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Evaluation of Heavy Metals Ions in *Calopogonium mucunoides*, *Manihot esculenta*, *Psidium guajava* and *Mangifera indica* Plant Species Within Quarry Site, Akamkpa, Nigeria and Phyto-remediation Potential

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Abstract: *The exploration of mineral resources like quarrying has a serious negative impact on the ecosystem. Phytoremediation has become one of the eco-friendly mitigation measures used to revegetate heavy metal-polluted soil. This study evaluates the levels of heavy metals in selected plant species (Calopogonium mucunoides, Manihot esculenta and Psiduim guajava L and Mangifera indica L with potential for phyto-remediation within SEEPCO Quarry site, Obung, Akamkpa, Nigeria. The plant's leaves were harvested with secateurs within the vicinity (0km) of the quarry, while the control sample was harvested (2.5km) away from any quarry. Two (2) soil samples, each weighing 1 kg, were scooped using an auger from a depth of 0–15 cm at a distance of 0km and 2.5km (control) away from the quarry crushing area. Heavy metal content in the soil and plant samples was determined using the Atomic Absorption Spectrophotometric (AAS) method. Results: The results showed that Nickel concentration in Calopogonium mucunoides, Manihot esculenta C., guava Psiduim guajava L. and Mangifera indica L harvested in the quarry site (0km) had concentration of (4.58± 0.02, 9.75± 0.01, 12.75± 0.00, 24.76± 0.00) mg/kg respectively and was higher in concentration than the samples harvested from the control site (2.5km) with (1.82± 0.02, 4.18± 0.01, 2.15± 0.04, 7.23± 0.01) mg/kg respectively. The results also showed that all heavy metals in the soil samples investigated (Nickel, cadmium, Zinc, Lead and copper) at the sampling point of (0km) recorded higher levels of heavy metal (3.15± 0.01, 7.95± 0.02, 20.13± 0.02, 31.66± 0.03, 89.89± 0.03) mg/kg respectively than those at the control site (2.5km) with (2.11± 0.00, 1.23± 0.01, 11.95± 0.02, 4.76± 0.00, 80.45± 0.01) mg/kg respectively. This suggests that the concentration of heavy metals in the plants and soil declines as the distance from the quarry increases. The high concentration of heavy metals in the parts of the plants may be due to the absorption/ phytoremediation ability of the plants.*

Keywords: *Plant species, Heavy metals, Soil, Quarry, contamination*

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1.0 Introduction

In Nigeria, mineral resources are one of the major sources of income and have greatly contributed to the country's economy. Despite the benefits of generating significant revenue for the economy activities of humans (such as deforestation, quarrying and burning of fossil fuels), the exploration of mineral resources is having a serious negative impact on the ecosystem, as environmental and safety measures are not usually observed when carrying out these activities (Peter *et al.*, 2018). Effluents are one of the factors that pollute the environment and significantly affect soil fertility, plant physiology, development, and productivity. They are released into the environment, causing surface and subsurface water contamination. They eventually find their ways into the food chain through uptake by plants in small quantities, which accumulate across trophic levels, thereby posing serious health dangers to man, public health and the environment (Adepoju, 2002). Industrial waste is a major source of soil pollution that originates mostly from mining, chemical and metal processing industries. These wastes include chemicals like effluents, heavy metals, phenolic etc. (Ekpo *et al.*, 2012).

Anthropogenic activities such as mining, quarrying and other industrial operations contribute significantly to environmental contamination. These anthropogenic activities by man have induced the accumulation of heavy metals in soil, which invariably have resulted in the disturbance of living organisms' biochemical and physiological function (Ekpo *et al.*, 2012).

Quarrying as a land use method is concerned with the extraction of non-fuel minerals from rocks. Soils formed in quarries, among other unfavourable features, have high levels of heavy metals. Quarry effluents are typically rich in minerals and pollutants like heavy metals, suspended solids, and acidic or alkaline substances, which can influence the growth and chemical composition of plants (Nzegbule *et al.*, 2007; Zhao, F. J., 2016). Naturally occurring toxic substances embedded in rocks and minerals are usually released during the quarry process in the form of dust, gaseous emissions, and airborne particulates (Kalu, 2018). Soil polluted with heavy metals has become common across the globe due to an increase in geological and anthropogenic activities. Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, sewage sludge pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition (Khan *et al.*, 2008, Uffia, *et al.*, 2013). Heavy metals are non-biodegradable; they persist in the environment, have the potential to enter the food chain through uptake by plants and eventually may accumulate in the human body through biomagnification (Akubugwo, 2012). Phytoremediation is an eco-friendly approach and mitigation measure used to revegetate heavy metal polluted soil in a cost-effective way. Phytoremediation involves the use of plants to extract and remove elemental pollutants or lower their bioavailability in soil (Berti and Cunningham, 2000; Ali *et al.*, 2013). Since the onset of human existence, plants have been dependable sources of sustenance to human beings. Plants play an important role as sources of food and maintenance of good health and ecosystem services. In Nigeria and most African countries, indigenous people traditionally use a wide range of plants (particularly non-timber forest products) as food and medicine (Uffia, *et al.,* 2021; Udofia, *et al.,* 2023; Nsien, 2024). The enormous genetic diversity of the indigenous leaf vegetables in Nigeria has been documented by many workers (Elijah *et al*., 2023; Adebooye *et al.*, 2003).

Wild bean *(Calopogonium mucunoides)* is a leguminous plant with distinct morphological and ecological characteristics, making it an important species in various agricultural and environmental applications. It belongs to the family Fabaceae, which is one of the largest plant families, commonly known as the legume, pea, or bean family. *Calopogonium mucunoides* is known for its ability to fix nitrogen in the soil via a symbiotic relationship with Rhizobium bacteria in its root nodules. *Calopogonium mucunoides* is a species of leguminous vine native to tropical and subtropical regions. Legumes are staple foods for many people in different parts of the world. The seeds have an average of twice as much protein as cereals by percentage and usually contain a more balanced profile of essential amino acids (Uffia *et. al.*, 2024; Awak *et al.,* 2017). *Calopogonium mucunoides* possesses important agronomic traits, such as tolerance to high and low temperatures and adaptation to different soil and climate conditions (Singh, 2020).

Cassava *(Manihot esculenta* Crantz) is a woody perennial root crop, and it is being cultivated abundantly in the tropics and subtropics, where it plays a primary role in human diet as well as for use in animal feeds. Cassava is easily propagated using stem cuttings where adventitious roots form and the plant grows up to a height of 5m (Eggum, R. O. 1970; Alcantaraa *et al*., 2017). It is the major staple food crop in Nigeria, supplying about 70% of the daily calories of about 50 million Nigerians. *Manihot esculenta* Crantz survives long droughts by shedding its leaves and going dormant until rain returns. It is also a plant capable of growing in soils that is very acidic, low in nutrients and high in toxic Aluminium compounds (Udoetok *et al*., 2012).

Guava *(Psidium guajava* L.) is a Neotropical fruit that is widely consumed around the world. However, its evolutionary history and domestication process are unknown. Guava needs full sunlight, warm temperatures, and well-distributed rainfall throughout the year to grow, but tolerates drought. *Psidium guajava* L. is an important perennial fruit tree whose distribution extends from Mexico and the Antilles to Argentina and Uruguay (Landrum, 2017). It is valued for fresh consumption because of the fruits' aroma and sweet flavor, but many of its products (pulp concentrate or jelly) have export potential. The consumption of guava fruits around the world and their medicinal properties have made it the most important among the minor tropical fruits (Arévalo-Marín, 2021).

Mango (*Mangifera indica* L) is one of the most important fruit crops worldwide. It is the most important species of the genus *Mangifera*, which produces the most delicious fruit called the mango. Morphologically, the genus could be separated into two sections based on the character of the flower disc: the first, with 34 species, has flowers with a well-developed swollen disc, and the second, with 7 species, has an obsolete or pedicellate disc. The mango is a member of the Anacardiaceae family, which includes poison ivy, cashews, and pistachios (Om Prakash, 2005).

Since heavy metal contamination poses a serious threat to human health and the ecosystem because of its toxic nature, therefore, remediation of land contamination is of paramount importance. The present study was designed to evaluate the levels of heavy metals in selected plant species (*Calopogonium mucunoides*, *Manihot esculenta* and *Psiduim guajava* L and *Mangifera indica* L with potential for phyto-remediation within

SEEPCO Quarry site, Obung, Akamkpa, Nigeria.

2.0 Materials and Methods

2.1 Study Area

The study was conducted in the Obung community in Akamkpa LGA of Cross River State. The area lies between latitudes 6°50N and 07°30S. The maximum annual mean daily temperature of the area is between 29°C and 34°C. One of the major companies carrying out quarrying in the area is SEEPCO (Sterling Oil Exploration and Energy Production Company (NPC, 1999; UNEP, 2007).

2.2 Sample collection

Samples were collected during the dry season, but before collections, pans were kept for 48 hours at different distances in order to ascertain the amount of dust produced during quarrying process that could settle on the pans to delineate the position where the samples were to be collected. The pans were kept 0km and 2.5km away from the quarry site. This was done to determine the extent of the spread of dust arising from the quarry operation and to establish the point of control. The contents of the pan were checked after the 48hours and a point without settlement of dust particles was used as control. Plant species of economic value were identified to be occurring in the two sampling positions were selected as screening material for levels of heavy metal. The leaves of *Calopogonium mucunoides*, *Manihot esculenta* C. , *Psiduim guajava* L. and *Mangifera indica* L were harvested with secateurs within the vicinity (0km) of SEEPCO (Sterling Oil Exploration and Energy Production Company) quarry at Obung community, while the Control sample was harvested (2.5km) away from any quarry site. The fresh leaves were washed and drained. Two (2) soil samples, each weighing 1 kg, were scooped using an auger from a depth of 0–15 cm at a distance of 0km and 2.5km (control) away from the quarry crushing area (Poggio *et al*., 2008. Each soil sample was collected in a labeled polyethylene bag. The soil and plant samples were oven-dried at 60°C for a day, pulverized to coarse powder using a mortar and pestle and sieved using a 2 mm sieve and homogenized. The homogenized soil samples were stored in clean and dry containers till digestion. The homogenized powdered samples were weighed, milled and digested and extracted using 0.1% perchloric acid for further analysis. The digested samples were analyzed for heavy metals using the atomic absorption spectrophotometer model (AAS) Schimadu A-A6701 (Skoop 2007; Street, 2008).

2.3 Data Analysis

Results obtained were analyzed using descriptive and inferential statistical techniques. Descriptive techniques were used to represent the data for easy comparison.

3.0 Results and Discussion

3.1 Results

The levels of heavy metals investigated in the leaves and soils of the collected samples of *Calopogonium mucunoides, Manihot esculenta, Psiduim guajava* and *Magnifera indica* were based on dry weight and the results are presented in the tables below. The results are mean of three replicates as presented in Table 4.I below. Table 1 revealed that Nickel concentration in Wild beans (*Calopogonium mucunoides*), Cassava (*Manihot esculenta* C.), guava (*Psiduim guajava* L.) and Mango (*Mangifera indica* L) harvested in the quarry site (0km) had higher concentration. of (4.58± 0.02, 9.75± 0.01, 12.75± 0.00, 24.76± 0.00) mg/kg respectively and was higher in concentration than the samples harvested from the control site with (1.82± 0.02, 4.18± 0.01, 2.15± 0.04, 7.23± 0.01) mg/kg respectively. Nickel concentration in the quarry site (0km) and the control site (2.5km) was still within WHO permissible level of 10 mg/kg except *Psiduim guajava* L and *Magnifera indica* L that was higher than WHO permissible level. Cadmium concentration in all the plants samples was higher than WHO permissible level of 0.02 mg/kg, except in *Calopogonium mucunoides (*0.01± 0.01 mg/kg) harvested from the control site. Zinc concentration in all the plant samples was also higher than WHO permissible level of 0.60 mg/kg, except in *Calopogonium mucunoides (*0.32± 0.00 mg/kg) harvested from the control site. The same trend was seen in the concentration of Pb^{2+}, which showed higher concentrations for samples from the quarry site(0km) than control site (2.5) and higher than WHO permissible level of 0.1 mg/kg, except in *Calopogonium mucunoides (*0.05± 0.45mg/kg) harvested from the control site. Copper concentration was within WHO permissible level of 10.00mg/kg except in *Calopogonium mucunoides (*19.20± 0.01 mg/kg) and *Magnifera indica* L (19.49± 0.45 mg/kg) harvested from the control site. This indicates that the quarry effluents might contain more sources of these metals.

Table 1:Mean Concentration (mg/kg) **of some heavy metals in selected plant species**

Plant Species	Location	Ni	Cd	Zn	Pb	Cu
Calopogonium mucunoides	Control (2.5 km)	1.82 ± 0.02	0.01 ± 0.01	0.32 ± 0.00	0.05 ± 0.45	4.76 ± 0.01
	Quarry (0 km)	4.58 ± 0.02	0.63 ± 0.06	7.24 ± 0.05	5.37 ± 0.00	19.20 ± 0.01
Manihot esculenta	Control (2.5 km)	4.18 ± 0.01	2.25 ± 0.01	1.75 ± 0.03	2.35 ± 0.00	5.30 ± 0.47
	Quarry (0 km)	9.75 ± 0.01	12.15 ± 0.00	12.13 ± 0.03	10.15 ± 0.02	9.00 ± 0.01
Psidium guajava	Control (2.5 km)	2.15 ± 0.04	1.46 ± 0.01	1.35 ± 0.03	2.15 ± 0.01	5.20 ± 0.04
	Quarry (0 km)	12.75 ± 0.00	11.87 ± 0.03	10.68 ± 0.00	6.90 ± 0.01	9.16 ± 0.04
Mangifera indica	Control (2.5 km)	7.23 ± 0.01	1.15 ± 0.03	2.35 ± 0.00	1.76 ± 0.01	4.37 ± 0.02
	Quarry (0 km)	24.76 ± 0.00	8.18 ± 0.04	22.16 ± 0.01	7.15 ± 0.02	19.49 ± 0.45
WHO Limit	-	10.00	0.02	0.60	0.10	10.00

** **Values are presented as means ± standard deviation (SD).**

Table 2 revealed that all heavy metals in the soil samples investigated (Nickel, cadmium, Zinc, Lead and copper) at the sampling point of (0km) recorded higher levels of heavy metal (3.15± 0.01, 7.95± 0.02, 20.13± 0.02, 31.66± 0.03, 89.89± 0.03) mg/kg respectively than those at the sampling point of 2.5mg/km (2.11± 0.00, 1.23± 0.01, 11.95± 0.02, 4.76± 0.00, 80.45± 0.01) mg/kg respectively but only level of heavy metals in Cadmium and Copper were higher than WHO permissible limit of 0.80 mg/kg and 36.00 mg/kg respectively at the sampling point of (0km) and at sampling point 2.5mg/km. This suggests that the concentration.of this heavy metals decline as the distance from the quarry increases.

Table 2 Mean Concentration (mg/kg) of some heavy metals in the soil at different sampling points from the quarry

Sampling positions	Ni (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)
0km	3.15± 0.01	7.95± 0.02	20.13± 0.02	31.66± 0.03	89.89± 0.03
2.5km (Control)	2.11± 0.00	1.23± 0.01	11.95± 0.02	4.76± 0.00	80.45± 0.01
WHO(mg/kg)	35.00	0.80	50.00	85.00	36.00

****Values are means ± SD**

4.2 *Discussion*

Quarry effluents are typically rich in minerals and pollutants like heavy metals, suspended solids, and acidic or alkaline substances, which can influence the growth and chemical composition of plants (Zhao, 2016). Quarry effluents can induce various physiological changes in Wild beans (*Calopogonium mucunoides*), Cassava (*Manihot esculenta* C.), guava (*Psiduim guajava* L.) and mango (*Mangifera indica* L.). Heavy metal toxicity in the effluent can disrupt chlorophyll biosynthesis and reduce photosynthesis rates. Heavy metals interfere with the electron transport chain in chloroplasts, reducing the plant's ability to generate energy. In this research, *Calopogonium mucunoides* collected within the quarry site had high concentration of Copper, Zinc and Nickel which can cause an imbalance in nutrient uptake, particularly reducing the uptake of essential nutrients such as nitrogen (N), phosphorus (P), and potassium (K) (FAO, 2010; Igwenagu-Ifeanyi, 2021). The high values recorded in this research clearly showed that probably, the plant harvested within the quarry vicinity was probably contaminated with heavy metals. This is because plants growing around contaminated areas take up heavy metals by absorbing minute deposits on the parts of the plants exposed to the air in the polluted environments and during nutrient uptake from contaminated soils (Zurayk *et al*., 2001). *Manihot esculenta* C., *Psiduim guajava* L. and *Mangifera indica* L. might accumulate toxic metals from quarry effluents, especially Lead and Cadmium in high concentration, which can affect their growth and survival (Singh & Kalamdha, 2011). Most of the metals were observed to be above WHO permissible limits (WHO, 1999), especially those harvested within the quarry vicinity, which suggests that the waste generated from the quarry is a major contributor of heavy metals to the vegetation and soil. This implies that the activities on the quarry site are harming the vegetation. The higher concentrations of toxic metals recorded in sampling positions within the quarry site confirm the relationship between metal concentrations and distance from the quarry, which is in good agreement with the report of Ekpo *et al*. (2012). Most of the Heavy metals assessed here were lower in concentration compared to work reported by Nzegbule *et al.* (2007). This study is in line with the report of Zhang *et al.* (2018) that heavy metals like Lead (Pb), Cadmium (Cd), Copper (Cu), and Zinc (Zn) are prevalent in environments impacted by industrial activities, mining, and agricultural runoff. Wild beans (*Calopogonium mucunoides*), Cassava (*Manihot esculenta* C.), guava (*Psiduim guajava* L.) and mango (*Mangifera indica* L.) have shown some capacity for heavy metal accumulation in their tissues, an indication that it can be beneficial for remediation purposes since they are capable of absorbing and storing large amounts of heavy metals without suffering from toxicity (Zhang *et al.,* 2018; Baker, 2019). The study also affirmed the work of Alcantaraa *et al.*,

(2007) that *Manihot esculenta* Crantz (cassava) has the potential to phytoextract Hg and Au from the soil. The level of heavy metals in vegetables varies by the ability of plants to selectively accumulate some of these elements, indicating the phytoremediation potential of the plant species. Bioavailability of the elements depends on the nature of their association with the constituents of a soil (Aken, 2019; Yang *et al*., 2022). The high concentration of heavy metals in the parts of the plants may be due to the absorption/ phytoremediation ability of the plants to get the trace heavy metals from the polluted soils, which is similar to the work of Milkessa (2013) who reported from his research that concentration of zinc in soil samples range between 60.09-414.12 mg/kg

Comparison of heavy metal level in the soil samples within the quarry site with that of the control soil samples indicates that the higher levels obtained from all samples could possibly be attributed to the high levels of heavy metal in the quarry effluents. Golow (2002) reported that plants that grow in mining areas have enhanced concentrations of heavy metals/metalloids as a consequence of soil, water and atmospheric contamination. Decline in concentration of heavy metals as the distance of quarry increases further shows that quarrying operation is strongly associated with the build- up of metal in soil and plants. This study also affirmed the work of Nzegbule (2007) who reported that in most instances concentration of heavy metal in soil is lesser than that of plants.

4.0 Conclusion

Heavy metal contamination has posed a serious threat to human health and the ecosystem because of their toxic nature, therefore, remediation of land contamination is of paramount importance. The levels of heavy metals in selected plant species (*Calopogonium mucunoides*, *Manihot esculenta* and *Psiduim guajava* L and *Mangifera indica* L with potential for phyto-remediation within SEEPCO Quarry site, Obung, Akamkpa, Nigeria were studied. Understanding these determinants is essential for monitoring metal pollution, utilizing plants in phytoremediation, and ensuring food safety. The effects of quarry effluents on plants and soil may lead to environmental and health risks posed by industrial pollution. Immediate action, including the use of phytoremediation strategies, proper waste management, and stricter environmental regulations, is crucial for minimizing the long-term impact of these pollutants on the ecosystem and public health. The careful monitoring and management of quarry effluents will help protect both the environment and human communities from the harmful effects of heavy metal contamination. In general, the plants accumulated and tolerated high amounts of lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) in their leaves, especially making Cassava (*Manihot esculenta* C.), guava (*Psiduim guajava* L.) and mango (*Mangifera indica* L) making them potential candidate for phytoremediation in polluted soil. It is therefore recommended that cash crops and related crops should not be planted close to where quarrying, dredging industrial waste and other anthropogenic activities to save the life of the consumers except for the purpose of phytoremediation.

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