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CHEMICAL ANALYSIS OF BAUXITE AND RUTILE ORES, CONTAMINATED VICINITY SOIL, SEDIMENT AND PLANTS (*VIGNA UNGUICULATA*) IN KANAM AND WASE, PLATEAU STATE-NIGERIA

Bulus E.D, Itodo A.U, Wuana R.A, Eneji I.S
Department of Chemistry Joseph Sarwuan Tarka University Makurdi, Benue State-Nigeria

Abstract;
Contamination of agricultural soils, water and sediments and depletion of the environment through unregulated mining activities poses a great threat on the environment and human. A non-destructive analytical technique (XRF) was employed to characterize bauxite and rutile ores and their vicinity soil and sediment, plant (vigna unguiculata) roots and stems. Bauxite ore had high clay (23.5%) content, suggesting that the ore cannot be utilized directly unless it is beneficiated to meet metallurgical required grade. The elemental composition of farmland soil within bauxite mineral vicinity revealed silicon (20.9%), Fe (10.7%), Al (9.4%), K (9.0%), Mg (2.5%), Ca (1.6%) and Ti (1.0%) as major components of the soil. Toxic heavy metals residues such as V (0.06%), Cr (0.02%) and Ba (0.19%) were also recorded. Soil contamination with Cr due to bauxite ore mining considerably affects the biological activity of the soil. ED-XRF for soil sediment within this proximate mining vicinity revealed higher value for Fe (16.6%) compared to bauxite vicinity soil. Similarly the characterization of rutile ore using this technique unveiled the interlocking of soil minerals such as Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, Ta and W in various proportions with titanium oxide having a relatively high concentration (25.3%). Although lower soil contamination was observed in the rutile vicinity soil and sediment compared to the former (bauxite vicinity soil), titanium contamination was recorded (2.9) higher than the Russian general toxicology and Dutch standards for soils (<1). Soil contamination in this mineral vicinity was due to continuous interference of the soil and soil organic matter. The chemical characterization of plant (vigna unguiculata) roots from the mineral exploration vicinity also revealed the usual soil elements Mg, Al, Si, K, Ca and Fe as major elements as well as Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, W and Ta as trace or minor elements respectively, and of great concern is the presence of Cr (0.03), Ni (0.004), Co (0.02), Mn (0.16) Cu (0.256) and Zn (0.06) in the roots and stems. . Low values observed for most metals in the stem XRF are due to the fact that metals (essential and non-essential) are trapped through the roots then subsequently transported to other sections of the plants. XRF analysis of the soil control samples (500 m away from bauxite and rutile ores vicinities) unveiled low values for most heavy metals, this suggests that mineral mining exploration in this location is the major source of soil heavy metals contamination. Contamination factor (C_f^i<1), ecological risk (Er^i<40) and geo-accumulation index ($I_{geo.}$) for heavy metals Cr, Cu. Ni and Zn revealed low contamination, low ecological risk and Igeo values. However, the pollution load index (PLI) suggests that the entire mineral exploration area soil and sediment were moderately polluted with Cr (>1) and unpolluted with Cu, Ni and Zn metals. The enrichment factor (EF) ranged between depletion to mineral enrichment-very high enrichment.

Keywords: Bauxite and Rutile Ores, Soil and Sediment, Plant (*Vigna Unguiculata*), Mining Exploration, Environmental Contamination, Characterization, X-Ray Fluorescence.

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INTRODUCTION;

Mining activities are one of the most important pollution sources of metals in countries with a tradition of ore extraction. Millions of tons of wastes deposited on river shores may release toxic elements to the rivers. Once in the water, metals and metalloids may be transported long distances affecting ecosystems (Aurora *et al.*, 2007). Solid mineral exploration in Nigeria began during the pre-colonial era (1903/1904) when the British colonial government organize mining operation covering both the northern and southern protectorate. This grew and metamorphosed leading to classification of Nigeria as a leading producer of coal, columbite and tin in 1940s (Itodo *et al*., 2019). In plateau state, solid minerals which have been given lesser attention and they also generate a significant level of environmental impact include; bauxite, rutile, gemstone, dimension stone, feldspar, monazite, clay, kaolin, dolomite, mica, zircon, marble, ilmenite, barites, talc, galena, quartz, bismuth ore, gamet, tourmaline, copper, topaz, silica, sharp sand and granite (Dateer, 2017).

Soil and sediment are a complex matrix that can adsorb pollutants and pollution due to heavy or toxic metals has generated much concern in most metropolitan and urban complexes. It is believed that the concentrations of these metals released into the ecosystem may lead to geoaccumulation, bioaccumulation, biomagnification and phytoaccumulation (Lokeshwari *et al*., 2012). Plants from mineral exploration areas and industries that burn their waste on-site are known to be responsible for the release of heavy metals into the atmosphere, which settle in the soil, thus leaving behind lasting effects for years, since they are environmentally stable, non-biodegradable, and tend to cause accumulation in soils. When the surface soils are accumulated, they consequently serve as a transmitter of pollutants to surface water, groundwater, atmosphere, and food. These accumulated pollutants in the surface can as well be transported to different environmental components such as deep soils, plants, and dust particles (Kodom *et al*., 2012).

Sample Collection and site description

A total of 20 samples from the Kanam and Wase LGAs were carefully collected during the rainy season using stainless-steel core-samplers(push probes and bucket augers) at regular intervals from the surface soils (0-15 cm depth)around mineral exploration sites. Control soil samples were collected 500 m away from the mining areas. Mineral samples (bauxite and rutile) were collected directly from the miners at the exploration sites. Plants samples were taken from agricultural farms around the mineral vicinities. In all, a total of 10 samples were selected from the total number collected from these locations for laboratory characterization and elemental analysis. The location of the sampling done directly at some points in Kanam and Wase is based on field survey and determination of location before using Google earth and the Global Positioning System (GPS). This was done to find the location of the distribution of the samples that have been taken.

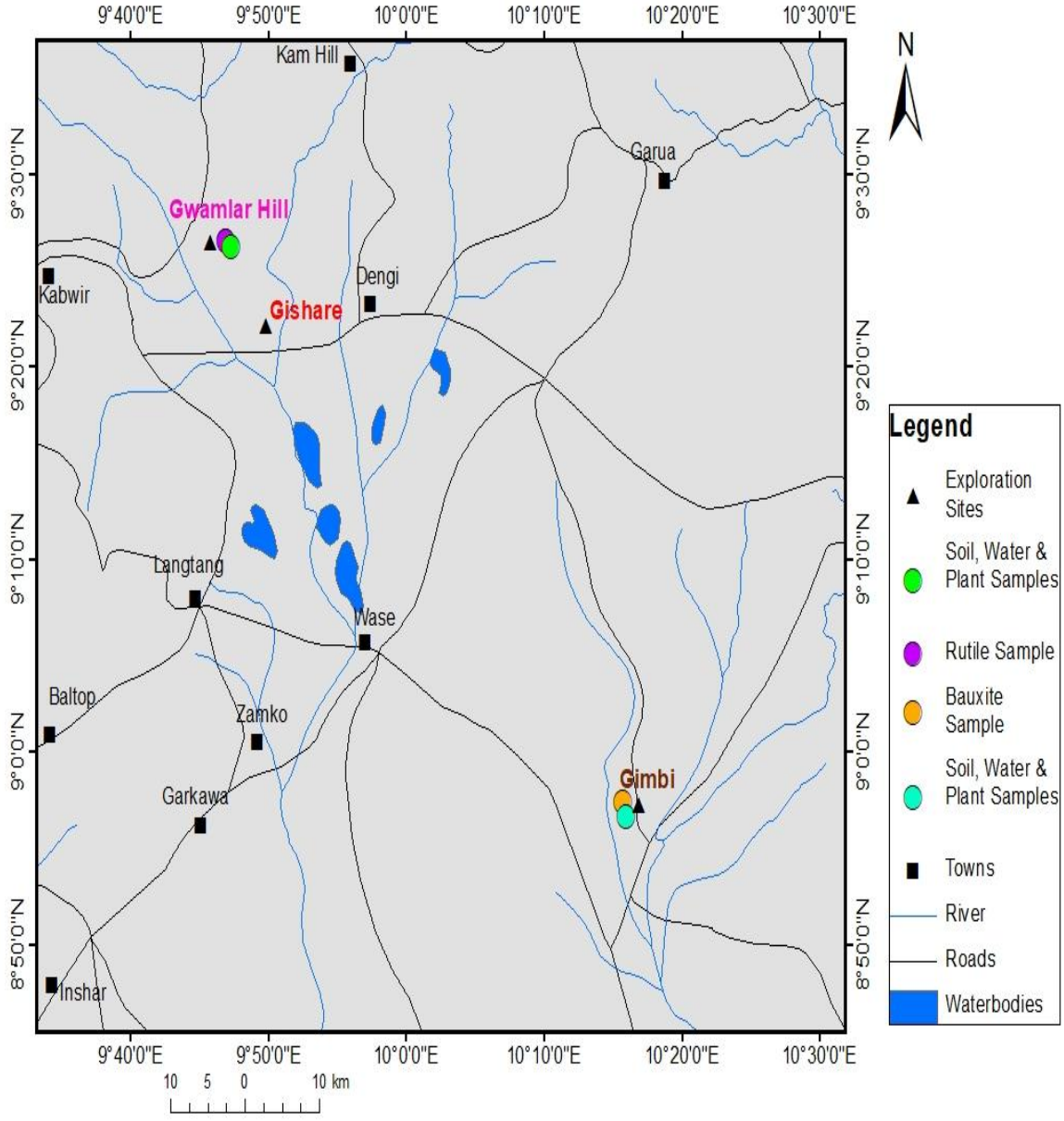


Figure 1: GPS map showing sampling location

Sample Preparation and Analysis

Soil samples were air-dried in open air for seven days, to ensure proper drainage and to decrease the moisture content below 20%. This is due to the fact that moisture content above 20% could interfere with the XRF analysis and also alter the soil matrix for which the XRF spectrometer has been calibrated with respect to solid (powdered) samples. To achieve this goal, the samples were prepared for drying by breaking them down into aggregates and spreading them evenly on a plywood tray in open air, and ensuring with great circumspection that there was no sample cross-contamination or contamination from any external sources (Kodom *et al*., 2010).

Plant samples were dried at 105^{o}c to constant weight, ground and homogenized. The obtained powder was ground topass through a 200-250 mesh sieve size. (Sykorova *et al*., 2006)

Method

The method adopted for this research is a field survey, sampling, and laboratory using X-Ray Fluorescence (XRF) analysis (Jamaluddin *et al*., 2018). 20.0 g of the ore samples were finely grinded to pass through a 200-250 mesh sieve. It was dried in an oven at 105℃ for at least 1hr and allowed to cool. The sample was intimately mixed with a binder in the ratio of 5.0 g sample(s) to 1.0 g cellulose flakes binder and pelletized at a pressure of 10-15 tons/inch^2 in a pelletizing machine. At this stage the pelletized sample(s) were stored in a desiccator for analysis. The ED-XRF model Genius IF by xenometrix Ltd Israel was used to characterize the bauxite and rutile ore samples respectively. The machine was switched on and allowed to warm up for 2hrs. Appropriate programs for the various elements of interest were at this point employed to analyze the ore samples for their presence or absence respectively. This procedure was also employed to determine the presence of metallic ions in the African bean (cowpea) [*Vigna unguiculata* (L.) Walp] sample, soil and sediment samples sourced from bauxite and rutile mineral mining vicinities and control soil (500m) away from mining site.

Results and Discussion

Table 1: XRF Result Showing Chemical Composition of Oxides in Bauxite Ore

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	50.40	62.60
2	V_2O_5	0.095	0.039
3	Cr_2O_3	0.048	0.024
4	MnO	0.143	0.150
5	Fe_2O_3	5.867	2.742
6	Co_3O_4	0.023	0.007
7	NiO	0.002	0.002
8	CuO	0.038	0.036
9	Nb_2O_3	0.018	0.006
10	MoO_3	0.005	0.003
11	P_2O_5	0.079	0.041
12	SO_3	0.183	0.170
13	CaO	1.464	1.949
14	K_2O	15.70	12.43
15	BaO	0.353	0.172
16	Al_2O_3	23.13	16.93
17	Ta_2O_5	0.022	0.004
18	TiO_2	1.143	1.068
19	ZnO	0.022	0.020
20	Ag_2O	0.042	0.014
21	Cl	0.609	1.281
22	ZrO_2	0.034	0.021
23	SnO_2	0.570	0.282

Table 2: XRF Result Showing Chemical Composition of elements in Bauxite Ore

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	43.48
2	Al	71.04	12.24
3	Si	603.6	23.56
4	P	2.093	0.034
5	S	8.726	0.073
6	Cl	96.79	0.609
7	K	2983	13.03
8	Ca	269.4	1.047
9	Ti	385.6	0.685
10	V	40.95	0.053
11	Cr	32.17	0.033
12	Mn	133.8	0.110
13	Fe	5981	4.104
14	Co	28.95	0.017
15	Ni	3.417	0.002
16	Cu	61.31	0.030
17	Zn	39.44	0.018
18	Zr	50.19	0.025
19	Nb	25.65	0.015
20	Mo	6.250	0.004
21	Ag	6.604	0.039
22	Sn	32.97	0.449
23	Ba	43.96	0.316
24	Ta	9.866	0.018

Table 3: XRF Result for Soil Sample from Bauxite Mine Site Showing Chemical Composition of Oxides

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	44.91	55.32
2	V_2O_5	0.114	0.046
3	Cr_2O_3	0.039	0.019
4	MnO	0.342	0.357
5	Fe_2O_3	15.33	7.109
6	Co_3O_4	0.068	0.021
7	NiO	0.009	0.009
8	CuO	0.104	0.097
9	Nb_2O_3	0.022	0.007
10	MoO_3	0.008	0.004
11	SO_3	0.085	0.079
12	CaO	2.241	2.958
13	MgO	4.240	7.784
14	K_2O	10.93	8.588
15	BaO	0.219	0.106
16	Al_2O_3	17.87	12.97
17	Ta_2O_5	0.046	0.008
18	TiO_2	1.751	1.622
19	ZnO	0.042	0.038
20	Ag_2O	0.062	0.020
21	Cl	1.287	2.687
22	ZrO_2	0.167	0.100
23	SnO_2	0.092	0.045

Table 4: XRF Result for Soil Sample from Bauxite Mine Site Showing Chemical Composition of Elements

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	42.17
2	Mg	0.550	2.557
3	Al	22.64	9.458
4	Si	244.1	20.99
5	S	1.963	0.034
6	Cl	97.92	1.287
7	K	1000.	9.075
8	Ca	221.4	1.602
9	Ti	322.3	1.049
10	V	27.62	0.064
11	Cr	14.99	0.027
12	Mn	170.3	0.265
13	Fe	8387	10.72
14	Co	47.26	0.050
15	Ni	5.505	0.007
16	Cu	75.96	0.083
17	Zn	34.83	0.034
18	Zr	160.0	0.123
19	Nb	21.14	0.017
20	Mo	6.433	0.005
21	Ag	12.79	0.058
22	Sn	2.632	0.073
23	Ba	15.34	0.196
24	Ta	9.908	0.038

Table 5: XRF Result of Sediment Sample from Bauxite Mine Site Showing Chemical Composition of oxides

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	42.11	54.19
2	V_2O_5	0.133	0.057
3	Cr_2O_3	0.068	0.034
4	MnO	0.423	0.461
5	Fe_2O_3	23.75	11.50
6	Co_3O_4	0.124	0.040
7	NiO	0.011	0.011
8	CuO	0.228	0.221
9	Nb_2O_3	0.050	0.017
10	MoO_3	0.012	0.006
11	CaO	7.383	10.17
12	K_2O	6.994	5.741
13	BaO	0.002	0.001
14	Al_2O_3	13.45	10.20
15	Ta_2O_5	0.148	0.026
16	TiO_2	2.676	2.591
17	ZnO	0.065	0.061
18	Ag_2O	0.075	0.025
19	Cl	2.059	4.491
20	ZrO_2	0.225	0.141

Table 6: XRF Result of Sediment Sample from Bauxite Mine Site Showing Chemical Composition of elements

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	40.64
2	Al	13.082	7.120
3	Si	185.439	19.68
4	Cl	128.618	2.059
5	K	529.173	5.806
6	Ca	625.727	5.277
7	Ti	375.942	1.604
8	V	23.859	0.075
9	Cr	18.518	0.046
10	Mn	147.233	0.328
11	Fe	8505.752	16.61
12	Co	54.687	0.091
13	Ni	3.683	0.008
14	Cu	91.127	0.182
15	Zn	29.003	0.052
16	Zr	79.171	0.166
17	Nb	16.819	0.040
18	Mo	3.139	0.008
19	Ag	2.796	0.070
20	Ba	0.080	0.001
21	Ta	16.712	0.121

Table 7: XRF Result of Bauxite Control Soil Sample (500 m away from mining site) Showing Chemical Composition of oxides

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	56.55	69.43
2	V_2O_5	0.047	0.019
3	Cr_2O_3	0.046	0.022
4	MnO	0.046	0.048
5	Fe_2O_3	15.688	7.247
6	Co_3O_4	0.065	0.020
7	NiO	0.004	0.004
8	CuO	0.098	0.091
9	Nb_2O_3	0.268	0.085
10	MoO_3	0.030	0.015
11	CaO	0.729	0.958
12	K_2O	1.199	0.939
13	BaO	0.433	0.208
14	Al_2O_3	20.30	14.68
15	Ta_2O_5	0.138	0.023
16	TiO_2	1.409	1.302
17	ZnO	0.024	0.022
18	Ag_2O	0.058	0.019
19	Cl	2.122	4.416
20	ZrO_2	0.738	0.442

Table 8: XRF Result of Bauxite Control Soil Sample (500 m away from mining site) Showing Chemical Composition of Elements

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	45.786
2	Al	21.61	10.745
3	Si	245.7	26.436
4	Cl	116.8	45.786
5	K	82.41	10.745
6	Ca	67.16	26.436
7	Ti	249.4	45.786
8	V	11.07	10.745
9	Cr	16.59	26.436
10	Mn	21.43	45.786
11	Fe	8015	10.97
12	Co	42.35	0.048
13	Ni	1.946	0.003
14	Cu	63.41	0.078
15	Zn	17.69	0.019
16	Zr	618.5	0.547
17	Nb	226.7	0.213
18	Mo	21.31	0.020
19	Ag	9.839	0.054
20	Sn	0.000	0.000
21	Ba	29.20	0.388
22	Ta	26.28	0.113

Table 9: XRF Result Showing Chemical Composition of Oxides in Rutile Ore

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	14.76	21.29
2	$V2O_5$	0.824	0.392
3	MnO	0.681	0.832
4	Fe_2O_3	25.18	13.66
5	Co_3O_4	0.121	0.044
6	NiO	0.008	0.009
7	CuO	0.035	0.038
8	Nb_2O_3	0.682	0.253
9	WO_3	0.133	0.050
10	P_2O_5	0.272	0.166
11	SO_3	0.058	0.063
12	CaO	6.068	9.375
13	K_2O	0.590	0.543
14	BaO	0.578	0.327
15	Al_2O_3	6.976	5.928
16	Ta_2O_5	0.209	0.041
17	TiO2	42.19	45.77
18	ZnO	0.065	0.069
19	Cl	0.427	1.045
20	ZrO_2	0.122	0.086

Table 10: XRF Result Showing Chemical Composition of elemental in Rutile Ore

S/N	Elememt	Intensity(c/s)	Concentration(mol/m^3)
1	Al	11.58	3.692
2	Si	121.4	6.904
3	K	109.4	0.49
4	Ca	1354	4.337
5	Ti	1106	25.29
6	V	263.0	0.461
7	Mn	225.0	0.527
8	Fe	8505	17.61
9	Co	47.74	0.089
10	Ni	2.711	0.006
11	Cu	12.277	0.028
12	Zn	24.83	0.052
13	Zr	3.119	0.091
14	Nb	3.824	0.524
15	Mo	0.241	0.001
16	Ba	56.13	0.518
17	Ta	18.89	0.171
18	W	11.92	0.106

Table 11: XRF Result for Soil Sample from Rutile Mine Site Showing Chemical Composition of Oxides

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	48.564	55.421
2	V_2O_5	0.140	0.053
3	Cr_2O_3	0.037	0.017
4	MnO	0.277	0.268
5	Fe_2O_3	11.618	4.989
6	Co_3O_4	0.043	0.012
7	NiO	0.014	0.013
8	CuO	0.067	0.058
9	Nb_2O_3	0.057	0.017
10	MoO_3	0.006	0.003
11	SO_3	0.292	0.250
12	CaO	6.097	7.455
13	MgO	6.547	11.137
14	K_2O	7.260	5.285
15	BaO	0.148	0.066
16	Al_2O_3	12.443	8.368
17	Ta_2O_5	0.084	0.013
18	TiO_2	4.842	4.157
19	ZnO	0.024	0.020
20	Ag_2O	0.026	0.008
21	Cl	1.166	2.254
22	ZrO_2	0.250	0.139

Table 12: XRF Result for Soil Sample from Rutile Mine Site Showing Chemical Composition of Elements

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	43.177
2	Mg	1.031	3.948
3	Al	18.635	6.586
4	Si	329.261	22.701
5	S	8.008	0.117
6	Cl	105.461	1.166
7	K	799.359	6.027
8	Ca	768.278	4.357
9	Ti	1043.646	2.903
10	V	39.680	0.078
11	Cr	15.818	0.026
12	Mn	157.010	0.214
13	Fe	7328.250	8.126
14	Co	34.220	0.031
15	Ni	10.444	0.011
16	Cu	61.242	0.053
17	Zn	25.162	0.019
18	Zr	302.001	0.185
19	Nb	69.528	0.045
20	Mo	6.096	0.004
21	Ag	6.631	0.024
22	Ba	12.134	0.132
23	Ta	22.552	0.069

Table 13: XRF Result of Sediment Sample from Rutile Mine Site Showing Chemical Composition of oxides

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	24.074	30.127
2	V_2O_5	0.173	0.072
3	Cr_2O_3	0.084	0.042
4	MnO	0.274	0.290
5	Fe_2O_3	17.286	8.139
6	Co_3O_4	0.082	0.026
7	NiO	0.017	0.017
8	CuO	0.145	0.137
9	Nb_2O_3	0.102	0.033
10	MoO_3	0.013	0.007
11	WO_3	0.015	0.005
12	SO_3	17.302	16.249
13	CaO	6.543	8.773
14	MgO	5.031	9.385
15	K_2O	11.745	9.375
16	Al_2O_3	9.842	7.258
17	Ta_2O_5	0.008	0.001
18	TiO_2	4.088	3.849
19	ZnO	0.032	0.030
20	Ag_2O	0.067	0.022
21	Cl	2.838	6.018
22	ZrO_2	0.239	0.146

Table 14: XRF Result of Sediment Sample from Rutile Mine Site Showing Chemical Composition of elements

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	40.839
2	Mg	0.465	3.034
3	Al	8.916	5.209
4	Si	103.885	11.253
5	S	353.827	6.929
6	Cl	165.134	2.838
7	K	788.621	9.750
8	Ca	465.123	4.677
9	Ti	502.767	2.451
10	V	28.011	0.097
11	Cr	20.725	0.057
12	Mn	88.904	0.212
13	Fe	6148.919	12.091
14	Co	36.986	0.060
15	Ni	6.641	0.013
16	Cu	69.150	0.116
17	Zn	17.537	0.026
18	Zr	149.606	0.177
19	Nb	64.618	0.081
20	Mo	7.045	0.009
21	Ag	8.871	0.062
22	Ta	1.170	0.007
23	W	2.214	0.012

Table 15: XRF Result of Rutile Control Soil Sample (500 m away from mining site) Showing Chemical Composition of oxides

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	61.473	73.448
2	V_2O_5	0.049	0.020
3	Cr_2O_3	0.259	0.123
4	MnO	0.042	0.043
5	Fe_2O_3	13.612	6.119
6	Co_3O_4	0.060	0.018
7	NiO	0.019	0.018
8	CuO	0.113	0.102
9	Nb_2O_3	0.217	0.067
10	MoO_3	0.012	0.006
11	CaO	0.411	0.526
12	MgO	0.000	0.000
13	K_2O	0.793	0.604
14	BaO	0.058	0.027
15	Al_2O_3	19.078	13.432
16	Ta_2O_5	0.074	0.012
17	TiO_2	1.160	1.043
18	ZnO	0.039	0.034
19	Ag_2O	0.036	0.011
20	Cl	2.007	4.063
21	ZrO_2	0.487	0.284

Table 16: XRF Result of Rutile Control Soil Sample (500 m away from mining site) Showing Chemical Composition of Elements

S/N	Element	Intensity (c/s)	Concentration (mol/m^3)
1	O	0.000	46.887
2	Al	20.732	10.097
3	Si	273.622	28.735
4	Cl	109.043	2.007
5	K	54.122	0.658
6	Ca	38.042	0.294
7	Ti	208.424	0.696
8	V	11.723	0.028
9	Cr	97.544	0.178
10	Mn	20.640	0.033
11	Fe	7281.789	9.521
12	Co	40.647	0.044
13	Ni	10.818	0.015
14	Cu	79.140	0.091
15	Zn	31.294	0.031
16	Zr	447.109	0.360
17	Nb	201.309	0.172
18	Mo	9.361	0.008
19	Ag	6.796	0.033
20	Ba	4.000	0.052
21	Ta	15.131	0.060

Table 17: XRF Result Showing Chemical Composition of Oxides in Plant Root

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	5.668	6.490
2	Cr_2O_3	0.045	0.020
3	MnO	0.206	0.200
4	Fe_2O_3	2.548	1.098
5	Co_3O_4	0.030	0.008
6	NiO	0.005	0.005
7	CuO	0.320	0.277
8	Nb_2O_3	0.043	0.013
9	MoO_3	0.024	0.011
10	WO_3	0.007	0.002
11	P_2O_5	2.313	1.121
12	SO_3	1.301	1.118
13	CaO	27.593	33.850
14	MgO	10.068	17.185
15	K_2O	37.576	27.443
16	Al_2O_3	8.493	5.731
17	TiO_2	0.492	0.424
18	ZnO	0.082	0.070
19	Ag_2O	0.004	0.001
20	Cl	2.345	4.550
21	ZrO_2	0.029	0.016
22	SnO_2	0.808	0.369

Table 18: XRF Result Showing Chemical Composition of Elements in Cowpea (*Vigna Unguiculata*) Plant Root

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	28.660
2	Mg	1.314	6.072
3	Al	10.323	4.495
4	Si	34.045	2.649
5	P	44.512	1.009
6	S	43.396	0.521
7	Cl	247.934	2.345
8	K	3687.491	31.194
9	Ca	1708.252	19.721
10	Ti	42.870	0.295
11	Cr	7.922	0.031
12	Mn	52.453	0.160
13	Fe	708.258	1.782
14	Co	10.275	0.022
15	Ni	2.155	0.004
16	Cu	154.705	0.256
17	Zn	44.550	0.066
18	Zr	12.508	0.022
19	Nb	17.568	0.034
20	Mo	7.893	0.016
21	Ag	0.181	0.004
22	Sn	23.190	0.636
23	W	0.970	0.005

Table 19: XRF Result Showing Chemical Composition of Oxides in Cowpea (*Vigna Unguiculata*) Plant Stem

S/N	Component	Concentration (mol/m^3)	Mole%
1	SiO_2	6.490	7.419
2	V_2O_5	0.006	0.002
3	Cr_2O_3	0.032	0.014
4	MnO	0.333	0.322
5	Fe_2O_3	1.699	0.731
6	Co_3O_4	0.004	0.001
7	NiO	0.004	0.004
8	CuO	0.269	0.233
9	Nb_2O_3	0.042	0.012
10	MoO_3	0.012	0.006
11	WO_3	0.027	0.008
12	P_2O_5	1.390	0.673
13	SO_3	1.254	1.076
14	CaO	24.968	30.585
15	MgO	9.773	16.656
16	K_2O	41.273	30.098
17	Al_2O_3	7.477	5.037
18	TiO_2	0.279	0.240
19	ZnO	0.079	0.067
20	Ag_2O	0.014	0.004
21	Cl	3.187	6.175
22	ZrO_2	0.044	0.024
23	SnO_2	1.344	0.612

Table 20: XRF Result Showing Chemical Composition of Elements in Cowpea (*Vigna Unguiculata*) Plant Stem

S/N	Element	Intensity(c/s)	Concentration (mol/m^3)
1	O	0.000	27.620
2	Mg	1.437	5.894
3	Al	10.269	3.957
4	Si	44.458	3.034
5	P	30.205	0.607
6	S	47.585	0.502
7	Cl	379.954	3.187
8	K	4403.545	34.264
9	Ca	1634.522	17.845
10	Ti	26.486	0.167
11	V	0.779	0.004
12	Cr	6.147	0.022
13	Mn	92.634	0.258
14	Fe	517.625	1.188
15	Co	1.643	0.003
16	Ni	2.005	0.003
17	Cu	144.517	0.215
18	Zn	47.505	0.064
19	Zr	0.741	20.032
20	Nb	18.742	0.033
21	Mo	4.478	0.008
22	Ag	0.730	0.013
23	Sn	42.257	1.058
24	W	4.178	0.021

Table 21: General oxides concentrations of the mineral ore, plant root and stems, vicinity soils, sediment and control soil.

S\N	Oxides	Conc.in B	Conc. In R	BVS.Conc	RVS.Conc	Plantroot	Plantstem	B.Sediment	R.Sediment	B.C.S	R.C.S
1	SiO_2	50.4	14.769	44.91	48.56	5.668	6.49	42.11	24.07	56.55	61.47
2	V_2O_5	0.095	0.824	0.114	0.14	ND	0.006	0.133	0.173	0.047	0.049
3	Cr_2O_3	0.048	ND	0.039	0.037	0.045	0.032	0.068	0.084	0.046	0.259
4	MnO	0.143	0.681	0.342	0.277	0.206	0.333	0.423	0.274	0.046	0.042
5	Fe_2O_3	5.867	25.189	15.33	11.61	2.548	1.699	23.75	17.28	15.68	13.61
6	Co_3O_4	0.023	0.121	0.068	0.043	0.03	0.004	0.124	0.082	0.065	0.06
7	NiO	0.002	0.008	0.009	0.014	0.005	0.004	0.011	0.017	0.004	0.019
8	CuO	0.038	0.035	0.104	0.067	0.32	0.269	0.228	0.145	0.098	0.113
9	Nb_2O_3	0.183	0.682	0.022	0.057	0.043	0.042	0.05	0.102	0.268	0.217
10	MoO_3	0.005	ND	0.008	0.006	0.024	0.012	0.012	0.013	0.03	0.012
11	P_2O_5	0.079	0.272	ND	ND	2.313	1.39	ND	ND	ND	ND
12	SO_3	0.183	0.058	0.085	0.292	1.301	1.254	ND	17.3	ND	ND
13	CaO	1.464	6.068	2.241	6.097	27.59	24.96	7.383	6.543	0.729	0.411
14	K_2O	15.7	0.59	10.93	7.26	37.57	41.27	6.994	11.74	1.199	0.793
15	BaO	0.353	0.578	0.219	0.148	ND	ND	0.002	ND	0.433	0.058
16	Al_2O_3	23.13	6.976	17.87	12.44	8.493	7.477	13.45	9.842	20.3	19.07
17	Ta_2O_5	0.022	0.209	0.046	0.084	ND	ND	0.148	0.008	0.138	0.074
18	TiO_2	1.143	42.19	1.751	4.842	0.492	0.279	2.676	4.088	1.409	1.16
19	ZnO	0.022	0.065	0.042	0.024	0.082	0.079	0.065	0.032	0.024	0.039
20	Ag_2O	0.042	ND	0.062	0.026	0.004	0.014	0.075	0.067	0.058	0.036
21	Cl	0.609	0.427	1.287	1.166	2.345	3.187	2.059	2.838	2.122	2.007
22	ZrO_2	0.034	0.122	0.167	0.25	0.029	0.044	0.225	0.239	0.738	0.487
23	SnO_2	0.57	ND	0.092	ND	0.808	1.344	ND	ND	ND	ND
24	WO3	ND	0.133	ND	ND	0.007	0.027	ND	ND	ND	ND
25	MgO	ND	ND	4.24	6.547	10.06	9.773	ND	ND	ND	ND

Note: Conc. in B and R is the oxides concentrations in bauxite and rutile ores, BVS and RVS conc are the respective bauxite and rutile vicinity soil concentrations, B and R sediment is the oxides concentrations for soil sediment from each of bauxite and rutile mine site vicinities, while BCS and RCS represents bauxite and rutile control soil.

Table 22: General elemental concentrations of the mineral ore, plant root and stems, vicinity soils, sediment and control soil.

S/N	Element	Conc.in B	Conc. In R	BVS.Conc	RVS.Conc	Plantroot	Plantstem	B.Sediment	R.Sediment	B.C.S	R.C.S
1	O	43.48	ND	42.17	43.177	28.66	27.62	40.64	40.839	45.786	46.887
2	Al	12.24	3.692	2.557	6.586	4.495	3.957	7.12	5.209	10.745	10.097
3	Si	23.56	6.904	20.99	22.701	2.649	3.034	19.68	11.253	26.436	28.735
4	P	0.034	ND	ND	ND	1.009	0.607	ND	ND	ND	ND
5	S	0.073	ND	0.034	0.117	0.521	0.502	ND	6.929	ND	ND
6	Cl	0.609	ND	1.287	1.166	2.345	3.187	2.059	2.838	45.786	2.007
7	K	13.03	0.49	9.075	6.027	31.194	34.264	5.806	9.75	10.745	0.658
8	Ca	1.047	4.337	1.602	4.357	19.721	17.845	5.277	4.677	26.436	0.294
9	Ti	0.685	25.29	1.049	2.903	0.295	0.167	1.604	2.451	45.786	0.696
10	V	0.053	0.461	0.064	0.078	ND	0.004	0.075	0.097	10.745	0.028
11	Cr	0.033	ND	0.027	0.026	0.031	0.022	0.046	0.057	26.436	0.178
12	Mn	0.11	0.527	0.265	0.214	0.16	0.258	0.328	0.212	45.786	0.033
13	Fe	4.104	17.61	10.72	8.126	1.782	1.188	16.61	12.091	10.97	9.521
14	Co	0.017	0.089	0.05	0.031	0.022	0.003	0.091	0.06	0.048	0.044
15	Ni	0.002	0.006	0.007	0.011	0.004	0.003	0.008	0.013	0.003	0.015
16	Cu	0.03	0.028	0.083	0.053	0.256	0.215	0.182	0.116	0.078	0.091
17	Zn	0.018	0.052	0.034	0.019	0.066	0.064	0.052	0.026	0.019	0.031
18	Zr	0.025	0.091	0.123	0.185	0.022	20.032	0.166	0.177	0.547	0.36
19	Nb	0.015	0.524	0.017	0.045	0.034	0.033	0.04	0.081	0.213	0.172
20	Mo	0.004	ND	0.005	0.004	0.016	0.008	0.008	0.009	0.02	0.008
21	Ag	0.039	ND	0.058	0.024	0.004	0.013	0.07	0.062	0.054	0.033
22	Sn	0.449	ND	0.073	ND	0.636	1.058	ND	ND	ND	ND
23	Ba	0.316	0.518	0.196	0.132	ND	ND	0.001	ND	0.388	0.052
24	Ta	0.018	0.171	0.038	0.069	ND	ND	0.121	0.007	0.113	0.06
25	W	ND	0.106	ND	ND	0.005	0.021	ND	0.012	ND	ND
26	Mg	ND	ND	ND	3.948	ND	5.894	ND	3.034	ND	ND

Note: Conc. in B and R is the elemental concentrations in bauxite and rutile ores, BVS and RVS conc are the respective bauxite and rutile vicinity soil concentration s, B and R sediment is the elemental concentrations for soil sediment from each of bauxite and rutile mine site vicinities, while BCS and RCS represents bauxite and rutile control soil respectively.

Table 23: Pollution Indices

Samples	Heavy metals	C^iF	Er^i	I*geo*	*EF*	PLI
BV Sample	Cr	0.0003	0.0006	-3.467	9.333	1.164
	Cu	0.0020	0.0100	-2.615	5.437	0.288
	Ni	0.0004	0.0020	-3. 585	2.114	0.184
	Zn	0.0002	0.0002	-4.000	18.421	0.083
RV Sample	Cr	0.0003	0.0006	-3.376	1.316	1.161
	Cu	0.0010	0.0050	-2.824	8.000	0.230
	Ni	0.0006	0.0030	-3.366	2.909	0.137
	Zn	0.0001	0.0001	-3.677	28.80	0.104

Note: BV= Bauxite vicinity, RV= Rutile vicinity

DISCUSSION

Chemical Composition of elements in Bauxite Ore

The analytical result for the chemical characterization of bauxite ore as seen in table 2 revealed aluminium (12.2%), potassium (13.0%), calcium (1.0%), silicon (23.5%) and iron (4.1%) as the most predominant metals and metalloid in concentration both as oxides and in elemental forms. This analytical result also suggests that the bauxiteore cannot be utilized directly because of low Al (12.2%) content unless it is beneficiated to meet metallurgical required grade. This is because the bauxite ore has a high clay (23.5%) content. This mineral ore varies in proportion from deposit to deposit depending on the geochemical composition of soil minerals that form the parent rock of the area.This result compared to other literatures cited in this research, compete favourably showcasing bauxite ore as an alternative source of Iron, Titanium, Vanadium, Manganese, Nickel, Niobium, Zircon Cobalt, Tin and Silver minerals as 1%-10% of these minerals can be added in steel as alloying elements (Itodo *et al*., 2019). Bauxite is commonly used as abrasive made by crushing it to form powder and as oil-field propellent (Donoghue *et al*., 2014).

Bauxite Mine Site Soil Elemental Composition

The result for the elemental composition of soil samples from vicinities around bauxite mine site as presented in the table (4) above revealed silicon (20.9%), Fe (10.7%), Al (9.4%), K (9.0%), Mg (2.5%), Ca (1.6%) and Ti (1.0%) as the dominant components of the soil. Other normal soil elements also present were Mn, Co, Ni, Cu, Zn, Zr, Mo, Nb, Ag, Sn and Ta in no order of concentrations. The considerably high percentage of aluminium in the soil is from Al_2O_3 which is the principal ore of alumina. Under natural conditions because aluminium is abundant in most soils, toxicity is largely dependent on the exchangeable amount present due to low soil pH. Worthy of note is that the concentrations of aluminium in the soil solutions are in most cases very small, even at low pH values. Of great concern is the presence of the radionuclide K-40 in the soil. Seeing the current hazards through inland sand mining, the contamination of this soil by radionuclides, toxic residues from other heavy metals like vanadium (0.06%), chromium (0.02%) and barium (0.19%) as revealed leads to negative

influence on the soil characteristics and can limits production and environmental functions (Chanada *et al*., 2010).Soil contamination with Cr due to disturbances from mining activities considerably affects the biological activity of the soil. The catalase activity of chernozems and the soil's ability for cellulose decomposition decrease thus exerts a highly toxic effect on the chernozem's biota (Kolesnikov, 2010).Bioaccumulation of Barium from soil, water, and food (especially in combination with excess Strontium) may disturb the calcium metabolism and results in a serious skeletal system disease known as endemic osteoarthritis. Vanadium is referred to as a hazardous heavy element in soils, it forms anionic complexes. The vanadyl cation VO_2^+ is more stable in acidic soils, it is firmly fixed by humus but the situation becomes more dangerous in a neutral medium (Vodyanitskii, 2012). Similar analysis carried out for soil at Ugwuegu site asserts that the typical elements normally present in clay mineral analysis were present, although magnesium was absent in all the samples analysed in the study, the elemental contents of the clay as found include K, Ca, V, Cr, Ti, Mn, Fe, Ni, Cu, Zn, Al, Ga and Si (Ikegwu and Uzuegbu, 2015).

Bauxite Mine Site Sediment

The result obtained for the elemental analysis of soil sediment around bauxite mining exploration site showed that except for manganese, tin and sulphur, all the elements in the ED-XRF of agricultural soil sample around bauxite mine site were present. Fe (16.6%) has a slightly high concentration in the sediment than in the agricultural soil. This is likely due to runoff or erosion of the weathered particles of bauxite mineral and other sources into the surface water. Under natural condition aluminium is abundant in most soils and its toxicity is largely dependent on the exchangeable amount present due to low soil pH. Slightly high concentrations for vanadium, chromium and barium in the Wase bauxite mine site suggest contamination of water sources.

Bauxite Control Soil Sample (500 m away from mining site)

XRF analysis was used to determine the chemical composition of elements in agricultural control soil (500 m away from bauxite mine site). The result in table 8 revealed the presence of heavy metals (Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, Ta) and as lightly high concentration of Si (metalloid) in various proportions. Comparing this result with that of soil and sediment around bauxite exploration vicinity, low values were recorded for heavy metals such as Iron, Titanium, Calcium, potassium, Vanadium, Chromium, Molybdenum among others. The slight decrease in concentration of these metals confirms the suspicion that bauxite mineral exploration exerts adverse effects on soil and its properties. A similar analysis of soil using the XRF technique at Galati revealed a large variation in the quantities of V and Zn determined in the investigated soils, for all depths. As and Ni concentrations were greater than the normal values (5 mg/kg for As and 20 mg/kg for Ni for all studied sites (including the control site) and depths (Antoaneta *et al.,* 2009).

Chemical Composition of Elements in Rutile Ore

The analytical result for the chemical characterization of rutile ore using XRF technique as seen in table 10 unveiled the interlocking of soil minerals such as Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, Ta and W in various proportions with titanium oxide having a relatively high concentration (25.3%) in the sample. This is a confirmation that rutile ore is predominantly an oxide of titanium or titania (TiO_2) occurring in forms such as sedimentary or igneous (Carruzzo *et al*., 2006). This analysis also suggests that the ore cannot be utilized directly unless it is further beneficiated to meet metallurgical required grade or standard. Comparing this analytical result to other literatures cited in this

research, one can conveniently conclude that it compete favourably showcasing titanium (rutile) ore as an alternative source of Copper, Iron, Chromium, Titanium, Vanadium, Manganese, Nickel, Niobium, Zircon, Cobalt, Tin and Silver minerals as 1%-10% of these minerals can be added in steel as alloying elements (Itodo *et al*., 2019). This is because a considerably high amount of Fe (17.6%), Si (6.9%), Al (3.7%) and Ca (4.3%) is recorded. Metallurgical grade rutile ore has numerous applications such as in welding rod coatings, manufacture of carbides, chemicals and as photoactive semiconductors (Moses *et al.*, 2015).Similar analysis of rutile ore at Ilesa southwest Nigeria showed that the major component of the mineral deposit was indeed rutile with maximum titanium Ti concentration of 49.4 wt% which converts to TiO_2 concentration 82.45% wt% in the homogenised samples. The black brownish colour is location dependent and attributed to the reduction state of TiO_2 as well as the oxidation states of some of the trace elements present (Yilleng *et al.*, 2015).

Rutile Mine Site Soil Chemical Composition of Elements

The result for the chemical analysis of soil around rutile mineral site using x-ray fluorescence technique as seen in table 12 revealed the usual soil mineral (oxides) or elements. These elements (V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, Ta, W) appears in various concentrations with predominantly silicon, aluminium, potassium, titanium, iron, calcium and magnesium. As revealed from this analysis, the vicinity soil contamination largely depends on continuous interference of the soil and soil organic matter over a prolong period of time. This is because the recorded concentrations of the elements except for Ti (2.9) which is slightly above the Russian general toxicology and Dutch standards for soils (<1), all other elements were observed to fall within their moderate to low contamination limits (Vodyanitskii, 2012). Comparing this analytical result with that of soil from bauxite mine site vicinity, the current hazards through inland sand mining, the contamination of this soil by radionuclides, toxic residues from other dangerous heavy metals such as vanadium, chromium and barium including moderately hazardous metals in soils can lead leads to negative influence on the soil characteristics thereby limiting production and environmental functions (Chanada *et al*., 2010). Soil contamination with Cr due to disturbances from mining activities considerably affects the biological activity of the soil.

Rutile Vicinity Sediment

As seen in table 14, the result for the analysis of rutile vicinity soil sediment unveiled the presence of chemical oxides which translates to normal soil elements (Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, Ta, W) in different concentrations. Worthy of note is that unlike the result of soil sediment from bauxite mine site, these heavy metals were believed to be held tightly to the rutile vicinity soil limiting their leaching into the surrounding stream channels, hence the low concentration in the soil sediment. Virtually all the chemical elements and oxides observed in the analysis of rutile ore as well as soil samples around rutile mine site vicinity were also noticeable in the soil sediment analytical result. Comparing this research result with that of Lower Ganges River Floodplain and Ganges Tidal Floodplain, the results revealed that SiO_2, Al_2O_3, Fe_2O_3, P_2O_5, K_2O CaO and TiO2 were the major elements characterizing the soils, while small amounts of S, Cr, Zr, Zn, Ni and Cu were also found as trace elements. The mineralogy and chemical composition of soil samples at both regions were nearly the same and quite similar to the soil samples collected at several locations suggesting that the soil samples in both locations were similar to the parent materials (Shamiha *et al.*, 2019).

Rutile Control Soil Sample (500 m away from mining site)

The result for the rutile control soil obtained through the use of X-ray fluorescence technique unveiled oxides of most soil heavy metals which also translates to elements such as K, Ca, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, W and Ta as trace metals, while Al (10.1%), Fe (9.5%), and Si (28.7%) as major elements characterizing the soil. As observed, the control soil is considerably less contaminated evident from the lower values recorded compared to those of soil sediment around rutile mine site and the rutile ore itself and they fall within the low hazardous range according to the Russian general toxicology and Dutch standards for soils (Vodyanitskii, 2012). A similar research around river Tiva however demonstrated that the soil was largely characterized by deposits of sands that were magnetic and indicative of heavy minerals. The geology of the study area indicates the presence of the igneous and sedimentary rocks associated with the occurrence of the heavy minerals. The results of the EDXRF analyses showed that Fe concentration was dominant followed Ti and Zr (Kiprotich, 2016).

Chemical Composition of Elements in Cowpea (*Vigna Unguiculata*) Plant Root

The chemical characterization of plant (*vigna unguiculata*) roots from the mineral exploration vicinity to ascertain the presence and levels of heavy metals toxicity through the use of a non-destructive analytical technique (XRF)as seen in table 18 revealed Mg, Al, Si, K, Ca and Fe as major elements as well as Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Sn, Ba, W and Ta as trace or minor elements present. Based on the values recorded, of great concern is the presence of Cr (0.03), Ni (0.004), Co (0.02), Mn (0.16) Cu (0.256), Zn (0.06) among other unfriendly heavy metals in the roots of these plants, although within acceptable limits, it is reported that cobalt (Co) produces toxicity to plants when the amounts available to the plant is high or exceed certain low levels (Milena and Mirosław, 2020). Continuous disturbance of the natural environment through mining activities poses more accumulation of these heavy metals in plants through the roots, stems and leaves. At toxic levels (that is available to the plants or animals in a form that can enter tissues of the organism either in solution “generally aqueous” as a gas, or “uncommonly” as a solid or emitting ionizing radiation), these are passed on to animals including man through the food chain resulting to severe health related challenges. Cr occurs most commonly in forms of trivalent Cr^{3+} and hexavalent Cr^{6+}. Both states are considered toxic to plants, animals and humans with the latter being highly soluble in water hence readily absorptive (Monalisa *et al.*, 2013).

Similar research for medicinal plants subjected to trace elements analysis in Turkey using energy dispersive x-ray fluorescence revealed K, Ca, Al, Ti, V, Rb, Sr, Nb, Mo, In, Sn, and Ce (Neslihan *et al*., 2004).

Chemical Composition of Elements in Cowpea (*Vigna Unguiculata*) Plant Stem

The chemical analysis of cowpea (*vigna unguiculata*) stems obtained from mine site vicinities in table 20 revealed K, Ca, Fe, Al, Mg and Si as major metals and metalloids respectively, while Ti, V, Mn, Co, Zn, Zr, Nb, Mo, Ag, Sn, Ba, Ta and W represents trace or minor metals as obtained from the result. With the exception of silicon, it was noted that low values for most heavy metals such as Cr (0.02) and other major and trace elements were recorded compared to the values obtained for the previous (x-ray fluorescence for the roots) analysis. The low values are due to the fact that metals (essential and non-essential) are trapped through the roots then subsequently transported to other sections of the plants. Also,

chromium at oxidation states (Cr^{3+}) shows low mobility ability in its transport from the root to green parts of the plant its distribution therefore was as root > stem (Monalisa *et al.*, 2013). As reported in other literatures as cited in this research, similar analysis was carried out in Kadin Creek, for plant roots, stems and leafs, the result of the analysis revealed that the distribution of elements by their concentrations in plant organs was as root > leaf > stem except for chromium which was asroot > stem > leaf (Murat *et al.*, 2014).

Pollution Indices

The estimated pollution indices for the most toxic heavy metals (Chromium, Copper. Nickel and Zinc) found in the surrounding soil revealed values in all categories of low to moderate pollution, moderate to high and extremely enrichment.

Contamination factor C_f^i

The contamination factor (C_f^i) was used to describe the contamination of the toxic metal substance in the mineral vicinity soil given by;

$$C^i_f = C^i_{0\text{-}2}/C^i_n \quad (1)$$

Where; C^i_{0-1} is the mean content of the substance *i* from at least 5 sample sites, and C^i_n is the pre-industrial reference level for the substance. The pre-industrial reference level determined from various European and American lakes (Gong *et al*., 2008).

The result revealed that the heavy metals (Cr, Cu. Ni and Zn) as estimated were within the (C_f^i<1) low contamination factor range (Gong *et al*., 2008). Although the contamination factor shows little or low contamination, heavy metals have many adverse health effects and last for long period of time, their exposure continuous and is increasing in many parts of the world. Metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Jaishankar *et al*., 2014).

Ecological risk factor

Consequently, the ecological risk factor (Er^i) estimated to quantitatively express the potential ecological risk of these metal contaminant also suggested (Er^i<40) low potential ecological risk. This was computed from the formula suggested by Håkanson (1980) is

$$Er^i = Tr^i \cdot C_f^i \quad (2)$$

Where Tr^i is the toxic-response factor for a given substance, and C_f^i is the contamination factor.

Index of geo-accumulation

Similarly, the geo-accumulation index (I_{geo}) computed to determine and define the metal contamination in sediments by comparing current concentrations with pre-industrial levels revealed that the heavy metals (Cr, Cu, Ni and Zn) showed low to no pollution in the soil. Also revealing is the fact that relatively less toxic and essential metals such Al, Ca, K, Fe, Ti, Mn, Mg, V and Zr however showed higher concentrations in the soil and are therefore believed to have high values of I*geo* (Buccolieri *et al*., 2006). Estimated through the equation;

$I_{geo}=\log_2[C_i/(1.5C_{ri})]$ (3)

As earlier cited in this literature.

Where C_i is the measured concentration of the examined metal *i* in the sediment, and C_{ri} is the geochemical background concentration or reference value of the metal *i*. Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences.

Pollution load index

The PLI determine for the most toxic metals in the soil revealed values ranging between 0.104 and 1.164 as minimum and maximum estimated values. These imply that the entire mineral exploration area soil and sediment were moderately polluted with Cr (>1) and unpollution with Cu, Ni and Zn metals. This suggests that metal toxicity due to Cu, Ni and Zn as revealed in this study could only be due to long term exposure resulting to bioaccumulation. The entire pollution level of these mine site areas were also attributed to the high concentrations of the heavy metals Cr (2.68), Al (5.44), Ti (8.09), Ca (8.55), K (12.1), Fe (9.27), Mn (4.78), Zr (2.17) and Mg (1.28) recorded in the XFR results. Calculated as the nth root of the product of the n CF, pollution load index is given by;

$PLI= (CF_1 \times CF_2 \times CF_3 \times .. . \times CFn)^{1/n}$ (4)

Where CF is contamination factor (Caeiro *et al*., 2005).

Enrichment factor (*EF*)

The enrichment factor (*EF*) initially developed to speculate on the origin of elements in the atmosphere, precipitation, or seawater, progressively extended to the study of soils, lake sediments, peat, tailings, and other environmental materials (Zhang *et al*., 2007). Computing for these toxic heavy metals revealed values between the ranges $EF<2$ (depletion to mineral enrichment), $2\leq EF<5$ (moderate enrichment) $5\leq EF<20$ (significant enrichment) and $20\leq EF<40$ (very high enrichment) in both the bauxite and rutile mineral vicinity soil (Chatterjee *et al*., 2007).

The following formula was used to calculate *EF;*

$EF=(C_i/C_{ie})_S/(C_i/C_{ie})_{RS}$ (5)

Where C_i is the content of element *i* in the sample of interest or the selected reference sample, and C_{ie} is content of immobile element in the sample or the selected reference sample. So $(C_i/C_{ie})_S$ is the heavy metal to immobile element ratio in the samples of interest, and $(C_i/C_{ie})_{RS}$ is the heavy metal to immobile element ratio in the selected reference sample (Zhang *et al*., 2007).

CONCLUSION

Chemical characterization of bauxite mineral ore revealed a high clay (23.5%) content, this suggests that the ore cannot be utilized directly unless it is beneficiated to meet metallurgical required grade. The elemental composition of soil and sediment samples within the bauxite mine site vicinity revealed soil natural elements Si, Fe, Al, K, Mg, Ca and Ti as the major heavy metals. Under natural conditions and because aluminium is abundant in most soils, toxicity is largely dependent on the exchangeable amount present due to low soil pH. Low content heavy metals in these mineral vicinity soil and sediment such as V (0.06%), Cr (0.02%) and Ba (0.19%) over a long period of time leads to negative influence on soil characteristics and can limit production and environmental functions. Soil contamination with

Cr as a result of bauxite mineral exploration activities considerably affects the biological activity of the soil as observed in the soil physicochemical parameters in our earlier research. However, slight decrease in concentration of metals were obtained in the soil control sample (500 m away from mine site), this suggests that bauxite ore exploration exerts adverse effects on soil functions.

In the same vein, elemental analysis of rutile ore also unveiled the interlocking of soil minerals in various proportions with titanium oxide having a relatively high concentration (25.3%). This is because rutile ore is predominantly an oxide of titania (TiO_2). This also showcased rutile ore as an alternative source of Copper, Iron, Chromium, Titanium, Vanadium, Manganese, Nickel, Niobium, Zircon, Cobalt, Tin and Silver minerals as 1%-10% of these minerals can be added in steel as alloying elements. Soil contamination is largely as a result of continuous interference and disruption of the soil and soil organic matter within the proximate mineral vicinity. Higher concentration of heavy metals in the mineral vicinity plant (*vigna unguiculata*) roots compared to the stems suggest that metals (essential and non-essential) are trapped through the roots then subsequently transported to other sections of the plants and its distribution therefore is as root>stem.The pollution load index (PLI) suggests that the entire bauxite and rutile mineral exploration area soils and sediment were moderately polluted with Cr (>1) and Ti and unpolluted with Cu, Ni and Zn metals and the enrichment factor (*EF*) ranged between depletion to mineral enrichment-very high enrichment.

Test of significance

Anova test at 95% confidence interval for metals and radionuclides obtained from the XRF results indicates that even though rutile vicinity soil concentration had higher metals and radionuclides from XRF compared to bauxite vicinity soil, the difference is not statistically significant. BVS Conc. (Mean 2.47 S±5.44), RVS (Mean 2.72±5.52), p>.05.

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