

Quarry soil and quarry stream water baseline level parameters around Chestedi Quarry, F.A.U.C. Golden Ltd Quarry, Fakunle Quarry and River Oyanmi in Igarra, Akoko Edo

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World Journal of Advanced Research and Reviews, 2024, 21(03), 2360–2384

Publication history: Received on 19 February 2024; revised on 28 March 2024; accepted on 30 March 2024

Article DOI: <https://doi.org/10.30574/wjarr.2024.21.3.0994>

Abstract

The primary objective of this research was to investigate the initial levels of chemical parameters surrounding quarry operations in Igarra, Akoko-Edo, Edo State. Specifically, three prominent quarries (Chestedi, F.A.U.C. Golden Ltd, and Fakunle) were examined, along with the water of River Onyami flowing through these quarries from the Ojirami dam. Each quarry site yielded four soil samples collected at a various depth (between 0 – 15 cm) and different geographical coordinates, while four water samples were obtained from River Onyami. These samples underwent analysis for their physicochemical properties and the chemical speciation of Fe, Zn, Cu, Pb, Cr, and Mn. As Tessier et al. (1978) described, a sequential extraction method was employed to partition the heavy metals into five different fractions. Total concentrations of heavy metals in both soil and water samples were determined. The distribution of heavy metals in the soil exhibited the following order of accumulation: Fe > Zn > Mn > Cu > Pb > Cr, whereas in water samples, the order was Fe > Zn > Cu > Mn > Pb > Cr. Iron and zinc emerged as the predominant heavy metals in the soil, with iron within permissible limits but zinc, copper, manganese, lead, and chromium exceeding their respective limits. In the stream water, iron and lead surpassed their permissible limits, while Zn, Cu, Cr, and Mn remained below theirs. Comparative analysis against WHO, NIS DPR, and CCME maximum contamination/permissible limits was conducted for heavy metal concentrations and physicochemical properties in both soil and water samples. Mobility Factors (MF), Environmental Risk Factors (ERF), Contamination Factors (CF), Pollution Load Index (PLI), and Geoaccumulation Index (GI) were computed. Results from this study indicate that the soil is conducive to supporting growth and is nutrient-rich for various applications, while the water is suitable for irrigation and other domestic purposes.

Keywords: Quarry Soil; Quarry Stream Water; Environment, Mobility; Environmental Risk Factors; Contamination Factors; Contamination Factors; Pollution Load Index; Geoaccumulation Index

1. Introduction

A quarry represents an open-pit mining site where rock or minerals are extracted, typically utilized for obtaining building materials like dimension stone, construction aggregate, riprap, sand, and gravel. Limestone, primarily composed of calcite (CaCO₃), is formed through organic or inorganic processes (Serra, 2006). Global quarry mining operations encompass various activities that can disrupt the environment if not properly designed, constructed, operated, and monitored. This disruption is attributed to fine dust particles and surface disturbances caused by

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explosive blasting, posing health hazards to workers. Hence, it is crucial to assess the soil in such areas to ensure environmental sustainability (Bayrami et al., 2008).

Marble, a metamorphic rock primarily composed of calcite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], or a combination, exhibits a fine to coarse-grained crystalline texture (Serra, 2006). Calc-gneisses, which are marble with impurities, are commonly associated with marble, particularly around Geoworks quarry sites (Obasi, 2012). Limestone exists in diverse forms, with chalk being a porous marine limestone predominantly comprised of microscopic fossils. Travertine, a freshwater sedimentary limestone, is characterized by thin, crenulated layers, often forming at springs. While calcite is the primary mineral in limestone, it frequently contains dolomite [$\text{CaMg}(\text{CO}_3)_2$] and aragonite (CaCO_3). Impurities such as sand, clay, and organic materials give limestone its various colors.

The geological makeup of Nigeria consists of three main litho-petrological components: the Basement Complex (Precambrian), Younger Granites, and Sedimentary Basins (Cretaceous to Tertiary). Efforts to address issues related to abandoned quarry pits involve characterizing the effects of blasting and quarry operations and implementing measures to control these effects during active and inactive periods. Additionally, measures such as fencing off abandoned quarry pits are essential for safety. Mining operations, both indigenous and organized, have been ongoing in Nigeria since the 20th century, with increasing interest in resource exploitation leading to numerous mines of minerals such as limestone, granite, iron ore, and gemstones. However, this has resulted in vast areas of bare and degraded land (>10 hectares per mine) at the cessation of mining operations (FME, 1999). Various physical, chemical, and biological technologies exist for treating mined-out areas, with the selection of treatment depending on factors such as degradation severity, site characteristics, regulatory requirements, cost, and time constraints (Steffen et al., 2004). The technical approaches to reclamation are as diverse as the minerals being extracted, with sand and gravel operators addressing post-mining land use due to the proximity of operations to urban areas, often incorporating site-planning principles into mining and reclamation operations. Given the physicochemical and biological intricacies involved, alongside the technical utilization of machinery for the extraction and processing of quarried materials, the quarry industry emerges as a significant enterprise. However, it is characterized by relatively low remuneration for its employees. Consequently, only workers who are highly motivated are likely to express interest in employment at such sites (Onivefu, 2023).

1.1. Igarra Quarries (Grey Calcite)

The quarries are situated in Igarra town within the Akoko-Edo Local Government Area of Edo State, approximately 6km away from the town center. These quarries exploit a calcite deposit spanning an area of approximately 500 feet by 500 feet square meters, boasting a production capacity of 50 tons of crude material per day. Among the prominent quarry sites in Igarra, Akoko-Edo, Edo State are Chestedi, F.A.U.C. Golden Ltd, and Fakunle quarries.

1.2. Heavy Metals in the Vicinity of Quarry Industries

Although many heavy metals serve as essential elements at low concentrations, they can become harmful when present at higher-than-permitted levels in the environment (Anegebe et al., 2014). Particularly during dry seasons, these metals may be released into the atmosphere, posing potential risks (Okuo and Okolo, 2011).

1.3. Environmental Impact of Quarrying in Surrounding Communities

There has been a tremendous increase in the level of industrial activities (such as mining) and vehicular traffic in most Nigerian cities. Most of the industrial processes involve the use of chemicals that are prone to emit VOCs into the atmosphere (Okuo and Olumayede, 2010). According to Omosanya and Ajibade (2011), the environmental impacts of quarrying on the surrounding communities are;

- Boulders and gravels produced during quarrying, some of them do travel in the air during blasting thereby constituting a major hazard to nearby settlers.
- Dust produced during the quarrying work has contributed hugely to air pollution. Dusts can be seen on the vegetation some distances away from the Quarry.
- Various levels of damage caused by quarrying activities, including the potential collapse of buildings in the vicinity.

Aim of the studies

The objective of this study is to assess the baseline levels of chemical parameters in the vicinity of quarry industries, specifically focusing on the Chestedi, F.A.U.C. Golden Ltd, and Fakunle quarries in Igarra, Akoko Edo, Edo State. Additionally, the study aims to investigate how these baseline levels may influence the surrounding environment.

2. Experimental and analysis of the study

The primary objectives of this research are as follows:

- Collect composite soil samples from each of the three quarries (Chestedi, F.A.U.C. Golden Ltd, and Fakunle, coded as Site 1, Site 2, and Site 3).
- Gather composite water samples from the River Onyami, which flows through the quarries.
- Identify key physicochemical parameters in the soils of the quarries and the River Onyami water surrounding the quarries.
- Fractionate the quarry soil samples to analyze heavy metals such as Fe, Zn, Cu, Mn, Pb, and Cr.
- Analyze the stream water samples for heavy metals including Fe, Zn, Cu, Mn, Pb, and Cr.
- Subject the collected data to statistical and graphical analysis.
- Determine the mobility factors (MF) of heavy metals in the soil samples from the quarries.
- Assess the environmental risk factors (ERF) associated with heavy metals in the soil samples from the quarries.
- Calculate the contamination factors (CF) of heavy metals in the soil samples from the quarries.

3. Material and methods

3.1. Study Area

The study area, situated in Igarra, falls within the geographical coordinates between Latitudes $N7^{\circ}16.547'$ and Longitudes $E6^{\circ}06.467'$. Positioned at the northern edge of Akoko Edo Local Government Authority in Edo State, Southwest Nigeria, Igarra is home to the quarry industries and stream water sources under investigation. The River Onyami, often referred to as the Upako stream by the locals, originates from the Ojirami dam, traverses through Igarra, and continues to Ososo. These sites can be located relative to Geoworks Industries

- Fakunle quarry,
- F.A.U.C. Golden Ltd,
- Chestedi and
- River Onyami water.

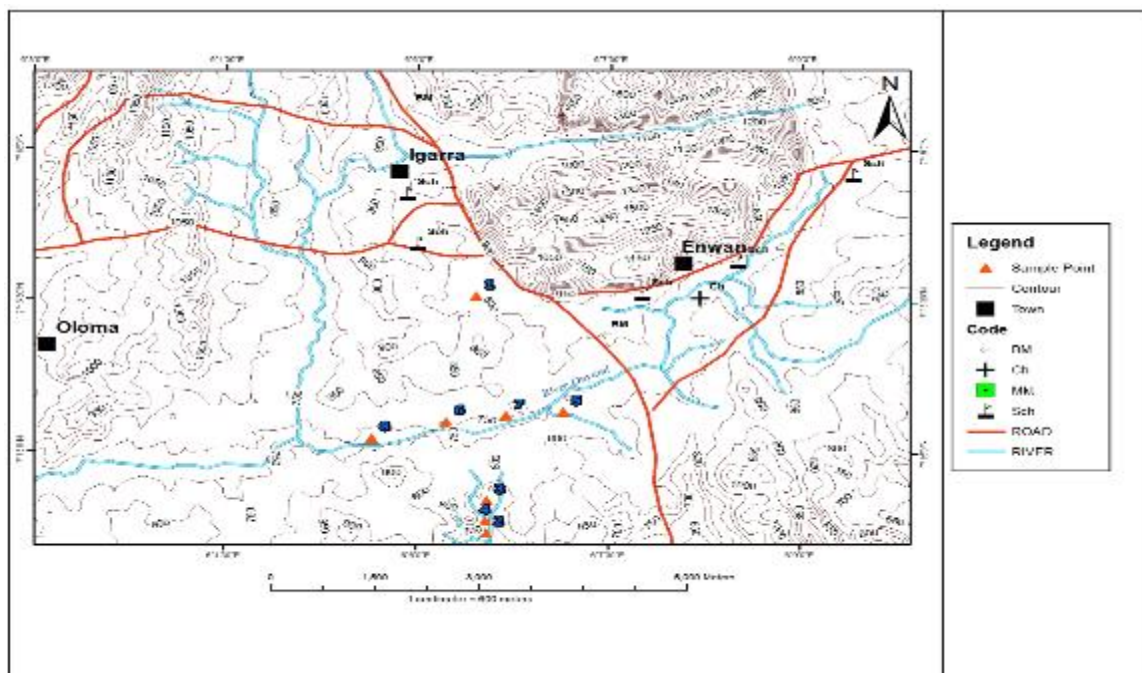


Figure 1 Map of Igarra showing the study area and the sampling site

Table 1 The quarries, site code and coordinates

Quarries	Site Code	Coordinate
Chestedi quarry	Site 1	N7°14.2868' E6°06.5103'
F.A.U.C. Golden Ltd quarry	Site 2	N7°14.5205' E6°06.5557'
Fakunle quarry	Site 3	N7°14.3004' E6°06.5275'

Table 2 The stream water samples, site code, coordinates and temperatures

Stream Water Samples	Site Codes	Coordinate	Temperature
River Onyami Water Sample 1	Site 5	N7°15.3947' E6°07.1488'	22°C
River Onyami Water Sample 2	Site 6	N7°15.3935' E6°06.1421'	21°C
River Onyami Water Sample 3	Site 7	N7°15.3898' E6°06.1396'	25°C
River Onyami Water Sample 4	Site 8	N7°15.3948' E6°06.1492'	29°C

3.2. Sampling procedure: sample collection, Preparation and sampling design

3.2.1. Soil Sample Collection and Preparation

Soil samples were systematically collected from each of the three quarries, and divided into four quadrants. Using a Dutch soil auger and hand trowel, samples were randomly taken at various distances within each quadrant at various depth (between 0 - 15cm) and at different geographical coordinates. These samples were combined and homogenized in clean plastic buckets to create composite samples for each quarry. Following this, all composite samples underwent air drying and sorting to eliminate plant materials and pebbles. Subsequently, the dried samples were ground using an agate mortar to a size suitable for passing through a 2mm sieve. The resulting particles were then packed into polythene bags and appropriately labeled for subsequent analyses. Temperature programmed can be particularly useful for understanding the thermal properties and behavior of volatile and semi-volatile compounds present in soils but this will be discussed in another research (Onivefu, 2023).

3.2.2. Water Samples Collection and Preparation

Water samples were gathered from the River Onyami near the quarry at distinct sampling locations spaced 5 meters apart: Site 5, Site 6, Site 7, and Site 8, utilizing one-liter plastic containers. Prior to water sample collection, the containers underwent washing with detergent, followed by rinsing with water to remove detergent residue, and then soaking overnight with chromic acid to ensure thorough removal of impurities and contaminants. The plastic containers were subsequently rinsed again with distilled water and rinsed three times with water from the stream before being filled with the water samples. Sampling was conducted midstream by immersing each sample bottle approximately 20 cm below the water surface, positioning the container mouth against the direction of the river's flow. Following sample collection, 2mL of concentrated nitric acid (HNO₃) was added to each one-liter container of stream water as a preservative for metal ions. Subsequently, the samples were shielded from direct sunlight and transported in a cooler box containing ice packs to the laboratory for analysis. All samples were stored at 4°C and analyzed within 48 hours of collection. The levels of available elements in the soil and water samples, post-analysis, were compared against the standards set by the World Health Organization (WHO), European Regulatory Standard Maximum Contamination Limits (EURS), United States Environmental Protection Agency (USEPA), Canadian Council of Ministers of the Environment (CCME), and the Department of Petroleum Resources Nigeria (DPR) to determine their environmental toxicity levels.

3.3. Method of Analysis for the Quarry Soil Samples

3.3.1. pH

Twenty grams of the soil aggregate were measured and placed into a 50mL beaker, followed by the addition of 20mL of distilled water. The soil-to-water mixture, with a ratio of 1:1, was allowed to stand for 30 minutes while being occasionally stirred with a glass rod. pH measurement was conducted using a digital pH meter (Jenway 3020 pH meter), calibrated with buffer solutions of pH 4 and pH 7. After calibration, the electrodes were rinsed and then submerged into the soil-water mixture, and the pH value was recorded as per the methodology outlined by Black (1965).

3.3.2. Particle size analysis – Hydrometer method

Fifty grams of soil samples were measured and placed into a 250 mL beaker. To this, 100 mL of distilled water and 10mL of concentrated H₂O₂ were added. The contents of the beaker were heated until frothing ceased. After cooling, the mixture was transferred into shaking bottles. Subsequently, 20 mL of sodium hexametaphosphate solution was added, and the mixture was shaken for one hour. The suspension was then transferred to a 1 L sedimentation cylinder and brought to the mark with water. An agitator was used to stir the suspension. A hydrometer was lowered into the suspension, and its reading was taken after 40 seconds while noting the temperature. The initial reading (R1) provided the percentage of clay and silt. After allowing the suspension to stand for two hours, the hydrometer reading was taken again, providing the second reading (R2), which aided in estimating the percentage of clay content, following the methodology described by Bouyoucos (1962).

3.3.3. Exchangeable

Five grams of air-dried soil were carefully measured and placed into a 150 mL plastic bottle. Subsequently, 50 mL of 1 M KCl solution was added, and the mixture was mechanically shaken for one hour. Afterwards, the mixture was filtered using a Whatman No. 1 filter paper into a 25 mL conical flask. Three drops of phenolphthalein indicator (prepared by dissolving 0.1 g of the dry indicator in 100 mL of 95% ethanol) were added into the conical flask. The solution was then titrated against 0.05M NaOH until the colorless solution turned pink, following the protocol outlined by Logana et al. (1985).

3.3.4. Cation Exchange Capacity (C.E.C)

Five grams of soil sample were accurately weighed and placed into a 250 mL polypropylene bottle. Following this, 100 mL of 1M NH₄OAc solution was added to the bottle, which was then stopped. The mixture underwent shaking for 30 minutes in a mechanical shaker (Heldoph) at a speed of 200 rpm. Subsequently, the supernatant was filtered through Whatman No. 1 filter paper. The concentrations of K⁺ and Na⁺ in the extract were determined using a Flame photometer, while Mg²⁺ and Ca²⁺ were determined using an Atomic Absorption Spectrophotometer (Buck Scientific VGP 210 model). Prior to the analysis, the equipment was calibrated using various concentrations of the metals ranging from 2 to 20 ppm, prepared from analytical grade reagents (Sigma, BDH, and Buck Scientific). The summation of the various cations was reported as the cation exchange capacity, following the methodology described by Black (1965).

3.3.5. Phosphorus

Five grams of soil were measured and placed into a polypropylene bottle, followed by the addition of 40 mL of the extracting solution (0.03 M NH₄F in 0.025 M HCl), which was then stopped. The mixture underwent manual shaking for one minute and was subsequently filtered using Whatman filter paper No. 1. The clear supernatant obtained after filtration was retained for phosphorus determination.

The concentration of phosphorus in the extract was assessed using a volumetric method. Specifically, 5 mL of the filtrate or supernatant was transferred into a 50 mL conical flask, and the pH was adjusted to 5 by adding three drops of p-nitrophenol and several drops of 2 M NH₄OH until a yellow coloration appeared. Following this, 30 mL of water was added, followed by the addition of 10 mL of ascorbic acid reagent. The solution was then brought up to the 100 mL mark with distilled water, and the absorbance was measured in a spectrophotometer at 660 nm, following the methodology described by Bray and Kurtz (1965).

3.3.6. Nitrogen

0.2 grams of finely ground soil were precisely weighed into a 100 mL Kjeldahl digestion flask. A single tablet of selenium catalyst and 4 mL of concentrated H₂SO₄ were then added to the flask, and the mixture was shaken thoroughly to ensure complete mixing of the soil and catalyst. The flask was subsequently placed on a micro Kjeldahl heater and digested for approximately 45 minutes until the mixture became clear. Once digestion was complete, the mixture was allowed to

cool until it was just warm to the touch, and then 10 mL of distilled water was added. The mixture was filtered through a single Whatman No. 1 filter paper into a 100 mL volumetric flask. The flask was further rinsed with distilled water, and the filtrate was made up to the mark. The concentration of nitrogen in the filtrate was determined using a colorimetric method. Specifically, 5 mL of the filtrate was pipetted into a 25 mL volumetric flask. To this, 2.5 mL of alkaline phenol, 1 mL of sodium potassium tartrate, and 2.5 mL of sodium hypochlorite were added and shaken well. The solution was then made up to the mark with distilled water and read calorimetrically at 630 nm. A nitrogen standard solution (1000 ppm) was prepared by dissolving 4.7 g of dried ammonium sulfate in a 1 L volumetric flask with distilled water and making up the volume. From this 1000 ppm nitrogen stock solution, a 100 ppm nitrogen standard was prepared. This standard solution was further used to prepare 5, 10, 15, and 25 ppm nitrogen standards. Each standard solution received the same treatment as the sample above, with the addition of 4 mL of H₂SO₄ and 0.95 g of anhydrous sodium sulfate, before being made up to 100 mL. A blank solution was also prepared without nitrogen but with the same quantities of acid and anhydrous sodium sulfate, following the procedure outlined by Vogel (2008).

3.3.7. Organic Carbon

In a 250 mL conical flask, 5 mL of K₂Cr₂O₇ solution was combined with 1 g of soil sample and gently swirled to ensure thorough wetting of the sample. Subsequently, 20 mL of concentrated H₂SO₄ was added, and the mixture was allowed to cool. Following this, 10 mL of distilled water and 5 mL of phosphoric acid were sequentially added. Then, 8-10 drops of diphenylamine indicator were introduced into the mixture. The prepared mixture was titrated against 0.5M iron (II) sulfate solution until reaching a green endpoint. A blank determination was conducted simultaneously, comprising 50 mL of the K₂Cr₂O₇ solution, 20 mL of concentrated H₂SO₄, 100 mL of distilled water, and 5 drops of Ferroin indicator, following the procedure described by Walkey and Black (1934).

3.4. Sequential Extraction Procedure (SEP)

The study followed the procedure outlined by Tessier et al. (1979), which involves separating heavy metals into five operationally defined fractions. One gram of soil sample was utilized for the sequential extraction process. Following each extraction step, centrifugation at 1500 rpm for 15 minutes facilitated the separation of the liquid-solid phases. The supernatant containing the extracted metals was decanted into a polypropylene bottle for subsequent metal analysis, while the residue underwent further extraction steps.

Five-step extraction schemes were employed, defining various geochemical fractions:

- Exchangeable Fraction (F1)
- Bound to Carbonates Fraction (F2)
- Bound to Iron and Manganese Fraction (F3)
- Bound to Organic Matter Fraction (F4)
- Residual Fraction (F5)

These fractions represent distinct chemical forms in which heavy metals may be present in the soil, providing valuable insights into their distribution and potential bioavailability.

3.4.1. Fraction F1 – Exchangeable

This fraction represents the soil's capacity to adsorb or desorb heavy metals concerning variations in the ionic composition of the soil. The sediment underwent extraction at room temperature for one hour, with 8mL of either magnesium chloride solution (1 M MgCl, pH 7.0) or sodium acetate solution (1 M NaOAc, pH 8.2), under continuous agitation.

3.4.2. Fraction F2 – Metals Bound to Carbonate

The residue obtained from fraction 1 (F1) was subjected to leaching at room temperature using 8 mL of 1 M sodium acetate (NaOAc) solution, which was adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained throughout the process, and the time required for complete extraction was assessed.

3.4.3. Fraction F3 – Metals Bound to Fe-Mn Oxides

The residue obtained from fraction 2 (F2) underwent extraction with either 20 mL of 0.3 M Na₂S₂O₄ + 0.175 M Na-citrate + 0.025 M H-citrate or 0.04 M NH₂OH.HCl in 25 % (v/v) HOAc. The experiments employing the latter solution were conducted at 96 °C with occasional agitation, and the duration required for complete dissolution of the free iron oxides was assessed.

3.4.4. Fraction F4 –Metals Bound to Organic Matter

To the residue from fraction 3 (F3), 3 mL of 0.02 M HNO₃ and 5 mL of 30 % H₂O₂ adjusted to pH 2 with HNO₃ were added. The mixture was then heated to 85 °C for 2 hours with occasional agitation. Subsequently, a second 3-mL aliquot of 30 % H₂O₂ (pH 2 with HNO₃) was added, and the sample was heated again to 85 °C for 3 hours with intermittent agitation. After cooling, 5 mL of 3.2 M NH₄OAc in 20% (v/v) HNO₃ was added, and the sample was diluted to 20 mL and continuously agitated for 30 minutes. The addition of NH₄OAc is intended to prevent the adsorption of extracted metals onto the oxidized sediment.

3.4.5. Fraction F5 – Residual Bound Metals

The residue obtained from fraction 4 (F4) underwent digestion with an HF-HClO₄ mixture, following the procedure outlined below for total metal analysis. These "selective" extractions were performed in centrifuge tubes made of polypropylene with a capacity of 50 mL to minimize the loss of solid material. After each successive extraction, separation was achieved by centrifugation at 4000 rpm for 30 minutes. The supernatant containing trace metals was carefully removed using a pipette and subjected to analysis. Meanwhile, the residue was washed with 8 mL of deionized water. Following another centrifugation step for 30 minutes, the second supernatant was discarded.

4. Result and discussions

4.1. The physical and chemical characteristics of the quarry soils and water.

The outcomes derived from the physicochemical assessment of soil samples from Chestedi, F.A.U.C Golden Ltd, and Fakunle quarries, designated as Site 1, Site 2, and Site 3 correspondingly, are presented in Table 3.1 below:

Table 3 The physicochemical properties of the quarry soils samples

Parameters	Units	CHESTEDI	F.A.U.C	FANKULE	Mean	STDV
		Site 1	Site 2	Site 3		
pH		6.5.00	6.70	7.20	6.80	0.36
EC	µS/cm	226.00	263.00	304.00	264.33	39.02
Ca	mg/kg	147.40	138.60	160.9	148.97	11.23
Mg	mg/kg	106.20	98.18	125.7	110.03	14.15
Na	mg/kg	45.20	52.60	60.80	52.87	7.80
K	mg/kg	58.76	68.38	79.04	68.73	10.14
PO ₄	mg/kg	5.73	7.44	3.62	5.60	1.91
SO ₄	mg/kg	12.90	16.13	11.42	13.48	2.41
CL	mg/kg	158.20	133.8	146.5	146.17	12.20
Alkalinity	mg/kg	106.00	97.40	118.3	107.23	10.50
NH ₄ -N	mg/kg	7.46	13.67	9.31	10.15	3.19
EA	mg/kg	98.65	110.40	103.14	104.06	5.93
CEC	mg/kg	357.56	357.76	426.44	380.59	39.71
TOC	%	0.63	0.47	0.41	0.50	0.11
Clay	%	6.21	8.22	6.18	6.87	1.17
Silt	%	3.61	4.30	6.70	4.87	1.62
Sand	%	90.18	87.48	87.12	88.26	1.67
POM	%	0.97	0.74	0.68	0.80	0.15

Note: **POM** – Particulate organic matter

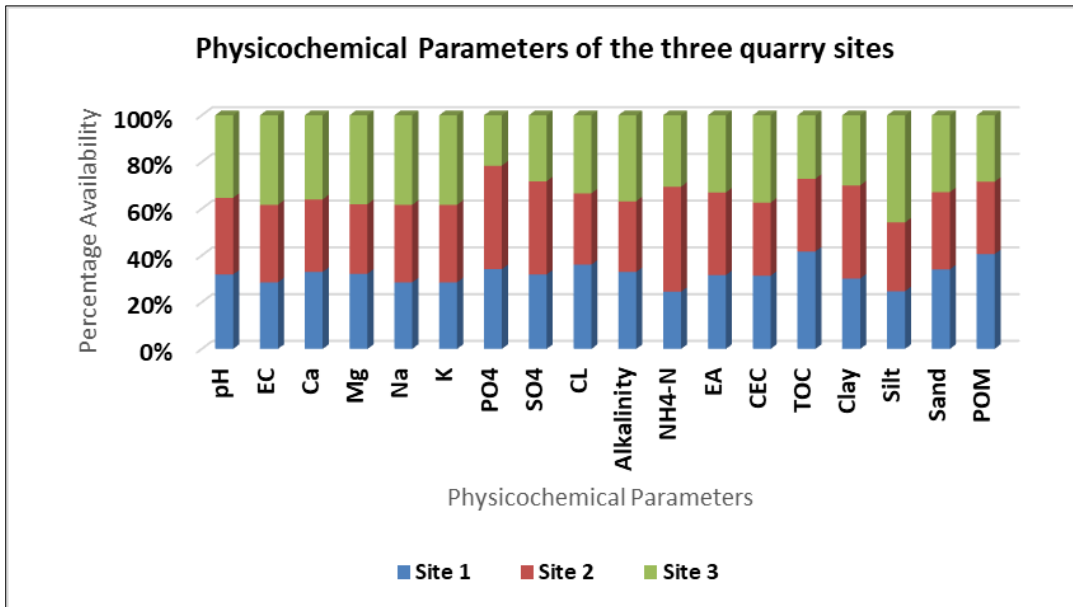


Figure 2 The physicochemical properties of the quarry soils samples

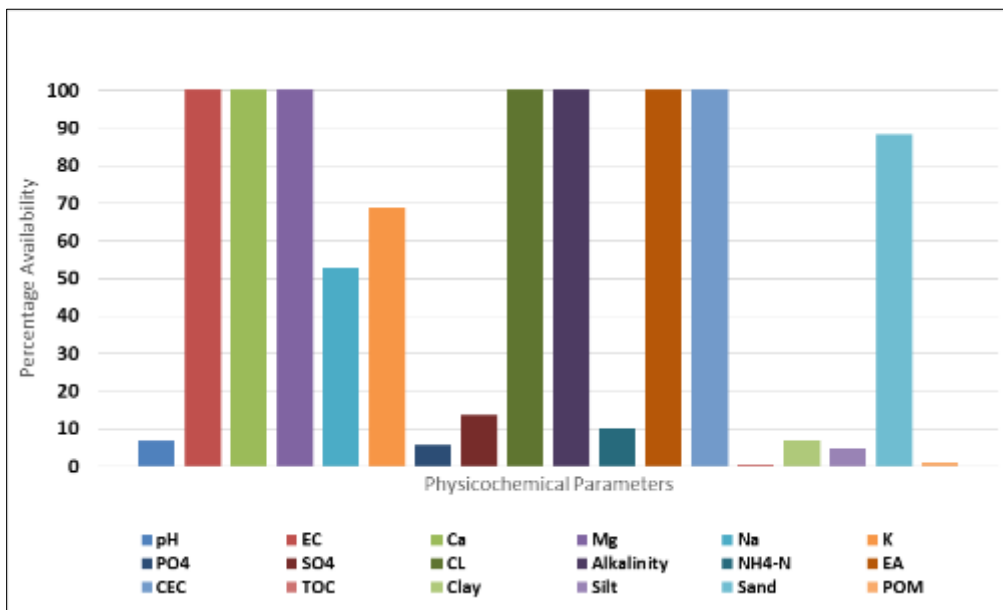


Figure 3 Average Values of the Physicochemical Parameters of the three sites

The soil physicochemical analysis depicted in Table 3.1 illustrates that the pH values of the soil samples range from 6.5 to 7.2 pH units, indicating a slightly acidic to neutral nature across all samples. pH plays a crucial role in soil properties, significantly influencing solute concentration and the sorption/desorption of contaminants within the soil matrix (Kadem et al., 2004). Elevated pH levels may restrict the mobility of certain metal species within the soil profile, whereas lower pH values typically promote the distribution and transport of metals. The proximity of the obtained pH values suggests that the influence of pH on metal availability is minimal. Soil pH, or soil reaction, serves as an indicator of soil acidity or alkalinity and is measured in pH units. It represents the negative logarithm of the hydrogen ion concentration or nutrient content. Most minerals and nutrients exhibit greater solubility or availability in acidic soils compared to neutral or slightly alkaline soils. Soil acidity tends to increase due to the leaching of basic ions (e.g., Ca^{2+} , Mg^{2+} , K^+ , and Na^+) by rainwater (Bickelhaupt, 2015).

Alkaline soils, primarily clayey soils, with a pH above 9, exhibit poor soil structure and low infiltration capacity. They are typically non-saline, with no excessive accumulation of soluble salts, particularly sodium chlorides. Often, these soils possess a hard-calcareous layer at depths of 0.5 to 1 meter (Oosterbaan, 2003). The alkalinity concentration in the soil

samples ranges from 97.4 mg/kg to 118.3 mg/kg, indicating very low levels, attributed to soil pH values below 9 pH units.

Analysis of particle size distribution in the quarry soil samples reveals that sand content ranges from 87.12 % to 90.18 %, representing the predominant fraction. Silt content ranges from 3.61 % to 6.70 %, while clay content ranges from 6.31 % to 8.22 %. Consequently, all soils examined exhibit less than 10 % of silt and clay, with a significant proportion comprising sand (80 % and above). Soils characterized by high sand content exceeding 70% often display weak surface aggregation and high porosity, facilitating efficient water infiltration and air circulation (Gbadegesin and Abua, 2011).

Electrical Conductivity (EC) values range from 226 $\mu\text{S}/\text{cm}$ to 304 $\mu\text{S}/\text{cm}$ across the three quarry soil samples, indicating relatively high values. These values exceed critical thresholds of 2 $\mu\text{S}/\text{cm}$ for sensitive crop species (FAO, 1994) and 4 $\mu\text{S}/\text{cm}$ for identifying saline soils (Donahue et al., 1994). Thus, the soil samples from Site 1, Site 2, and Site 3 exhibit high electrical conductivity levels, indicating salinity. Elevated electrical conductivity can induce water stress, disrupt nutrient balance, and impede nutrient uptake by soils (Agronomic Spotlight, 2015).

The cation exchange capacity (C.E.C) observed in the soils ranges from 357.56 mg/kg to 426.44 mg/kg, indicating the availability of metal cations such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ in the soil, influenced by its porous nature and pH. Soils with low C.E.C are prone to deficiencies in potassium (K^+), magnesium (Mg^{2+}), and other cations, whereas high C.E.C soils are less susceptible to the leaching of these cations (CUCE, 2007). Although the addition of organic matter can enhance C.E.C, the sandy fraction's low organic content contributes to its low C.E.C. Exchangeable bases are generally high in such soils. C.E.C is directly associated with the capacity to adsorb heavy metals, as adsorption behavior depends on soil properties and specific element characteristics (Barry et al., 1995).

Exchangeable acidity (EA) in the quarry soil samples ranges from 98.65 mg/kg to 110.4 mg/kg, indicating the total amount of C.E.C occupied by acidic cations such as H^+ and Al^{3+} . The relatively low exchangeable acidity compared to C.E.C suggests that a smaller portion of the exchange sites is occupied by acidic ions, with the majority being occupied by basic cations (Clemson Public Service Activities, 2015).

Particulate Organic Matter ranges from 0.68 % to 0.97 %, indicating very low levels (< 3%). Particulate Organic Matter (POM) significantly influences soil physical characteristics, with higher levels associated with improved structure, moisture retention, and water infiltration (Spargo et al., 2013).

Total organic carbon (TOC), representing carbon stored in soil organic matter, ranges from 0.41% to 0.49% in the quarry soil samples. Organic carbon enters the soil through decomposition of plant and animal residues, root exudates, microorganisms, and soil biota.

Calcium concentration ranges from 138.60 mg/kg to 160.90 mg/kg, exceeding the critical limit of 80 mg/kg recommended by Adulaji and Ekong (1981). Magnesium concentration ranges from 98.18 mg/kg to 125.70 mg/kg, significantly surpassing the critical value of 15 mg/kg suggested by Akande and Awojobi (2003), particularly noted in the topsoil.

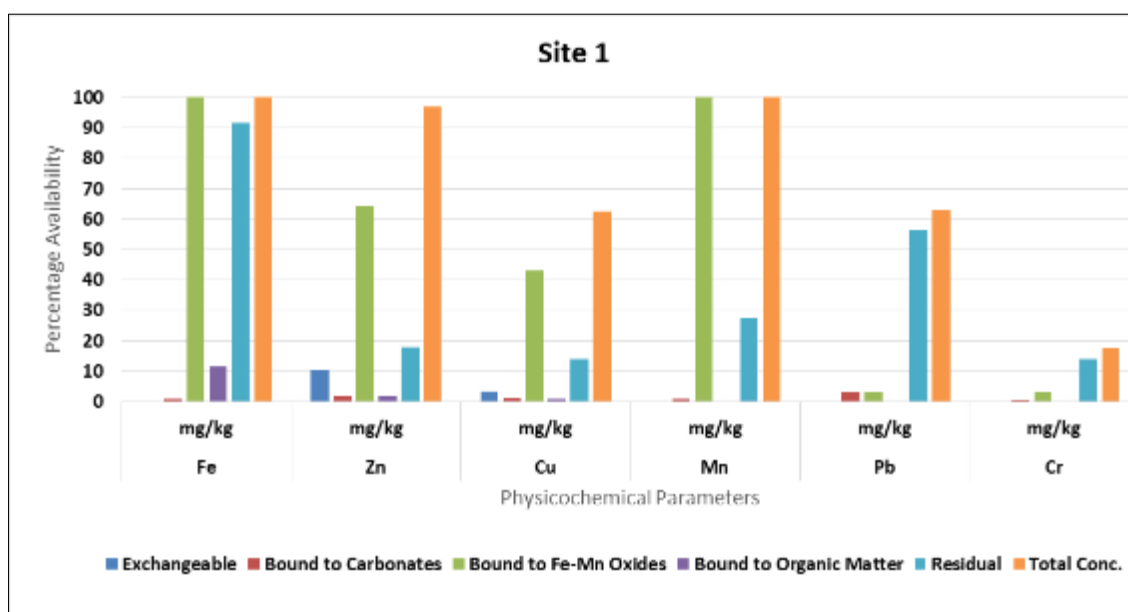
Potassium concentration ranges from 58.76 mg/kg to 79.04 mg/kg, close to or slightly below the acceptable limit of 58.50 mg/kg suggested by Sobulo and Osiname (1981). Sodium concentration ranges from 45.20 mg/kg to 60.80 mg/kg, falling below the permissible limit of 80 mg/kg as suggested by Tisade and Werner (1985).

Phosphate concentration ranges from 3.62 mg/kg to 7.44 mg/kg, exceeding the permissible limit of 0.40 mg/kg (WHO, 1983; Ministry of Agriculture, Fisheries and Food, 1987). Sulfate concentration ranges from 11.42 mg/kg to 16.13 mg/kg, within the permissible limits set by WHO (1983) and the Ministry of Agriculture, Fisheries and Food, London (1987) of 200.00 mg/kg.

The concentration of chloride ions ranges from 133.80 mg/kg to 158.20 mg/kg, which falls within permissible limits of 250 mg/kg (WHO, 1983). Common soluble salts found in the environment include chlorides and sulphates of calcium, magnesium, sodium, and potassium. While salt contamination typically doesn't pose a direct hazard to human health, it can have adverse and long-lasting environmental effects on soil and groundwater resources. Chloride, being highly soluble, doesn't adsorb onto soil particles, doesn't degrade, and can inhibit biological processes. When salt is released onto the ground, it can damage soil by disrupting its structure and permeability. High concentrations of soluble salts can also inhibit seed germination and a plant's ability to uptake water. Salt-contaminated soil near the surface may lose its ability to support agricultural crops, native grasses, or other vegetation, particularly if salt levels are sufficiently high, potentially contributing to surface erosion (BER, 2004).

Table 4 The concentration of heavy metal presents in the operationally defined area (Site 1, Quarry soil)

Metals	Units	Exchangeable	Bound to Carbonates	Bound to Fe-Mn Oxides	Bound to Organic Matter	Residual	Total Conc.
Fe	mg/kg	0.04	0.80	172.0	11.40	91.75	275.99
Zn	mg/kg	10.54	1.85	64.33	2.11	18.06	96.89
Cu	mg/kg	3.40	1.11	43.24	0.92	13.89	62.56
Mn	mg/kg	0.05	0.82	123.34	0.32	27.60	152.13
Pb	mg/kg	0.23	3.12	3.08	0.074	56.60	63.10
Cr	mg/kg	0.14	0.58	3.04	0.03	13.88	17.67

**Figure 4** The concentration of heavy metals present in the operationally defined area (Site 1, Quarry soil)

The concentration of $\text{NH}_4\text{-N}$ in Site 1 is 7.46 mg/kg, in Site 2 it is 13.67 mg/kg, and in Site 3 it is 9.31 mg/kg, all falling within the permissible limits of 10-50 mg/kg set by WHO (1983) and the Ministry of Agriculture, Fisheries and Food, London (1987).

4.2. Fractionation and Distribution of Heavy Metals in the Soil Samples

According to Table 3.3, the total metal concentration in this site follows the order of $\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cr}$. Fe, Zn, Cu, and Mn are predominant in the Fe-Mn oxide reducible fractions compared to the other labile fractions. This occurrence may be attributed to Fe and Mn oxides constituting a significant sink for heavy metals in aquatic systems under oxidizing conditions, as explained by Gibbs et al., (1997). The higher concentration of elements such as Fe, Zn, Cu, and Mn associated with this fraction suggests their adsorption to Fe-Mn colloids, which are thermodynamically unstable under anoxic conditions (Jenne, 1968). This illustrates the ability of Fe-Mn oxides to scavenge trace metals from solution through processes such as adsorption and co-precipitation (Lim and Kiu, 1995). Site-to-site variations in metal concentration in this fraction may be due to changes in redox potential, affecting the mechanisms of adsorption and co-precipitation and rendering them moderately mobile, thus influencing their relative concentration. This fraction carries a significant burden of metals, potentially available to biota with changes in environmental conditions. Pb and Cr are found to be highest in concentration in the residual phase.

Heavy metals bound to the residual fractions are considered to be the most stable, less reactive, and less available since they are occluded within the crystal lattice layer of silicates and well-crystallized oxides (Terus, 1995).

The total heavy metal concentrations in this site from Table 3.4 follow the order of Fe > Zn > Cu > Mn > Pb > Cr. The total concentration (Exchangeable + Bound to carbonate + Bound to Iron and Manganese oxide + Bound to organic matter + Residual) of the heavy metals in this analysis is the sum of all the concentrations in each fraction.

Fe, Zn, and Cu exhibit the highest concentrations in the bound to Fe-Mn oxides reducible phase. The organic and Iron-Manganese oxide (Fe-Mn oxide) fraction may be considered relatively very stable, slowly mobile, and poorly available, but changes with variations in the redox conditions (Horsfall and Spiff, 2005). The concentration of zinc in this fraction is sufficiently high to potentially pose serious environmental problems for underground water (Wangboje et al., 2014).

Table 5 The concentration of heavy metals present in the operationally defined area (Site 2, Quarry soil)

Metals	Units	Exchangeable	Bound to Carbonates	Bound to Fe-Mn Oxides	Bound to Organic Matter	Residual	Total Conc.
Fe	mg/kg	0.05	2.20	154.80	10.60	72.00	239.65
Zn	mg/kg	11.21	0.98	60.10	3.04	17.21	92.54
Cu	mg/kg	1.99	2.03	37.95	0.12	10.21	52.30
Mn	mg/kg	0.08	5.78	0.35	11.20	17.33	34.74
Pb	mg/kg	0.15	1.12	0.76	0.39	17.72	20.14
Cr	mg/kg	0.16	0.94	4.30	0.04	9.40	14.84

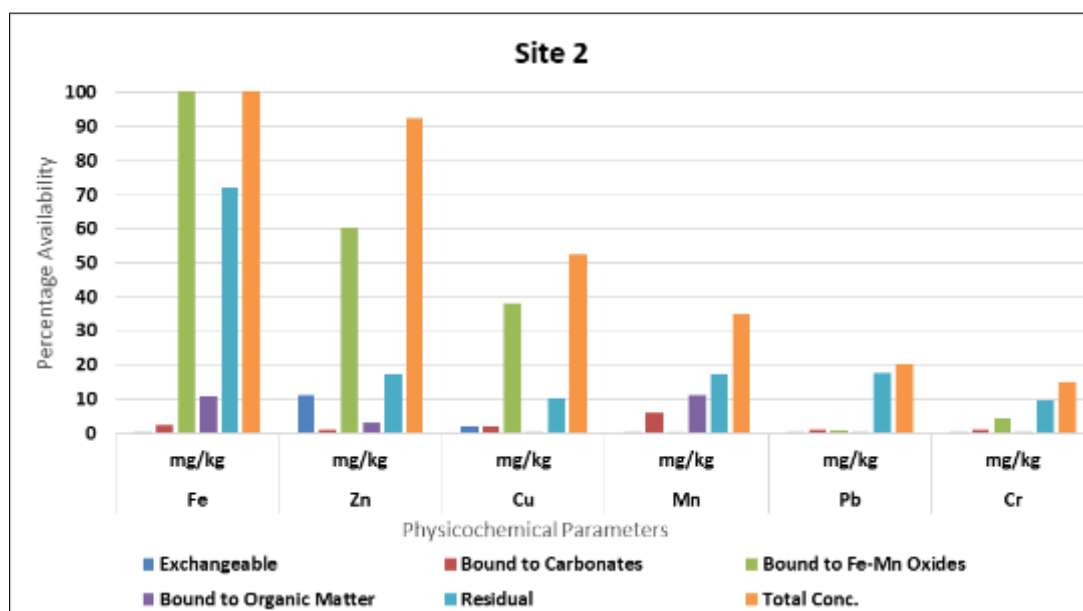


Figure 5 The concentration of heavy metals present in the operationally defined area (Site 2, Quarry soil)

Manganese (Mn) demonstrates the highest concentration within the organic matter fraction. Substantial quantities of trace metals are sequestered within this fraction, which is comparatively less mobile, owing to its association with higher molecular weight, stability, and humic nature, resulting in gradual metal release (Zhang, 1989). Conversely, lead (Pb) and chromium (Cr) exhibit their highest concentrations in the residual fractions. The residual fraction is widely regarded as the most stable, less reactive, and less bioavailable due to its occlusion within the crystal lattice layer of silicates and well-crystallized oxide minerals (Segarra et al., 2008).

Table 6 The concentration of heavy metals present in the operationally defined area (Site 3, Quarry soil)

Metals	Units	Exchangeable	Bound to Carbonates	Bound to Fe–Mn Oxides	Bound to Organic Matter	Residual	Total Conc.
Fe	mg/kg	0.10	2.80	224.00	14.00	81.25	322.15
Zn	mg/kg	5.92	2.01	98.21	0.51	22.01	128.66
Cu	mg/kg	7.20	2.04	62.32	1.02	9.58	82.16
Mn	mg/kg	0.12	8.72	91.04	0.04	7.70	107.62
Pb	mg/kg	0.02	2.03	6.89	0.20	7.61	16.75
Cr	mg/kg	0.26	0.86	0.76	0.01	9.38	11.27

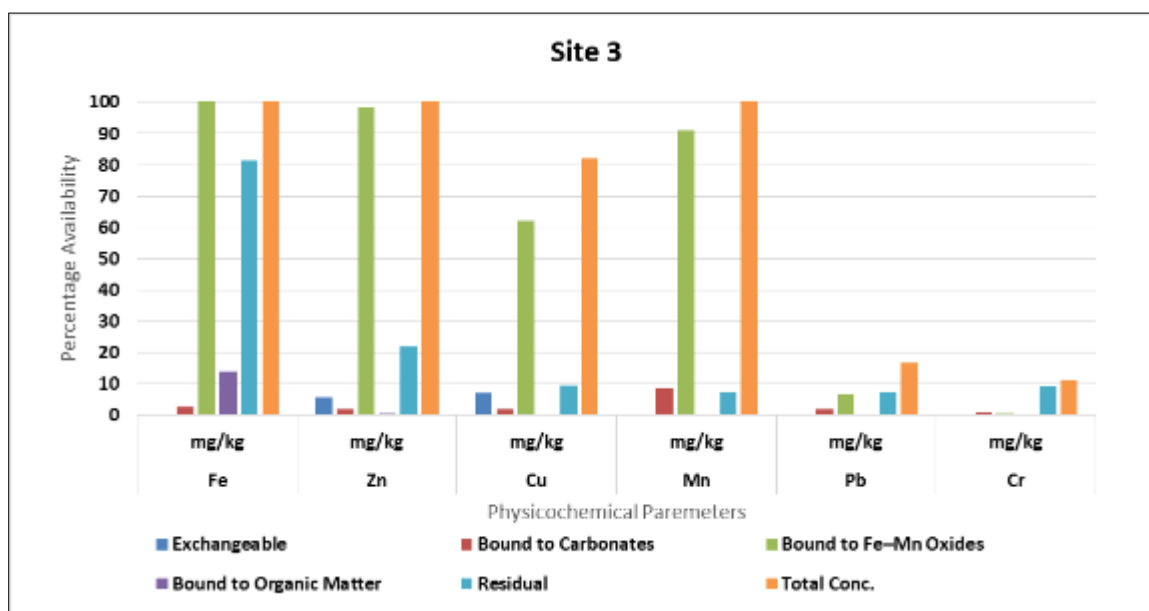


Figure 6 The concentration of heavy metals present in the operationally defined area (Site 2, Quarry soil)

The total heavy metal concentrations at this site, as indicated in Table 3.4, follow the order of Fe > Zn > Mn > Cu > Pb > Cr. Fe, Zn, Cu, and Mn exhibit the highest concentrations within the Fe–Mn oxide reducible fractions, whereas Pb and Cr are most concentrated in the residual fractions.

4.3. Mobility Factors of the Heavy Metals in the Quarry Soil Samples

The mobility of heavy metals in soils can be assessed by considering both the absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility is calculated as a mobility factor (MF) using the equation below:

Mobility Factor

$$= \frac{\text{Exchangeable} + \text{Bound to Carbonate}}{\text{Exchangeable} + \text{Bound to Carbonates} + \text{Bound to Fe – Mn Oxides} + \text{Bound to Organic matter} + \text{Residual}} \times 100$$

The Mobility Factor (MF) value for heavy metals in soil is often interpreted as evidence of relatively high lability and biological availability (Ma and Rao, 1997; Kabala and Singh, 2001). Below are the mobility factors of the heavy metals in the three quarry soils:

The mobility factors for heavy metals in the three quarry soils are as follows:

Table 7 The relative index of metal mobility (Mobility Factor)

Mobility Factors for the three quarry soils sample			
Metals	Site 1 (%)	Site 2 (%)	Site 3 (%)
Fe	0.04	0.94	0.90
Zn	12.80	13.17	6.16
Cu	7.20	7.69	11.25
Mn	0.57	16.87	8.21
Pb	5.07	6.31	12.24
Cr	4.08	7.41	9.94

The results obtained from Table 3.11 above indicate a low mobility factor within the range of 0.04 % - 16.87 %. This suggests a lower biological availability and mobility of heavy metals in the soils of the three quarries.

4.4. Environmental Risk Factor (ERF)

The Environmental Risk Factor (ERF) was utilized to assess the environmental risk and establish the potential threat posed by heavy metals (Saenz et al., 2003). The Environmental Risk Factor (ERF) was calculated using the formula:

$$\mathbf{ERF} = \mathbf{CSQV} - \frac{\mathbf{Ci}}{\mathbf{CSQV}} \quad \text{or} \quad \mathbf{ERF} = \mathbf{F5} - \frac{\mathbf{F1+F2+F3+F4}}{\mathbf{F5}}$$

Where **CSQV** = The Concentration of Sediments Quality Value refers to the heavy metal concentration in the residual fraction of sediment, which is equivalent to the background or pre-industrial concentration (F5).

Ci = Heavy metal concentration from the first four fractions of sediments (F1 + F2 + F3 + F4).

Table 8 Environmental Risk factors for heavy metals in the three quarry soils

Soil samples			
Metals	ERF for Site 1	ERF for Site 2	ERF for Site 3
Fe	89.74	69.67	78.29
Zn	13.70	12.83	17.17
Cu	10.39	6.09	2.00
Mn	23.09	16.33	-5.28
Pb	56.49	17.58	6.41
Cr	13.61	8.82	9.18

Key: ERF < 0 = Potential Ecological Threat; ERF > 0 = No Potential Ecological Threat

Based on the results provided, manganese in the Site 3 quarry soil may indeed pose a potential threat to the environment. This is inferred from its Environmental Risk Factor (ERF) value, which is calculated as -5.28 and falls below zero, indicating a potential environmental risk.

4.5. Contamination Factor

The contamination factor (CF), as defined by Lin et al. (2009), was employed to assess the degree of soil contamination by heavy metals.

The contamination factor was calculated as:

$$CF = \frac{\text{Metal concentration in sediment}}{\text{Background concentration of heavy metals in sediment}} \text{ OR}$$

$$CF = \frac{F1 + F2 + F3 + F4}{F5}$$

Table 9 Contamination factors for heavy metals in the three quarry soil samples

Contamination Factor for the three quarry soils sample			
Metals	CF for Site 1	CF for Site 2	CF for Site 3
Fe	2.01	2.33	2.97
Zn	4.35	4.38	4.85
Cu	3.50	4.12	7.58
Mn	4.51	0.98	12.98
Pb	0.12	0.14	1.20
Cr	0.28	0.58	0.20

Key: CF < 1 = low contamination
 1 < CF < 3 = moderate contamination
 3 < CF < 6 = considerable contamination
 CF > 6 = very high contamination

CF < 1 = Lowly contaminated
 = For Site 1 (Pb, Cr)
 = For Site 2 (Mn, Pb, Cr)
 = For Site 3 (Cr)

1 < CF < 3 = Moderately contaminated
 = For Site 1 (Fe)
 = For Site 2 (Fe)
 = For Site 3 (Fe, Pb)

3 < CF < 6 = Considerably contaminated
 = For Site 1 (Zn, Cu, Mn)
 = For Site 2 (Zn, Cu)
 = For Site 3 (Zn)

CF > 6 = Very highly contaminated
 = For Site 1 (null)
 = For Site 2 (null)
 = For Site 3 (Cu, Mn)

From the provided information, it can be observed that Pb and Cr in Site 1, Mn, Pb, and Cr in Site 2, and Cr in Site 3 have contamination factors less than unity. This indicates that they are very low in contamination with their respective heavy metals listed above. On the other hand, the other heavy metals in the quarry soil samples, based on the calculation of their contamination factors, are contaminated.

4.6. Pollution Load Index

The Pollution Load Index (PLI), proposed by Tomlinson et al. (1980), was calculated to compare the pollution levels of heavy metals between the different quarry sites. It was determined as the contamination factor of each heavy metal with respect to the background value in the soil.

$$PLI = \sqrt[n]{Cf1 \times Cf2 \times Cf3 \times Cf4 \dots \dots \dots Cf n}$$

In this formula:

n = the total number of heavy metals under investigation.

CF₁, CF₂, CF₃, CF₄....CF_n are the contamination factors of each respective heavy metal. According to Tomlinson et al. (1980), the interpretation of PLI values is as follows:

- PLI < 1 indicates perfection, suggesting that pollution levels are minimal.
- PLI = 1 suggests that only baseline levels of pollutants are present.
- PLI > 1 indicates a deterioration of site quality, indicating elevated pollution levels.

Table 10 The Pollution Load Index of metals in the three quarries

Pollution Load Index (PLI) for the three quarry soils sample		
PLI for Site 1	PLI for Site 2	PLI for Site 3
1.29	7.49	16573.70

The Pollution Load Index (PLI) values calculated for all sites were found to be above or equal to 1. Site 1 exhibited high PLI values, while site 2 had slightly higher values, and site 3 had very high values. These results indicate that all sites have metal concentrations that could potentially cause pollution to the environment.

4.7. Index of geoaccumulation (I_{geo})

The Geoaccumulation Index (I_{geo}) was employed to assess heavy metal pollution by comparing present concentrations with reference or control values (Müller, 1969).

$$I_{geo} = \text{Log}_2 \frac{C_n}{1.5 B_n}$$

The Geoaccumulation Index (I_{geo}) represents the metal's level of geoaccumulation, with C_n denoting the measured concentration of the element in the sample, and B_n representing the geochemical background value. The inclusion of the constant 1.5 enables the examination of natural variations in the substance's content in the environment, including minor anthropogenic influences. As described by Müller (1969), this index is structured across seven scales (0–6), spanning from unpolluted to very highly polluted. Metal pollution levels are categorized into seven enrichment classes based on this scale.

Table 11 The Geoaccumulation Index for the three quarry soil samples

Geoaccumulation Index for the three quarry soils sample			
Metals	I _{geo} for Site 1	I _{geo} for Site 2	I _{geo} for Site 3
Fe	1.00	1.15	1.40
Zn	1.83	1.84	1.96
Cu	1.59	1.77	2.52
Mn	1.87	0.42	3.22
Pb	-0.43	-0.40	0.55
Cr	-0.24	0.07	-0.32

The interpretation of the result above was made based on the scale below in comparison with the control/refers sample.

Table 12 The Geo accumulation Index scale

I _{geo} Value	I _{geo} Class	Designation of sediment quality
>5	6	Extremely contaminated
4-5	5	Strongly to extremely contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately to strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated to moderately contaminated
0<	0	Uncontaminated

The data indicates that Site 1 exhibits no contamination with Cr and Pb, and moderate contamination with Fe, Zn, Cu, and Mn. Site 2, on the other hand, shows no contamination with Cr, Pb, and Mn, with moderate contamination observed for Cu, Zn, and Fe. Site 3 demonstrates no contamination with Cr and Pb, moderate contamination with Fe and Zn, moderate to strong contamination with Cu, and strong contamination with Mn.

The analysis suggests significant variability in I_{geo} values across the soil samples from the quarries, ranging from uncontaminated to moderately contaminated, with the heavy metals under examination. Additionally, the I_{geo} assessment highlights that, except for the soil samples from Sites 1 and 2, Cu and Mn concentrations in Site 3 fall into class 3 and 4, respectively, indicating moderate to strong contamination and strong contamination, respectively.

4.8. Stream water analysis

The results obtained from physicochemical analysis of the stream water labelled as Site 5, Site 6, Site 7 and Site 8 respectively are shown in table 3.6 below:

Table 13 The physicochemical properties of the stream water samples

PARAMETERS	UNIT	Site 5	Site 6	Site 7	Site 8	Mean	STDV
pH		6.50	7.10	6.60	6.80	6.75	0.27
EC	uS/cm	26.00	30.00	22.00	28.00	26.50	3.42
TDS	mg/l	13.00	15.00	11.00	14.00	13.25	1.71
TSS	mg/l	0.06	0.18	0.07	0.11	0.11	0.06
DO	mg/l	8.00	7.60	2.80	6.40	6.20	2.37
BOD	mg/l	4.80	3.20	0.40	2.10	2.63	1.85
Ca	mg/l	3.64	4.28	2.66	3.56	3.54	0.67
Mg	mg/l	1.78	2.16	0.78	1.21	1.48	0.61
T. HARDNESS	mg/l	5.40	7.10	3.60	5.73	5.46	1.44
PO ₄	mg/l	0.08	0.13	0.10	0.06	0.09	0.03
SO ₄	mg/l	0.32	0.40	0.39	0.33	0.36	0.04
NO ₃	mg/l	0.68	2.70	1.77	0.52	1.4175	1.02
NH ₄ -N	mg/l	0.13	0.15	0.07	0.12	0.1175	0.03
Na	mg/l	5.00	6.31	4.40	5.60	5.3275	0.82
K	mg/l	6.50	8.20	5.72	7.30	6.93	1.06

Alkalinity	mg/l	19.30	30.60	23.80	15.5	22.3	6.49
Chloride	mg/l	26.40	37.10	14.70	12.16	22.59	11.49
Fe	mg/l	0.32	0.66	0.08	0.16	0.305	0.26
Zn	mg/l	0.12	0.25	0.02	0.07	0.115	0.10
Cu	mg/l	0.06	0.11	<0.05	0.05	0.0675	0.03
Pb	mg/l	<0.05	<0.05	<0.05	<0.05	0.05	0.00
Cr	mg/l	0.01	0.04	0.02	0.03	0.02	0.01
Mn	mg/l	<0.05	0.08	<0.05	<0.05	0.0575	0.015
Temperature	°C	22°C	21°C	25°C	29°C	24.25	3.593976

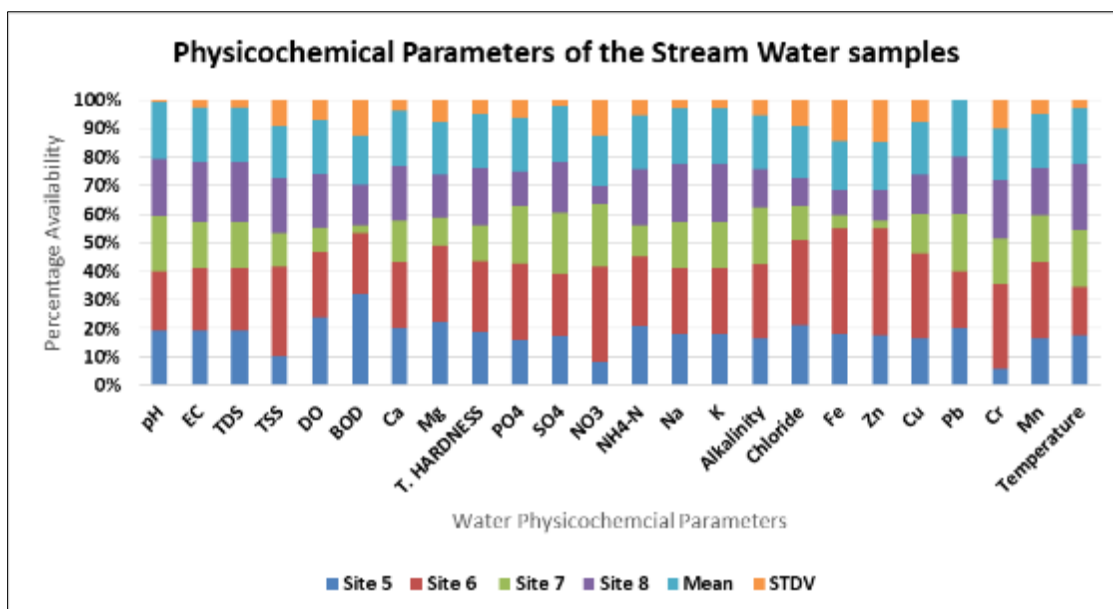


Figure 7 The physicochemical properties of the stream water samples

The pH is a metric used to quantify the acidity or alkalinity of a solution. The pH of the quarry water samples was determined by the calculation of the concentration of hydrogen ions ($[H^+]$) present in the quarry water samples. Mathematically, pH is calculated as:

$$pH = -\log [H^+]$$

The pH value represents the negative exponent to which 10 must be raised to match the hydrogen ion concentration (Kumar & Puri, 2012). Across stream water samples from site 5 to site 8, the overall pH ranges from 6.5 to 7.1. Specifically, stream water samples at Site 5, Site 7, and Site 8 exhibit slight acidity, while stream water at site 6 is neutral according to Table 3.6. The average pH of the water samples is 6.8, indicating slightly acidic water along the quarry. Interaction of stream water with metal ions from minerals and rock mass, in the presence of atmospheric air, results in the formation of acidic waters mixed with heavy metals. pH significantly influences metal concentration by altering their availability and toxicity (Swier and Singh, 2014). Exposure to higher pH either by drinking or any other condition can be adverse to human life and health (Onivefu, 2024). The mean pH of 6.8 falls within the pH range of 6.5 to 8.5, as per WHO (2012) and Nigerian Industrial Standard (NIS, 2007) requirements for consumable water (Das et al., 2012).

The temperature recorded during sampling of the four River Onyami water samples was 22 °C, 21 °C, 25 °C, and 29 °C, resulting in a mean temperature of 24.3 °C. According to WHO's (2008) guideline for drinking water, the maximum temperature limit for potable water should be below 30 °C. The water temperature (24.3 °C) meets this requirement. Water temperature regulates aquatic ecosystem metabolism and affects the ability of water to hold essential dissolved

gases like oxygen (Kumar & Puri, 2012). It also influences chemical and biochemical reactions in water bodies, with high temperatures increasing the toxicity of heavy metals and the sensitivity of living organisms to toxic substances (Momba et al., 2006).

Electrical conductivity (EC) in the study area ranges from 22 $\mu\text{S}/\text{cm}$ to 30 $\mu\text{S}/\text{cm}$ based on data from Table 3.6. EC of stream water is the cumulative ionic conductance of all ionic constituents, dependent on dissolved nutrients and micronutrients. The mean EC of the four stream water samples is 27 $\mu\text{S}/\text{cm}$, indicating a very low conductivity. The Nigerian Industrial Standard (2007) sets a maximum permissible limit of 1000 $\mu\text{S}/\text{cm}$. Higher EC values may indicate the dissolution of minerals due to quarrying of rock mass, or the presence of high amounts of dissolved inorganic substances in ionized form, while lower EC may suggest the absence of dissolved inorganic substances and nutrients (Kerketta et al., 2013). These findings contrast with observations by Rao et al. (2012) and Patil and Patil (2010), who recorded higher conductivity in stream water samples.

Dissolved oxygen (DO) analysis quantifies the amount of gaseous oxygen (O_2) dissolved in an aqueous solution, primarily entering water through diffusion from the surrounding air, aeration, and as a byproduct of photosynthesis. The DO values for stream water samples at sites 5, 6, 7, and 8 are 8, 7.6, 2.8, and 6.4 mg/l respectively (Table 3.6). A DO level below 3 mg/l can be stressful to most aquatic organisms, while a minimum of 5-6 mg/l is typically required for their growth (Tekade et al., 2011). According to WHO (2008) guidelines, the minimum permissible limit for Dissolved Oxygen in drinkable water is 5.0 mg/l (WHO, 2008), a standard met by the mean DO of 6.3 mg/l in the stream water samples. The high DO may result from the stream's low temperature, reduced molecular activities, and minimal presence of aquatic organisms. Conversely, low DO levels can stem from metal contamination and poor water aeration, leading to downstream decreases. DO is crucial for sustaining higher forms of aquatic life and is a vital parameter for assessing water quality.

Biochemical Oxygen Demand (BOD) indicates the extent of organic pollution in aquatic systems, adversely affecting water quality (Igbinsosa et al., 2012). BOD values for stream water samples range between 0.4 to 4.8 mg/l, with a mean of 2.6 mg/l (Table 3.6). This aligns with research by Usharani et al., (2010), who reported BOD ranges from 0.16 to 11.6 mg/l. BOD levels below 4 mg/l are considered unpolluted and safe (Kurup et al., 2011), while elevated BOD can produce ammonia and hydrogen sulfide, detrimental to fish (Boyd and Lichikoppler, 1979). Increased BOD may indicate elevated organic matter from industrial discharge and wastewater effluents, hindering self-purification (Phiri et al., 2005; Akan et al., 2007; 2008). With a mean BOD of 2.6 mg/l, the quarry stream water meets the universal water requirement index of 3 mg/l BOD (Boyacioglu, 2007).

Calcium concentrations in stream water samples range from 3.64 to 4.28 mg/l, with a mean of 3.50 mg/l (Table 3.6), below the WHO (1973) maximum level of 70 mg/l for drinkable water. Sulphate concentrations in the four River Onyami water samples range from 0.32 to 0.40 mg/l, with a mean concentration of 0.36 mg/l (Table 3.6), well below the permissible limit of 100 mg/l as prescribed by NIS (2007). Total hardness (T-Hardness) values of the water samples range from 3.60 to 7.10 mg/l, with a mean of 5.5 mg/l (Table 3.6), not exceeding the NIS (2007) standard of 150 mg/l. Water hardness has no known adverse environmental effects but can pose challenges for human usage (Das et al., 2012).

The phosphate levels in the quarry stream water, ranging from 0.06 mg/l to 0.13 mg/l, differ from the values reported by Das et al. (2012). Phosphate, a vital nutrient for the growth of water microorganisms like algae, can lead to eutrophication at high concentrations. The average phosphate concentration in the stream water samples is 0.09 mg/l, below the WHO's maximum permissible limit of 5mg/l for potable water yet surpassing the FEPA's (1991) guideline of < 0.05 mg/l for aquatic life and other uses.

Total Dissolved Solids (TDS) levels in the four stream water samples vary between 11 and 15 mg/l, with an average of 13.25 mg/l, well below the WHO's (1973) limit of 1000 mg/l and the NIS's (2007) 500 mg/l standard. This is contrary to the findings of Kerketta et al. (2013), who noted TDS levels between 67 mg/l and 1846 mg/l. High TDS levels can lead to taste issues and scaling in water pipes and appliances, often resulting from the presence of various organic and inorganic compounds.

The alkalinity of the water samples, ranging from 15.5 mg/l to 30.6 mg/l with an average of 22.3 mg/l, contrasts with higher values reported in other studies, suggesting variations due to the presence of bicarbonate, carbonate, and hydroxide compounds of calcium, sodium, and potassium.

Nitrate concentrations vary from 0.52 mg/l to 2.70 mg/l, averaging 1.42 mg/l, within the acceptable limit of 4.5 mg/l. Excessive nitrate levels, possibly from agricultural runoff or waste leaching, can pose health risks, including methemoglobinemia in infants.

Ammonium-nitrogen levels in the samples are between 0.07 mg/l and 0.15 mg/l, with an average of 0.09 mg/l. High levels of ammonium-nitrogen and nitrate can foster unwanted plant growth, leading to eutrophication, which may negatively impact recreational water use.

The average chromium concentration of 0.022 mg/l in the water samples is below the critical limit of 0.1 mg/l set by the USEPA (1999) and the WHO's (1982) maximum limit of 0.05 mg/l.

Zinc concentration averages at 0.12 mg/l, under the international standard of <1.0 mg/l and well below the WHO's (1996) and NIS's (2007) permissible limits, indicating the water's suitability for drinking and domestic use.

Table 14 Soil quality criteria for some standard organisations compared with the present study

Soil Permissible limits by various Standard Organizations and Research												
Parameters	Units	Range of this study	Mean of this study	WHO (2012)	WHO (2008)	WHO (1973)	WHO (1986)	USEPA (1999)	NIS (2007)	DPR (2002)	Boyacioglu <i>et al.</i> , (2007)	Robillard <i>et al.</i> , (2007)
pH		6.5-7.1	6.75	6.5-8.5				6.5-8.5	6.5-8.5			
EC	uS/cm	22.0 -30.0	26.50				300		1000			
TDS	mg/l	11.0 -15.0	13.25	1000			1000		500			
TSS	mg/l	0.06-0.18	0.11									
DO	mg/l	2.80-8.00	6.20		5.0					7.5-8.5		
BOD	mg/l	2.1-4.8	2.63								3	
Ca	mg/l	2.66-4.28	3.54			70	75					
Mg	mg/l	0.78-2.16	1.48		50		30		0.2			
T-HARDNESS	mg/l	3.60-7.10	5.46				500					
PO ₄	mg/l	0.06-0.13	0.093	5.0								
SO ₄	mg/l	0.32-0.40	0.36				500					
NO ₃	mg/l	0.52-2.70	1.42			45	50					
NH ₄ -N	mg/l	0.07-0.15	0.12									
Na	mg/l	4.40-6.31	5.33						200			
K	mg/l	5.72-8.20	6.93				20					
Alkalinity	mg/l	15.5-30.6	22.3			250	200					
Chloride	mg/l	12.16-37.10	22.59			250	250	250	250			250
Fe	mg/l	0.08-0.66	0.31			0.3	0.1		0.30			
Zn	mg/l	0.02-0.25	0.12				5.0			0.8		
Cu	mg/l	0.05-0.11	0.068				1.0	1.3		0.08		

Pb	mg/l	0.05-0.05	0.05				0.05		0.01	0.08		
Cr	mg/l	0.007-0.036	0.022				0.4	0.1	0.2	0.03		
Mn	mg/l	0.05-0.08	0.058				0.5					
Temp.	°C	21-29	24.30		30							

Table 15 Water quality criteria for some standard organisations compared with the present study

Water Permissible limits values by some various standard organisations and research													
Parameters	Units	Range of this study	Mean of this study	WHO (1983)	WHO (1998)	DPR (1991)	CCME (1999) Agric. Site	CCME (1999) Commercial	CCME (1999) Residential	CCME (1999) Industrial	FAO (1994)	Anyakora <i>et al.</i> 13) - EURS	Dona Hu e <i>et al.</i> , 1990
pH		6.5–7.2	6.80				6-8	6-8	6-8	6-8			
EC	uS/cm	226–304	264.33				2	4	2	4	2		4
Ca	mg/l	138.6–160.90	148.97										
Mg	mg/l	98.18 -125.70	110.03										
Na	mg/l	45.20-125.70	52.87										
K	mg/l	58.76-79.04	68.73										
PO ₄	mg/l	3.62-7.44	5.60	0.4							0.4		
SO ₄	mg/l	11.42-16.13	13.48	200									
Cl	mg/l	133.80-158.20	146.17	250									
Alkalinity	mg/l	97.40 -118.3	107.23										
NH ₄ -N	mg/l	7.46-13.67	10.15	10-50									
EA	mg/l	98.65-110.40	104.06										
CEC	mg/l	357.76-426.44	484.65										
TOC	mg/l	0.41-0.49	0.50										
Clay	mg/l	6.31-8.22	6.87										
Silt	mg/l	3.61-6.70	4.87										
Sand	mg/l	87.12-90.18	88.26										
POM	mg/l	0.68-0.97	0.80										
Fe	mg/l	239.65-322.15	279.26		200							1500	
Zn	mg/l	92.54-128.60	106.03			146	200	360	200	360			
Cu	mg/l	52.30-82.16	65.67			36	63	91	63	91		30	
Pb	mg/l	16.75-63.10	33.33			85	70	260	140	600		150	

Cr	mg/l	11.27-17.67	14.59			100	64	87	64	87	100	100	
Mn	mg/l	34.74-152.13	98.16		200		64	87	64	87		200	

5. Conclusion and Suggestions

The initial assessment of chemical parameters in the vicinity of the quarry industries in Igarra has shown that the concentrations of heavy metals and their physicochemical properties are relatively stable and do not exhibit significant fluctuations. According to the findings, the levels of physicochemical properties in the soil samples generally remain within acceptable limits, except phosphate levels. The high proportion of sand in the soil indicates a likelihood of poor surface aggregation, leading to a higher rate of water infiltration. This condition could facilitate the leaching of metal ions into the subsoil and eventually into the groundwater, potentially causing pollution.

In comparison to standard benchmarks for metals, the concentrations of heavy metals in the stream water from this study are predominantly below permissible limits, with the notable exception of iron, which exceeds its acceptable threshold. Among the metals analyzed, manganese presents a potential environmental risk due to its relatively high contamination factor in the stream water.

Given these observations, it is crucial to maintain ongoing evaluation of the nature, use, transportation, volume, and direct environmental impact of these substances. Since the physicochemical analysis of River Onyami conforms to the essential criteria for potable water, its use for irrigation and other domestic applications is deemed suitable.

However, to ensure safety, it is imperative to continuously monitor the stream water quality and regulate quarrying operations closely. This proactive approach is necessary to address any deviations that might emerge, potentially averting significant environmental threats in the future.

Future Idea

For the future ideas, surface functionalization of quarry soil can offer a comprehensive understanding of its environmental factors and content, crucial for assessing its ecological impact and devising effective remediation strategies. By modifying the surface of quarry soil particles with specific chemical groups or ligands, researchers can explore the interactions between functionalized soil particles and environmental constituents such as organic matter, minerals, and contaminants (Onivefu, 2024 (a) and Onivefu, 2024 (b)). This approach enables the investigation of adsorption and desorption dynamics, providing insights into the retention and release mechanisms of pollutants present in quarry soil. Moreover, surface-functionalized soil particles can serve as sorbents for contaminants, aiding in the assessment of their remediation potential and facilitating the development of tailored soil remediation techniques. Understanding the environmental fate and transport of functionalized quarry soil particles under different conditions further elucidates their behavior in natural ecosystems, informing sustainable management practices aimed at mitigating the environmental impact of quarry activities.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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