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Monitoring the Distribution of Potentially Toxic Elements in Soil and Accumulation in Fodder and Medicinal Plant Species at a Quarry site in Ebonyi State, Nigeria

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ABSTRACT

The study monitored the distribution of PTEs (Pb, Cd, As, Ni, Fe and Zn) in soil and accumulation in plant samples collected at the distance of 1 m, 180 m, and 360 m in south east (SE), south central (SC) and southwest (SW) directions of China quarry site in Ngwogwo in Ebonyi State, Nigeria. The soil and plant samples were dried, grinded, sieved, and digest separately in the laboratory to determine the concentrations of Pb, Cd, As, Ni, Fe and Zn using Atomic Absorption Spectrometer. The highest concentration of Pb, Cd, As, Ni, Fe and Zn in soil was obtained at a distance of 1 m from the edge of the quarry. The values of heavy metals in soil were below the Dutch criteria and permitted limits of FAO/WHO, NESREA and FEPA except for Cd. Cotolaria retusa assimilated highest level of Pb (2.42±0.00 mg/kg), As (0.43±0.01 mg/kg) and Zn (5.52±0.00 mg/kg) while Cd (0.09±0.00 mg/kg), Ni (1.13±0.00 mg/kg) and Fe (54.70±0.00 mg/kg) were highest in Pennisetum polystachion. The values of Pb (0.60±0.00 to 2.42±0.00 mg/kg) and As (0.11±0.00 to 0.43±0.01 mg/kg) in plants was higher than the permissible limit of 0.30 mg/kg (Pb) and 0.2 mg/kg (As) established by FAO/WHO, thus posing a serious health risk to man and animals that depend on such plants for food and medicine.

1. INTRODUCTION

Quarrying is an anthropogenic activity that involves the removal of soil (and most times vegetation) to extract non-metal and nonfuel minerals from rock. The mining of precious metals and other types of solid minerals forms an important part of many countries' economy (Ogbonna *et al*., 2011). Notwithstanding this, quarrying may have contributed to the observed disequilibrium between the rate of generation of contaminants by man and natures inherent ability to decontaminate the soil-plant system. Continual loading of pollutants into the environment is of great concern to man since contaminants such as heavy metals persist in the environment due to its chemical structure (Ali *et al*., 2013; Hashem *et al*., 2017; Ogbonna *et al*., 2020). Such contaminants include mercury, dioxin, cadmium and lead that does not degrade over a long time, thus heavy metal pollution is a global phenomenon that poses serious health hazards to aquatic and terrestrial ecosystems (Ogbonna *et al*., 2011; Ogbonna *et al*., 2020).

The atmosphere is one of the major pathways for transport of dust contaminated with heavy metals and the major external input of bio-available metals in the environment, which are potential threats to the health and survival of people living in proximity to quarry sites (Ogbonna *et al*., 2018a). This is because quarry atmosphere is subjected to large inputs of heavy metals arising from stationary source such as blasting of rock and large volume of tailing dust at quarry site. The heavy metals are deposited on soils which are absorbed from soil solution into plants via the roots (Ogbonna *et al*., 2018b). The covering of leaf surfaces with dust may result to blocking of leaf stomata and inhibiting gaseous exchange with its concomitant effect on photosynthetic processes. Loss of vegetative cover via extensive excavation and dumping of large volumes of tailings may expose barren soil to erosive force of water runoff, thus reducing the nutrient content of soil through leaching. Poor nutrient composition of quarry or mining site may result to slow rate of plant regeneration and biodiversity conservation since the soil seed banks may either be destroyed or rendered dormant due to harsh soil condition (Ogbonna *et al*., 2019).

The large number of quarrying activities in Nigeria are located in the rural areas and their operations might be releasing environmental contaminants that are deposited on plants (including medicinal plants) and their growing media (soil). Undoubtedly, people living in the rural areas relied heavily on medicinal plants for their primary health care because of the low price and active ingredients in plant materials and they can easily scavenge for it (medicinal plants) in bush fallows in proximity to their homes (Ogbonna *et al*., 2018a). The use of medicinal plants contaminated with potentially toxic elements may be a route of entry into human body. In a developing country like Nigeria, large percentage of the population particularly the rural dwellers lack access to information on the danger of using plants and plant products growing near or around sources of pollution.

The four plants sampled in this study (*Crotolaria retusa* L., *Boerhavia eracta* L., *Pennisetum polystachion* (L) Schult. and *Paspalum scrobiculatum* L.) are important medicinal and fodder plant species. For instance, the whole plant of *Crotolaria retusa* L. is used for treatment of skin infections. The powdered seeds are used to cure flatulence, leprosy and as analgesic against pain of scorpion stings and snake venom (Maregesi *et al*., 2016), leaves and flowers for the treatment of fever and lung diseases while root is used against coughing up blood (Nuhu *et al*., 2009; Wiedenfeld, 2011). The root of *Boerhavia eracta* L. is used as febrifuge, diuretic, hepatoprotective, treatment of gonorrhea, stomachic, jaundice, expectorant, anthelmintic, laxative, enlarged spleen, cardiotonic, and internal inflammations (Nisha *et al*., 2018). *Pennisetum polystachion* L. Schult is grazed and also cut for use as a fresh fodder or hay, as well as for controlling erosion, especially on slopping land while *Paspalum scrobiculatum* L. is a fodder plant and the debranned grain is primarily cooked as rice (Gomez and Gupta, 2003).

Several recent studies were carried out on bryophytes of adjacent serpentine and granite outcrops on the deer isles, Maine in United States of America (Briscoe *et al*., 2009), heavy metal contamination of agricultural soils around a chromite mine in Vietnam (Kien *et al*., 2010), heavy metal concentration in soil and woody plants in a quarry in Ebonyi State, Nigeria (Ogbonna *et al*., 2011), multiple exposure and effects assessment of heavy metals in the population near mining area in south China (Zhuang *et al*., 2014). The assessment of heavy metal pollution of granite quarrying operations in Nigeria (Oluyemi *et al*., 2014), assessment of toxicity level in selected heavy metal in volcanic soils of Tawau, Malaysia (Husin *et al*., 2015), effects of open cast quarrying technique on vegetation cover and the environment in South-Eastern Nigeria (Akanwa *et al*., 2016), ecological and human health risks associated with abandoned gold mine tailings contaminated soil in Krugersdorp, South Africa (Ngole-Jeme and Fantke, 2017). More so, characterization of soil physico-chemical parameters and limitations for revegetation in serpentine quarry soils, North West Spain

(Rodríguez-Seijo and Andrade, 2017), critical issues of sustainability associated with quarry activities in Nigeria (Nwachukwu *et al.*, 2018). Some studies on human health risk assessment of heavy metals in soils and commonly consumed food crops from quarrying sites in Nigeria (Onyedikachi *et al.*, 2018), assessment of the distribution of potentially harmful trace elements in bedrocks and stream sediments in Nigeria (Ayodele *et al.*, 2018) and preliminary assessment of the trace element composition of dust from two granite quarries from Jos Plateau and their possible health implications (Daspan *et al.*, 2018) were carried out in Nigeria. Furthermore, there was assessment of heavy metals content and pollution in tin tailings from Singkep Island, Riau, Indonesia (Irzon *et al.*, 2018), the influence of wind direction on the level of trace metals in plants collected around a quarry site in South Africa (Raimi *et al.*, 2019) and assessment of concentrations of heavy metals in soils around ESPRO asphalt production and quarry site in Nigeria (Alabi *et al.*, 2019). However, literature search showed that no apparent studies were carried out on potentially toxic element in soil and accumulation in medicinal and fodder plant species (*Crotolaria retusa* L., *Boerhavia eracta* L., *Pennisetum polystachion* (L) Schult. and *Paspalum scrobiculatum* L.) at any quarry site the world over. More so, none of these studies determined the potentially toxic elements in granites from their study sites Therefore, this study is aimed at investigating the impact of quarrying activities on potentially toxic element in soil and medicinal plants growing around the vicinity of China quarry site in Ishiagu in Ebonyi State, Nigeria.

2. MATERIALS AND METHODS

2.1. Study Area

The study was carried out at China quarry in Ngwogwo in Ishiagu, Ivo Local Government area of Ebonyi State, Nigeria. It is located on the plains of the south-eastern savannah belt and lies within latitudes 5°51' and 5°59' N and longitudes 7°24' and 7°40' E. The wet season starts from April and end in November while dry season commence from December to March. It has an average temperature of 27 °C and annual precipitation of about 1,925 mm (Ofomata, 2002). The vegetation consists of mainly tall grasses, some trees and shrubs. The crops commonly grown are rice, yam, cassava, and vegetables such as *Telfaria occidentales* (fluted pumpkin), *Vernonia amydalina* (bitter leaf), spinach among others. The area is underlain by two rock formations viz the Abakiliki Formation and the Ezeaku Formation. The Abakaliki formation comprises of shales and sandstones units. The shale unit consists of clay, siltstones and dark grey calcareous shales while the sandstone unit consists of fine to medium grained calcareous sandstone. The composition of the igneous rocks at Ishiagu range from intermediate to basic (Ofoegbu, 1985). The people of the area depend primarily on surface water bodies such as streams, wetlands and pit lakes. The pit lakes were formed by the activities of quarrying and mining companies.

2.2. Sample Collection

Reconnaissance survey was carried out prior to sample collection to determine wind direction, the terrain and plant species common in the study area. Surface soil (0-15 cm) samples were collected at the distance of 1 m, 180 m, and 360 m in south east (SE), south central (SC) and southwest (SW) directions of the quarry site. The control (background) sample was collected in a home garden about 4 km from the China quarry site where there was no visible source of contamination. Samples from each particular distance (e.g. 0-15 cm at 1 m in SE, SC and SW) were bulked together to form a composite sample and placed in large polythene bags (about 60 g), properly tied, labeled well, placed in a wooden box and covered to avoid contamination from external sources. The samples in the wooden box were transferred to the laboratory for pre-treatment and analysis.

Fresh leaves were sampled from different parts of four (4) plant species. The leaves of four species, *Crotolaria retusa* L. (rattleweed, Fabiaceae), *Boerhavia eracta* L. (erect spiderling, Nyctagynaceae), *Pennisetum polystachion* (L) Schult. (mission grass, Poaceae), and *Paspalum scrobiculatum* L. (rice grass or kodo millet or cow grass) were randomly collected in February 2019 (dry season) from each plant using well-cleaned stainless secateurs. These four plant species were collected because they were common among all sampling distance, thus, the plants were growing around the points where soil samples were collected from the China quarry site. Samples from each plant species was placed separately in large envelopes, labeled well, properly sealed, placed in a wooden box and covered to avoid contamination from external sources. The samples in the wooden box were transferred to the laboratory for pre-treatment and analysis.

2.3. Soil and Plant Digestion and Analysis

Each bulked soil sample was freed from foreign objects such as stones, seeds, roots etc. and air-dried at room temperature until all moisture was completely eliminated. The samples were subjected to crushing and grinding and then homogenized using a porcelain pestle and mortar. The homogenized soil samples were sieved (<2 mm) and analyzed for potentially toxic elements (Pb, Cd, As, Ni, Fe and Zn) using standard laboratory methods described in IITA (1979).

Two (2) g of soil samples from each particular distance were digested with 10 ml 30 % HCl and 3.5 ml 65 % HNO_3 on a Tecator Model 20 Digestor system at 150 °C for 1 hour 30 minutes before heating at 230 °C for another 30 mins. The digestion tubes were removed and allowed to cool before washing the contents into 50 ml volumetric flasks. The heavy metals in the digests were determined in triplicates with Atomic Absorption Spectrophotometer (Unicam Solar 969 with acetylene air flame). Potassium and sodium were determined using flame photometer, calcium and magnesium were determined using the versanate EDTA complexometric titration method while Mn was determined by differential pulse cathodic voltammetry method (Opydo, 2008) and Co by extraction-spectrophotometric method (Dospatliev *et al.*, 2010).

The leaves were rinsed with deionized water to remove pollen particles, dust, sand and oven-dried at 30 °C for 120 hours. The dried leaves samples were milled to fine powder (<1 mm) in an agate mortar with pestle. The procedure of Raimi *et al.* (2019) was adopted for the analysis. About 0.5 g of each of the plant samples were weighed separately into a beaker. A mixture of 3 ml concentrated HNO_3, 5 ml $HClO_4$ and 4 ml H_2O_2 was added to the sample and the solution was placed on a hot plate for about 7 mins until a clear solution was obtained. The digested sample was allowed to cool and filtered into a 100 ml volumetric flask using Whatman filter paper and made up to the mark with distilled water. The analyses for heavy metals in the samples were carried out in triplicates using the Atomic Absorption Spectrophotometer (Unicam Solar 969 with acetylene air flame).

For quality assurance and control (QA/QC) measures, high purity reagents of analytical grades were obtained from BDH Chemicals Ltd., UK. All glassware was thoroughly washed and oven-dried and cooled in a desiccator. Reagent blanks and a series of standard solutions of 0.5, 1.0, 2.0, 5.0, 10.0 and 100 mg/l were prepared from the stock standard solution of each test metal by diluting known volumes of the stock solution in 100 ml volumetric flasks using distilled water. The blank reagent and standard reference soil materials were included in each sample batch to verify the accuracy and precision of the digestion procedure. The blanks and standard solutions were aspirated directly into the atomic absorption spectrometer. The following working wavelengths were used: Pb (283.3 nm), Fe (248.3 nm), Ni (232.0 nm), Cd (228.8 nm), As (193.7 nm) and Zn (213.9 nm) and accepted recoveries ranged from 81.0% to 109%.

2.4. Experimental Design and Statistical Analysis

A simple factorial experiment was conducted in a randomized complete block design with three replications. Data generated from the experiment were subjected to one way analysis of variance (ANOVA) using special package for social sciences (SPSS) v. 20 and means were separated (Steel and Torrie, 1980) at $P<0.05$ using Duncan Multiple Range Test (DMRT) while Correlation analysis was used to determine the relationship between the means of the parameters analyzed in soil and plants.

3. RESULTS AND DISCUSSION

3.1. Distribution of Potentially Toxic Element in Soil

The distribution of potentially toxic element in soil at various distance from the China quarry site is presented in Table 1. The results show that concentration of potentially toxic element in soil were raised to different levels and significant differences at $p<0.05$ was evident amongst the sampling distance in this study. The various quarrying activities such as excavation and dumping of overburden, blasting, crushing, haulage, transportation and dumping of chippings at the site resulted to release of potentially toxic element (Pb, Cd, As, Ni, Fe and Zn) that are distributed along the sampling points through wind, leaching and water runoff. Wind, rainfall and surface run-off from urban roadways carrying heavy metals in both particulate and dissolved forms result to metal pollution of soil, water bodies and sediment (Sansalone and Buchberger, 1997; Turer *et al*., 2001; Ogbonna *et al*., 2013). The result indicate that highest and lowest concentration of potentially toxic element were observed at the quarry site and control site, respectively for (Pb, Cd, As, Ni, Fe and Zn). Some pollution survey showed that soils within or around source of pollutants has high concentration of heavy metals (Nwachukwu *et al*., 2010; Ogbonna *et al*., 2011; Ogbonna *et al*., 2013; Nwachukwu *et al*., 2018; Ogbonna *et al*., 2018c; Ogbonna *et al*., 2020). Since there were no other sources of contamination in the area, the high concentration of heavy metal in soil around the quarry area unlike the control may be attributed to generation and distribution of heavy metal (Pb, Cd, As, Ni, Fe and Zn) from tailing dust and quarry water.

The concentration of six (6) heavy metals tested in this study was observed to peak within 1 m followed by their (heavy metals) values at the distance of 180 m and 360 m while the control site had the lowest concentration of the heavy metals. The pattern of leaching or migration of the heavy metals in soil suggest that the concentration of heavy metals from soil samples were decreasing with increasing distance from the quarry. Similar trend in distribution of heavy metals (Pb, Cr, Fe, Ni and Cu) with highest concentration at 0 m and decreased with distance has been reported in granite quarry at Ikole-Ekiti in Ekiti State, Nigeria (Ayodele *et al*., 2014). Furthermore, Bada and Fagbayigbo (2009) also reported similar decrease of heavy metal concentration with distance from a stone quarry. This might be due to heavy metals emitted in particulate matter from chippings and dust from China quarry (Table 2) which settled under gravity near the point source. Heavy metals released in particulate matter settle under gravity very few meters from the point source (Haygarth and Jones, 1992). The highest concentration of Pb (21.48 ± 0.96 mg/kg), Cd (1.69 ± 0.08 mg/kg), As (8.40 ± 1.07 mg/kg), Ni (11.16 ± 1.39 mg/kg), Fe (211.55 ± 0.66 mg/kg) and Zn (18.58 ± 0.74 mg/kg) was recorded at 1 m and the values are significantly ($P<0.05$) higher than their corresponding values at 180 m (10.62±0.30, 0.80±0.08, 2.30±0.14, 3.78±0.23, 201.69±0.72 and 5.05±1.06 mg/kg), 360 m (2.04±0.06, 0.31±0.01, 0.45±0.04, 0.69±0.04, 191.49±0.03 and 0.47±0.07 mg/kg), and the control (0.00±0.00, 0.00±0.00, 0.00±0.00, 0.03±0.01, 71.10±0.01 and 0.00±0.00 mg/kg), respectively for Pb, Cd, As, Ni, Fe and Zn. The heavy metals from the heaps of tailing dust at the quarry site may have provided a source for continued dispersion (by wind and water runoff) and have resulted to various level of contamination of Pb, Cd, As, Ni, Fe and Zn at the various distance of 1, 180, and 360 m. For instance, heavy metal are part of the composition of tailings in mine sites and elevated levels of metals are found in and around mines due to discharge and dispersion of mine wastes such as tailings (Martinez-Sanchez *et al*., 2009; Ogbonna *et al*., 2018). Quarry activities release harmful minerals and chemicals that contaminate soil and air quality (Ezeaku, 2012). Heavy metal contamination by mining is a major environmental concern on a global scale and high concentration of Cd in rice on the Chinese market is attributed to fields contaminated with heavy metals from acid mine drainage (Zhuang *et al*., 2014). The concentration of Pb in soil at the quarry area of China quarry Ishiagu, Nigeria was 2.04±0.06 to 21.48±0.96 mg/kg, which is below the accepted limit (i.e. target value) of 80 mg/kg (Pb) as described by Dutch criteria for soil (Ogbonna *et al*., 2018) and the maximum permitted level of 50 mg/kg (Pb) established by Codex Alimentarius Commission (FAO/WHO, 2001) (Table 3). The concentration of Pb (21.48±0.96 mg/kg) at 1 m is 2.02, 10.53 and 21.48 times higher than its values at 180 m, 360 m from the quarry site and control, respectively. The concentration of Pb (2.04±0.06 to 21.48±0.96 mg/kg) in soils at the various distance from the quarry site is well below 21 to 1,050 mg/kg Pb in soil at Mahad AD'Dahab mine in Saudi Arabia (Al-Farraj and Al-Wabel, 2007), 149,740.3 to 250,311.3 mg/kg Pb in soil at Sungai Lembing tin mine in Malaysia (Alshaebi and Wan Yaacob, 2009), 7.04 to 36.05 mg/kg Pb in soil at a quarry site in Nigeria (Ogbonna *et al*., 2011) and 2.0 to 24.0 mg/kg in volcanic soil at Tawau in Sabah, Malaysia (Husin *et al*., 2015). However, the concentration of Pb in soil is higher than 8.04 to 17.36 mg/kg Pb in soil at a tin mining area in Singkep Island, Indonesia (Irzon *et al*., 2018), 7.75 to 17.75 mg/kg at a granite quarry site in Ikole-Etiti, Nigeria (Ayodele *et al*., 2018) and 0.00±0.00 to 9.80±0.20 mg/kg Pb in soil at a quarry area in Ishiagu, Ebonyi State, Nigeria (Onyedikachi *et al*., 2018).

Table 1: Heavy metals concentration (mg/kg) in soil

Distance (m)	Pb	Cd	As	Ni	Fe	Zn
1	21.48±0.96^{a}	1.69±0.08^{a}	8.40±1.07^{a}	11.16±1.39^{a}	211.55±0.66^{a}	18.58±0.74^{a}
180	10.62±0.30^{b}	0.80±0.08^{b}	2.30±0.14^{b}	3.78±0.23^{b}	201.69±0.72^{b}	5.05±1.06^{b}
360	2.04±0.06^{c}	0.31±0.01^{c}	0.45±0.04^{c}	0.69±0.04^{c}	191.49±0.03^{c}	0.47±0.07^{c}
Control	0.00±0.00^{d}	0.00±0.00^{d}	0.00±0.00^{d}	0.03±0.01^{d}	71.10±0.01^{d}	0.00±0.00^{d}

Values are mean ± standard deviation of 3 replicates; ^{a,b,c,d} Means in the same column with different superscripts are significantly different (P<0.05)

Table 2: Heavy metals concentration (mg/kg) in chippings

Samples	Pb	As	Zn	Fe	Cd	Ni
Dust	2.00±0.05^{a}	0.33±0.01^{e}	6.85±0.06^{a}	3,461.65±3.61^{a}	0.03±0.01^{b}	0.62±0.01^{b}
0.50 (unmixed)	0.73±0.04^{c}	0.42±0.00^{b}	3.97±0.01^{de}	2,415.60±36.20^{e}	0.02±0.00^{b}	0.48±0.00^{bc}
0.50 (mixed)	1.73±0.23^{b}	0.40±0.01^{c}	5.71±0.39^{c}	3,154.71±28.72^{b}	0.09±0.02^{a}	1.44±0.03^{a}
3/8 inch	0.72±0.01^{c}	0.42±0.00^{b}	3.72±0.04^{e}	2,332.20±60.95^{f}	0.01±0.00^{b}	0.57±0.01^{b}
3/4 inch	0.70±0.00^{c}	0.41±0.00^{bc}	3.63±0.12^{e}	2,517.25±5.73^{d}	0.02±0.00^{b}	0.42±0.00^{bc}
½ inch	0.61±0.05^{cd}	0.47±0.00^{a}	6.15±0.06^{b}	2,592.63±12.13^{c}	0.03±0.01^{b}	0.60±0.01^{b}
1 inch	0.69±0.00^{c}	0.32±0.01^{e}	5.76±0.06^{c}	2,389.65±2.05^{ef}	0.03±0.01^{b}	0.44±0.01^{bc}
Hardcore	0.47±0.01^{d}	0.39±0.00^{d}	4.27±0.02^{d}	2,427.55±1.06^{e}	0.01±0.00^{b}	0.39±0.00^{bc}

Values are mean ± standard deviation of 3 replicates; ^{a,b,c,d,e,f,g,h} Means in the same column with different superscripts are significantly different (P<0.05)

Table 3: Comparison of concentration of heavy metals in soils with international and national standards (*ECDGE 2010; Ogbonna *et al*., 2019)

Heavy metals	This study	Dutch Criteria (target Value) mg/kg	FAO/WHO 2001, 2006, 2007	FEPA 1999	NESREA 2011	*UK	Austria	*Netherlands	*Sweden
Cd	0.31±0.01–1.69±0.08	0.8	0.1	0.01	3	3	1-2	0.5	0.4
Pb	2.04±0.06–21.48±0.96	85	50	1.6	NA	300	100	40	40
As	0.45±0.04–8.40±1.07	36	100	70-80	100	135	NA	40	40
Ni	0.69±0.04–11.16±1.39	100	100	NA	100	400	50-70	30	60
Fe	191.49±0.0–211.55±0.66	NA	NA	400	NA	NA	NA	NA	NA
Zn	0.47±0.07–18.58±0.74	140	60	NA	421	NA	NA	NA	NA

NA = Not available

The concentration of Cd in soil at the quarry area of China quarry Ishiagu, Nigeria was 0.31±0.01 to 1.69±0.08 mg/kg, which is higher than the accepted limit of 0.8 mg/kg (Cd) as described by Dutch criteria for soil (,; Ogbonna *et al*., 2018) and the maximum permitted level of 0.1 mg/kg (Cd) established by the Codex Alimentarius Commission (FAO/WHO, 2001). The concentration of Cd (1.69±0.08 mg/kg) at 1 m is 2.11, 5.45, and 169 times higher than its values at 180 m, 360 m from the quarry site and control, respectively. The concentration of Cd in soils increased from 0.31±0.01 (360 m) to 1.69±0.08 mg/kg (1 m) and the values are well below 0.4 to 30 mg/kg Cd in soil at Mahad AD'Dahab mine in Saudi Arabia (Al-Farraj and Al-Wabel, 2007) and 1.48 to 12.31 mg/kg Cd in soil (Ogbonna *et al*., 2011) but higher than 0.00 to 1.50 mg/kg Cd in soil at ESPRO quarry site in Osun State, Nigeria (Alabi *et al*., 2019) and 0.00±0.00 mg/kg Cd in soil at a quarry area in Ishiagu, Ebonyi State, Nigeria (Onyedikachi *et al*., 2018).

The concentration of As and Ni in soil at the quarry area of China quarry of Ishiagu, Nigeria were 0.45±0.04 to 8.40±1.07 and 0.69±0.04 to 11.16±1.39 mg/kg, respectively for As and Ni which are below the target value of 29 mg/kg (As) and 35 mg/kg (Ni) as described by Dutch criteria for soil (Ogbonna *et al*., 2018). The concentration of As (8.40±1.07 mg/kg) at 1 m is 3.65, 18.67 and 840 times higher than its values at 180 m, 360 m and control, respectively while the concentration of Ni (11.16±1.39 mg/kg) at 1 m is 2.95, 16.17 and 372 times higher than its values at 180 m, 360 m and control, respectively. The concentration of As (0.45±0.04 to 8.40±1.07 mg/kg) in soils at the various distance from the quarry site is well below 10.54 to 62.83 mg/kg As in soil at ESPRO quarry site in Osun State, Nigeria (Irzon *et al*., 2018) but relatively lower than 5.0 to 10.0 mg/kg As in soil at tin mining area in Singkep Island, Riau, Indonesia (Husin *et al*., 2015). The concentration of Ni (0.69±0.04 to 11.16±1.39 mg/kg) in soils at the various distance from the quarry site is lower than 9.0 to 23.0 mg/kg Ni in soil at a tin mining area in Singkep Island, Riau, Indonesia (Husin *et al*., 2015) but higher than 2.25 to 5.75 mg/kg Ni in soil at a granite quarry site in Ikole-Etiti, Nigeria (Olufemi *et al*., 2014). Nickel occurs in igneous rocks as a free metal or together with iron and it is released into the environment by anthropogenic activities such as metal mining, smelting, fossil fuel burning, vehicle emissions, disposal of household, municipal and industrial wastes, fertilizer application and organic manures

(Alloway, 1995; Salt *et al*., 2000; Chen *et al*., 2009). The concentration of Fe in soil at the quarry area of China quarry of Ishiagu, Nigeria was 191.49±0.03 to 211.55±0.66 mg/kg, which is below the accepted limit of 400 mg/kg (Fe) set by Federal Environmental Protection Agency (FEPA, 1991) of Nigeria for Fe. The concentration of Fe in soil increased from 191.49±0.03 (360 m) to 211.55±0.66 mg/kg (1 m) and the values are lower than 148.00±0.00 to 7,148.45±0.05 mg/kg Fe in soil at a quarry area in Ishiagu, Ebonyi State, Nigeria (Onyedikachi *et al*., 2018) and 56.4 to 323.2 mg/kg Fe in soil at ESPRO quarry site in Osun State, Nigeria (Alabi *et al*., 2019) but higher than 0.36 to 1.62 % Fe in soil at a granite quarry site in Ikole-Etiti, Nigeria (Olufemi *et al*., 2014).

The concentration of Zn in soil at the quarry area of China quarry of Ishiagu, Nigeria was 0.47±0.07 to 18.58±0.74 mg/kg, which is well below the accepted limit (target value) of 140 mg/kg (Zn) as described by Dutch criteria for soil (; Ogbonna *et al*., 2018), the maximum permitted limit of 60 mg/kg (Zn) established by Codex Alimentarius Commission (FAO/WHO, 2001) and 421 mg/kg (Zn) set by National Environmental Standards and Regulations Enforcement Agency (NESREA, 2011) of Nigeria for Zn. The concentration of Zn (18.58±0.74 mg/kg) at 1 m is 3.68, 39.53, and 1,858 times higher than its values at 180 m, 360 m, and control, respectively. The concentration of Zn in soil increased from 0.47±0.07 (360 m) to 18.58±0.74 mg/kg (1 m) and the values are lower than 74.0 to 132.0 mg/kg Zn in soil at a tin mining area in Singkep Island, Riau, Indonesia (Husin *et al*., 2015), 2.10 to 101.0 mg/kg Zn in soil at a quarry in Nigeria (Ogbonna *et al*., 2011) and 2.70±0.10 to 53.95±0.05 mg/kg Zn in soil at a quarry area in Ishiagu, Ebonyi State, Nigeria (Onyedikachi *et al*., 2018) but higher than 3.50 to 14.55 mg/kg Zn in soil at a granite quarry site in Ikole-Etiti, Nigeria (Olufemi *et al*., 2014). Generally, the order of abundance of heavy metals in soil is as follows: Pb>Zn>Ni>Fe>As>Cd.

3.2. Potentially Toxic Element (mg/kg) in Fodder and Medicinal Plants

The concentration of heavy metals in plants collected at different sampling points in the vicinity of China quarry site is presented in Table 4. From the results, there were no plants growing at 1 m distance from the edge of the quarry due to high impact of quarrying activities. Significant differences at P<0.05 exist in the concentration of heavy metals in plants but the highest and lowest concentration of heavy metals were observed in plants samples collected from the quarry area and control site, respectively. The result also indicate that the plant species assimilated different levels of concentration of heavy metals at various distances from the emission source (i.e., quarry) and the concentration of heavy metals decreases with increasing distance from the quarry. This result corroborates the findings of Ogbonna *et al*. (2018) that reported a decrease in concentration of heavy metals with increasing distance in a related study. The result clearly indicates that *Crotolaria retusa* assimilated the highest concentration of Pb (2.42±0.00 mg/kg), As (0.43±0.01 mg/kg) and Zn (5.52±0.00 mg/kg) and the values are significantly (P<0.05) different from the values of Pb, As and Zn, respectively for *Boerhavia erecta* (2.37±0.00, 0.33±0.00 and 4.58±0.00 mg/kg), *Paspalum scrobiculatum* (1.26±0.00, 0.19±0.00 and 2.71±0.00 mg/kg) and *Pennisetum polystachion* (1.25±0.00, 0.26±0.00 and 3.50±0.07 mg/kg) at 180 m. Furthermore, the values of *C. retusa* is significantly (P<0.05) higher than the values of *B. erecta* (0.92±0.01, 0.17±0.00 and 2.12±0.00 mg/kg), *C. retusa* (0.69±0.00, 0.11±0.00 and 1.43±0.00 mg/kg), *P. scrobiculatum* (0.60±0.00, 0.20±0.00 and 2.15±0.00 mg/kg) and *P. polystachion* (0.68±0.00, 0.16±0.00 and 2.65±0.00 mg/kg) at 360 m as well as *B. erecta* (0.01±0.00, 0.01±0.00 and 0.18±0.00 mg/kg), *C. retusa* (0.01±0.00, 0.01±0.00 and 0.21±0.00 mg/kg), *P. scrobiculatum* (0.09±0.00, 0.08±0.00 and 0.38±0.00 mg/kg) and *P. polystachion* (0.03±0.00, 0.02±0.00 and

0.44±0.00 mg/kg) at control site. The high concentration of Pb, As and Zn in *C. retusa* may be attributed to the inherent ability of the plant (*C. retusa*) to absorb and translocate more Pb, As and Zn to the aerial plant parts (leaves) than other plant species since the concentration of these metals (Pb, As and Zn) peaked in soil at 180 m. Ogbonna *et al.* (2013) reported that inherent ability of *Baphia nitida* resulted to absorption of high concentrations of Cr, Zn and Cd in its roots and their (Cr, Zn and Cd) translocation to the leaves than other plants. Further, the bushy nature of the plant (*C. retusa*) as well as its alternate and simple leaves that are slightly stalked and oblanceolate in shape may have provided more surface area for deposition of dust (from quarry) and subsequently assimilated into its tissues via the stomata than other plants (Hutchinson *et al.*, 1958; Devendra and Srinivas, 2011). Heavy metal accumulation in plants is dependent on type of metal and plant species involved (Juste and Mench, 1992; Ogbonna and Okezie, 2011). The highest concentration of Pb (2.42±0.00 mg/kg) in *C. retusa* is 1.94, 1.92 and 1.02 times higher than its (Pb) concentration in *P. polystachion, P. scrobiculatum* and *B. erecta* at 180 m, and 3.56, 4.03 and 2.63 times higher than the values of *P. polystachion, P. scrobiculatum* and *B. erecta* at 360 m, as well as 80.67, 26.89 and 242 times higher than the values of *P. polystachion, P. scrobiculatum* and *B. erecta* at the control site, respectively.

The concentration of Pb in plants increased from 0.60±0.00 in *P. scrobiculatum* at 360 m to 2.42±0.00 mg/kg in *C. retusa* at 180 m. The concentration of Pb (0.60±0.00 to 2.42±0.00 mg/kg) in this study is lower than 0.30±0.00 to 212.7±0.06 mg/kg in *Manihot esculenta, Discorea rotundata, Calocacia antiquorm, Telfarie occidentalis, Vernonia amygdalina, Talinum triangulare, Citrus sinensis, Chrysophyllum albidum, Carica papaya, Cocos nicifera, Cola acuminate* and *Elaies guineensis* at a quarry in Ebonyi State, Nigeria (Onyedikachi *et al.*, 2018), 2.9 to 89 mg/kg in *Pergularia tomentosa, Calotropis procera, Acacia tortilis, Ochradenus baccatus, Salsola* sp., *Rhiza strica, Convolvulus* sp., *Euculeprus* sp., and *Prosopis juliflora* in Mahad AD'Dahab mine, Saudi Arabia (Al-Faraj and Al-Wabel, 2007).

Table 4: Potentially toxic elements in plant

Distance (m)	Plant species	Pb (mg/kg)	As (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Fe (mg/kg)
1M	*P. polystachion*	NA	NA	NA	NA	NA
	P. scrobiculatum	NA	NA	NA	NA	NA
	C. retusa	NA	NA	NA	NA	NA
	B. eracta	NA	NA	NA	NA	NA
180	*P. polystachion*	1.25 ± 0.00^{c}	0.26 ± 0.00^{c}	3.50 ± 0.07^{c}	20.03 ± 0.01^{a}	54.70 ± 0.00^{a}
	P. scrobiculatum	1.26 ± 0.00^{c}	0.19 ± 0.00^{d}	2.71 ± 0.00^{d}	15.42 ± 0.00^{b}	45.60 ± 0.14^{b}
	C. retusa	2.42 ± 0.00^{a}	0.43 ± 0.01^{a}	5.52 ± 0.00^{a}	12.81 ± 0.00^{c}	40.06 ± 0.00^{c}
	B. eracta	2.37 ± 0.00^{b}	0.33 ± 0.00^{b}	4.58 ± 0.00^{b}	10.20 ± 0.00^{d}	35.20 ± 0.00^{d}
360	*P. polystachion*					
	P. scrobiculatum	0.60 ± 0.00^{g}	0.20 ± 0.00^{d}	2.15 ± 0.00^{f}	10.19 ± 0.00^{e}	24.37 ± 0.00^{g}
	C. retusa	0.69 ± 0.00^{e}	0.11 ± 0.00^{f}	1.43 ± 0.00^{g}	8.45 ± 0.00^{g}	19.01 ± 0.00^{h}
	B. eracta	0.92 ± 0.01^{d}	0.17 ± 0.00^{e}	2.12 ± 0.00^{f}	8.71 ± 0.00^{f}	32.30 ± 0.00^{e}
Control	*P. polystachion*					
	P. scrobiculatum	0.09 ± 0.00^{h}	0.08 ± 0.00^{g}	0.38 ± 0.00^{i}	1.31 ± 0.00^{i}	10.66 ± 0.00^{j}
	C. retusa	0.01 ± 0.00^{j}	0.01 ± 0.00^{i}	0.21 ± 0.00^{j}	1.01 ± 0.00^{k}	10.30 ± 0.00^{k}
	B. eracta	0.01 ± 0.00^{j}	0.01 ± 0.00^{i}	0.18 ± 0.00^{j}	0.92 ± 0.00^{l}	10.10 ± 0.00^{l}

Values are mean ± standard deviation of 3 replicates; ^{a,b,c,d,e,f,g,h,I,j,k,l}Means in the same column with different superscripts are significantly different (P<0.05)

The values of Pb in this study is also lower than 7.0 to 13.0 mg/kg in *Sida scabrida, Aspilia africana, Synedrella nodiflora, Chromolaena odorata* and *Talinum triangulare* in Ikole-Etiti, Etiti State, Nigeria

(Olufemi *et al*., 2014), 0.01±0.00 to 10.37±0.52 mg/kg in *Irvingia gabonensis, Dialium guinense, Mangifera indica, Icacina trichantha, Alchornea cordifolia, Andropogon gayanus* and *Manihot esculenta* in Akwuke and Iva coal mine sites, Enugu State, Nigeria (Ogbonna *et al*., 2018), 3.90 to 6.01 mg/kg in *Terminalia ivorensis, Ceiba pentandra, Milicia excelsa, Newbouldia laevis* and *Ficus exasperata* in quarry site in Ebonyi State, Nigeria (Ogbonna *et al*., 2011) but higher than <0.04 to 0.07±0.01 mg/l in *Anogeissus leiocarpus, Bauhinia reticulate, Prosopis oblonga, Sterculia tomentosa* and *Tamarindus indica* in quarry site in Demsa, Adamawa State, Nigeria (Mustapha *et al*., 2016).

The concentration of Pb in plants (0.60±0.00 to 2.42±0.00 mg/kg) in this study is higher than the permissible limit of 0.30 mg/kg (Pb) established by the Codex Alimentarius Commission (FAO/WHO, 2007). Consequently, the concentration of Pb in *C. retusa* that is used for medicinal purposes will constitute a serious health problem to the inhabitants of Ngwogwo in Ebonyi State. Exposure to lead could lead to weakness of the joints and reproductive failure in human (Adelekan and Abegunde, 2011).

The concentration of Zn (5.52±0.00 mg/kg) in *C. retusa* is significantly (P<0.05) higher than values recorded for *B. eracta* (4.58±0.00 mg/kg), *P. scrobiculatum* (2.71±0.00 mg/kg) and *P. polystachion* (3.50±0.07 mg/kg) at 180 m, the values of *B. eracta* (2.12±0.00 mg/kg), *C. retusa* (1.43±0.00 mg/kg), *P. scrobiculatum* (2.15±0.00 mg/kg) and *P. polystachion* (2.65±0.00 mg/kg) at 360 m, as well as the values of *B. eracta* (0.18±0.00 mg/kg), *C. retusa* (0.21±0.00 mg/kg), *P. scrobiculatum* (0.38±0.00 mg/kg) and *P. polystachion* (0.44±0.00 mg/kg) at the control site. The value of Zn (5.52±0.00 mg/kg) in *C. retusa* is 1.21, 2.04, 1.58 times higher than its (Zn) values in *B. eracta, P. scrobiculatum, P. polystachion* at 180 m, and 2.6, 3.86, 2.57, 2.08 times higher than its (Zn) values in *B. eracta, C. retusa, P. scrobiculatum, P. polystachion* at 360 m, as well as 30.67, 26.29, 14.53 and 12.55 times higher than its (Zn) values in *B. eracta, C. retusa, P. scrobiculatum* and *P. polystachion* at the control site, respectively. The concentration of Zn in this study increased from 2.12±0.00 in *B. eracta* at 360 m to 5.52±0.00 mg/kg in *C. retusa* at 180 m, and the values are lower than 40.4 to 720.6 mg/kg in *Pergularia tomentosa, Calotropis procera, Acacia tortilis, Ochradenus baccatus, Salsola* sp., *Rhiza strica, Convolvulus* sp., *Euculeprus* sp., and *Prosopis juliflora* in Mahad AD'Dahab mine, Saudi Arabia (Al-Faraj and Al-Wabel, 2007), 105.8±24.65 to 232.3±97.35 mg/kg in *Lantana camara, Panicum maximum* and *Datura stramonium* around a quarry site in Pretoria North, South Africa (Raimi *et al*., 2019). The concentration of Zn in this study is also lower than 3.23±0.03 to 27.71±0.01 mg/kg in *Manihot esculenta, Discorea rotundata, Calocacia antiquorm, Telfarie occidentalis, Vernonia amygdalina, Talinum triangulare, Citrus sinensis, Chrysophyllum albidum, Carica papaya, Cocos nicifera, Cola acuminate* and *Elaies guineensis* at a quarry in Ebonyi State, Nigeria (Onyedikachi *et al*., 2018), 5.5 to 12.0 mg/kg in *Sida scabrida, Aspilia africana, Synedrella nodiflora, Chromolaena odorata* and *Talinum triangulare* in Ikole-Etiti, Etiti State, Nigeria (Olufemi *et al*., 2014), and 0.02 to 9.10 mg/kg in *Terminalia ivorensis, Ceiba pentandra, Milicia excelsa, Newbouldia laevis* and *Ficus exasperata* in quarry site in Ebonyi State, Nigeria (Ogbonna *et al*., 2011).

The concentration of Zn (2.12±0.00 to 5.22±0.00 mg/kg) is below the permissible limit of 50 mg/kg (Zn) established by the Codex Alimentarius Commission (FAO/WHO, 2006) (Table 5). The level of Zn in this study may have enhanced the growth and development of the plants since zinc is an essential micronutrient for enzymatic activities and deoxyribonucleic acid (DNA) transcription in plants (Mengel and Kirkby, 1982; Kobayashi *et al*., 1998; Yanagisawa, 2004; Ogbonna *et al*., 2011). Similarly, the use of the plant species for medicinal purposes by man or as forage plants for feeding of animals will supply zinc to their body. Zinc helps to activate or enhances the reproductive system of man (Barminas *et al*., 1998).

The concentration of As (0.43±0.01 mg/kg) in *C. retusa* is significantly (P<0.05) higher than values observed in *B. eracta* (0.33±0.00 mg/kg), *P. scrobiculatum* (0.19±0.00 mg/kg) and *P. polystachion* (0.26±0.00 mg/kg) at 180 m, and the values of *B. eracta* (0.17±0.00 mg/kg), *C. retusa* (0.11±0.00 mg/kg), *P. scrobiculatum* (0.20±0.00 mg/kg) and *P. polystachion* (0.16±0.00 mg/kg) at 360 m, as well as the values of *B. eracta* (0.01±0.00 mg/kg), *C. retusa* (0.01±0.00 mg/kg), *P. scrobiculatum* (0.08±0.00 mg/kg) and *P. polystachion* (0.02±0.00 mg/kg) at the control site.

Table 5: Comparison of concentration of heavy metals in plants with international and national standards

Heavy metals	This study	Similar studies	FAO/WHO 2001, 2006, 2007	FEPA	NESREA	DPR
Pb	0.60±0.00 to 2.42±0.00	0.30-212.7 Onyedikachi *et al*. (2018) 2.9 to 89 Al-Faraj and Al-Wabel, 2007 7.0-13.0 Olufemi *et al*., 2014 0.01-10.37 Ogbonna *et al*. (2018) 3.90-6.01 Ogbonna *et al*. (2011) <0.04 to 0.07 Mustapha *et al*., 2016	0.3	NA	NA	NA
Ni	0.25±0.00 to 1.18±0.00	55.4-136.7 Raimi *et al*. (2019) 7.0-13.0 Olufemi *et al*. (2014 <0.005 Mustapha *et al*., 2016	1.63	NA	NA	NA
Zn	2.12±0.00 to 5.22±0.00	40.4-720.6 Al-Faraj and Al-Wabel, 2007 105.8-232.3 Raimi *et al*. (2019) 3.23-27.71 Onyedikachi *et al*. (2018) 5.5-12.0 Olufemi *et al*., 2014 0.02-9.10 Ogbonna *et al*. (2011)	50	NA	NA	NA
As	0.11±0.00 to 0.43±0.01	49-7,521 González-Chávez *et al*. (2015) 0.8-114 Kampouroglou and Economou-Eliopoulos (2013) 0.0-0.42 Arhin *et al*. (2017)	0.2	NA	NA	NA
Cd	0.0000±0.00 to 0.09±0.00	54.1-134.3 Raimi *et al*. (2019) 0.51-1.12 Ogbonna *et al*. (2011) BDL-0.23 Onyedikachi *et al*. (2018) <0.01 Mustapha *et al*., 2016	0.2	NA	NA	NA
Fe	19.01±0.00 to 54.70±0.00	205-9,432 Olufemi *et al*. (2014) 196.5-2,925 Raimi *et al*. (2019) 31.95-2,654.11 Onyedikachi *et al*. (2018)	425	NA	NA	NA

The value of As (0.43±0.01 mg/kg) in *C. retusa* is 1.30, 2.26, 1.65 times higher than its (As) values in *B. eracta, P. scrobiculatum, P. polystachion* at 180 m, and 2.53, 3.91, 2.15, 2.69 times higher than its (As) values in *B. eracta, P. scrobiculatum, P. polystachion* at 360 m, as well as 43, 43, 5.38 and 21.5 times higher than its (As) values in *B. eracta, P. scrobiculatum, P. polystachion* at the control site, respectively. The concentration of As in this study increased from 0.11±0.00 in *C. retusa* at 360 m to 0.43±0.01 mg/kg in *C. retusa* at 180 m, and the values are well below 49 to 7,521 mg/kg in *Pteridium* sp., *Juniperus sp., Cuphea* *lanceolata, Dichondra argentea, Brickellia veronicifolia, Ruta graveolens, Dalea bicolor, Viguiera dentate, Aster gymnocephalus, Gnaphalium* sp. and *Crotalaria pumila* in mine tailings at Zimapan, Central Mexico in Hidalgo State, Mexico (González-Chávez *et al*., 2015). The value of As in this study is also below the values of 0.8 to 114 mg/kg *Sonchus oleraceus, Cichorium intybus, Scolymus hispanicus, Brachypodium ramosum, Erica* sp., and *Sinapis arvensis* at limestone quarry in Greece (Kampouroglou and Economou-Eliopoulos, 2013) but higher than 0.0 to 0.42 mg/l in millet, sorghum, Guinea corn, groundnuts, maize, rice and soya bean at gold belt region in Ghana (Arhin *et al*., 2017). The concentration of As in this study (0.11±0.00 to 0.43±0.01 mg/kg) is relatively higher than the permissible limit of 0.2 mg/kg (As) recommended by Codex Alimentarius Commission (FAO/WHO, 2006). *Crotalaria retusa* is an important medicinal plant species in South east Nigeria. Consequently, the use of such metal-contaminated plant for therapeutic purposes can be a route of entry of arsenic in the bodies of those living around China quarry area. Herbal medicines are currently collected from wild fields by large sections of population and used with poor care, since these plants are not regulated for medicines (González-Chávez, 2015). The main route of entry of arsenic in human system is consumption of contaminated food plants (Gupta and Gupta, 2013). Arsenic does not have any essential function to plants or humans (González-Chávez *et al*., 2015) and high level of arsenic hinders plant growth by distorting plant metabolism and germination of seeds in soil (Shah *et al*., 2010; Kampouroglou and Economou-Eliopoulos, 2013). The Agency for Toxic Substances and Disease Registry considers arsenic as one of the most harmful contaminants to human health (ATSDR, 2013). Some health challenges associated with ingestion of high amount of arsenic in human include lesions, neurological defects, atherosclerosis (Zhongiun *et al*., 2016), dehydration, weakness, lethargy (Gupta and Gupta, 2013), cardiovascular, gastrointestinal, hepatic and renal diseases (Vamerali *et al*., 2010) and promote bladder, lung and skin cancer (WHO, 2015).

The highest concentration of Cd (0.09±0.00 mg/kg) was obtained in *P. polystachion* at 180 m and the value is significantly (P<0.05) higher than its corresponding values in *P. scrobiculatum* (0.02±0.00 mg/kg), *C. retusa* (0.002±0.00 mg/kg) and *B. eracta* (0.001±0.00 mg/kg) at 180 m, and the values of *P. polystachion* (0.0009±0.00 mg/kg), *P. scrobiculatum* (0.0002±0.00 mg/kg), *C. retusa* (0.0001±0.00 mg/kg) and *B. eracta* (0.0001±0.00 mg/kg) at 360 m, as well as the values of *P. polystachion* (0.00001±0.00 mg/kg), *P. scrobiculatum* (0.0000±0.00 mg/kg), *C. retusa* (0.0000±0.00 mg/kg) and *B. eracta* (0.0000±0.00 mg/kg) at control site. The concentration of Cd increased from 0.0000±0.00 to 0.09±0.00 mg/kg, which is well below 54.1±2.15 to 134.3±14.57 mg/kg in *Lantana camara, Panicum maximum* and *Datura stramonium* around a quarry site in Pretoria North, South Africa (Raimi *et al*., 2019), 0.51 to 1.12 mg/kg in *Terminalia ivorensis, Ceiba pentandra, Milicia excelsa, Newbouldia laevis* and *Ficus exasperata* in quarry site in Ebonyi State, Nigeria (Ogbonna *et al*., 2011) and 0.00±0.00 to 0.23±0.03 mg/kg in *Manihot esculenta, Discorea rotundata, Calocacia antiquorm, Telfarie occidentalis, Vernonia amygdalina, Talinum triangulare, Citrus sinensis, Chrysophyllum albidum, Carica papaya, Cocos nicifera, Cola acuminate* and *Elaies guineensis* at a quarry in Ebonyi State, Nigeria (Onyedikachi *et al*., 2018) but higher than <0.01 mg/l in *Anogeissus leiocarpus, Bauhinia reticulate, Prosopis oblonga, Sterculia tomentosa* and *Tamarindus indica* in quarry site in Demsa, Adamawa State, Nigeria (Mustapha *et al*., 2016). The values of Cd (0.0000±0.00 to 0.09±0.00 mg/kg) in this study is lower than the permissible limit of 0.2 mg/kg (Cd) recommended by the Codex Alimentarius Commission (FAO/WHO, 2007). Cadmium is a non-essential element in plant metabolism and has no nutritional benefit in human body.

The highest concentration of Ni (1.13±0.00 mg/kg) was recorded in *P. polystachion* at 180 m and the value is significantly ($P<0.05$) higher than its corresponding values in *P. scrobiculatum* (0.60±0.00 mg/kg), *C. retusa* (0.57±0.00 mg/kg) and *B. eracta* (0.48±0.00 mg/kg) at 180 m, and the values of *P. polystachion* (0.36±0.00 mg/kg), *P. scrobiculatum* (0.42±0.00 mg/kg), *C. retusa* (0.29±0.00 mg/kg) and *B. eracta* (0.25±0.00 mg/kg) at 360 m, as well as the values of *P. polystachion* (0.002±0.00 mg/kg), *P. scrobiculatum* (0.004±0.00 mg/kg), *C. retusa* (0.001±0.00 mg/kg) and *B. eracta* (0.000±0.00 mg/kg) at control site. The concentration of Ni increased from 0.25±0.00 in *B. eracta* at 360 m to 1.18±0.00 mg/kg in *P. polystachion* at 180 m, which is below 55.4±2.82 to 136.7±13.32 mg/kg in *Lantana camara, Panicum maximum* and *Datura stramonium* around a quarry site in Pretoria North, South Africa (Raimi *et al*., 2019) and 7.0 to 13.0 mg/kg in *Sida scabrida, Aspilia africana, Synedrella nodiflora, Chromolaena odorata* and *Talinum triangulare* in Ikole-Etiti, Etiti State, Nigeria (Olufemi *et al*., 2014) but higher than <0.005 mg/l in *Anogeissus leiocarpus, Bauhinia reticulate, Prosopis oblonga, Sterculia tomentosa* and *Tamarindus indica* in quarry site in Demsa, Adamawa State, Nigeria (Mustapha *et al*., 2016). The concentration of Ni (0.25±0.00 to 1.18±0.00 mg/kg) in this study is relatively lower than the permissible limit of 1.63 mg/kg (Ni) recommended by the Codex Alimentarius Commission (FAO/WHO, 2001). Persistence use of *P. polystachion* as fodder plants may pose a serious health risk to animals around Ngwogwo and its neighboring communities because of the level of Ni in the plant species. Nickel occurs in igneous rocks as a free metal or together with iron and it is released into the environment by anthropogenic activities such as metal mining, smelting, fossil fuel burning, vehicle emissions, disposal of household, municipal and industrial wastes, fertilizer application and organic manures (Alloway, 1995; Salt *et al*., 2000; Chen *et al*., 2009). Nickel is an essential nutrient for plants (Eskew *et al*., 1983; Brown *et al*., 1987; Ragsdale, 1998) but the amount of Ni required for normal growth of plants is very low (Chen *et al*., 2009). The uptake of Ni in plants is carried out mainly by root systems via passive diffusion and active transport (Seregin and Kozhevnikova, 2006). The ratio of uptake between active and passive transport varies with species, nickel form and concentration in the soil or nutrient solution (Dan *et al*., 2002; Vogel-Mikus *et al*., 2005). Exposure of plants to nickel lead to inhibition of mitotic activities (Madhava Rao and Sresty, 2000), reductions in plant growth (Molas, 2002) and adverse effects on fruit yield and quality (Gajewska *et al*., 2006; Chen *et al*., 2009). The influence of Ni on photosynthesis is pervasive, occurring both in isolated chloroplasts and whole plants (Tripathy *et al*., 1981; Singh *et al*., 1989; Molas, 2002; Boisvert *et al*., 2007). Nickel damages the photosynthetic apparatus at almost every level of its organization, including destroying cells of mesophyll and epidermal tissue (Bethkey and Drew, 1992) and decreasing chlorophyll content (chlorophyll a, b, total chlorophyll and chlorophyll a/b ratio) (Krupa *et al*., 1993; Pandey and Sharma, 2002; Gopal *et al*., 2002; Gajewska *et al*., 2006; Gajewska and Sklodowska, 2007; Chen *et al*., 2009). Nickel also damages the thylakoid membrane and chloroplast grana structure (Molas, 2002; Szalontai *et al*., 1999) reducing the size of grana and increasing the number of non-appressed lamellae (Molas, 1997; Chen *et al*., 2009).

The highest concentration of Fe (54.70±0.00 mg/kg) was obtained in *P. polystachion* at a distance of 180 m, and the value is significantly ($P<0.05$) higher than its corresponding values in *P. scrobiculatum* (45.60±0.14 mg/kg), *C. retusa* (40.06±0.00 mg/kg) and *B. eracta* (35.20±0.00 mg/kg) at 180 m, and the values of *P. polystachion* (27.80±0.00 mg/kg), *P. scrobiculatum* (24.37±0.00 mg/kg), *C. retusa* (19.01±0.00 mg/kg) and *B. eracta* (32.30±0.00 mg/kg) at 360 m, as well as the values of *P. polystachion* (10.91±0.00 mg/kg), *P. scrobiculatum* (10.66±0.00 mg/kg), *C. retusa* (10.30±0.00 mg/kg) and *B. eracta* (10.10±0.00 mg/kg) at control site. The concentration of Fe in plants may be attributed to its (Fe) higher concentration in soil. Notwithstanding this, the concentration of Fe may also be attributed to aerial deposition of dust particles from quarry activities. The concentration of Fe increased from 19.01±0.00 in *C. retusa* at 360 m to 54.70±0.00 mg/kg in *P. polystachion* at 180 m, and the values are well below 205 to 9,432 mg/kg in *Sida scabrida, Aspilia africana, Synedrella nodiflora, Chromolaena odorata* and *Talinum triangulare* in Ikole-Etiti, Etiti State, Nigeria (Olufemi *et al*., 2014). The concentration of Fe in this study is also well below the values of 196.5±64.34 to 2,925±7.07 mg/kg in *Lantana camara, Panicum maximum* and *Datura stramonium* around a quarry site in Pretoria North, South Africa (Raimi *et al*., 2019) and 31.95±0.05 to 2,654.11±0.11 mg/kg in *Manihot esculenta, Discorea rotundata, Calocacia antiquorm, Telfarie occidentalis, Vernonia amygdalina, Talinum triangulare, Citrus sinensis, Chrysophyllum albidum, Carica papaya, Cocos nicifera, Cola acuminate* and *Elaies guineensis* at a quarry in Ebonyi State, Nigeria (Onyedikachi *et al*., 2018). The concentration of Fe (19.01±0.00 to 54.70±0.00 mg/kg) in plants in this study is well below the permissible limit of 425 mg/kg (Fe) recommended by the Codex Alimentarius Commission (FAO/WHO, 2001) (Table 5). Iron is not easily available in neutral to alkaline soils, hence, rendering plants iron-deficient despite its abundance (Rout and Sahoo, 2015) in soil. It (Fe) plays a significant role in basic biological processes such as photosynthesis, chlorophyll synthesis, respiration, nitrogen fixation, uptake mechanisms (Kim and Rees, 1992), and DNA synthesis through the action of the ribonucleotide reductase (Reichard, 1993). It is also an active cofactor of many enzymes that are necessary for plant hormone synthesis, such as ethylene, lipoxygenase, 1-aminocyclopropane acid-1-carboxylic oxidase (Siedow, 1991), or abscisic acid (compounds that are active in many plant development pathways and their adaptive responses to fluctuating environment conditions). Iron deficiency severely affects plant development and growth, and excess iron in cells is toxic (Rout and Sahoo, 2015). Considering the fact that the concentration of Fe in plants is well below the FAO/WHO permissible limit, the Fe in plants is required by human for a number of highly complex processes that continuously take place on a molecular level and that are indispensable to human life, for instance, the transportation of oxygen in human body in which Fe is an important prosthetic group in both protein carriers; myoglobin and hemoglobin (Zagar *et al*., 2015). Fe is the most important cofactor for the production of red blood cells, conversion of blood sugar to energy and also plays an important role in production and functioning of various enzymes (Zagar *et al*., 2015).

4. CONCLUSION

The result of the study show that quarrying activities release potentially toxic element into the terrestrial environment. The values of heavy metals (Pb, Cd, As, Ni, Fe and Zn) in soil are below the Dutch criteria and permitted limits of Codex Alimentarius Commission, the Nigerian Environmental Standard and Regulatory Enforcement Agency and Federal Environmental Protection Agency except for Cd in soil. The values of Pb in *Crotolaria retusa* and As in *Pennisetum polystachion* is higher than the permissible limit of 0.30 mg/kg (Pb) and 0.2 mg/kg (As) established by the Codex Alimentarius Commission. Consequently, prolong consumption of *Crotolaria retusa* and *Pennisetum polystachion* may result to serious health challenges. Therefore, it is recommended that periodic monitoring of potentially toxic element in soil and plants in Ngwogwo in Ivo Local Government Area of Ebonyi State, Nigeria be done since the soil is used for the cultivation of food crops while plants are used as fodder and therapeutic purposes.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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