

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

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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.

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 organized mining operations covering both the northern and southern protectorates. This grew and metamorphosed leading to classification of Nigeria as a leading producer of coal, columbite and tin in the 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, garnet, 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. Plant 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.

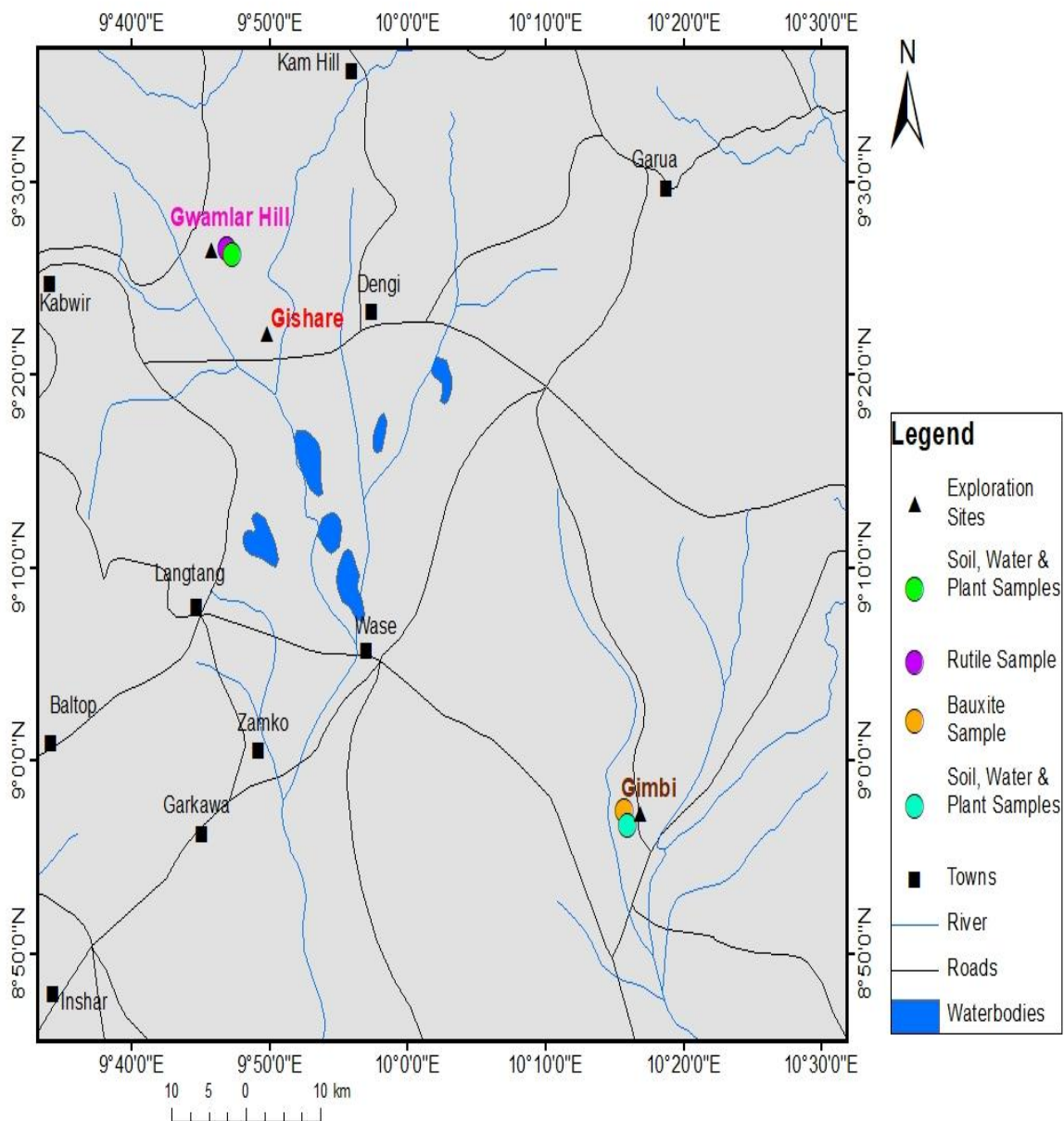


Figure 1: GPS map showing sampling location

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°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°C 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/inch² 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 ₂ O ₅ | 0.095 | 0.039 |
| 3 | Cr ₂ O ₃ | 0.048 | 0.024 |
| 4 | MnO | 0.143 | 0.150 |
| 5 | Fe ₂ O ₃ | 5.867 | 2.742 |
| 6 | Co ₃ O ₄ | 0.023 | 0.007 |
| 7 | NiO | 0.002 | 0.002 |
| 8 | CuO | 0.038 | 0.036 |
| 9 | Nb ₂ O ₃ | 0.018 | 0.006 |
| 10 | MoO ₃ | 0.005 | 0.003 |
| 11 | P ₂ O ₅ | 0.079 | 0.041 |
| 12 | SO ₃ | 0.183 | 0.170 |
| 13 | CaO | 1.464 | 1.949 |
| 14 | K ₂ O | 15.70 | 12.43 |
| 15 | BaO | 0.353 | 0.172 |
| 16 | Al ₂ O ₃ | 23.13 | 16.93 |
| 17 | Ta ₂ O ₅ | 0.022 | 0.004 |
| 18 | TiO ₂ | 1.143 | 1.068 |
| 19 | ZnO | 0.022 | 0.020 |
| 20 | Ag ₂ O | 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 ₂ O ₅ | 0.114 | 0.046 |
| 3 | Cr ₂ O ₃ | 0.039 | 0.019 |
| 4 | MnO | 0.342 | 0.357 |
| 5 | Fe ₂ O ₃ | 15.33 | 7.109 |
| 6 | Co ₃ O ₄ | 0.068 | 0.021 |
| 7 | NiO | 0.009 | 0.009 |
| 8 | CuO | 0.104 | 0.097 |
| 9 | Nb ₂ O 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 ₂ O | 10.93 | 8.588 |
| 15 | BaO | 0.219 | 0.106 |
| 16 | Al ₂ O ₃ | 17.87 | 12.97 |
| 17 | Ta ₂ O ₅ | 0.046 | 0.008 |
| 18 | TiO ₂ | 1.751 | 1.622 |
| 19 | ZnO | 0.042 | 0.038 |
| 20 | Ag ₂ O | 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 ₂ O ₅ | 0.133 | 0.057 |
| 3 | Cr ₂ O ₃ | 0.068 | 0.034 |
| 4 | MnO | 0.423 | 0.461 |
| 5 | Fe ₂ O ₃ | 23.75 | 11.50 |
| 6 | Co ₃ O ₄ | 0.124 | 0.040 |
| 7 | NiO | 0.011 | 0.011 |
| 8 | CuO | 0.228 | 0.221 |
| 9 | Nb ₂ O ₃ | 0.050 | 0.017 |
| 10 | MoO ₃ | 0.012 | 0.006 |
| 11 | CaO | 7.383 | 10.17 |
| 12 | K ₂ O | 6.994 | 5.741 |
| 13 | BaO | 0.002 | 0.001 |
| 14 | Al ₂ O ₃ | 13.45 | 10.20 |
| 15 | Ta ₂ O ₅ | 0.148 | 0.026 |
| 16 | TiO ₂ | 2.676 | 2.591 |
| 17 | ZnO | 0.065 | 0.061 |
| 18 | Ag ₂ O | 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 ₂ O ₅ | 0.047 | 0.019 |
| 3 | Cr ₂ O ₃ | 0.046 | 0.022 |
| 4 | MnO | 0.046 | 0.048 |
| 5 | Fe ₂ O ₃ | 15.688 | 7.247 |
| 6 | Co ₃ O ₄ | 0.065 | 0.020 |
| 7 | NiO | 0.004 | 0.004 |
| 8 | CuO | 0.098 | 0.091 |
| 9 | Nb ₂ O ₃ | 0.268 | 0.085 |
| 10 | MoO ₃ | 0.030 | 0.015 |
| 11 | CaO | 0.729 | 0.958 |
| 12 | K ₂ O | 1.199 | 0.939 |
| 13 | BaO | 0.433 | 0.208 |
| 14 | Al ₂ O ₃ | 20.30 | 14.68 |
| 15 | Ta ₂ O ₅ | 0.138 | 0.023 |
| 16 | TiO ₂ | 1.409 | 1.302 |
| 17 | ZnO | 0.024 | 0.022 |
| 18 | Ag ₂ O | 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 | V ₂ O ₅ | 0.824 | 0.392 |
| 3 | MnO | 0.681 | 0.832 |
| 4 | Fe ₂ O ₃ | 25.18 | 13.66 |
| 5 | Co ₃ O ₄ | 0.121 | 0.044 |
| 6 | NiO | 0.008 | 0.009 |
| 7 | CuO | 0.035 | 0.038 |
| 8 | Nb ₂ O ₃ | 0.682 | 0.253 |
| 9 | WO ₃ | 0.133 | 0.050 |
| 10 | P ₂ O ₅ | 0.272 | 0.166 |
| 11 | SO ₃ | 0.058 | 0.063 |
| 12 | CaO | 6.068 | 9.375 |
| 13 | K ₂ O | 0.590 | 0.543 |
| 14 | BaO | 0.578 | 0.327 |
| 15 | Al ₂ O ₃ | 6.976 | 5.928 |
| 16 | Ta ₂ O ₅ | 0.209 | 0.041 |
| 17 | TiO ₂ | 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 | Element | 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 ₂ O ₅ | 0.140 | 0.053 |
| 3 | Cr ₂ O ₃ | 0.037 | 0.017 |
| 4 | MnO | 0.277 | 0.268 |
| 5 | Fe ₂ O ₃ | 11.618 | 4.989 |
| 6 | Co ₃ O ₄ | 0.043 | 0.012 |
| 7 | NiO | 0.014 | 0.013 |
| 8 | CuO | 0.067 | 0.058 |
| 9 | Nb ₂ O 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 ₂ O | 7.260 | 5.285 |
| 15 | BaO | 0.148 | 0.066 |
| 16 | Al ₂ O ₃ | 12.443 | 8.368 |
| 17 | Ta ₂ O ₅ | 0.084 | 0.013 |
| 18 | TiO ₂ | 4.842 | 4.157 |
| 19 | ZnO | 0.024 | 0.020 |
| 20 | Ag ₂ O | 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 ₂ O ₅ | 0.173 | 0.072 |
| 3 | Cr ₂ O ₃ | 0.084 | 0.042 |
| 4 | MnO | 0.274 | 0.290 |
| 5 | Fe ₂ O ₃ | 17.286 | 8.139 |
| 6 | Co ₃ O ₄ | 0.082 | 0.026 |
| 7 | NiO | 0.017 | 0.017 |
| 8 | CuO | 0.145 | 0.137 |
| 9 | Nb ₂ O 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 ₂ O | 11.745 | 9.375 |
| 16 | Al ₂ O ₃ | 9.842 | 7.258 |
| 17 | Ta ₂ O ₅ | 0.008 | 0.001 |
| 18 | TiO ₂ | 4.088 | 3.849 |
| 19 | ZnO | 0.032 | 0.030 |
| 20 | Ag ₂ O | 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 ₂ O ₅ | 0.049 | 0.020 |
| 3 | Cr ₂ O ₃ | 0.259 | 0.123 |
| 4 | MnO | 0.042 | 0.043 |
| 5 | Fe ₂ O ₃ | 13.612 | 6.119 |
| 6 | Co ₃ O ₄ | 0.060 | 0.018 |
| 7 | NiO | 0.019 | 0.018 |
| 8 | CuO | 0.113 | 0.102 |
| 9 | Nb ₂ O 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 ₂ O | 0.793 | 0.604 |
| 14 | BaO | 0.058 | 0.027 |
| 15 | Al ₂ O ₃ | 19.078 | 13.432 |
| 16 | Ta ₂ O ₅ | 0.074 | 0.012 |
| 17 | TiO ₂ | 1.160 | 1.043 |
| 18 | ZnO | 0.039 | 0.034 |
| 19 | Ag ₂ O | 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 ₂ O ₃ | 0.045 | 0.020 |
| 3 | MnO | 0.206 | 0.200 |
| 4 | Fe ₂ O ₃ | 2.548 | 1.098 |
| 5 | Co ₃ O ₄ | 0.030 | 0.008 |
| 6 | NiO | 0.005 | 0.005 |
| 7 | CuO | 0.320 | 0.277 |
| 8 | Nb ₂ O ₃ | 0.043 | 0.013 |
| 9 | MoO ₃ | 0.024 | 0.011 |
| 10 | WO ₃ | 0.007 | 0.002 |
| 11 | P ₂ O 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 ₂ O | 37.576 | 27.443 |
| 16 | Al ₂ O ₃ | 8.493 | 5.731 |
| 17 | TiO ₂ | 0.492 | 0.424 |
| 18 | ZnO | 0.082 | 0.070 |
| 19 | Ag ₂ O | 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 ₂ O ₅ | 0.006 | 0.002 |
| 3 | Cr ₂ O ₃ | 0.032 | 0.014 |
| 4 | MnO | 0.333 | 0.322 |
| 5 | Fe ₂ O ₃ | 1.699 | 0.731 |
| 6 | Co ₃ O ₄ | 0.004 | 0.001 |
| 7 | NiO | 0.004 | 0.004 |
| 8 | CuO | 0.269 | 0.233 |
| 9 | Nb ₂ O ₃ | 0.042 | 0.012 |
| 10 | MoO ₃ | 0.012 | 0.006 |
| 11 | WO ₃ | 0.027 | 0.008 |
| 12 | P ₂ O 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 ₂ O | 41.273 | 30.098 |
| 17 | Al ₂ O ₃ | 7.477 | 5.037 |
| 18 | TiO ₂ | 0.279 | 0.240 |
| 19 | ZnO | 0.079 | 0.067 |
| 20 | Ag ₂ O | 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 ₂ O ₅ | 0.095 | 0.824 | 0.114 | 0.14 | ND | 0.006 | 0.133 | 0.173 | 0.047 | 0.049 |
| 3 | Cr ₂ O 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 ₂ O ₃ | 5.867 | 25.189 | 15.33 | 11.61 | 2.548 | 1.699 | 23.75 | 17.28 | 15.68 | 13.61 |
| 6 | Co ₃ O 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 ₂ O 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 ₂ O 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 ₂ O | 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 ₂ O ₃ | 23.13 | 6.976 | 17.87 | 12.44 | 8.493 | 7.477 | 13.45 | 9.842 | 20.3 | 19.07 |
| 17 | Ta ₂ O 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 ₂ O | 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 | WO ₃ | 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 ⁱ F | 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 bauxite ore 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 propellant (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 Al₂O₃ 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 limit 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 competes 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 prolonged 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 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 TiO_2 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;

$$C_f^i = C_{0-2}^i / C_n^i \quad (1)$$

Where; C_{0-1}^i is the mean content of the substance i from at least 5 sample sites, and C_n^i 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 ($Er < 40$) 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;

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

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 n th root of the product of the n CF, pollution load index is given by;

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (4)$$

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;

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

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 (TiO₂). 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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