

Physicochemical Properties of Mineral Vicinity Soil, Water and Sediment and the Morphology (SEM) and Functional Group (FTIR) Analysis of Bauxite and Rutile Ore in Kanam and Wase Mining Sites, Plateau State-Nigeria.

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Abstract;

Physicochemical properties of soil and sediment as well as water quality parameters, microbial and biochemical properties were carried out to ascertain the levels of metal contamination from Kanam and Wase mineral ore (bauxite and rutile) exploration sites. pH, and E.C, revealed contamination of water sources within bauxite and rutile ore vicinities. Values obtained were higher than that received for water control sample, the observed nitrate values were alarmingly higher than the global acceptable 10 mg/L limit. Turbidity results of bauxite and rutile vicinity water were also higher than the control sample (4.7 NTU) and above FAO/WHO acceptable limits of below 5NTU and <1 for drinking water. TBC and TCC of water samples sourced within bauxite mining exploration site revealed high MPN for bacteria and coliform (28, 32 MPN) slightly higher than the control (25 MPN). Similar results were received for rutile vicinity water. The biochemical property DO of water samples sourced within bauxite and rutile mine site areas unveiled values above the acceptable limit (3 mg/L). The BOD varied between 1.98 to 2.1 and 1.9-2.1mg/l for bauxite and rutile vicinity stream channel water respectively, both lower than the water control sample (3.2 mg/L) and the EU guideline standard values of 3.0 to 6.0 mg/L. COD values ranged between (4.9 mg/l-5.05 mg/l) for bauxite vicinity water samples and (5.2 to 5.5 mg/L) for rutile mine site. The physicochemical property pH of soil and sediment received within bauxite mining vicinity varied between the slightly acidic ranges (6.1 to 6.2), while that of soil and sediment sample from rutile ore mine site and control were observed to vary between the recommended ranges of 6.6 to 7.5. The average E.C of soil and sediment within both bauxite and rutile mining vicinities revealed similar levels of metal contamination which were slightly higher than the control sample (27 $\mu S/cm$). Soil samples CEC had lower values than the control. Bauxite vicinity soil, sediment and control unveiled averagely Sandyclay-loam in various proportions of sand, clay and silt whereas, rutile vicinity soil revealed Sandyloam. SEM characterization of bauxite ore revealed the interlocking of various associated minerals within the crystal aggregate, while the surface morphology of rutile ore suggested that rutile consist of nano-sized primary particles. FTIR analysis of bauxite and rutile ore within the absorption spectra 650-4000 cm^{-1} due to symmetrical stretching is as result of azide $[N=N=N]^-$, sodium nitrosonium ion $(Na+[NO_2]^+)$, (Phosphane) PH_3 and $[C=N]^-$ ion. While predominantly nitrosyl chloride, nitrogen and linear isocyanate functional groups were revealed for rutile ore.

Keywords: Physicochemical Properties, Scanning Electron Microscopy, Infrared Spectroscopy, Bauxite and Rutile Ores, Soil, Sediment and Water.

1.0 Introduction

Heavy metals occur naturally in the environment, but may also be introduced as a result of land use activities such as solid mineral exploration (the extraction of valuable minerals or other geological materials from the earth crust). The mining industry throughout history has seriously caused immense environmental pollution in industrialized and developing countries. According to the Environmental Data Report of the United Nations Environmental Programme (UNEP, 2013), there is an increasing awareness that the health of human population is at risk from pollution hazards. Mining generates 2.7 billion tons of waste, an amount which far exceeds the world's total accumulated municipal garbage and is responsible for an increase in certain heavy metals in soils, sediments and groundwater reserves occurring within the influence sphere of the mine (Ukpe *et al.*, 2022).

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 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 (Bulus *et al.*, 2023). The large volumes of contaminated wastes generated through solid mineral extraction processes, which are generally stored on the surface can release dangerous pollutants that can persist in the environment for along period of time (Nieva *et al.*, 2018). Mining waste can pose a serious threat to the surrounding soils and biota. The pollutants contained in these wastes can also affect the quality of surface water and groundwater, leading to local contamination of rivers and sediments through erosion and leaching of mining wastes and can lead to a further water pollution by the transport of solid particles such as suspended solids. Even years after mining ceases, most of its adverse effects e to persist over large areas of land (Benidire *et al.*, 2020).

According to Brandy and Weil (2009), the soil is a multi-component system consisting of solid, liquid and gaseous phases as well as living organisms. It is dynamic and sensitive to almost every aspect of its surroundings and represents a chemical system where mineral transformation occurs continuously. Thus, when environmental changes occur, such as mining activity, the soil responds. Any such change produces a gradual alteration of soil characteristics until a new balance is reached. As a complex matrix, soil and sediment can adsorb pollutants and pollution due to heavy or toxic metals and 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 (Bulus *et al.*, 2023). 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 (Itodo *et al.*, 2023).

Site Description

The location of the sampling done directly at some points in these areas was 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.

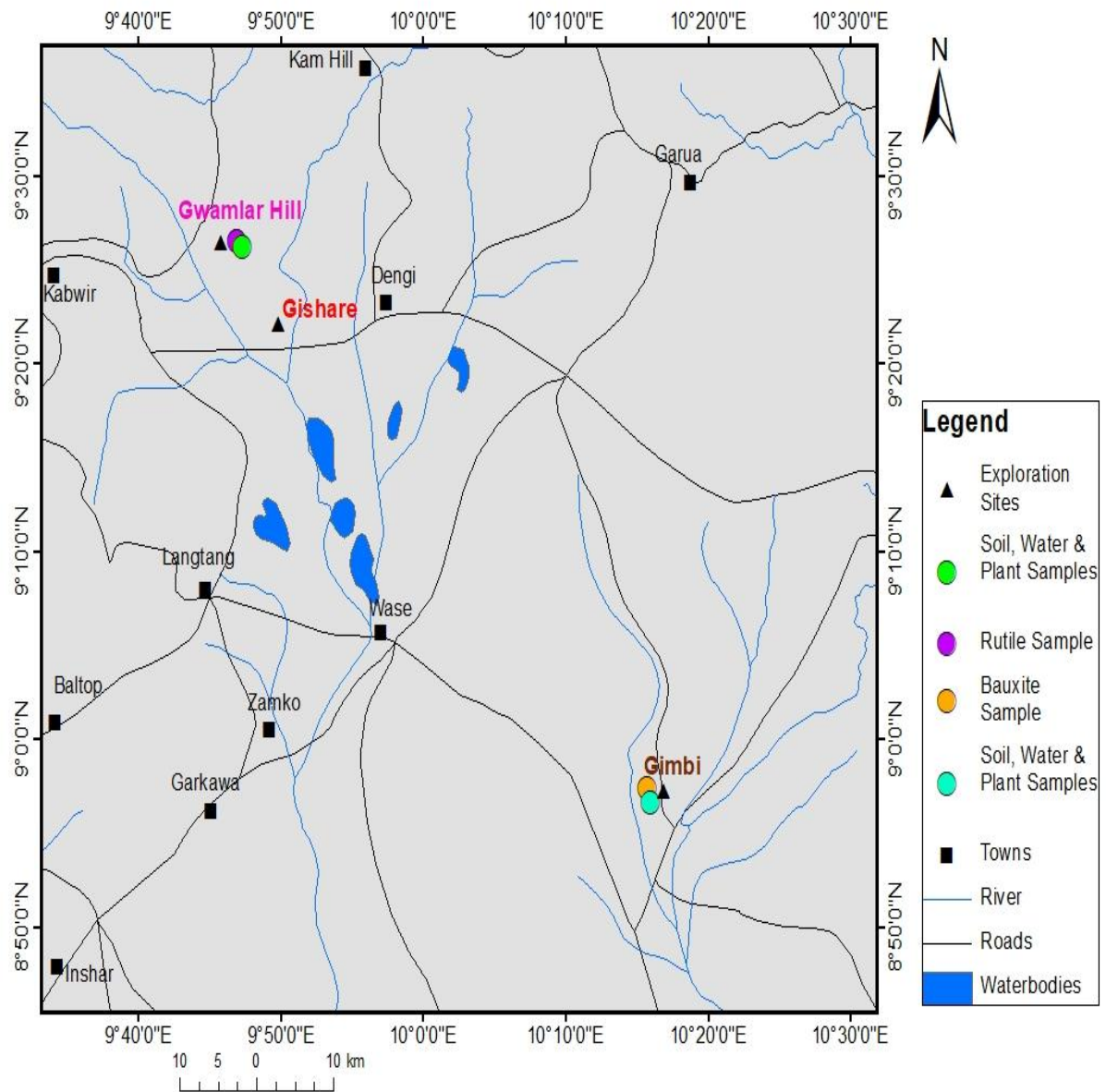


Figure 1: GPS map showing sampling location





Plate 1; Pictorial Representation of (a) Bauxite Exploration site within farm Land Soil (b) Water Samples Collection sites (c) African Beans farm around Mineral mine site (d) Rutile Mineral site.

1.1 MATERIALS AND METHOD

Sample Collection

Bauxite and Rutile ore samples were collected directly from the mineral exploration vicinities of Kanam and Wase LGAs. These minerals were identified at Bass and Matt Mineral Limited Yingi-Rayfield, Jos Plateau State. A total of 30 soil and sediment samples from the Gwamlar (Kanam) and Gimbi (Wase) bauxite and rutile mineral mining vicinities were carefully collected for physicochemical analysis 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). Control soil samples were collected 500 m away from the mining area. Method employed by Environmental Protection Agency (EPA) as reported by Bala (2008) was adopted for the collection of water samples with slight modification. The immediate source of water within the mineral exploration was used. The sources include the effluents pumped by the miners for the purpose of washing/separation of the mineral and also from any channels leading away from the exploration processes. The water from the control site were directly collected from a stream (500 m) away from the mining area. The composite samples of water were collected in prerinsed plastic containers and mixed to make representative samples.

1.2 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 soil properties and also alter the soil matrix for which the measuring instruments were 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 plywood trays in open air, and ensuring with great circumspection that there was no sample cross-contamination or contamination from any external sources (Buluset *al.*, 2023).

2.0 SEM Characterization

Morphological and qualitative analyses of bauxite and rutile ore samples were carried out using the phenomProx model MVE016477830 by Phenom World Eindhoven, the Netherlands at the Ahmadu Bello University Zaria. All the samples were carbon coated in order to make the

minerals surface conductive. To determine the mineral morphology and identifying their mode of occurrence, the crushed carbon coated minerals were examined directly with scanning electron microscopy without polishing. Qualitative chemical analysis of samples was then carried out to produce Backscattered images (BSI).

Results

The surface morphology of bauxite and rutile ore through the use of scanning electron microscopy revealing the interlocking minerals is described in plates 2 and 3.

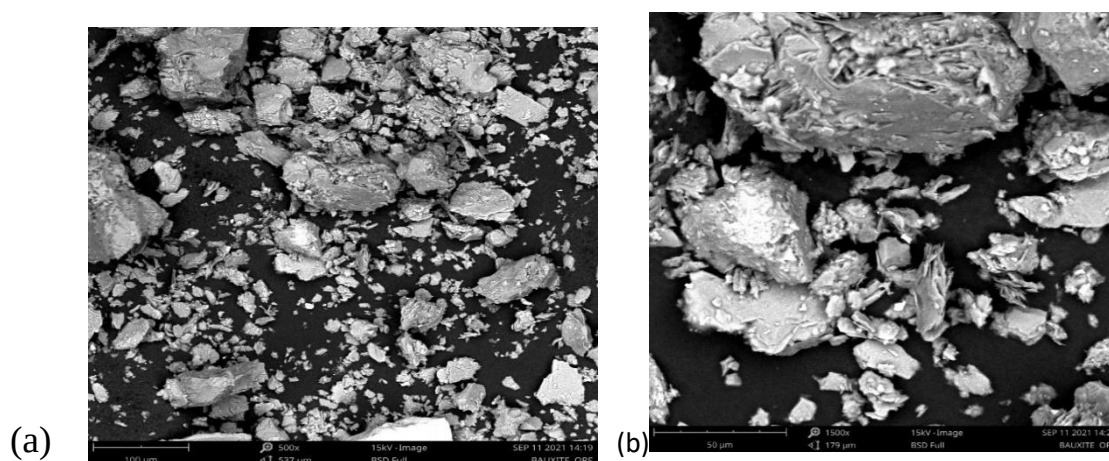


Plate 2; SEM Images of Bauxite Ore at (a) 750x and (b) 1000x magnifications.

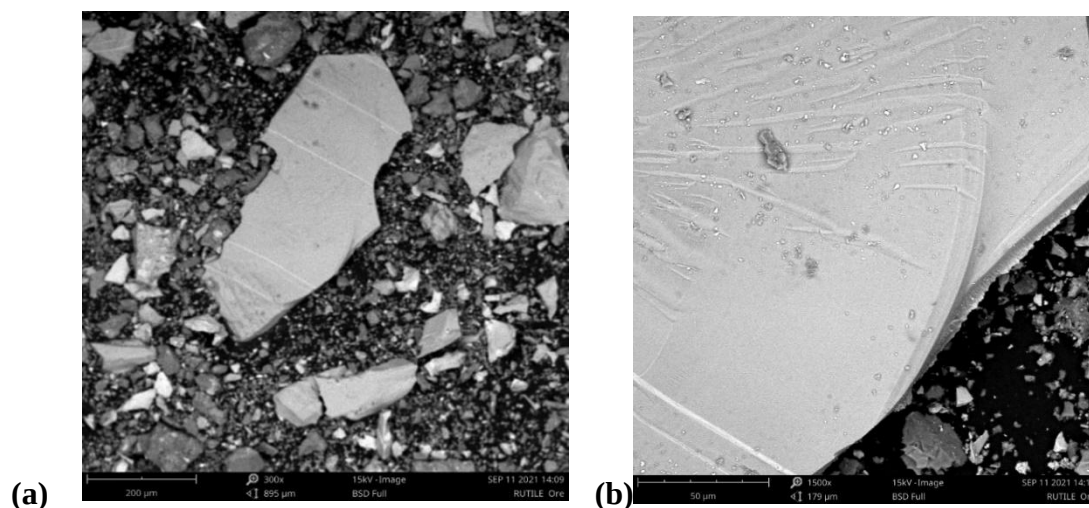


Plate 3; SEM Images of Rutile Ore at (a) 300x and (b) 1500x magnifications.

Discussion

Investigating the surface morphology of bauxite ore through the use of scanning electron microscopy revealed the interlocking of various minerals within the crystal aggregate. This heterogeneous surface is likely a magnetic matrix interspersed with silica, hematite and/or pyrite. This is because the irradiation of fine solid minerals (bauxite residue) containing hard-

like colloidal particles and other noble metals results in cluster (agglomeration) processes with the formation of coarse particles in the form of a drop-like shape with particle size one to two orders of magnitude larger than the original ones (Oglaet *et al.*, 2020). Similar analysis carried out for bauxite ore in Lages, Santa Catarina revealed that gibbsites aggregate were predominant all over the sample. Some semi crystals of goethite which can reach over 100um in size were also observed (Thiago *et al.*, 2011).

The result for the surface morphology of rutile ore through the use of scanning electron microscopy presented in plate 3 showed that rutile consist of nano-sized primary particles with a spherical shape of agglomerated powder, which are packed on layers of cubic flakes. This is because the irradiation of fine solid minerals containing hard-like colloidal particles and other noble metals results in cluster (Oglaet *et al.*, 2020). However, unlike bauxite it is observed to have somewhat smooth surface which is in layers. Another scanning electron microscopy analysis of rutile ore in Middle belt Nigeria revealed that a close look into the powder micrographs shows a degree of rod like shape are also formed. A patchy rusty brown veneer Iron oxide commonly coats the rutile ore. The Backscatter SEM images shown Depicts the zoning of the texture of the rutile ore is produced by concentrations of heavy metals (Moses *et al.*, 2015).

3.0 FTIR Characterization

Functional groups analysis of the ore (bauxite and rutile) were investigated using the furrier transform infra-red spectrometer Cary 360 by Agilent Technologies Inc USA carried out at the Ahmadu Bello University Zaria. The samples were ground using a pestle and a mortar and sieved employing a US standard test sieve with an ASTM E-11 speciation. The sampling station of the instrument was equipped with overhead ATR accessory, the ATR diamond crystal was carefully cleaned with pure Isopropanol inbetween measurements. 10 mg of a powdered sample was cautiously placed on the diamond crystal surface while each spectrum was recorded as absorbance under 100 N.

Result

Table 1; FTIR Spectral Information of Bauxite Ore Sample

Group Frequency (Cm ⁻¹)	Functional Group	Observed frequency of Relative ore (Cm ⁻¹)	Intensity	Assignment
750-650	Azide ion	749.2	S	[N=N=N]-
828-800	Sodium ion, Nitrosonium ion	823.7	S Vs	Na+[NO ₂]-
969-892	Fluoride	909.5	w=m, vw=m	F ₂ , Cl ₂ O
990-980	Phosphane	980.3	m + s	PH ₃ [C=N]-
2250-2050	Cyanide	1982.9	s-band	(NO)+
3500-2220	Nitrosonium ion	2076.1	s, band	

Intensity abbreviations: s=strong, vs= very strong, vw= very weak, m=medium, w=weak

Table 2: FTIR Spectral Information of Rutile Ore Sample

Group Frequency (Cm ⁻¹)	Functional Group	Observed frequency of Relative ore (cm ⁻¹)	Intensity	Assignment
1020-990	Phosphane	998.9	S, m-S	PH ₃
2100-1800	Nitrosylchloride	1871.1	S	NOCl
2100-1815	Cyanide	1982.9	S, Sharp	DCN, [C=N] ⁻
2140-2100	Potassium ion, Isocyanate	2102.2	S, vw-w, broad	K+[NCO] ⁻
3335-2260	Nitrogen, Carbondioxide	2322.1	S, sharp, broad	CO ₂ , N ₂ ¹⁴

Intensity abbreviations: s=strong, vs= very strong, vw= very weak, m=medium, w=weak

Discussion

The reflectance spectra of bauxite mineral specie sourced from the Wase exploration site. This reflectance was ascertained to validate the spectra obtained from the entire spotlight range of 650 cm⁻¹ to 4000 cm⁻¹. The lowest absorption spectrum was observed at 749.2 cm⁻¹, while the higher absorption was recorded at 2076.1 cm⁻¹. Clearly visible were the main peaks between 749.2 cm⁻¹-980.3 cm⁻¹ accompanied by a broad peak at much higher wavelength and transmittance (2076.1) cm⁻¹. The lower absorption spectra 749.2 cm⁻¹ due to symmetrical stretching is as result of azide [N=N=N]⁻ and sodium nitrosonium ion (Na+[NO₂]⁺) (Hallam *et al.*, 2002). Whereas the higher absorption spectra observed at 1982.9 and 2076.1 cm⁻¹ were due to the presence of (Phosphane) PH₃ and [C=N]⁻ ion. This is also the reason for the observed broad peak and strong hydrogen bonding (Brian Smith, 2018). Similar analysis carried out for other minerals/compounds of bauxite (boehmite, gibbsite and kaolinite) revealed major peaks between 1200-900 cm⁻¹ but no peaks were observed for hematite. This is because hematite cannot be studied using FTIR imaging spotlight as its major peaks fall below the mid IR range 700 cm⁻¹ (Pannirselvam *et al.*, 2014).

The spectra were obtained to validate the observed spectral information from the spotlight range of 650 cm⁻¹-4000 cm⁻¹ for the rutile ore. Unlike the result obtained for bauxite ore where the spectral peaks revealed predominantly nitrosyl chloride, nitrogen and linear isocyanate functional groups. The lower and broad absorption spectra observed for the crushed rutile ore sample (998.9) cm⁻¹ is as a result of PH₃ linkage (Brian smith, 2017). Similar analysis was carried out for rutile ore and the characteristic bands occurring at 3417 cm⁻¹, 3182 cm⁻¹, 3000 cm⁻¹, 2963 cm⁻¹, 2907 cm⁻¹, 2809 cm⁻¹, and 1600 cm⁻¹, and in the ranges (1500–1400) cm⁻¹ and (1300–1000) cm⁻¹. The bands between 3417 cm⁻¹ and 3000 cm⁻¹ were due to hydroxyl stretching vibration bands. The band at 3000 cm⁻¹ belongs to the C-H bond stretching vibration. The bands at 2963 cm⁻¹, 2907 cm⁻¹, and 2809 cm⁻¹ correspond to stretching vibration of functional groups CH, CH₂, and CH₃. The vibration at 1600 cm⁻¹ corresponds to C=C bond stretching vibration in the aromatic ring (Andrea *et al.*, 2017)

4.0 Physicochemical Parameters of Water Samples

Method described by El-Harouny *et al* (2009), was employed for this analysis. The pH, conductivity, nitrate and turbidity of the samples were determined using the standard protocols and methods by the American Public Health Organization (APHO) and American Society for Testing and Materials (ASTM).

4.1 pH

Procedure described by El-Harouny *et al* (2009), was adopted for this analysis with little modification. The pH of the water samples were measured using a pH meter model 3345 manufactured by JENWAY Bibby scientific Ltd-UK calibrated with three standard solutions (pH 4.0, 7.0, and 10.0), before taking the measurements. The value of each sample was taking after submerging the pH probe in the water sample and holding for a couple of minutes to achieve a stabilized reading. After the measurement of each sample, the probe was rinsed with deionized water to avoid cross contamination among different samples.

4.2 Conductivity

Method adopted by El-Harouny *et al* (2009), was used without alteration where the conductivity of the samples were measured with a conductivity meter calibrated using a standard solution with a known conductivity. The probe was submerged in the water sample and the reading recorded after the disappearance of stability indicator. After the measurement of each sample, the probe was rinsed with deionized water to avoid cross contamination among different samples. Conductometer model DDS-11D MC JEFFERSON of the National Veterinary Research Institute (NVRI) Vom was used for this analysis.

4.3 Turbidity

As described by El-Harouny *et al* (2009), the turbidity of the water samples were measured using a turbidity meter. Each sample was poured in the sample holder and kept inside for a few minutes. After achieving the reading stability, the value were then recorded.

4.4 Nitrates

According to the procedure reported by Badiadka and Kenchaiah (2009), A UV-Visible spectrophotometer model 6405 designed by JENWAY Bibby scientific Ltd-UK of the Biochemistry Department, NVRI Vom was used for the analysis of nitrates in water samples for the absorbance measurements. Exactly 10 mL of nitrate stock solution was pippered to a beaker, 5 mL of Conc. HCl and 2 mL of Zn/NaCl granular mixture were added, and allowed to stand for 30 minutes with occasionally stirring to form nitrite, then the solution was filtered to 100 mL standard flask using Whatman No 41 filter paper and diluted up to the mark. Aliquots of stock solution containing 0.26-10.7 $\mu\text{g mL}^{-1}$ of reduced nitrate were transferred in to series of 10 mL standard flask. 1 mL of 0.5% sulfanilic acid and 1 mL of 2 mol L⁻¹ HCl solution were added, shaken thoroughly for 5 minutes for the diazotization reaction to go to completion. Then, 1 mL of 0.5% methyl anthranilate and 2 mL of 2 mol L⁻¹ sodium hydroxide solution were also added to form an azo dye and the contents diluted to 10 mL with water. After dilution to 10 mL with water, the absorbance of the red colored dye were measured at 493 nm using the UV-Visible spectrophotometer against the corresponding reagent blank.

5.0 Microbial Parameters

The microbial examination of water samples were carried out to ascertain the quality of water from bauxite and rutile ores mineral mining vicinities. Bacteria and coliform count were verified to know whether these stream channels were safe for drinking and other purposes.

5.1 Bacterial count

Method proposed by Abubakar (2015), was adopted for this analysis. Petri plates of nutrient agar medium containing (g/L): casein hydrolyzate 4.0, yeast extract 3.0, glucose 2.0, beef extract 1.5, peptone 6.0 and agar 20.0 (pH 7.0) were used to determine viable bacterial count. 0.5 ml of each of water samples was transferred to the individual plates for determination of total viable counts (TVC) followed by incubation at 37°C for 24-48 h. for accurate result, each sample was run in triplicates. Total number of colonies on each plate were counted with the help of colony counter.

Colony Forming Unit (CFU) was then estimated/counted using formula:

$$\text{CFU} = \text{No. of colonies} \times \text{Dilution factor} / \text{sample volume (ml)} \quad (16)$$

5.2 Coliform count

Method suggested by (Feng *et al.*, 2002) was used for this research. Coliform count was carried out using lactose broth medium containing malt extract (3.0 g/L), peptone (10 g/L), lactose (5.0 g/L) and Bromothymol blue indicator (1.0 g/L). 10 ml of lactose broth medium were transferred in test tubes. Thereafter inverted Durhams tubes and 5 ml of water sample in it was added. After 24 h incubation at 37°C the test tubes were examined for the presence of acid and gas. Acid production was indicated by a change in color while the gas production was also indicated by the accumulation of gas bubbles in the inverted Durham tubes.

$$\text{CFU} = \text{No. of colonies} \times \text{Dilution factor} / \text{sample volume (ml)} \quad (1)$$

6.0 Biochemical parameters of water samples

The biochemical and microbial analysis such as chemical oxygen demand (COD), oxygen demand (DO) and biochemical oxygen demand (BOD) were carried out using standard laboratory procedures described in literature. Method adopted by Sawyer *et al* (2000), was used for this research work.

6.1 Chemical oxygen demand

Method described by Sawyer *et al* (2000), were adopted with slight modification where the culture tubes and caps were washed with 20% H₂SO₄ before using to prevent contamination. The sample were placed in a culture tube or ampule and a digestion solution was added. Sulfuric acid reagent was carefully being run downed inside the vessel so an acid layer is formed under the sample-digestion solution layer and tightly cap tubes or seal ampules, each was invert several times to mix completely. The tubes or ampules hence placed in block digester preheated to 150°C and reflux for 2 h behind a protective shield. These sealed vessels were viewed to be under pressure from gases generated during digestion. A face and hand protection were worn against the dangerous pressures that was generated at 150°C. Allow to cool to room temperature and vessels placed in test tube rack. Some mercuric sulfate may precipitate out but this will not affect the analysis. Culture tube caps were then removed and small TFE added and covered with magnetic stirring bar. Ampules were at this point removed and the contents transferred to a larger container for titrating. 0.05 to 0.10 mL (1 to 2 drops)

ferroin indicator was added and stirred rapidly on magnetic stirrer then titrated with a standardized 0.10 M FAS (ferrous ammonium sulfate).

COD was computed by the formula:

$$\text{COD as mg/L O}_2\text{/L} = [(A-B) \times M \times 8000] / (V_{\text{sample}}) \quad (2)$$

Where: A = volume of FAS used for blank (mL);

B= volume of FAS used for sample (mL);

M=molarity of FAS; 8000= miliequivalent weight of oxygen $\times 1000$ mL/L Analyze samples in duplicates because of small sample size.

6.2 Dissolved oxygen

The approach described by Sawyer *et al* (2000), was adopted without modification. A dilution water was first of all produced by adding 2 mL/L Phosphate buffer solution, Magnesium sulfate solution, Calcium chloride solution, Ferric chloride solution and Sodium Sulfite solution reagents in a distilled water. For each given sample bottle, 1 mL of alkali-iodide-azide was added and then 1 mL manganous sulfate solution. The bottle then well shaken and kept open for 5 minutes to settle the precipitate. 2 mL concentrated H_2SO_4 was added and the cap placed on the bottle. The bottle was shaken very well till all the precipitates were observed to be completely dissolved. Then 203 mL of sample was measured in a conical flask and titrated with standard sodium thiosulfate solution (0.025 N) and observed until the colour changed from dark yellow to light yellow. Few drops of starch indicator were also added and the process (titration) continued until the color of the solution became colorless and later changed to its original sample colour and the volume of 0.025 N sodium thiosulfate consumed was noted down.

Dissolved oxygen is given by; Dissolved oxygen (DO) (in mg/L) = mL of sodium thiosulfate (0.025N) consumed. (3)

6.3 Biochemical oxygen demand

Method described by Sawyer *et al* (2000), was adopted with slight modification where BOD dilution water referred to as the blank was prepared, 5 mL sample in 300 mL BOD bottle was measured then filled up with dilution water. Another 15 mL sample in 300 mL BOD bottle was also measured and filled up with dilution water as well as 20 mL sample in another 300 mL BOD bottle, fill up also to the mark with dilution water. Two sets of this samples were prepared. One set was used for DO analysis and another sample in BOD incubator for 5 days at 20°C . DO was measured immediately for the different samples at $t=0$ while the dissolve oxygen values (readings) for the BOD samples Incubated in 20°C for 5 days was also record from the incubator and reported in a table form.

Results

Table 3: Nitrate, PH, Turbidity and E.C Analysis in Water Sources around Bauxite Mine Site

Parameters	Sample 1	Sample 2	Sample 3	Control	Mean	SD
Nitrate (mg/L)	12.45	12.20	12.40	21.3	12.350	0.132
PH	7.24	7.15	7.20	7.99	7.197	0.045
Turbidity (NTU)	14.0	12.0	13.0	4.00	13.0	3.600
E.C (us/cm)	0.11	0.12	0.11	0.10	0.113	0.006

Table 4: Nitrate, Turbidity, PH and E.C Analysis in Water Sources around Rutile Mine Site

Parameters	Sample 1	Sample 2	Sample 3	Control	Mean	SD
Nitrate (mg/L)	12.08	11.36	12.06	11.56	11.83	0.410
PH	7.91	8.01	7.82	8.21	7.913	0.095
Turbidity (NTU)	10.0	13.0	13.0	4.00	12.00	2.944
E.C (us/cm)	0.22	0.23	0.22	0.20	0.223	0.006

Table 5: Bacteria and Coliform Count from water sources/stream channels around bauxite mine site.

Sample	TBC (CFU/ML)	TCC (CFU/ML)	MPN of Coliform/100ML	Bacterial Isolates
Control	1.3 x 10 ²	1.5 x 10 ¹	25	<i>Klebsiella aerogenes</i> , <i>Micrococcus luteus</i> , <i>Staphylococcus species</i> .
Sample 1	8.9 x 10 ¹	1.4 x 10 ¹	28	<i>Klebsiella aerogenes</i> , <i>Escherichia coli</i> , <i>Bacillus circulans</i> .
Sample 2	1.4 x 10 ²	2.7 x 10 ¹	32	<i>Klebsiella aerogenes</i> , <i>Staphylococcus species</i> , <i>Escherichia coli</i>

Key: TBC Total Bacterial Count, TCC Total Coliform Count, CFU/Ml Colony Forming Unit per Mililitre, MPN Most Probable Number

Table 6: Bacteria and coliform count from water sources/stream channels around rutile mine site

Sample	TBC (CFU/ML)	TCC (CFU/ML)	MPN of Coliform/100ML	Bacterial Isolates
Control	1.6×10^2	< 10	14	<i>Bacillus species</i> , <i>Micrococcus luteus</i> , <i>Klebsiella species</i> .
Sample 1	6×10^1	0	0	<i>Bacillus species</i> .
Sample 2	5.2×10^1	0	0	<i>Staphylococcus species</i> , <i>Bacillus species</i> .

Key: TBC Total Bacterial Count, TCC Total Coliform Count, CFU/ML Colony Forming Unit Per Mililitre, MPN Most Probable Number

Table 7: Biochemical parameters of Water Samples from Bauxite Mine Site

Parameter	S-1	S-2	S-3	Mean	S.D	Control
DO	4.04	4.5	4.3	4.26	0.23	10.8
BOD	1.98	1.98	2.1	1.36	0.35	3.2
COD	4.9	5.05	4.9	3.31	0.09	4.0

Table 8: Biochemical parameters of Water Samples from Rutile Mine site

Parameter	S-1	S-2	S-3	Mean	S.D	Control
DO	4.3	4.2	4.3	4.2	0.06	10.8
BOD	2.0	1.9	2.1	1.3	0.1	3.2
COD	5.5	5.2	5.2	5.3	0.14	4.0

Discussion

Physicochemical Parameters of Water Samples

The physicochemical and chemical parameters of water ascertained in this research for both samples and control were pH, Electrical conductivity, turbidity and Nitrate contamination of water sources around bauxite and rutile ore vicinities of Wase and Kanam respectively;

pH of Water

The pH of water in the study area (bauxite mine-site) as seen in table 4 ranged between 7.1-7.2 (neither acidic nor basic) having a standard deviation (SD) of 0.045. Bauxite being the principal ore of aluminium exerts no significant effect on the pH of water as seen in this result. This is because Aluminium sticks to soil particles and enters drinking water only if the water is acidic or soft. The pH for the control sample shows a slightly higher value of 7.99 (alkaline) declaring that the water is far from being acidic hence not allowing for the dissolution of aluminium (Udiba *et al.*, 2013). In the same vein, the pH values for water samples sourced from the rutile mine-site vicinity of Kanam (table 5) revealed values between 7.91, 8.01 and 7.82 for the control sample with mean and standard deviations (SD) of 7.91 and 0.09 respectively. Both the water samples and the control were seen to be alkaline (8.01) possibly due to high value of aluminium earlier recorded in the soil samples. Similar test for water in the Cyeru River revealed that the pH of water in the study area ranged between acidic (5.3) to basic (7.6) with the highest pH values found in the downstream region as 7.6 and 7.2 (Hirwa *et al.*, 2019).

Electrical Conductivity (E.C)

The maximum value for the electrical conductivity of water from bauxite mine-site was equal to $0.12 \mu\text{Scm}^{-1}$, whereas the minimum value was found to be $0.11 \mu\text{Scm}^{-1}$ with a mean and standard deviations of $0.113 \mu\text{Scm}^{-1}$ and $0.006 \mu\text{Scm}^{-1}$ respectively. Comparing these values with that of the control ($0.10 \mu\text{Scm}^{-1}$), it was noted that the EC values for the analytical samples were found to be higher due to high concentration of heavy metals leached into the stream channel water through unregulated mining activities. In the same vein, the EC of water samples from the Kanam rutile mine-site as seen in (table 5) unveiled ($0.22, 0.23, 0.22 \mu\text{Scm}^{-1}$) and $0.20 \mu\text{Scm}^{-1}$ for the control sample with a mean and standard deviations (SD) of $0.223 \mu\text{Scm}^{-1}$ and $0.006 \mu\text{Scm}^{-1}$ respectively. These analyses seemingly revealed values within the same range for both samples and control. It however showed slightly higher EC values than were recorded at the Wase bauxite mine-site. The fairly higher values could be due to leached heavy metals through indiscriminate mineral exploration and through other unverified sources for the control. Comparing the E.C results of this research with others cited in literature, the electrical conductivity of water in Gifurwe mining and processing site for downstream water revealed values as high as $54 \mu\text{Scm}^{-1}$ whereas the lowest value ranges between $35 \mu\text{Scm}^{-1}$ to $36 \mu\text{Scm}^{-1}$ upstream respectively. This is due to high level of metals released through mining and processing channels whose effects were often felt downstream of the mine far away from the source of pollution (Nkuli *et al.*, 2019).

Nitrates

The analysis of nitrate (NO_3^-) in water from the bauxite mine-site of Wase in table 4 revealed 12.45 mg/L, 12.20 mg/L, 12.40 mg/L while the value for the water control sample was recorded to be 21.30 mg/L with a deviation of 0.132 mg/L. From the results, the nitrate in the control sample is by far higher than that recorded for the near mine-sites waters. The nitrate contamination of water at the control side is believed to be due to other anthropogenic activities (such as from inorganic fertilizers, industrial waste etc.) which contribute most of

the NO_3^- that accumulates in different localized water bodies, resulting in devastating environmental and health impacts (Withers *et al.*, 2014). The result for that of Kanam rutile mine-site unveiled 12.08 mg/L, 11.36 mg/L and 12.06 mg/L for the samples while 11.56 mg/L was recorded for the water control sample at a deviation of 0.41. Nitrate in both samples and control showed values within the same range hence could have a similar or same source of nitrate contamination in the water. Contaminations in this case is through rutile mining and other sources like organic fertilizers sourced from decomposing organic material and byproducts such as cattle manure and/or through natural environmental sources (Moloantoa *et al.*, 2022). Worthy of note is that for both samples and control in the Kanam and Wase rutile and bauxite mine-sites, the nitrate concentrations in the water were both higher than the global acceptable 10 mg/L limit.

Comparing this research finding to a recent study conducted revealed the impact of NO_3^- contamination of over 50 mg/L from one mine that was detected in water supplied to a village situated close to a mine in the Limpopo province of South Africa. Groundwater sampled around the Selian mining area in China revealed a maximum NO_3 concentration of 109 mg/L, which is alarmingly higher than the global acceptable 10 mg/L limit (Feng *et al.*, 2020).

Turbidity

The minimum and maximum turbidity of the water samples sourced from the bauxite mine site vicinity ranged from 12 – 14 NTU with a mean value of 13.3. Whereas that of water control sample was recorded at 4.7 NTU. Similarly, the recorded values for samples from rutile mineral mine site ranged between 10 – 13 NTU with a mean value of 12 NTU. Although these studies revealed fairly low turbidity values, these are however above the FAO/WHO standard of below 5NTU and <1 for drinking water. These slightly high figures were believed to be connected to wind action blowing lots of debris and man-made contamination of the water sources through bauxite and rutile ore mineral mining operations (Mafuyai *et al.*, 2020).

Microbial Parameters of Water Samples.

The total bacteria and coliform count for water samples sourced from bauxite mining exploration site revealed the bacteria causative isolates *Klebsiella aerogenes*, *Escherichia coli*, *Bacillus circulans* and *Staphylococcus* species, while in the control water sample *Klebsiella aerogenes*, *Micrococcus luteus* and *Staphylococcus* species were reported. The colony forming units for bacteria in these samples were recorded to be 8.9×10 and 1.4×10^2 . That of coliform were found to be 1.4×10 and 2.7×10 while control sample had 1.3×10^2 and 1.5×10 for bacteria and coliform respectively. High MPN (most probable number) for coliform in the samples signifies more contamination in the water sourced from bauxite mineral vicinity (28, 32 MPN) than in the control (25 MPN) believed to be due to disturbance in the stream channels and metal contamination of these water sources through unregulated activities of mineral mining. This alters the general physico-chemical properties of water such as Ph, electrical conductivity, nitrates and nitrites. Routine total bacteria counts (TBC) and total coliform counts (TCC) are commonly done to indicate the microbiological quality of water in rivers or streams affected by anthropogenic activities. MPN indicates the possibility of contamination with human or animal waste, and also pathogenic bacteria (Sanders *et al.*, 2013). Coliform bacteria generally belong to four genera of Enterobacteriaceae (*Citrobacter freundii*, *Enterobacter cloacae*, *Enterobacter aerogenes*, *E. coli* and *Klebsiella pneumoniae*). While others are associated with the intestine (colon) of animals others relates to plants. Coliforms are considered as indicator organisms (used to test the

quality of water and food) because their presence in foods indicates or signifies poor sanitary conditions or fecal contamination (Sui *et al.*, 2018).

Similarly, the total bacterial count for water samples sourced from rutile mine-site vicinity revealed 6×10 , 5.2×10 . The control sample unveiled the bacteria count of 1.6×10^2 and a coliform count of < 10 . Bacterial isolates *Staphylococcus* species and *Bacillus* species were present in the water samples while *Bacillus* species, *Micrococcus luteus* and *Klebsiella* species were found in the control sample with an MPN of 14. Unlike the samples from the bauxite mine-site, no colony forming unit (CFU) per millilitre were recorded for coliform in these samples, this implies that surface inland rutile ore mining was seen to generate minimum impact on the microbiological quality of water compared to bauxite ore mining. A similar research at northwest coast of Borneo revealed that high coliform counts recorded from the river samples indicated the occurrence of faecal contamination. Three of the sampling sites of the water sources complied with DOE standard while none of the sites comply with WHO standards for coliform/bacteria in water (Sanders *et al.*, 2013).

Biochemical Parameters of Water Samples

The biochemical parameters of water samples sourced from the Kanam and Wase mineral mining sites were checked. Parameters such as dissolve oxygen, biochemical oxygen demand and chemical oxygen demand were ascertain to verify the levels of possible water contamination due to surface inland mining of bauxite and rutile ores.

Dissolved Oxygen

The dissolved oxygen for water samples sourced from the Wase bauxite mine site varies from 4.04, 4.5 and 4.3 mg/l. The lowest value 4.04 mg/l was observed at pont S-1 while the highest value 4.5 mg/l was recorded at point S-2. The value for the control sample was found to be 10.8 mg/l. Generally, DO levels less than 3 mg/L are stressful to most aquatic organisms and as a result of this most cyprinids die at 1 - 2 mg/L. However, fish can move away from low DO areas. Water with low DO from 0.2 - 0.5 mg/L are considered hypoxic whereas waters with less than 0.5 mg/L are anoxic. The standard for sustaining aquatic life is stipulated at 5 mg/L therefore a concentration below this value adversely affects aquatic biological life and a concentration below 2 mg/L may lead to death for most fishes (Joseph *et al.*, 2012).

In the same vain, the DO values for rutile ore mining stream channel of Gwamlar-Kanam varies from 4.3 mg/l, 4.2 mg/l and 4.3 mg/l respectively at sampling points S1, S2 and S3 with the same sample used as the control (10.8 mg/l). The higher value was observed at 4.3 mg/l at sample points S1 and S3, whereas the lower value was found to be 4.2 mg/l at sample point S2. Comparing the values obtained from this research with other literature reveals that only the control sample (10.8 mg/l) meets the standard for DO in water out of all the sampling points. Lower values obtained for DO in this research are attributed to the unnatural (man-made) disturbance of the water sources due to mineral exploration activities. Similar studies carried out for water samples at Ganga river Uttarakhand (mg/l) revealed that DO varies from 8.2 to 10.1 mg/l with the average value meeting the criteria (above 5 mg/l) at all monitoring locations and points. The effect of oxygen depletion was more on site 1 & 2 as compared to 3 & 4 and the first observation made was that fishes from site of low DO lacking swim bladder which led to increase in mortality on these sites. Another observation was that most of the fishes of sites 1 & 2 were suffering from oxygen deficiency disease called Asphyxiation (disease more common in cyprinids). Symptom of these diseases are fish do not take food, skin became pale in color, congestion of cyanotic blood in the gill, adherence of

gill lamellae, small hemorrhages in the front of the ocular cavity and in the skin of gill covers (Priyanka *et al*, 2014).

Biochemical Oxygen Demand

The biochemical oxygen demand varies between 1.98 and 2.1 mg/l for samples S1, S2 and S3 respectively. The value observed for the control sample was 3.2 mg/l. Generally, aside the value recorded for the control sample, the BOD levels recorded in the entire sampling points were below the EU guidelines of 3.0 to 6.0 mg/L (BOD) for the protection of fisheries and aquatic life and for domestic water supply (Chapman *et al*, 2012). The variations in the levels of BOD between the three sampling points might be due to run-off from agricultural activities within this area of study. Biochemical Oxygen Demand is a measure of the quantity of oxygen consumed by microorganisms during the decomposition of organic matter (Akan *et al*, 2007).

The values for BOD sourced from the stream channels (rutile ore mine site) of Gamlar, Kanam as observed were 2.0, 1.9 and 2.1mg/l. Just as in the other part of this research, the entire sampling points were also lower than the EU guidelines standard values of 3.0 to 6.0 mg/L for biochemical oxygen demand. Similarly, a research in the Baga, Lake Chad basin north eastern Nigeria revealed that the biochemical oxygen demand (BOD) of 83.66 mg/L was significantly high at point S5, while point S2 shows the least concentration. The variations in the levels of BOD between the five sampling points of study were attributed to be due the run-off from agricultural activities within this area (Joseph *et al*, 2012).

Chemical Oxygen Demand

The chemical oxygen demands for water samples sourced from bauxite ore mining vicinity were recorded to be within the range of 4.9 mg/l for S1, S3 and 5.05 mg/l for S2. The control sample was observed to be 4.0 mg/l. These values detected at all sampling points including the control sample were observed to be within the WHO limit of 200 mg/L (Priyanka *et al*, 2014).

Similarly, the values recorded for water samples from the Kanam rutile ore mining vicinities varies between 5.2 to 5.5 mg/l with the lower values obtained at 5.2 mg/l (point S2 and S3), while the higher value of 5.5 mg/l obtained at sample point S1 and the control at 4.0 mg/l. Although these values were observed to be slightly higher than the former, they also did not exceed the WHO standard value of 200 mg/l for COD. The COD levels observed in the present study are likely to be inconsistency depending on the season at which the sampling was carried out. Previous research carried out by (Joseph *et al*, 2012) in Vrishabhavathy River, Ban-galore reported many fold increase of COD in downstream which ranged between 662 and 366 mg/L than upstream in summer, and decreased to 74 and 180 mg/L in rainy season.

7.0 Physicochemical Properties of Soil, Sediment and Control

The physiochemical parameters of the soil samples such as pH, conductivity, bulk density, cation exchange capacity and texture content were carried out using standard laboratory procedures. Method explained by Ahmedna *et al.*, (2000) was adopted for use in this research.

7.1 pH

The pH of the soil and sediment samples were determined by weighing 5.0 g of sample into 100 mL distilled water in a beaker stirred for 5mins. Analytical pH meter model PHS-3C of the

Federal College of Land Resources Technology Vom was used to record the pH for each soil sample (Itodo *et al.*, 2019).

7.2 Conductivity

The conductivities of the soil and sediment samples were recorded using a conductivity meter model HI86304 of the Federal College of Land Resources Technology Vom. 5.0 g of the analytical samples of (soil and sediment) were mixed/suspended in distilled water, stirred and allowed to settle for 10 minutes and the conductivity values recorded. This was repeated successively for each sample (Itodo *et al.*, 2019).

7.3 Bulk Density

The bulk densities of the soil and sediment samples were determined using the tamping method by Ahmedna *et al.* (2000). A 5.0 g portion of the soil sample was packed in 25 mL measuring cylinder to a specific volume and tapped until a minimum volume is occupied. The readings were taken and analyzed thus;

$$\text{Bulk Density (g/cm}^3\text{)} = M_d / V \quad (4)$$

M_d = Mass of dry soil sample (grams)
 V = Soil volume.

7.4 Cation Exchange Capacity

Cation exchange capacity (CEC) of the soil samples were determined using the method adopted by Morteza (2017), with slight modification. Exactly 25.0 g of soil were measured in a 500 mL Erlenmeyer flask, 125 mL of the 1 M NH_4OAc was added and shaken thoroughly and allowed to stand 16 hours (or overnight), a 5.5 cm Buchner funnel with retentive filter paper, moistened and with a light suction was used to filter the soil. These soil samples were gently washed four times with 25 mL additions of the NH_4OAc , allowing each addition to filter through but not allowing the soil to crack or dry. Suction was applied to ensure slow filtering. The soil is again washed exactly with about eight separate additions of 95% ethanol to remove excess saturating solution. Enough of it was added to cover the soil surface, and allow each addition to filter through before adding more. The leachate discarded and the receiving flask rinsed properly. The adsorbed NH_4 was extracted by leaching the soil with eight separate 25 mL additions of 1 M KCl , leaching slowly and completely as above, the soil was discarded and the leachate transferred to a 250 mL volumetric flask and diluted to volume with additional KCl . The concentration of $\text{NH}_4\text{-N}$ in the KCl extract was determined by distillation or colorimetry. $\text{NH}_4\text{-N}$ in the original KCl was also determined by extracting solution (blank) to adjust for possible $\text{NH}_4\text{-N}$ contamination in this reagent.

$$\text{NH}_4\text{-N is reported in mg N/L: CEC (cmolc/kg)} = (\text{NH}_4\text{-N in extract} - \text{NH}_4\text{-N in blank}) / 14$$

Where $\text{NH}_4\text{-N}$ is reported in mg $\text{NH}_4\text{/L}$:

$$\text{CEC (cmolc/kg)} = (\text{NH}_4\text{-N in extract} - \text{NH}_4\text{-N in blank}) / 18 \quad (5)$$

7.5 Texture content of soil

Method reported by Andrés *et al.* (2014), was adopted for this analysis. In this procedure, the SOM were destroyed in a 70 g soil sample by applying successive aliquots (approximately three times) of 40 mL of hydrogen peroxide (H_2O_2 , 130 volumes) until the effervescence of the reaction appeared minimal. This procedure was performed on an 80 °C hotplate. The oxidized samples were placed in a forced-air oven and allowed to dry-off at 80 °C. Dispersion was obtained by shaking 50 g of dry soil sample with 100 mL of 25% sodium

hexametaphosphate for 16 hours in a reciprocating shaker. The mixture was then placed in a Bouyoucos' blender cup and stirred for two minutes with an electrical mixer. The contents of each cup transferred to a 2 L sedimentation cylinder and the cylinder filled with deionized water to the 2000 mL mark. The mixture was then homogenized using manual agitation. The solids in the suspension were measured with a hydrometer following 40 seconds of decantation with a second lecture taken after two hours. The measurement was made when the suspension is between 20 and 22 °C and then corrected due to the temperature. The first reading was for estimating the sand content, whereas the second one at two hours was to estimate the clay content. The silt fraction was calculated as the difference between those two measurements.

Sand%=100–(Lecture 40 s x 2 – blank Lecture) x 100/oven-dry wt.

Clay%= (Lecture at 2 hours x 2 – blank Lecture) x 100 / oven-dry wt.

Silt % = 100 – sand % - clay %. (6)

Results

Table 9: pH, E.C and CEC of Soil, Sediment and Control from Bauxite Mine Site

Parameters	S-1	S-2	S-3	Mean	S.D	Sediment	Control
pH _(H2O)	6.2	6.2	6.22	6.2	0.01	6.1	6.6
pH _(CaCl2)	4.98	4.96	4.96	4.96	0.012	5.28	4.92
E.C(us/c)	29	29	29	29	0	5.28	4.92
CEC(meq/100)	0.73	0.71	0.72	0.72	0.01	0.60	0.62

Meq=milliequivalent per100 grams of soil

Table 10: pH, E.C and CEC of Soil, Sediment and control around Rutile mine site

Parameters	S-1	S-2	S-3	Mean	S.D	Sediment	control
pH _(H2O)	6.98	6.96	6.96	6.96	0.012	6.81	6.42
pH _(CaCl2)	5.24	5.2	6.96	5.23	0.02	5.14	5.14
E.C	27	27	27	27	0	26	23
CEC(meq/100)	0.82	0.83	0.8	0.82	0.02	0.62	0.7

Meq=milliequivalent per100 grams of soil

Table 11: Texture of Soil, Sediment and Control from Bauxite Mine Site

Samples	Particle Size			Textural Class
	Sand	Clay	Silt	
Soil	69.44	26.00	4.56	Sandyclay loam
Sediment	65.62	23.84	10.54	Sandyclay loam
Control				
Soil	63.56	24.90	11.54	Sandyclay loam

Table 12: Texture of Soil, Sediment and Control from Rutile Mine Site

Samples	Particle Size			Textural Class
	Sand	Clay	Silt	
Soil	71.44	13.00	15.56	Sandyloam clay
Sediment	67.44	26.00	6.56	Sandyclay loam
Control Soil	65.44	24.10	10.55	Sandyclay loam

Discussion

Physicochemical Properties of Soil, Sediment Control.

The physicochemical properties of soil, sediment and control were ascertained to check the PH, electrical conductivity, texture and cation exchange capacities. These were carried out to verify the level of soil contamination through bauxite and rutile ores mineral exploration within the vicinities of Gwamlar, Kanam and Wase mining areas.

pH

The pH of the soils, sediment and control were carried out in two different mediums (H_2O and $CaCl_2$). In H_2O , the pH varies between 6.1 and 6.61. The average pH value for soils S1 to S2 is 6.2 while the values for sediment and control varies between 6.1 and 6.6. The respective PH of these samples in $CaCl_2$ at each sampling points were found to be within the ranges of 4.98, 4.96, 4.96 for soil, 5.28 and 4.92 for sediment and soil control samples. The values recorded in the calcium chloride medium were observed to be lower in comparison to the water medium samples. The pH(H_2O) values at S1, S2 and S3 and that of the sediment falls within the slightly acidic range (6.1 to 6.2) due to mineral (bauxite ore) mining activities, this could cause low forage growth due to soil metal toxicities such as aluminium or manganese, phosphorus fixation, and reduced population of N-fixing bacteria in legumes (Itodo *et al.*, 2019). While the observed value (6.6) for the control soil sample was within the pH recommended value range of 6.6 to 7.5 for optimum plant growth according to Queensland Department of Environment and Heritage Protection (QDEHP, 2019). Similarly, the pH values for soil, sediment and control collected within the proximity of rutile ore mine site varied between 6.98, 6.96 and 6.96 for S1, S2, S3 and 6.82, 6.42 for sediment and control soil sample. Also, the values obtained for pH ($CaCl_2$) averagely vary within 5.2 to 6.96 for soil samples, sediment and control. The pH (H_2O) values at each sampling point and that of sediment were however observed to be slightly higher than those recorded for samples collected from bauxite mine site vicinity. Unlike the former, the values are in agreement with the pH recommended value range of 6.6 to 7.5 for optimum plant growth.

Another research carried out in the Nigeria's Benue Trough (Ikwo LGA, Ebonyi State) indicates pH values within the acidic (5.2) and slightly acidic (6.3) range. This analysis revealed that the soil was also lacking in other key nutrients such as phosphate and potassium, soil containing such a very low amount of nitrogen, phosphorous and potassium indicates intensive leaching of the above mentioned nutrients (Gupta *et al.*, 2006).

Electrical Conductivity

The average electrical conductivity (E.C) value of the analytical soils and sediment samples at each sampling points within the proximity location of bauxite ore mining site was (29 $\mu S/cm$). The control sample was observed to be (27 $\mu S/cm$) slightly lower than those of the

analytical samples. The recorded values for the analytical samples as observed were relatively high due to high level electrical potential in soils; clays and other water saturated and unsaturated sediments, ionic layers, electro filtration, pH difference and electro osmosis (Pozdnyakova *et al.*, 2019). The E.C values also confirm the distribution of ionic species in soils and sediments due to run-off from bauxite ore exploration vicinity. In the same vain, the mean electrical conductivity (E.C) for soil samples and sediment collected around rutile ore surface mine site varies between (27 and 26) $\mu S/cm$ respectively, while that of control soil was recorded at 23 $\mu S/cm$ lower than the values observed for analytical samples. Comparing this result to that of samples collected within the proximity location of bauxite ore mine site, the E.C of soils, sediment and control within this area was fairly low. The above results were however, not in agreement with a research undertaken at Ebonyi Eastern Nigeria where the electrical conductivity (EC) for soil samples and sediment at wet and dry seasons were seen to be less than 2 $\mu S/cm$ due to relatively large deposit of carbon (coal) in the soil (Ukpe *et al.*, 2021).

Cation exchange capacity (CEC)

The cation exchange capacity of soil from the study area (bauxite mine site vicinity) revealed values for potassium, K varying between (50-52) meq/100 g for S1, S2, S3 and 64 meq/100 g for sediment. Mg and Ca recorded values within the range of 3.7 to 5.1 and 6.8 to 6.9 meq/100 g as seen in table 10. The average value for Na was 0.72 meq/100 g. Higher value of K in the sediment and control soil (sourced 500 m away from bauxite mine site) indicated the presence of high organic matter in the control possibly due to agricultural practices (polluted with K from sources such as run-off or direct application of inorganic chemicals/fertilizer from surrounding farms). Generally, humus soils are rich in organic matter and this is proportional to high CEC at any increasing humus. The cation exchange capacity of soil corresponds to the total capacity of a material (soil) to hold exchangeable cations, which gives information on the soil sorption capacity towards metal and metalloids. An increase in soil CEC due to increased organic matter causes a decrease in electrical conductivity (Moore *et al.*, 2008).

The CEC of soil collected from the Gwamlar, Kanam rutile mine side (table 11) also revealed figures varying from 62 to 63 meq/100 g for K, averagely 3.1 for Mg and 3.2 to 5.2 meq/100 g for Ca. while Na was observed to be 0.82, 0.83 and 0.80 meq/100 g respectively for S1, S2 and S3. Similar to that of soil samples received from the bauxite mine site area of Wase, the control soil sample was observed to have slightly higher value for K (81 meq/100 g) compared to sampling points S1,S2 and S3 also suggesting the presence of organic matter in the soil. The relative high CEC for K, Ca and Mg suggesting the presence of organic matter in the soil for both bauxite and rutile ores mine site locations confirm that the mineral exploration activities were carried out within agricultural farm land vicinities. This is also consistent with a research carried out in Benin, Nigeria for soil parameters before pollution with Pb and after remediation with *Eleusine indica*, It was observed that exchangeable acidity and CEC of humus soil was significantly higher than that of clayey soil ($P < 0.05$). It was also observed that the exchangeable acidity and CEC increased significantly with increasing proportions of humus soil before pollution with Pb. however, electric conductivity decreased (khajiagbe *et al.*, 2019).

Texture

The textural class of soil, sediment and control soil collected from the mineral vicinities of Wase local government area of Plateau State as observed were averagely sandyclay-loam in various proportions of sand (69.44), clay (26.0) and silt (4.56) for analytical soil samples,

while sediment and control soil samples were found to be sand (65.62), clay (23.84), silt (10.54) and sand (63.56), clay (24.90), silt (11.54) respectively. This suggests that bauxite ore mining does not exert so much impact on soil structure and texture. The result for the textural class of soil, sediment and control within the proximate mine site location of rutile ore shows sandyloam for vicinity soil as well as sandyclay loam for sediment and control soil in proportions of sand (71.44), clay (13.0), silt (15.56) for analytical soil whereas, sand (67.44), clay (26.0), silt (6.56) and sand (65.44), clay (24.10) silt (10.55) for sediment and control soil respectively. Slightly higher values recorded for clay and silt (loam) for the mineral mine vicinity soil implies that rutile ore mining alters soil texture. Generally, mineral exploration distorts vegetation, mining residue with fine particle-size (< 2 mm) and homogeneously distributed are subject to wide dispersion in the environment, and as such a potential source of metal contamination for the surrounding compartments (El Hachimi *et al.*, 2020). Similar research for at some mineral mines sites revealed that the textural class of soil at Ijero-Ekiti was sandy loam while that at Awo and Itagunmodi was loamy sand (Oluwatosin *et al.*, 2014).

Conclusion

Water quality parameters pH, Electrical conductivity, turbidity and Nitrate within the bauxite and rutile ore vicinities suggests that the water were contaminated with mineral mining residues. Total bacteria (TBC) and coliform count (TCC) revealed various bacteria causative isolates and colony forming units for bacteria and coliform exceeding the values obtained for the water control samples. High MPN for coliform in the samples signifies contamination in the mineral vicinity water sample compared to the control (25 MPN). Dissolved oxygen (DO) revealed lower values for both bauxite and rutile mines vicinity sampling points compared to the control 10.8 mg/L. The biochemical oxygen demand (BOD) unveiled values below the water control sample (3.2 mg/L) and the EU guideline standard values of 3.0 to 6.0 mg/L for the protection of fisheries and aquatic life and for domestic water supply. COD values detected at all sampling points including control were however within the WHO limit of 200 mg/L. Observed pH values for soil and sediment within the bauxite vicinity varied between the slightly acidic ranges (6.1 to 6.2) while that within the proximity of rutile ore exert little impact on soil pH. The average electrical conductivity (E.C) of soil and sediment received at both mining locations revealed higher values for soil and sediment samples from the bauxite and rutile ore vicinity mine sites than the control. Higher values of control soil where however observed for the CEC and this were attributed to sources such as inorganic fertilizer applied farmland soil and also industrial waste. Generally, humus soils are rich in organic matter and this is proportional to high CEC at any increasing humus. The textural class of bauxite vicinity soil, sediment and control unveiled largely Sandyclay-loam in various proportions whereas that within the rutile vicinity revealed Sandyloam. This is because silt recorded higher percentage than clay and by implication, rutile ore mining impact more on soil texture as seen from this study. SEM characterization of bauxite ore revealed the interlocking of various minerals within the crystal aggregate with a heterogeneous surface which is likely a magnetic matrix interspersed with silica, hematite and/or pyrite. Whereas, the surface morphology of rutile ore showed that rutile consist of Nano-sized primary particles with a spherical shape of agglomerated powder, which are packed on layers of cubic flakes. FTIR analysis of bauxite ore revealed that the entire absorption spectra within the spotlight range $650\text{--}4000\text{ cm}^{-1}$ was due to symmetrical stretching is as result of azide $[\text{N}=\text{N}=\text{N}]^-$ and sodium nitrosonium ion $(\text{Na}+[\text{NO}_2]^+)$, (Phosphane) PH_3 and $[\text{C}=\text{N}]^-$ ion. Validating the observed spectral information of rutile ore from the spotlight range of $650\text{ cm}^{-1}\text{--}4000\text{ cm}^{-1}$ revealed predominantly nitrosyl chloride, nitrogen and linear isocyanate

functional groups. The lower and broad absorption spectra observed for the crushed rutile ore sample (998.9) cm^{-1} is as a result of PH_3 linkage.

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