the associated rocks and leaching / concentration of metals due to mining operations within the study area, hence suggesting the area to be classified under the practically contaminated to moderately contaminated, the pie chart diagram obtained for the degrees of contamination of trace elements in the stream sediment of Awo study area also confirms the highest degree of contamination of [Cu] to be about 33^0 degrees. The geologic mapping of the area revealed the oldest lithologies in the study area to be Biotite Gneiss, Granite which was intruded by a younger sequence of Pegmatite bodies.

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