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# Spatial Distribution of Heavy Metals in Soil and Plant in a Quarry Site in Southwestern Nigeria

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## Abstract

*The study assessed the concentration of heavy metals in soil and plants around a quarry site in Southwestern Nigeria. Sample plots were established in a systematic method along a line transect at increasing distance of 1, 50, 100, 150, 200, 250 and 300 m from the quarry processing plant. A composite soil sample was drawn from a depth of 0 – 15 cm. These were air dried, passed through a 2 mm sieve and properly labeled. Plant samples in each plot were identified and collected for laboratory analysis. Both soil and plant samples were then analysed for heavy metals (Cd, Zn, Cu, Pb, Ni, Cr, Co, Fe, Se Mn) using Atomic Absorption Spectrophotometer (AAS). Four (4) soil samples were collected in each specified distance and 1 sample of soil and plants were collected 2 km away from the quarry site. Results showed that the concentrations of heavy metals from soil samples were decreasing with increasing distance from 1 to 300 m (Cd 0.21 – 0.04 mg/kg, Cr 0.23 – 0.03 mg/kg, Pb 0.25 – 0.03 mg/kg, Se 0.19 – 0.02 mg/kg, Ni 0.16 – 0.02 mg/kg, Co 0.13 – 0.02 mg/kg, Mn 7.82 – 5.40 mg/kg, Zn 5.01 – 2.82 mg/kg) with the exception of Fe and Cu, which decreased and increased randomly at various points. The study showed low concentrations of Cd 0.05 mg/kg, Cr 0.02 mg/kg, Pb 0.02 mg/kg, Se 0.01 mg/kg, Ni 0.01 mg/kg and Co 0.01 mg/kg in the plant tissue samples. The study concluded that quarrying activities elevated the soil heavy metal content up to the range of 300 m away from the quarrying site and the concentration of heavy metals in plant tissues around the quarry site were below the acceptable toxic level of heavy metals in plants. This can be attributed to the number of years quarry activities in the study area have been in operation.*

**Keywords**: Heavy metals, quarry, pollution.

## Introduction

Environmental pollution has been defined as the contamination of the biological, physical and chemical components of the atmospheric system to such an extent that normal environmental processes are adversely affected[1]. It is also the introduction of contaminants into the environment that cause discomfort to man and other living organisms, which can damage the environment. These can be in the form of chemical substances or energy such as noise, heat or light but are considered contaminants when in excess of natural levels. Any use of natural resources at a rate higher than nature's capacity to restore itself can result in pollution of the environment[2].

Quarrying of different useful minerals from underground deposits is an old technology that has been in existence since antiquity[3]. The Egyptians and the Romans of old used a lot of quarried materials in the construction of the huge pyramids of numbers, temples and monuments that are preserved till today. However, there are several adverse effects quarrying activities have brought to bear on humans and the entire ecosystem. Quarrying generates enormous amounts of particulates because of the method of extraction and this can be hazardous to plants and animals. These elements accumulate in the body tissues of living organisms and their concentrations increase as they pass from lower trophic levels to higher trophic levels (a phenomenon known as biomagnification). In soil, heavy metals cause toxicological effects on soil microbes, which may lead to a decrease in their numbers and activities[4].

Certainly, there is need to investigate the baseline concentrations of toxic heavy metals within the vicinity of the quarry, as the study assessed the levels of Cd, Cr, Pb, Se, Ni, Co, Mn, Fe, Zn and Cu in topsoil (0 – 15cm) of a major quarry in Irewole Local Government Area, Osun State, Nigeria. Therefore, the main goal of the present research was to assess the heavy metals' concentrations and their spatial variations (distance).

## Material and Methods

The study area situated at ESPRO Asphalt Plant and Quarry was selected because it is one of the largest functioning quarry industries in Southwestern Nigeria. The area lies at latitudes 7° 25' and 7° 30' N and longitudes 4° 16' and 4° 20' E. The study area falls within the humid tropics where the climate is seasonally damp, typical of South West Nigeria. The quarry plant/machines were first test-run in November/December 2009 and started processing and production operations in January 2010. Blasting operations are carried out daily due to the increase in demand of the finish products. The quarry is surrounded with rural settlement, with farming and animal rearing activities within the vicinity of the quarry.

**Sampling design, collection, and preparation: Soil Analyses:** Soil samples were collected using a Dutch soil auger in a systematic method along a line transect at increasing distance of 1, 50, 100, 150, 200, 250 and 300 m from the processing plant within the quarry site. Core soil samples were randomly collected at various distances, using a Dutch soil auger within each sampling point at 0 - 15 cm depth in the quarry. These core samples were homogenized in a clean plastic bucket and a composite sample was drawn from it. This process was repeated for all the experimental units. Four (4) soil samples were collected in each specified distance and 1 sample collected 2km away from the quarry site, in an undisturbed forest was taken as the control. All the composite samples were air dried and allowed to pass through a 2 mm sieve, which were then poured into polythene bags, labeled adequately and transported to the laboratory immediately for analyses. A total of 29 soil samples was analysed from the study area.

The sieved soil samples less than 2mm were then taken to the laboratory and analyzed for particle size, soil pH, organic matter and digested for heavy metals analysis. Three grammes of 2 mm sieved air dried soil were weighed into a digestion tube (50 mls in volume) and 1 ml of $HNO_3$ and 10 ml of HCl (aqua regia of ratio 1:2) were added to the samples. The content was heated on a digestion block in fume cupboard to dryness at 120°C [5]. The residue was allowed to cool and leached with 5 ml of 2 M HCl, placed inside the centrifuge machine for 10 minutes at 4500RPM (Revolution Per Minute) at 120°C for 1 hour, then increased to 250°C for I hour, allowed to cool before making it to volume with ultra-pure water. The extract was then poured into a set of vials for the determination of the metals (Cd, Cr, Pb, Se, Ni, Co, Mn, Fe, Zn and Cu) using a Buck 205 model Atomic Absorption Spectrophotometer (AAS). However, soil pH was determined using the electrolyte of a pH meter, calibrated using pH buffer 4 and 7. Organic matter was determined using the chromic acid oxidation method[6], while particle size distribution was performed on air-dry soil using the hydrometer method as described by Bouyoucos[7].

**Plant Analysis:** Plant samples identified in each of the sampling points were collected using a secateur and washed with deionised water to remove pollen, dust and soil particles. The plant samples were separated into leaves and fruits where applicable and then oven dried at 70°C to a constant weight. The dried leaves and fruits were then milled into powdery form using the laboratory stainless mill. Two grammes of the milled samples were then mixed with 2 ml of concentrated $H_2SO_4$ acid on the digestion block inside a fume cupboard[8] for digestion at 150°C for 3.5 hours. Drops of hydrogen peroxide as the oxidizing agent were added while heating until the sample became clear indicating complete digestion. The samples were allowed to cool down to temperature of 23°C and then made up to volume of 50 ml using an ultra-pure water and then swirled and transferred to a centrifuge machine for 10 minutes at 3000RPM. The extract was then poured in to a set of vials for the determination of heavy metals using Atomic Absorption Spectrophotometer (Buck 205).

**Statistical Analysis:** Data collected from the analysis of soil and plant samples were subjected to a comparison of means using analysis of variance (ANOVA) at 0.05 level of significance and treatment means were separated using Duncan Multiple Range Test (DNMRT) in Statistical Package for Social Sciences (SPSS) v.16.

## Results and Discussion

**Heavy metal concentration in soil:** Data shows the mean values of physico-chemical properties in soil at different distances from the quarry site. There was no significant difference in the soil pH ($H_2O$) relative to distances from the quarry site. The % sand distribution varied with distances from 1 m to 300 m from the quarry site and showed a higher distribution in the study area than % clay and % silt. Concentration of organic matter showed no variation from one distance to the other, being a storehouse of nutrients with exception in the control in table 1.

The concentration of heavy metals in soil in the study area is presented in table 2. The concentration of heavy metals in soil at a depth of 0 – 15 cm varied with distances (1, 50, 100, 150, 200, 250 and 300 m) to the quarry site. The concentration of Cd and Cr decreased with increase in distance to the quarry site, with the least value observed at 300 m for Cd (0.04 mg/kg) and Cr (0.03 mg/kg) while the highest value was observed at 1 m for Cd (0.21mg/kg) and Cr (0.23 mg/kg). The influence of the distance on Pb and Se concentrations in the soil did not follow a definite pattern. The concentration of Ni and Co also decreased with increasing distance from the quarry site, with the least value observed at 300 m for Ni (0.02 mg/kg) and Co (0.02 mg/kg) and the highest mean value was observed at 1 m for Ni (0.16 mg/kg) and Co (0.13 mg/kg). The effect of increasing distance on the concentration of Mn, Fe and Zn was rarely observed at 300 m from the quarry, although the values of Fe and Zn at 300 m were lower than the values at 1 – 250 m. However, Cu concentration was within a range of 3.79 mg/kg and 4.62mg/kg from the quarry site. The level of heavy metals in the control site varied significantly when compared to the various distances to the quarry site.

**Heavy metal concentration in plants:** The mean values of some nutrient contents in plants at various distances from the quarry site were shown in table 3. The concentration of P and Ca increased with increase in distance from the quarry site, with the least values observed at 100 m (P 18.46 mg/kg and Ca 1.09 cmol/kg) and the highest values were obtained at 300 m (P

30.57 mg/kg and Ca 1.78 cmol/kg). The effect of the distance on K, Mg and Na concentration in plants did not follow a definite pattern of distribution. Except for Na, the closer the distance from the quarry site, the lower the nutrient contents of the plants (table 3). However, there was a significant difference between the parameters analysed at different distances and the control values.

The concentration of heavy metals in plants is presented in table 4. There were no plant samples available at 1m and 50 m from the quarry site for analysis. There was a significant elevation of Cd content in the plant samples collected at 200 m away to the quarry site. Similarly, the Cr content of plants collected at 200 m and 300 m was also elevated, the Pb content of the plant samples at 150 m and 200 m to the quarry site was also increased compared with the distance. At 100 m away to the site, Ni could not be detected in the plant samples while Co was found in the plants irrespective of the distance. The Mg, Fe, Zn and Cu contents were more pronounced in the plants found at 150 m and 200 m away from the quarry. In all sample determinations, the heavy metals concentrations were reduced in the undisturbed forest than the concentrations in the quarry site.

**Table-1**
**Spatial Variation on the Distribution of Physico-Chemical Properties in Soil at the Quarry Site**

| Distance (m) | pH ($H_20$) | Sand | Clay % | Silt | Textural class | O. M. g/kg |
|---|---|---|---|---|---|---|
| | | 79.75ab | 14.75a | 5.63c | Sandy loam | 3.01ab |
| 50 | 6.26a | 77.00b | 16.63a | 6.38b | Sandy loam | 3.10ab |
| 100 | 6.29a | 76.25b | 16.88a | 7.00a | Sandy loam | 3.61a |
| 150 | 6.08a | 79.00ab | 14.75a | 6.00b | Sandy loam | 3.42a |
| 200 | 5.69b | 77.12b | 16.38a | 6.25b | Sandy loam | 3.04ab |
| 250 | 6.38a | 79.00ab | 14.88a | 5.50c | Sandy loam | 3.46a |
| 300 | 5.58b | 79.00ab | 14.50a | 6.50b | Sandy loam | 3.48a |
| Undisturbed forest | 6.45a | 84.50a | 11.50b | 5.00c | Sandy loam | 4.27b |

Values in the same column followed by the same letter are not significantly different (P<0.05) according to Duncan's Multiple Range Test. Unit mg/kg

**Table-2**
**Spatial Variation on the Distribution of Heavy Metals in Soil at the Quarry Site**

| Distance (m) | Cd | Cr | Pb | Se | Ni | Co | Mn | Fe | Zn | Cu |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.21a | 0.23a | 0.25a | 0.19a | 0.16a | 0.13a | 7.82ab | 8.50a | 5.01a | 3.92a |
| 50 | 0.16b | 0.13b | 0.08b | 0.08b | 0.14ab | 0.11ab | 9.01a | 7.35b | 4.83a | 4.19a |
| 100 | 0.12b | 0.11b | 0.13b | 0.04c | 0.12ab | 0.09ab | 8.90a | 8.37a | 4.93a | 4.62a |
| 150 | 0.11b | 0.10b | 0.08b | 0.03c | 0.06ab | 0.05ab | 8.45a | 8.15a | 4.88a | 4.50a |
| 200 | 0.09c | 0.08b | 0.08b | 0.03c | 0.06ab | 0.04ab | 8.75a | 8.82a | 4.93a | 4.41a |
| 250 | 0.07c | 0.05c | 0.10b | 0.04c | 0.05ab | 0.03ab | 8.69a | 8.10a | 4.77a | 3.79a |
| 300 | 0.04c | 0.03c | 0.03c | 0.02d | 0.02b | 0.02b | 5.40bc | 5.36c | 2.82b | 4.13a |
| Undisturbed forest | 0.01d | 0.02c | 0.01d | 0.01d | 0.01b | 0.01b | 4.41c | 2.85d | 2.69b | 1.28b |

Values in the same column followed by the same letter are not significantly different (P<0.05) according to Duncan's Multiple Range Test. Unit mg/kg

**Table-3**
**Spatial Variation on the Distribution of Nutrient Contents in Plants at the Quarry Site**

| Distance (m) | P mg/kg | K | Mg | Ca cmol/kg | Na | Plants |
|---|---|---|---|---|---|---|
| 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | - |
| 50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | - |
| 100 | 18.46c | 0.22c | 0.43c | 1.09d | 0.55c | *Talinum triangulare* |
| 150 | 21.62c | 0.32b | 0.67b | 1.35c | 0.77b | *Talinum triangulare* |
| 200 | 22.84c | 0.31b | 0.46c | 1.39c | 0.77b | *Talinum triangulare* |
| 250 | 28.24b | 0.24b | 0.69b | 1.71b | 0.68c | *Talinum triangulare* |
| 300 | 30.57b | 0.34b | 0.71b | 1.78b | 1.03a | *Talinum triangulare* |
| Undisturbed forest | 33.30a | 1.39a | 1.29a | 2.19a | 0.79b | *Talinum triangulare* |

Values in the same column followed by the same letter are not significantly different (P<0.05) according to Duncan's Multiple Range Test. Unit mg/kg.

**Table-4**
**Spatial Variation on the Distribution of Heavy Metals in Plants at the Quarry Site**

| Distance (m) | Cd | Cr | Pb | Se | Ni mg/kg | Co | Mn | Fe | Zn | Cu |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 100 | 0.01b | 0.01b | 0.01b | 0.01a | 0.01b | 0.01a | 12.11d | 37.42c | 31.15c | 3.91c |
| 150 | 0.01b | 0.01b | 0.02a | 0.01a | 0.01a | 0.01a | 33.72a | 72.18a | 43.02a | 5.02a |
| 200 | 0.05a | 0.02a | 0.02a | 0.01a | 0.01a | 0.01a | 27.56b | 61.83b | 37.98b | 4.62b |
| 250 | 0.01b | 0.01b | 0.01b | 0.01a | 0.01a | 0.01a | 18.88c | 46.83c | 28.02c | 3.02c |
| 300 | 0.01b | 0.02a | 0.01b | 0.01a | 0.01a | 0.01a | 10.33d | 27.08d | 25.19c | 3.03c |
| Undisturbed forest | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 11.95d | 16.51e | 13.61d | 0.66d |

Values in the same column followed by the same letter are not significantly different (P<0.05) according to Duncan's Multiple Range Test.

**Discussion:** The assessment of the concentration of heavy metals in soils showed significant differences between samples in different distances. Results of the this study showed that there was a marked decrease in concentration of Cd, Cr, Pb, Se, Ni, Co, Mn, Fe, Zn and Cu in soil as the sampling distance increases. The highest value of Cd (0.21 mg/kg) observed at 1m from the study site was lower than 0.63 mg/kg of Cd found 100 m from limestone quarry in Southwestern Nigeria[9], which was higher than 0.01 mg/kg at 1 m from Oyeama coal mine, Nigeria[10] and 0.15 mg/kg in Beijing[11], as well as the average concentration (0.06 mg/kg) in worldwide soils[12]. Soils at a distance of 300 m from the quarry plant site were still contaminated, but the concentration decreased exponentially with the distance. In Les Maine mine sites in Southern France, such non-linear decreasing metal concentration in topsoils with increasing distance to the emission source have been shown[13]. Cd concentration in this study could lead to stunted growth and chlorosis[14] of the plants and also high concentration intake of Cd can cause *itai itai* disease in man.

At 1 m from the quarry plant, Cr, Pb, Se and Ni showed the highest mean values from the corresponding distance in the site. These values were 2 to 5 times lower than the values of similar heavy metals of Cr, Pb, Se and Ni found in top soils sampled at the derelict Udege mines of Nasarawa State, Nigeria[15]. Higher values of Co at 100 m away from a limestone had also been reported by Etim and Adie[9].

Soil samples collected between 1 m and 150 m appeared to show higher concentration for most heavy metals, than samples father away, probably because of their proximity to the exploration area and leaching of metals from quarry tailings[9] (Etim and Adie, 2012). The composition of Mn, Fe and Zn sampled at various distances are decreasing with increasing distance except for Cu. Cu is an essential substance to human life but in high doses can cause anemia, liver and kidney damage.
However, the concentration of heavy metals in soil in dry season were significantly ($P < 0.05$) higher than concentration of metals in wet season. This is in agreement with the findings of Yahaya *et al.*[16]. This might be due to the run off effect that is capable of removing heavy metals from the site and the effect of rainfall which may facilitate the dilution of soil solution during the wet season and intense evaporation in the dry season makes soil solution more concentrated. Concentration of heavy metals was highest in the south direction of the study area with the exception of Mn which was highest in the east. This may be due to the topography of the area, atmospheric influence and farm land cultivation in the south and east direction of the study area.

**Plants:** Metal toxicity in plants varies with plant species, plant properties, specific metals, soil composition, pH and metals considered to be essential for plants growth[17]. They reduce the availability of nutrients to plants when present in high concentration in soils, as they affect biological processes in soil such as litter rate decomposition, soil respiration and nitrogen mineralization[18].

The concentration of heavy metals (Cd, Cr, Pb, Se, Ni and Co) in Talinum triangulare in the study area was below the general acceptable toxic levels in plants[19]. Selenium (Se), Ni, and Co are of very low values in the plant samples. This might be due to the selective absorption mechnism of the metals by various crops. The concentration of Cr fell within the natural occurrence in plant food[20]. The level of Cu in plants in the study area from the results, is lower than the Cu content in plants reported by Oluyemi *et al.*[21], and conforms to the Cu concentration levels in plants and plant foodstuffs[19,20].

The metal uptake in plants is influenced by the type of metal, plant species and plant part[21]. The study illustrates that the plant species Talinum traingulare accumulated different concentrations of heavy metals at different distances from the quarry. Zinc (Zn), Fe and Cu are essential micro nutrients to higher plants and are involved in several metabolic processes[22]. Above certain threshold these elements become toxic, but, due to its role of micro nutrient, plants cannot exclude its uptake. Leaf chlorosis, poor nutritional quality, stunted growth, as well as reduction in biomass production are symptoms and signs of metal toxicity to plants[23] which are not observed yet in the studied plants.

However, the absence of plants at 1 m and 50 m from the quarry plant may be as a result of closeness to the quarrying and processing unit. The vegetation within this distance must have accumulated enough dust, tailings and heavy metals over time, blocking the stomata on the leaves and tend to hinder photosynthetic processes, that may have resulted in death of the vegetation. Also, absence of plants during dry season could be attributed to the low water table and dust particles which may cause water stress and lack of nutrients uptake by the plants and leads to the death of plants during dry season.

## Conclusion

The results showed that the concentration of heavy metals from soil samples were decreasing with increasing distance from 1m to 300m with the exception of Pb, Fe and Cu, which decreased and increased randomly at various points. This may be due to the landscape topography, soil chemical composition, regional and microclimate effects on the study area. However, the level of concentration of heavy metals in the study area was observed to be lower than the concentration of metals in other quarrying/mining industrial site such as the limestone quarry in Southwest (Ibadan), Nigeria. This can be attributed to the number of years the quarry plant in the study area has been in operations.

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