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Assessment of Heavy Metal Contamination and Risk Associated with Quarrying Activities in Marksino Concession Area, Akamkpa

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ABSTRACT: *This study evaluates the environmental risks of quarrying activities in the Marksino Concession area, Akampka, with a focus on heavy metal contamination of the soil. Soil samples were collected at various distances from the quarry site and analyzed using atomic absorption spectrophotometry (FAAS; PG990) to determine concentrations of lead, chromium, copper, cadmium, cobalt, nickel, arsenic, and zinc. Pollution indices and ecological risk factors were calculated, along with hazard quotients and indices for non-carcinogenic impacts on children and adults.Results indicate that contamination values for all metals were below one, suggesting no significant impact at the sampling points. The geo-accumulation index values also indicated no significant impact for all metals. Furthermore, hazard quotient (HQ) and hazard index (HI) values for all metals were below the permissible value of 1, indicating non-carcinogenic risks for residents. However, children showed higher HI values compared to adults, emphasizing the need for targeted measures to protect this vulnerable group. Continuous monitoring and mitigation efforts are crucial for sustainable quarrying activities and prevention of environmental hazards in the Marksino Concession area.*

KEYWORDS: heavy metals, contamination, environment, natural, plastic

INTRODUCTION

One of the primary anthropogenic sources of heavy metals is mining (Naggar et al., 2018). Quarrying is a major land-use activity in the Akamkpa Local Government Area of the Cross River

(Ukpong, 2012). The Local Government Area undoubtedly has the highest deposits of limestone, granite, and other minerals in the cross-river state. Due to the huge deposits of these minerals, the area is home to many quarrying companies that produce large tones of chippings of different sizes for different engineering and construction projects within the Cross River State and nearby states of the South-South and Southeastern regions of Nigeria. However, with such a level of mechanical exploration of the mineral deposits in the area, the environmental and health consequences may have been considered a matter of concern. Quarrying activity provides a large tone of chippings of various sizes, as well as accompanying toxic wastes that affect both the environment and humans (Ekpo et al., 2012).

Mechanical mining in Nigeria began in 1939 with privately owned companies (Nwogha et al., 2017). Since then, health and environmental degradation due to mining or quarrying has been on the rise, with or without elaborate research aimed at creating awareness of the associated health and environmental implications of quarrying to man. Mechanized mining or quarrying has been in practice for many years in the Akamkpa Local Government Area. Such quarrying operations in developing countries, such as ours, have caused environmental hazards and have generated many wastes and different types of pollutants. Mining activities, particularly quarrying, have left devastated landscapes and exposed fertile lands, wells, streams, rivers, and food to minerals or heavy metal contamination (Nwogha, 2017).

Heavy metals enter the human body through the gastrointestinal tract, skin, or via inhalation. Toxic metals have proven to be a major threat to human health, mostly because of their ability to cause membrane and DNA damage and perturb protein function and enzyme activity. They find their way into our food when they are taken up by consumable plants, travel through the food chain or trophic level or/and contamination during food processing (Witkowska et al., 2021). Heavy metals are environmental contaminants that are found in small amounts in nature, but are harmful to humans and other living beings at large concentrations (Shakya and Agarwal, 2020). Unlike energy, which tends to deplete and become more dispersed at each step in the trophic level, to ensure safe food crops and feed for human and animal consumption, information on the heavy metal concentrations in the soil within and around quarry sites must be generated and given utmost publicity owing to the carcinogenic and other health effects of heavy metals on humans. They are usually present in trace amounts in natural waters, but many of them are toxic, even at very low concentrations. At high levels of toxicity, both essential and nonessential heavy metals can damage cell membranes, alter enzyme properties, disrupt cell function, and damage DNA structure (Wu et al., 2016). Heavy metal pollution in soil is frequently induced by human activities, such as industrial development, urbanization, sewage sludge consumption, composting, and agricultural chemical fertilizers, and when released into the environment, heavy metal pollution mostly ends up in the soil (Zorpas et al., 2021). The emission of greenhouse gases from industrial areas, mines, waste disposal, diesel and lead paint, agricultural fertilization applications, animal manure, sewage sludge, pesticides, sewage irrigation, coal combustion residues, petrochemicals, and atmospheric sediments can contaminate soil with heavy metals and metalloids (Gabarron et al., 2017). These metals have a long life in soil. Unlike organic pollutants, which are oxidized to carbon dioxide by

microbial activity, most heavy metals do not undergo microbial or chemical degradation and all heavy metal concentrations remain in the soil for a long time (Bolan and Duraisamy, 2003). Contamination of the environment by heavy metals is a more pronounced issue and has been reported to pose both intended and unintended impacts on living organisms. An increase in economic activities due to population growth and urbanization has been linked to a rapid increase in the presence of heavy metals in the environment. In most African countries, anthropogenic activities are a major source of heavy metal input into the environment. For example, Mercury in Algeria, Arsenic in Namibia and South Africa, Tin in Nigeria and Zaire and Copper in Zambia are the major heavy metal pollutants emanating from quarrying and mining operations in general (Taylor et al., 2005). However, of all the anthropogenic sources of heavy metals, Pradhan et al. (2020) stated that mining/quarry activities contribute to or release the highest number of heavy metals into the environment compared to other sources.

Quarrying is an activity that has immediate and long-term negative environmental impacts. These operations are associated with landscape destruction and deformation and the release of toxic minerals from the deep earth crust into the environment. However, these negative impacts are often ignored because of the enormous economic benefits of the operation.Shakir and Mohamed (2013) stated that quarrying has resulted in an increase in infrastructural and mineral resource development in several regions.However, Moibi (2007) stated that quarrying causes soil compaction, landscape degradation, soil erosion, and loss of vegetation and soil fauna. Similarly, Ekpo et al. (2012) enumerated the destruction of wildlife and biodiversity, loss of fertile soil, air and water pollution, degradation of farmland, impairment of human health, forced pollution migration, and damage to aquatic ecosystems as negative impacts of quarrying on the environment. Several studies (Ekpo et al., 2012; Ezenwa et al., 2014 and Tiimub et al., 2015; Nwogha et al., 2017) have reported increase in heavy metal content of soil and plant because of quarrying activities. Tiimub et al, (2015) obtained significantly ($p < 0.05$) higher and different metal concentration on quarry dust than the control dust in Ashanti region of Ghana.

Heavy metal contamination is becoming a serious issue of concern worldwide as it has gained momentum because of the increase in the use and processing of heavy metals during various activities to meet the needs of the rapidly growing population. Natural and human activities contaminate the environment and its resources, discharging more than what the environment can handle (Masindi et al., 2018), and health and mortality problems will break out, as well as the disturbance of food chains. Some metals are needed in small amounts for the body to function normally, but too many of them can cause poisoning (Egorova and Ananikov, 2017). They may frequently react with biological systems by losing one or more electrons and forming metal cations that have an affinity for the nucleophilic sites of vital macromolecules. Several acute and chronic toxic effects of heavy metals affect different body organs, gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, vascular damage, immune system dysfunction, birth defects, and cancer are examples of the complications of heavy metals toxic effects. Simultaneous exposure to two or more metals may have cumulative effects (Fernandes Azevedo et al. 2012; Cobbina et al. 2015). Exposure to high doses of heavy metals, particularly mercury and lead, may

induce severe complications, such as abdominal colic pain, bloody diarrhea, and kidney failure (Bernhoft, 2012).Heavy metals, including lead, aluminum, mercury, copper, cadmium, nickel, and arsenic, are first absorbed by phytoplankton, bacteria, fungi, and other small organisms, and then eaten by larger organisms. Eventually, by consuming crops grown in contaminated soils, they enter the food chain of consumers and endanger human and animal health (Cimboláková, 2020).

Most heavy metals are distributed in the body from the blood to tissues (Florea et al., 2006). Lead is carried by red blood cells to the liver and kidney and is subsequently redistributed to the teeth, bone, and hair, mostly as phosphate salt (Morais et al., 2012). Cd initially binds to blood cells and albumin and subsequently binds to metallothionein in the kidney and liver tissues. Following its distribution from the blood to the lungs, arsenic is distributed in the blood and accumulates in the heart, lung, liver, kidney, muscle, and neural tissues as well as in the skin, nails, and hair. For example, lead and zinc are known to cause health problems, ranging from hematological to neurological problems (Tchounwou, 2014). Pb can be hazardous to the body in trace quantities because it can affect virtually all organs in the body. At higher concentrations, zinc can be toxic, thereby leading to reduced cell division rates and the uncoupling of cell division and photosynthesis (Fisher et al., 1981).The accumulation of nickel and nickel compounds in the body through chronic exposure may be responsible for a variety of adverse effects on human health, such as lung fibrosis, kidney and cardiovascular diseases, and respiratory tract cancer (Zambelli et al., 2016).The fact that several metals have emerged as human carcinogens is another important aspect of chronic exposure. While the exact mechanism is unclear, aberrant changes in genome and gene expression are suggested as underlying processes. Carcinogenic metals such as arsenic, cadmium, and chromium can disrupt DNA synthesis and repair (Koedrith et al., 2013). The toxicity and carcinogenicity of heavy metals are dose dependent.In health risks assessment, it is necessary to identify the potential sources of risk - agents in the environment and estimate the amount of risk those in contact with the human environment. The determination of the health consequence of exposure is also very necessary (Khan et al., 2015).

Aim of the Study

This research work is aimed at investigating the level of toxic metal pollution, and carry out a risk assessment study of metals identified within the Marksino quarry concession area in Akamkpa, Cross River State.

Objectives of the Study

The specific objectives of the study are to:

1. To determine the concentrations of heavy metals at the quarry site.
2. To estimate heavy metal contamination and pollution levels using the enrichment factor (EF), geoaccumulation index (Igeo), and pollution load index (PLI).
3. To estimate the Average daily dose values for heavy metals in quarry soil via different exposure pathways for children
4. To assess human health risks (non-carcinogenic and carcinogenic) associated with each heavy metal in children and adults at quarry sites.

MATERIALS AND METHOD

Study area

The study area is located at the old Netim in the Akamkpa Local Government Area of the Cross River State, Nigeria. The area is in the southern part of the Cross River State and lies between latitude 5°24' N and Longitude 8°12'' E (Cross River State Diary 2005; Cross River State Bureau of Land 1997).

Sample Collection

Samples were collected at four different positions around the rock mining sites. The first point (MS1) used as a control was taken away from the quarry site, the second point (MS2) was 0m within the quarry site, the third point (MS3) was 100m and the fourth point (MS4) was 200m away from the quarry site. At each of the sampling positions (0m, 200m, 100m and outside the quarry site), 50 g soil samples were collected using a hand-driven auger from a depth of approximately 0–15 cm and packaged in clean polyethylene bags for onward analysis. The samples were taken to the laboratory, air-dried, sieved with a < 0.25 mm marsh, and then placed in an electric oven at a temperature of approximately 40 °C for approximately 30 min. The resulting fine powder was stored in desiccators prior to the analysis of heavy metals.

Determination of heavy metal concentration at study site

The concentrations of Lead (Pb), Chromium (Cr), Copper (Cu), Cadmium (Cd), Cobalt (Co), Nickel (Ni), Vanadium (V), Zinc (Zn), Selenium (Se) and Arsenic (As) were determined using atomic absorption spectrophotometry (FAAS). PG990) (Mafuyai et al., 2015). Various indices to assess the current pollution status and carcinogenic and non-carcinogenic risks were calculated using the models stated below.

Pollution Indices

Contamination factor (C_f), degree of contamination (Cd), geo-accumulation index (Igeo) and pollution load index (PLI) were the contamination indicators used for the assessment of the soil pollution in the present study.

Contamination factor (Cf)

The contamination factor of the studied site was estimated using the formula below as described by Hakanson (1980).

$$C_f = \frac{C_{metal}}{C_{backgrund}}$$

Where: C_f = contamination factor, C_f < 1 = low contamination factor, C_f ≤1<3 moderate contamination factor, 3≤ C_f < 6 = considerable contamination factor, C_f ≥ 6 = very high contamination factor.

Degree of contamination (Cd)

Degree of contamination (Cd) was also estimated according to the method of Hakanson (1980) through the equation below.

$$C_d = \sum_{i=1}^{n} C_f$$

Where: Cd<7 = low degree of contamination, 7≤Cd<14 = moderate degree of contamination, 14 ≤ Cd < 28 = considerable degree of contamination, Cd ≥28 = very high degree of contamination.

Pollution load index (PLI)

The pollution load index (PLI) of the studied heavy metals were calculated according to the formula below as described by Tomlinson et al., (1980)

$$PLI = \left(CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x } ... \text{ x } CF_n \right)^{1/n}$$

Where: PLI<1 = No metal pollution, PLI = 1 = Baseline levels of pollutants, PLI >1= indicates a polluted condition.

Geo-accumulation index (Igeo)

Geo-accumulation Index (Igeo) was calculated according to Muller (1969).

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 * B_n} \right)$$

Cn stands for measured concentration of the examined metal n in the soil and Bn stands for reference value or geochemical background concentration of the metal n (mg/kg) in the soil. Factor 1.5 was used to take into account the possible variations in background values for a given metal in the environment and the small anthropogenic influences.

Where: Class 0 = Igeo <0 = practically uncontaminated, Class 1= 0 < I_{geo} < 1 = uncontaminated to moderately contaminated, Class 2 = 1 < I_{geo} < 2 = moderately contaminated, Class 3 = 2 < I_{geo} < 3 = moderately to heavily contaminated, Class 4 = 3 < I_{geo} < 4 = heavily contaminated, Class 5 = 4 < I_{geo} < 5 = heavily to extremely contaminated, Class 6 = I_{geo}>5 = extremely contaminated.

Ecological Risk Factors and Index

The ecological risk factor for the control soil (i.e. soil outside the quarry site), and soils taken 0 m, 100 m, and 200 m away from quarry site was estimated as described by Hakanson (1980).

Er=TR×CF

$$RI = \sum_{i=1}^{n} E_r$$

Where: Er = ecological risk factor, TR = toxicity of heavy metals,
CF = pollution factor, RI = ecological risk index, RI< 150 <300 = low risk, 150 ≤ RI = moderate risk, 300≤ RI <600 = considerable risk, IR ≥600 = very high risk.

Human Health Risk Assessment of heavy metals in quarry site;
Determination of the Average daily dose.

The average daily dose was determined while considering the different routes of human exposure to these metals. The Ingestion, inhalation and Dermal absorption were considered. Heavy metal health risk assessment aimed at evaluating the carcinogenic and non-carcinogenic risks of the human body after full exposure to heavy metals was carried out as described by Zgłobicki and Telecka, (2021). These were estimated using the equations below:

$$ADD_{ingestion} = \frac{C \times R_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \ldots\ldots (1)$$

$$ADD_{inhalation} = \frac{C \times R_{inh} \times EF \times ED}{PEF \times BW \times AT} \quad \ldots\ldots (2)$$

$$ADD_{dermal} = \frac{C \times SA \times SL \times ABF \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \ldots\ldots (3)$$

Therefore, the total ADD can be evaluated by adding the ADD dermal +ADD inhalation + ADD ingestion.

Where C = the Concentration of metal (e.g. µg/kg, mg/kg); R_{ing} = ingestion rate, R_{inh} = inhalation rate, EF is Exposure Frequency (days/yr); SA = exposed skin area, ABF = the exposure duration (h/day), SL = the chemical-specific dermal permeability constant (cm/h) ED = Exposure Duration (yr); AT = Averaging Time (period over which exposure is averaged) (days); BW = Body Weight (kg).

Determination of the hazard quotient (HQ) and Index (HI) or non-carcinogenic risk

This is used to denote the risks associated with exposure to non-carcinogenic substances. It is the ratio between exposure and oral reference dose (RFD) in mg/kg/day and if it is above one, then there is a probability of the relevant substance causing adverse effects. The use of HQ to estimate risk was provided in USEPA region 3 risk-based concentration. The hazard index (HI) was determined to estimate the overall risk of exposure to the total heavy metals present in the sample. It was developed by USEPA and is calculated by aggregating the individual HQ from all the heavy metals examined.

$$HQ = \frac{ADD}{RfD} \quad \ldots\ldots (4)$$

HQ = hazard quotient, HQinh = hazard quotient for inhalation, HQing = hazard quotient for ingestion, HQdem = hazard quotient for dermal absorption, HQt = summation of hazard quotients from all routes of exposure, HI = hazard index.

Where HQ > 1 suggests a possibility of health effects, while HQ < 1 shows no possibility of health effects. HI value < 1 describes a very low risk, a HI value between 1 and 4 shows that the risk effects are possible, and HI values > 4 describe a high risk.

Carcinogenic risk assessment

The carcinogenic risk (CR) was estimated according to the method of Maeaba et al., (2019) and Weissmannova et al. (2019), to determine the possibility of developing cancer of any sort by exposure to heavy metal such as As, Ni, Pb, Cd, Co and Cr. The equations below were employed for this estimation for each exposure pathway:

$$CR = ADD \times SF \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where CR = cancer risk. ADD = average daily dose and SF = cancer slope factor

$$TCR = \sum CR = CR_{ing} + CR_{inh} + CR_{derm} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where, TCR, CR, and SF reflect total carcinogenic risk (no unit), carcinogenic risk (no unit), and slope factor for carcinogenic PTEs (mg/kg/d), respectively. A safe TCR values should be in the range of 1×10^{-6} to 1×10^{-4}. That is a reasonable standard that demonstrates no considerable risk to human health (Sager, 2020). However, values $\leq 1 \times 10^{-3}$ suggests the development of cancer.

Statistical Analysis

The mean and standard deviation of the collected data for the various estimated parameters were statistically analyzed using SPSS.

RESULTS

Heavy metals concentration in quarrying site

The concentration of heavy metals in quarrying sites with their respective world average shale values are shown in Table 1 below. The mean concentrations of Cr in soil samples collected over the study zones were 0.4667 ± 0.004, 2.45 ± 0.021, 1.667 ± 0.010, and 0.933 ± 0.008 mg/kg respectively for control soil (i.e. soil outside the quarry site), 0 m, 100 m and 200 m (i.e. soil within the quarry site). Soil outside the quarry site had the least Cr concentration. However, soil located 0 m within the quarry site had the highest Cr concentration, closely followed by those at 100 m and 200 m respectively. Nevertheless, among the sampling stations, none exceeded average shale value for Cr (90 mg/kg) and remained at relatively lower concentrations. Nevertheless, among the sampling stations, none exceeded average shale value for the metals and remained at relatively lower concentrations. Nickel recorded the highest level in all sampling points except for Chromium that had a higher concentration in MS3 (1.667 ± 0.010 mg/kg) than Nickel (1.538 ± 0.015 mg/kg)

Table 1. Heavy metal concentration in the studied sites

Sample	Cr	Cu	Zn	Ni	Pb	As	Cd	Se	V	Co
MS1	0.4667± 0.004	0.1617 ± 0.005	0.8225 ± 0.095	1.846 ± 0.018	0.1489 ± 0.001	0.67744 ± 0.003	0	0.112 ± 0.043	0.019 ± 0.078	0.5385 ± 0.003
MS2	2.45 ± 0.021	0.5173 ± 0.016	1.4632 ± 0.169	1.9487 ± 0.019	0.1489 ± 0.001	3.1613 ± 0.014	0.0357 ± 0.001	0.219 ± 0.051	0.012 ± 0.071	0.1795 ± 0.001
MS3	1.667 ± 0.010	1.0346 ± 0.032	1.2727 ± 0.147	1.538 ± 0.015	0.1489 ± 0.001	1.8065 ± 0.008	0	0.008 ± 0.025	0.007 ± 0.057	0.1795 ± 0.001
MS4	0.933 ± 0.008	0.485 ± 0.015	1.2727 ± 0.147	1.7436 ± 0.017	0.2979 ± 0.002	1.354 ± 0.006	0.0714 ± 0.002	0.216 ± 0.063	0.003 ± 0.053	0.8974 ± 0.005
ASV	90	45	95	68	20	13	0.3	300	130	19

ASV = Average shale values taken from Turekian and Wedepohl (1961)

Contamination indices

Contamination factor (CF), degree of contamination (Cd), geo-accumulation index (Igeo) and pollution load index (PLI) were the contamination indicators used for the assessment of the soil pollution in the present study. The Calculated values of the pollution indices are presented in Tables 3, 4 and 5 below. Based on classification scheme for contamination factor, the result of the study (Table 3) has clearly indicated that the Cf values are less than unity for Cr, Zn, Ni, Pb, As, Cd, Se, V, Co, and Cu for the studied heavy metals irrespective of the sampling point. Considering the contaminations level terminologies associated with Cf values, it can be inferring from the result that the soil in quarry site is low in Cr, Zn, Ni, Pb, As, Cd, Se, V, Co, and Cu.

Degree of contamination (Cd)

The result for degree of contamination and pollution load index (PLI) are presented in Table 2. Soil collected from control area (i.e. soil outside the quarry site), 0 m, 100m and 200 m (i.e. soil within the quarry site) all showed low degree of contamination for Cr, Zn, Ni, Pb, As, Cd, Se, V, Co, and Cu. The results of the pollution load index (PLI) calculated for each heavy metal from control soil (i.e. soil outside the quarry site), 0 m, 100 m and 200 m away from quarry site all showed their values to be less than 1, indicating an unpolluted condition for the assessed heavy metals. The results of the present evaluation revealed that the soil in quarry site in Akamkpa is unpolluted by heavy metals. However, the low PLI obtained for the present study are not static,

there is tendency for increase because of increased human input and activities and hence there is a need for regular check.

Table 2. Contamination factor in quarry soil

Sample	Cr	Zn	Ni	Pb	As	Cd	Se	V	Co	Cu
MS1	0.005186	0.008658	0.027147	0.007445	0.052111	0	0.000373	0.000146	0.028342	0.00359
MS2	0.027222	0.015402	0.028657	0.007445	0.243177	0.119	0.00073	9.23E-05	0.009447	0.01150
MS3	0.018522	0.013397	0.022618	0.007445	0.138962	0	2.67E-05	5.38E-05	0.009447	0.02299
MS4	0.010367	0.013397	0.025641	0.014895	0.104154	0.238	0.00072	2.31E-05	0.047232	0.01078

Table 3: Degree of contamination and pollution index of heavy metals

Sample	C degree	PLI
MS1	0.1294	0
MS2	0.4512	0.011
MS3	0.2105	0
MS4	0.4544	0.010

C_d = Degree of contamination; PLI = pollution load index

Geo-accumulation index (Igeo)

The calculated Geo-accumulation index (Igeo) values are presented in Table 4. The calculated results of Igeo of heavy metals in the quarry soil investigated showed that irrespective of heavy metal and sampling points, the Igeo values for all the heavy metals fell in class '0', indicating practically uncontaminated conditions in these sites.

Table 4. Geo-accumulation index and enrichment factor in quarry soil

Sample	Cr	Zn	Ni	Pb	As	Cd	Se	V	Co	Cu
MS1	-8.176	-7.437	-5.788	-7.654	-4.847	0.000	-11.972	-13.325	-5.726	-8.70542
MS2	-5.784	-6.606	-5.710	-7.654	-2.625	-3.656	-11.005	-13.988	-7.311	-7.02774
MS3	-6.340	-6.807	-6.051	-7.654	-3.432	0.000	-15.780	-14.766	-7.311	-6.02774
MS4	-7.177	-6.807	-5.870	-6.654	-3.848	-2.656	-11.025	-15.988	-4.989	-7.12076

Ecological Risk Factors and Index

The results from statistical calculation of the ecological risk factor (Table 5) for the control soil (i.e. soil outside the quarry site), and soils taken 0 m, 100 m and 200 m away from quarry site showed that all the sampling points were classified as having low potential ecological risk with respect to individual heavy metals (Cr, Zn, Ni, Pb, As, Cd, Se, V, Co, and Cu) considered. Similarly, the integrated ecological risk index also classified the soil of the area as having a low ecological risk value.

Table 5. Ecological risk factor of heavy metal in quarry soil

Sample	Cr	Zn	Ni	Pb	As	Cd	Se	V	Cu	Co	RI
MS1	0.010371	0.008658	0.135735	0.037225	0.521108	0	0.00224	0.000292	0.01796	0.141711	0.85734
MS2	0.054444	0.015402	0.143287	0.037225	2.431769	3.57	0.00438	0.000185	0.05747	0.047237	6.303929
MS3	0.037044	0.013397	0.113088	0.037225	1.389615	0	0.00016	0.000108	0.11495	0.047237	1.637874
MS4	0.020733	0.013397	0.128206	0.074475	1.041538	7.14	0.00432	4.62E-05	0.05388	0.236158	8.658874

Human health risk assessment

The health risks due to human exposure to heavy metals exposure in quarrying site included non-carcinogenic and carcinogenic risk. This assessment was done for children and adults as two receptor groups.

Determination of the Average daily dose (ADD) per heavy metal via different routes of exposure.

The average daily dose of the heavy metal from the quarrying site for three different exposure pathways (ingestion, dermal and inhalation) were calculated for both children and adult and summarized in Table 6 - 7. The ADD in children via the ingestion path, the control soil (i.e. soil outside the quarry site) in Table 6, ranged from 2.43 x 10^{-7} to 2.36 x 10^{-5} and decreased in this order: Ni ≥Zn>As≥Co ≥Cr ≥Cu≥Pb ≥Se>V. However, soils at 0 m, 100 m and 200 m within the quarry site ranged from 1.53 x10^{-7} to 4.04 x 10^{-5}; 8.95 x 10^{-8} to 2.31 x10^{-5} and 3.8 x10^{-8} to 2.23 x 10^{-5}, respectively. It decreases in the order of As≥Cr≥Ni≥Zn≥Cu≥Se≥Co≥Pb>Cd≥V, Ni≥As ≥Zn≥Cr≥Co>Cu≥Pb≥Se>Cd>V and Ni≥As≥Zn≥Cr≥Co>Cu≥Pb≥Se>Cd>V, respectively. Similarly, the ADD in children via the inhalation route of exposure showed that the control soil (i.e. soil outside the quarry site) ranged from 4.6 x 10^{-12} to 4.47 x 10^{-10} and decreased in this order: Ni ≥Zn>As≥Co ≥Cr ≥Cu≥Pb ≥Se>V. However, soils at 0 m, 100 m and 200 m within the quarry site ranged from 8.64 x10^{-12} to 7.66 x 10^{-5}, 1.7 x 10^{-12} to 4.37 x10^{-10} and 7.26 x10^{-13} to 4.22 x 10^{-}

^{10}. The ADD decreased in the order of As≥Cr≥Ni≥Zn≥Cu≥Se≥Co≥Pb>Cd≥V, As≥Cr≥Ni≥Zn≥Cu≥Co≥Pb>Se>V and Ni≥As≥Zn≥Cr≥Co>Cu≥Pb≥Se>Cd>V, respectively. In similar sequence, the ADD in children following dermal absorption for control soil (i.e. soil outside the quarry site) ranged from 3.4 x 10^{-9} to 3.3 x 10^{-7} and decreased in the order of Ni ≥Zn≥As>Co ≥Cr ≥Cu≥Pb ≥ Se>V. However, soils at 0 m, 100 m and 200 m within the quarry site ranged from 2.15 x10^{-9} to 5.66 x 10^{-7}, 1.25 x 10^{-9} to 3.23 x10^{-7} and 5.37 x10^{-10} to 3.12 x 10^{-7} and decreased in the order of As≥Cr≥Ni≥Zn≥Cu≥Se≥Co≥Pb>Cd≥V, As≥Cr≥Ni≥Zn>Cu>Co≥Pb>Se>V and Ni≥As≥Zn≥Cr≥Co>Cu≥Pb≥Se>Cd>V, respectively.

Table 6. Average daily dose via different exposure pathways for children in mg/Kg body weight/day

Pathways	Cr	Zn	Ni	Pb	As	Cd	Se	V	Co	Cu
ADDing										
MS1	5.97E-06	1.05E-05	2.36E-05	1.90E-06	8.66E-06	0	1.43E-06	2.43E-07	6.88E-06	2.07E-06
MS2	3.13E-05	1.87E-05	2.49E-05	1.90E-06	4.04E-05	4.56E-07	2.80E-06	1.53E-07	2.29E-06	6.61E-06
MS3	2.13E-05	1.63E-05	1.97E-05	1.90E-06	2.31E-05	0	1.02E-07	8.95E-08	2.29E-06	1.32E-05
MS4	1.19E-05	1.63E-05	2.23E-05	3.81E-06	1.73E-05	9.13E-07	2.76E-06	3.84E-08	1.15E-05	6.2E-06
ADDinh										
MS1	1.13E-10	1.99E-10	4.47E-10	3.61E-11	1.64E-10	0	2.71E-11	4.6E-12	1.3E-10	3.92E-11
MS2	5.93E-10	3.54E-10	4.72E-10	3.61E-11	7.66E-10	8.64E-12	5.3E-11	2.91E-12	4.35E-11	1.25E-10
MS3	4.04E-10	3.08E-10	3.72E-10	3.61E-11	4.37E-10	0	1.94E-12	1.7E-12	4.35E-11	2.51E-10
MS4	2.26E-10	3.08E-10	4.22E-10	7.21E-11	3.28E-10	1.73E-11	5.23E-11	7.26E-13	2.17E-10	1.17E-10
ADDdem										
MS1	8.35E-08	1.47E-07	3.30E-07	2.67E-08	1.21E-07	0	2.00E-08	3.40E-09	9.64E-08	2.89E-08
MS2	4.39E-07	2.62E-07	3.49E-07	2.67E-08	5.66E-07	6.39E-09	3.92E-08	2.15E-09	3.21E-08	9.26E-08
MS3	2.98E-07	2.28E-07	2.75E-07	2.67E-08	3.23E-07	0	1.43E-09	1.25E-09	3.21E-08	1.85E-07
MS4	1.67E-07	2.28E-07	3.12E-07	5.33E-08	2.42E-07	1.28E-08	3.87E-08	5.37E-10	1.61E-07	8.68E-08

The ADD in adult following ingestion path for control soil (i.e. soil outside the quarry site) in Table 8, ranged from 2.60 x 10-8 to 2.53 x 10 -6 and decreased in this order: Ni ≥Zn>As≥Co ≥Cr ≥Cu≥Pb ≥Se>V. However, soils at 0 m, 100 m and 200 m within the quarry site ranged 4.33 $x10^{-6}$ to 4 x 10^{-8}, 9.59 x 10^{-9} to 2.47 $x10^{-6}$ and 4.11 $x10^{-9}$ to 2.39 x 10^{-6}, and decreased in the order of As≥Cr≥Ni≥Zn>Cu≥Se≥Co≥Pb>Cd≥V, As≥Cr≥Ni≥Zn≥Cu>Co≥Pb>Se>V and Ni≥As≥Zn≥Cr≥Co>Cu≥Pb≥Se>Cd>V, respectively. Similarly, the ADD in adult following inhalation path for control soil (i.e. soil outside the quarry site) ranged 2.60 x 10^{-8} to 2.53 x 10 $^{-6}$ and decreased in this order: Ni ≥Zn>As≥Co ≥Cr ≥Cu≥Pb ≥Se>V. However, soils at 0 m, 100 m and 200 m within the quarry site ranged from 4.33 $x10^{-6}$ to 4 x 10^{-8}, 9.59 x 10^{-9} to 2.47 $x10^{-6}$, and 4.11 $x10^{-9}$ to 2.39 x 10^{-6}, and decreased in the order of As≥Cr≥Ni≥Zn>Cu≥Se≥Co≥Pb>Cd≥V, As≥Cr≥Ni≥Zn≥Cu>Co≥Pb>Se>V and Ni≥As≥Zn≥Cr≥Co>Cu≥Pb≥Se>Cd>V, respectively. In similar sequence, the ADD in adult following dermal pathway for control soil (i.e. soil outside the quarry site) ranged from 1.48 x 10^{-9} to 1.44 x 10^{-7} and decreased in this order: Ni ≥Zn≥As>Co ≥Cr ≥Cu≥Pb≥Se>V. However, soils at 0 m, 100 m and 200 m within the quarry site ranged from 9.37 $x10^{-10}$ to 2.46x 10^{-7}, 5.47 x 10^{-10} to 1.41 $x10^{-7}$ and 2.34 $x10^{-10}$ to 1.36 x 10^{-7}, and decreased in the order of As≥Cr ≥Ni≥Zn≥Cu≥Se≥Co≥Pb>Cd≥V, As≥Cr≥Ni≥Zn>Cu>Co≥Pb>Se>Vand Ni≥As≥Zn≥Cr≥Co>Cu ≥Pb≥Se>Cd>, respectiv

Table 7. Average daily dose values for heavy metals in quarry soil via different exposure pathways for adult

Pathways	Cr	Zn	Ni	Pb	As	Cd	Se	V	Co	Cu
ADDing										
MS1	6.39E-07	1.13E-06	2.53E-06	2.04E-07	9.28E-07	0	1.53E-07	2.60E-08	7.38E-07	2.22E-07
MS2	3.36E-06	2.00E-06	2.67E-06	2.04E-07	4.33E-06	4.89E-08	3.00E-07	1.64E-08	2.46E-07	7.09E-07
MS3	2.28E-06	1.74E-06	2.11E-06	2.04E-07	2.47E-06	0	1.10E-08	9.59E-09	2.46E-07	1.42E-06
MS4	1.28E-06	1.74E-06	2.39E-06	4.08E-07	1.85E-06	9.78E-08	2.96E-07	4.11E-09	1.23E-06	6.64E-07
ADDinh										
MS1	9.69E-11	1.71E-10	3.83E-10	3.09E-11	1.41E-10	0	2.32E-11	3.94E-12	1.12E-10	3.36E-11
MS2	5.09E-10	3.04E-10	4.04E-10	3.09E-11	6.56E-10	7.41E-12	4.55E-11	2.49E-12	3.73E-11	1.07E-10
MS3	3.46E-10	2.64E-10	3.19E-10	3.09E-11	3.75E-10	0	1.66E-12	1.45E-12	3.73E-11	2.15E-10
MS4	1.94E-10	2.64E-10	3.62E-10	6.18E-11	2.81E-10	1.48E-11	4.48E-11	6.23E-13	1.86E-10	1.01E-10
ADDdem										

MS1	3.64E-08	6.42E-08	1.44E-07	1.16E-08	5.29E-08	0	8.75E-09	1.48E-09	4.20E-08	1.26E-08
MS2	1.91E-07	1.14E-07	1.52E-07	1.16E-08	2.47E-07	2.79E-09	1.71E-08	9.37E-10	1.40E-08	4.04E-08
MS3	1.30E-07	9.94E-08	1.20E-07	1.16E-08	1.41E-07	0	6.25E-10	5.47E-10	1.40E-08	8.08E-08
MS4	7.29E-08	9.94E-08	1.36E-07	2.33E-08	1.06E-07	5.58E-09	1.69E-08	2.34E-10	7.01E-08	3.79E-08

Non-carcinogenic risk or hazard quotient

Non-carcinogenic risk for adults and children were calculated based on reference dose (RfD) values as presented. These results for the ingestion, inhalation and dermal pathways are all presented in terms of HQs and HI. The individual values of HQ and HI of the heavy metals for children and adults are presented in Table 8 – 9 below. In the case of the ingestion pathway, in control soil (i.e. soil outside the quarry site), the HQ for children ranged from 5.44 x 10^{-4} to 2.8 x 10^{-2} and was in the order of As > Zn > Cr > Ni > Pb, whereas for adult it ranged from 5.83 x 10^{-5} to 3.09 x 10^{-3}, and was in the order of As>Zn>Cr>Ni> Pb. However, for soils at 0 m within the quarry site, it ranged from 4.56 x10^{-4} to 1.35 x 10^{-1} and followed the order of As>Cr>Zn>Ni> Pb>Cd for children and ranged from 4.89 x10^{-5} to 1.44 x 10^{-2} and followed the order of As>Cr>Zn>Ni> Pb>Cd for adult. Further result indicated that at 100 m within the quarry site, HQ via ingestion route ranged 5.44 x 10^{-4} to 7.69 x10^{-2} and followed the order of As>Cr>Zn>Ni> Pb for children and ranged from 5.83 x 10^{-5} to 8.25 x10^{-3} and followed the order of As>Cr>Zn>Ni> Pb for adult. However, at 200 m within the quarry site, HQ via ingestion route ranged from 9.13 x10^{-4} to 5.77 x 10^{-2} and followed the order of As>Zn>Cr>Ni> Pb >Cd for children and ranged from 9.78 x10^{-5} to 6.18 x 10^{-3}, and followed the order of As>Zn>Cr>Ni> Pb >Cd for adult.

The inhalation pathway in the control soil (i.e. soil outside the quarry site) showed that the HQ for children ranged from 1.02 x 10^{-8} to 3.95 x 10^{-6} and was in the order of Cr>As>Zn>Ni> Pb. The HQ for adult ranged from 8.78 x 10^{-9} to 3.39 x 10^{6} and was in the order of Cr>As>Zn>Ni> Pb. However, soils at 0 m within the quarry site, it ranged from 8.64 x10^{-9} to 1.35 x 10^{-1} and followed the order of As>Cr>Zn>Ni> Pb>Cd for children and ranged from 7.41 x10^{-9} to 1.78 x 10^{-5} and decreased in the order of Cr>As>Zn>Ni> Pb>Cd for adult. Further result indicated that at 100 m within the quarry site, HQ via ingestion route ranged from 1.02 x 10^{-8} to 1.41 x10^{-5} and followed the order of Cr>As>Zn>Ni> Pb for children and ranged from 8.78 x 10^{-9} to 1.21 x10^{-5} and decreased in the order of Cr>As>Zn>Ni> Pb for adult. However, at 200 m within the quarry site, HQ via inhalation route ranged from 9.13 x10^{-4} to 5.77 x 10^{-2} and decreased in the order of As>Zn>Cr>Ni> Pb >Cd for children and ranged from 1.48 x10^{-8} to 6.77 x 10^{-6} and decreased in the order of Cr>As>Zn>Ni≥ Pb >Cd for adult.

However, the dermal pathway, in control soil (i.e. soil outside the quarry site), showed that the HQ for children ranged from 5.47 x 10^{-7} to 2.45 x 10 $^{-3}$ and was in the order of Zn>Cr>Ni> Pb>As. The adult ranged from 2.21 x 10^{-5} to 1.07 x 10^{-3} and decreased in the order of Zn>Cr>As>Ni> Pb.

However, soils at 0 m within the quarry site ranged from 4.56 $x10^{-4}$ to 1.35 x 10^{-1} and decreased in the order of As>Cr>Zn>Ni> Pb>Cd for children and for adult it ranged from 2.21 $x10^{-5}$ to 3.19 x 10^{-3} and decreased in the order of Cr>As>Zn>Cd>Ni> Pb. Further result indicated that at 100 m within the quarry site, HQ via dermal route ranged from 1.46 x 10^{-6} to 4.97 $x10^{-3}$ and decreased in the order of Cr>Zn>Ni>Pb>As for children and for adult it ranged from 2.21 x 10^{-5} to 2.17 $x10^{-3}$ and decreased in the order of Cr>Zn>As>Ni>Pb. However, at 200 m within the quarry site, HQ via dermal pathway ranged from 1.09 $x10^{-6}$ to 3.79 x 10^{-3} and decreased in the order of Zn>Cr>Cd> Pb >Ni>As for children and for adult it ranged from 2.52 $x10^{-5}$ to 1.65 x 10^{-3} and decreased in the order of Zn>Cr>As> Cd>Pb >Ni.

HQ of different elements was in the order of ingestion>dermal>inhalation. This indicates that ingestion was the most important pathway that heavy metals in soil enter the human body for both children and adults. Risks through ingestion and dermal contacts were higher than inhalation, and the risk to adult was lower than children. The higher HQ values of the HMs in children through ingestion pathway can be attributed to the more vulnerability of children to the toxic substances.

Further investigation showed that the HQt (inhalation + ingestion + dermal absorption) in control soil (i.e. soil outside the quarry site), ranged from 5.95 x 10^{-4} to 2.98 x 10^{-2} and decreased in the order of As >Zn>Cr>Ni> Pb for children. The adult HQt ranged from 8.04 x 10^{-5} to 3.52 x 10^{-3} and decreased in the order of As >Zn>Cr>Ni> Pb. However, at 0 m within the quarry site, HQinh + ing + dem ranged from 5.95 $x10^{-4}$ to 1.39 x 10^{-1} and decreased in the order of As >Cr>Zn>Ni>Cd> Pb for children and for adult it ranged from 8.04 $x10^{-5}$ to 1.64 x 10^{-2} and decreased in the order of As >Cr>Zn>Cd>Ni> Pb. Similarly, at 100 m within the quarry site, HI ranged from 5.95 x 10^{-4} to 7.96 $x10^{-2}$ and decreased in the order of As >Cr>Zn>Ni> Pb for children and for adult it ranged from 8.04 x 10^{-5} to 9.39 $x10^{-3}$ and decreased in the order of As >Cr>Zn>Ni> Pb. However, for 200m the HQt ranged from 1.17 $x10^{-3}$ to 5.97 x 10^{-2} and decreased in the As >Zn>Cr>Cd> Pb >Ni for children and for adult it ranged from 1.45 $x10^{-4}$ to 7.04 x 10^{-3} and decreased in the order of As >Zn>Cr>Cd> Pb >Ni.

Table 8. HQ and HI values for heavy metals in quarry soil via different exposure pathways for children

Pathways	Cr	Zn	Ni	Pb	As	Cd
HQing						
MS1	0.001989	0.003505	0.00118	0.000544	0.028871	0
MS2	0.010441	0.006236	0.001246	0.000544	0.134728	0.000456
MS3	0.007104	0.005424	0.000983	0.000544	0.076989	0
MS4	0.003976	0.005424	0.001115	0.001088	0.057705	0.000913
HQinh						
MS1	3.95E-06	6.64E-08	2.17E-08	1.02E-08	2.30E-06	0
MS2	2.07E-05	1.18E-07	2.29E-08	1.02E-08	1.12E-05	8.64E-09
MS3	1.41E-05	1.03E-07	1.81E-08	1.02E-08	6.71E-06	0
MS4	7.90E-06	1.03E-07	2.05E-08	2.05E-08	5.25E-06	1.73E-08

HQdem						
MS1	0.001392	0.002454	6.12E-05	5.08E-05	5.47E-07	0
MS2	0.007309	0.004365	6.46E-05	5.08E-05	2.55E-06	0.000639
MS3	0.004973	0.003797	5.10E-05	5.08E-05	1.46E-06	0
MS4	0.002783	0.003797	5.78E-05	0.000102	1.09E-06	0.001278
HI						
MS1	0.003385	0.005959	0.001241	0.000595	0.029858	0
MS2	0.017771	0.010601	0.00131	0.000595	0.139331	0.001095
MS3	0.012092	0.009221	0.001034	0.000595	0.07962	0
MS4	0.006768	0.009221	0.001172	0.00119	0.059676	0.002191

Table 9. HQ and HI values for heavy metals in quarry soil via different exposure pathways for adult

Sample	Cr	Zn	Ni	Pb	As	Cd
HQing						
MS1	0.000213	0.000376	0.000126	5.83E-05	0.003093	0
MS2	0.001119	0.000668	0.000133	5.83E-05	0.014435	4.89E-05
MS3	0.000761	0.000581	0.000105	5.83E-05	0.008249	0
MS4	0.000426	0.000581	0.000119	0.000117	0.006183	9.78E-05
HQinh						
MS1	3.39E-06	5.69E-08	1.86E-08	8.78E-09	4.69E-07	0
MS2	1.78E-05	1.01E-07	1.96E-08	8.78E-09	2.19E-06	7.41E-09
MS3	1.21E-05	8.81E-08	1.55E-08	8.78E-09	1.25E-06	0
MS4	6.77E-06	8.81E-08	1.76E-08	1.76E-08	9.37E-07	1.48E-08
HQdem						
MS1	0.000607	0.00107	2.67E-05	2.21E-05	0.00043	0
MS2	0.003188	0.001904	2.82E-05	2.21E-05	0.002007	0.000279
MS3	0.002169	0.001656	2.22E-05	2.21E-05	0.001147	0
MS4	0.001214	0.001656	2.52E-05	4.43E-05	0.00086	0.000558
HI						
MS1	0.000824	0.001446	0.000153	8.04E-05	0.003524	0
MS2	0.004325	0.002572	0.000162	8.04E-05	0.016444	0.000328
MS3	0.002943	0.002237	0.000128	8.04E-05	0.009397	0
MS4	0.001647	0.002237	0.000145	0.000161	0.007043	0.000655

The calculated TCR values for each exposure pathway in children and adults are listed in Table 1. Because of lack of the carcinogenic slope factors for Cu, Zn, V and Sr, only the carcinogenic risks for Cr, Ni, Pb, AS, Cd and Co were estimated (Table 10 -11). Based on this the risks surpassing 1×10^{-4} are viewed as unacceptable, whereas risks below 1×10^{-6} are not considered to pose significant health effects, and risks lying in the range of 10^{-6} to 10^{-4} are generally regarded as tolerable to some degree. The TCR in adult following ingestion path ranged from 4.98×10^{-7} to 2.43×10^{-6} and decreased in the order of MS2>MS3>MS4>MS1. However, for inhalation pathway it ranged from 2.37×10^{-9} to 1.13×10^{-8} and decreased in the order of MS2>MS3>MS4>MS1. In similar sequence, the TCR in adult following dermal pathway ranged from 6.91×10^{-7} to 3.29×10^{-6} and decreased in this order of MS2>MS3>MS4>MS1. Regardless of the sampling point, the TCR in adult for the studied heavy metals ranged from 3.51×10^{-10} to 1.23×10^{-5} and decreased in the order of As>Cd>Cr>Pb>Ni>Co. However, for the children group, the TCR in following ingestion path ranged from 1.11×10^{-6} to 5.43×10^{-6} and decreased in the order of MS2>MS3>MS4>MS1 . However, for inhalation pathway it ranged from 1.46×10^{-9} to 7.07×10^{-9} and decreased in the order of MS2>MS3>MS4>MS1. In similar sequence, the TCR in children following dermal pathway ranged from 3.80×10^{-7} to 1.81×10^{-6} and decreased in this order of MS2>MS3>MS4>MS1 . Regardless of the sampling point, the TCR in children for the studied heavy metals ranged from 2.833×10^{-10} to 1.545×10^{-5} and decreased in the order of As>Cd>Cr>Pb>Ni>Co.

Table 10. Carcinogenic risk for heavy metals in soil via different exposure pathways for children

Pathways	Cr	Ni	Pb	As	Cd	Co	TCR
Cing							
MS1			1.39E-09	1.11E-06	0		1.115E-06
MS2			1.39E-09	5.2E-06	2.39E-07		5.437E-06
MS3			1.39E-09	2.97E-06	0		2.971E-06
MS4			2.77E-09	2.23E-06	4.77E-07		2.706E-06
Cinh							
MS1	4.068E-10	8.37E-11	4.41E-13	8.92E-10	0	8.11E-11	1.464E-09
MS2	2.563E-09	9.51E-11	4.67E-13	4.36E-09	2.43E-11	2.77E-11	7.070E-09
MS3	2.034E-09	8.04E-11	4.93E-13	2.6E-09	0	2.85E-11	4.748E-09
MS4	1.301E-09	9.73E-11	1.04E-12	2.04E-09	5.23E-11	1.46E-10	3.635E-09
Cdem							
MS1				3.8E-07	0		3.804E-07
MS2				1.78E-06	3.34E-08		1.809E-06
MS3				1.01E-06	0		1.014E-06
MS4				7.6E-07	6.68E-08		8.27E-07
CR	6.305E-09	3.565E-10	6.938E-09	1.545E-05	8.163E-07	2.833E-10	

Table 11: Carcinogenic risk for heavy metals in soil via different exposure pathways for adult

Pathways	Cr	Ni	Pb	As	Cd	Co	TCR
Cing							
MS1			6.20E-10	4.97E-07	0		4.98E-07
MS2			6.19E-10	2.32E-06	1.07E-07		2.43E-06
MS3			6.19E-10	1.33E-06	0		1.33E-06
MS4			1.24E-09	9.94E-07	2.13E-07		1.21E-06
Cinh							
MS1	1.45E-09	1.15E-10	4.64E-13	7.58E-10	0	3.91E-11	2.37E-09
MS2	7.63E-09	1.21E-10	4.64E-13	3.54E-09	1.67E-11	1.30E-11	1.13E-08
MS3	5.19E-09	9.58E-11	4.64E-13	2.02E-09	0	1.30E-11	7.32E-09
MS4	2.90E-09	1.09E-10	9.27E-13	1.52E-09	3.33E-11	6.52E-11	4.63E-09
Cdem							
MS1				6.91E-07	0		6.91E-07
MS2				3.23E-06	6.07E-08		3.29E-06
MS3				1.84E-06	0		1.84E-06
MS4				1.38E-06	1.21E-07		1.50E-06
CR	1.85E-08	6.49E-10	3.10E-09	1.23E-05	5.02E-07	3.51E-10	

DISCUSSION

The concentration of Ni, Zn, As, Co, Cr, Cu, Pb, Se, Cd and V varied across the control soil and soil samples from the quarry site. Due to unavailability of background values of heavy metals concentration in Akamkpa soils, the metal concentration obtained in this study were compared with allowable limit for soil using allowable limits established for mineral soil environment (Lindsay 1979) and geochemical average shale values of the earth's crust as proposed by Turekian and Wedepohl (1961).

From the result of the investigation, the concentration of Cr in all the sampling points within and outside soils in Marksino Quarry Company were lower than its average shale value (90 mg/kg), background value (49.3 mg/ kg), and maximum level (100 mg/kg) that may be present in soil (Ali et al., 2015). These values were also lower than TEL–PEL (threshold effect level–probable effect level) and ERL–ERM (effect range low–effect range median) values (Long and Morgan 1991; Smith et al., 1996). From the result obtained, it is evidence that the Cr concentration in the studied soils is safe for crop cultivation. Similarly, the values of Pb obtained for this study were all below the maximum permissible limits of 200 mg/kg (Lindsay, 1979) established for mineral soil environments and far below the background level of 85 mg/kg (Turekian and Wedepohl, 1961). These low content values of Pb in the soils investigated are safe for crop cultivation. The Cd concentrations recorded were below its average concentration present in shale (0.3 mg/kg), background levels (0.12 mg/kg), and TEL (0.6 mg/kg); and those of PEL (3.5 mg/kg) and ERL (5)/ERM (9) values (Long and Morgan 1991; Smith et al., 1996).

The results of the study further suggested that the Ni concentrations obtained from the investigated samples were below its average concentration present in shale (68 mg/kg), and TEL (18 mg/kg), and those of PEL (36 mg/kg) and ERL (30)/ERM (50) values (Long and Morgan 1991; Smith et al. 1996). Similarly, from this investigation, it was also evidence that the concentration of Zn, As, Co, Cu, Se and V were all lower than their respective average shale values, background values and TEL–PEL (threshold effect level–probable effect level) and ERL–ERM (effect range low–effect range median) values. However, when these heavy metals in the studied quarry site were compared with other cities around the world (Arenas-Lago et al., 2014; Lago-Vila et al., 2017; Weissmannova et al., 2019), there were variations in their concentrations. For example, in the serpentinite quarry soils in the old Penas Albas quarry site, Moeche, NW Spain high Cr and Ni and moderate Co contamination were observed (Lago-Vila *et al.,* 2017. This variation maybe attributed to various factors such as a high population, unregulated waste burning, unplanned construction, emissions from nearby industrial areas, sewage waste. Lower concentration of heavy metal is always desirable for ensuring safe and healthy agricultural crops for human consumption. The problem of agricultural land contamination with heavy metals in Nigeria and elsewhere around the globe has raised serious concerns for scientific community over the years (Chonokhuu et al., 2019; Mafulul et al., 2022). This is so because, potentially toxic elements such as arsenic causes skin infections, vascular diseases and visceral cancers, cadmium that is a human carcinogen causes renal disorder and can damage the kidney. Furthermore, chromium causes nausea, vomiting, diarrhea and headache while copper has been associated with Wilson disease, gastrointestinal irritation, insomnia (sleeplessness), and liver damage. Additionally, nickel, a human carcinogen causes nausea, dermatitis, chronic asthma, and coughing; lead causes damage to the circulatory and nervous system, fetal brain, and diseases of the kidney; zinc causes lethargy, neurological signs, depression, and increased thirst (Eze et al., 2021). Although, the concentration of all the studied heavy metals were below the level that can cause harm to crop and human, it was found that soil outside the quarry site or the control sample had the least concentration of metals. The soil sampled obtained at 0 m (center of the quarry site) within the quarry site had the highest concentration, closely followed by those at 100 m and 200 m respectively. The result obtained herein differs from the studies of Lago-Vila et al. (2017) who reported high levels of heavy metals exceeding average concentration shale and background values in soils around mining and quarry sites.

The contamination factor (CF), degree of contamination (Cd), geo-accumulation index (Igeo) and pollution load index (PLI) of metals obtained in the different sampling points around the quarrying site were all low. The results obtained for this investigation corroborates with the reports of Chukwu and Oji (2018), Salman et al., (2019) and Proshad et al., (2019) who all recorded low Cf for Cr in Agricultural Soils in Katsina State (North-Western Nigeria), Mkpuma Ekwoku (South-eastern Nigeria), El Obour (Egypt) and Tarutia (Bangladesh) respectively. However, these findings were contrary to the studies of Omran (2016) who had both moderate contamination and considerable contamination for Cr in soils of Bahr El Baqar, Egypt. The result obtained by Salman et al., (2019) showed Arsenic to have very high contamination in the soil, which was contrary to the present study. However, Ephraim and Ayaji (2014) also had low Arsenic values in all the

studied sites in their research. The report of Mandeng et al., (2019) indicated sediments of Abiete-Toko watersheds, Cameroon to have been moderately contamination with Pb. Chukwu and Oji (2018) and Proshad et al., (2019) also had very high contamination for Cd in their studies. Soils contaminated by Cd can cause serious ecological risks and negatively impact on human health as Cd being highly toxic heavy metal can enter the food chain through soil-plant interaction (Shahid et al., 2017). Atayese et al. (2008) pointed out that increasing levels of soil contamination with heavy metals can result to its transformation and transportation into plant tissues and from plants passes into animals and human. The findings for the pollution load index is in line with those of Udofia et al., (2015) who reported that the sediment of Okporku River, Nigeria is unpolluted by heavy metals. The PI investigated however, differed from those of Barakat et al., (2012) in Day River, Morocco whose values lies between 1.57-2.20 and Salman et al. (2019) who had 1.25-2.40, indicating that the concentration levels of the studied metals in most of the stations exceeded the background values. Rabee et al. (2011) in Tigris River Sediment in Baghdad Region also obtained very low pollution load index ranging between 0.301-0.970. The results of Geo-accumulation index (Igeo) obtained for this study showed practically uncontaminated condition for the studied heavy metals. Mandeng et al. (2019) also had practically uncontaminated situation in their result.

There is lack of public enlightenment concerning the extent of heavy metal contamination, pollution, and ecological risk of soils in quarrying site, especially those utilized for agricultural cultivation in industrial area in Cross River State. The contamination of agricultural soils and crops by heavy metals most especially highly hazardous metals such Pb, Cd, Cr, As, etc. should be given priority due to their potential effects on human health. In Nigeria for instance, Galadima and Garba (2010) reported lead poisoning in Zamfara state that claimed the lives of over 500 children within seven months in 2010. Similarly, as found in Verla et al. (2020) report, in 2007, arsenic disaster in Bangladesh killed many persons including children in Bangladesh. Qadir et al., (2008) in a survey report along the Musi River in Hyderabad city, India, revealed the transfer of metal ions from wastewater to cow's milk using para grass as fodder, produced by irrigating with wastewater containing heavy metals.

The studied metals recorded hazard quotient values less than 1 for children and adults. Based on the health risk investigation of As, Cd, Cr, Ni, Pb, Zn, and Cu, the mean hazard quotients generally suggest an acceptable level of non-carcinogenic health risk in the soil samples collected from quarry site. According to USEPA (2010) and Maqbool et al., (2019) when HQ and HI values are less than 1, there is no obvious risk to the residents' health, but if the value exceeds one, there may be a concern for possible non-carcinogenic effects. The HQ and HI values of all metals were below maximum permissible value of 1, demonstrating no risk of non-carcinogenic impacts among children and adults residing in the Marksino quarrying site. Children displayed higher HI values for the studied heavy metals than adults. The higher risk of children than adult is pointing to the fact that children are more sensitive to heavy metals in indoor dust due to their behaviors such as hand-to-mouth activities and crawling (Alhazmi, 2022) than their adult counterpart. Moreover, Olujimi et al., (2015) reported ingestion as the main toxic metal exposure route for children as they prefer to play on the house floor and ingest the indoor dust directly. The findings of this study are

in line with the risk assessment conducted by Kurt-Karakus (2012), Ardashiri and Hashemi (2018), Olujimi et al. (2015), and Liu et al. (2017), who also reported a total hazard quotient (ΣHQ) less than one indicating that exposure to heavy metals in quarrying site poses no health hazards (non-carcinogenic risks) to children and adults.

Regardless of the sampling point, the TCR in adult for the studied heavy metals ranged from 3.51 x 10-10 to 1.23 x 10-5 and decreased in the order of As>Cd>Cr>Pb>Ni>Co, whereas for children it ranged from 2.833 x 10-10 to 1.545 x 10-5. For children and adult, the TCR values decreased in the order of As>Cd>Cr>Pb>Ni>Co. Potentially toxic elements such as As, Cd, Cr, Ni, and Pb can magnify the risk of cancer in humans (Chonokhuu et al., 2019). Long term exposure to dangerous metals could result in numerous kinds of cancer. In this research, As, Cd, Cr, Ni, Co, and Pb were investigated as the carcinogens. According to USEPA (2002), TCR values less than $1x10^{-6}$ are considered unimportant and can be disregarded, while a TCR value exceeding $1x10^{-4}$ is considered detrimental. From this study, the total cancer risks for As reported for both children and adults are generally within the acceptable limit of potentially toxic elements (10^{-6} and 10^{-4}) in the soil (USEPA 2002), while other heavy metals (Cd, Cr, Ni, Co, and Pb) showed values which were less than 10^{-6}. This indicates no significant carcinogenic health risks for both adults and children through ingestion, inhalation, and dermal contact exposure routes in the study area. However, the observed risk in soil around quarrying site was higher in children than in adults. The results of the present carcinogenic risk assessment are also in agreement with , Kurt-Karakus (2015) and Olujimi et al, (2015) who also reported carcinogenic risk for these heavy metals within the acceptable level (10^{-4}–10^{-6}) for the receptor groups. The higher risk of children than adult is not surprising as children are more sensitive to heavy metals in indoor dust due to their behavior such as hand-to-mouth activities and crawling (Alhazmi, 2022; Jena and Singh, 2018).

CONCLUSION

The investigation conducted revealed that the concentrations of heavy metals, such as chromium, zinc, nickel, lead, arsenic, cadmium, selenium, vanadium, cobalt, and copper, both within and outside the quarry site, were found to be below the average shale and background values. These heavy metals were present at relatively lower concentrations, indicating that there was no significant contamination of heavy metals in the soil. Additionally, the findings indicated that the soil studied in the area is safe for crop cultivation, and the crops grown around the quarry site are safe for consumption. This suggests that the potential uptake of heavy metals by crops from the soil was within safe limits. The pollution indices and ecological risk assessment conducted in the study yielded low values, indicating that the overall environmental contamination and associated risks were minimal. The mining operations did not seem to have had a considerable detrimental impact on the encompassing soil and ecosystem now, as it is a new site. Nevertheless, it was discovered that children exhibited greater Hazard Index (HI) values than adults, which implies that children might be more vulnerable to the potential health consequences arising from exposure to contaminated soil than adults. Although no substantial carcinogenic health hazards were identified

for both adults and children, the higher risk observed in children demands further attention and investigation.

Future Research

Future research should concentrate on elucidating the precise pathways and mechanisms through which children are more prone to the observed risks. Moreover, it would be beneficial to explore the potential long-term consequences of exposure to low concentrations of heavy metals in the soil on the health of both children and adults. Additional studies could also assess the efficacy of mitigation measures and remediation strategies to reduce the potential health risks associated with the mining activities in the region.

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APPENDIX

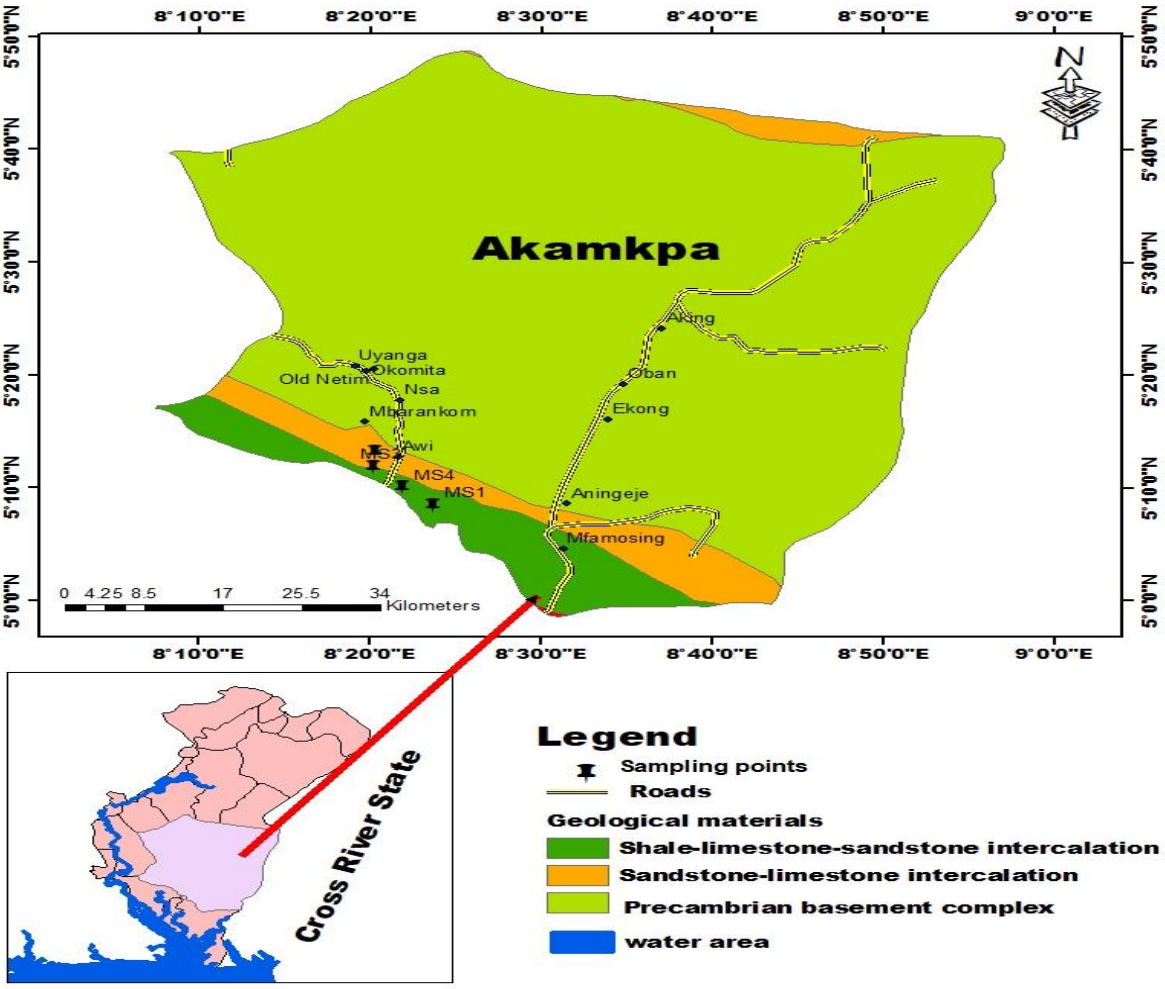

Figure 1. Map of Cross River State with Quarrying Sample Collection Points in Akamkpa (Yemi et al., 2022)

Table I. Values of the parameters used for cancer health risk assessment

Parameters	Unit	Values for adult	References
Rate of ingestion (RI)	mg/day	100.00	USEPA (2011)
Exposed skin area (ESA)	cm^2day	3300.00	Hue *et al*. (2014)
Skin adherence factor (SAF)	mg/cm^2	0.20	Man *et al* (2013)
Frequency of exposure (FE)	Days/year	312.00	Man *et al* (2013)
Duration of exposure (DE)	Year	30.00	Cao *et al*. (2019)
Time of exposure (ET)	h/day	8.00	Man *et al* (2013)
Averaging time (AT)	Day h/day	(70 yrs × 365 days/yr) = 25, 550	USEPA (2009)
Averaging time (AT^x)		70 yrs × 365 days/yr × 24 h	USEPA (2009)
Oral slope factor (OSF)	$(mg/kg\ day)^{-1}$	7.30	USEPA (2012)
Gastrointestinal absorption factor (GIAF) × (OSF)	$(mg/kg\ day)^{-1}$	7.30	USEPA (2012)
Dermal absorption factor DAF	$(mg/kg\ day)^{-1}$	0.13	Man *et al* (2013)
Inhalation unit risk (IUR)	$(mg/kg\ day)^{-1}$	1.1×10^{-6}	USEPA (2012)
Body weight (BW)	Kg		Onyedikachi *et al* (2019)
Particle emission factor (PEF)	m^3/kg	1.36×10^{-6}	Wang *et al*. (2018)
Conversion factor (CF)	kg/mg	1×10^{-6}	Man *et al* (2013)

Table II. Reference doses for non-cancer risks and slope factors for cancer risk assessment

Heavy metals	RFD(mg/kg/d)			SF(mg/kg/d)		
	RFDing	RFDinh	RfDderm	SFing	SFinh	SFderm
Cr	0.003	2.86E-05	6E-05		42	
Zn	0.003	0.003	6E-05			
Ni	0.02	0.0206	0.0054		0.84	
Pb	0.0035	0.0352	5.25E-4	0.0085	0.042	
As	0.0003	0.0003	1.23E-04	1.5	15.1	3.66
Cd	0.001	0.001	1E-05	6.1	6.3	6.1
Sr	0.6	-	0.12			
V	0.005	0.007	0.007			
Co	0.0003	0.02	0.0054		0.98	
Cu	0.04	0.04	0.012			

Ferreira-Baptista and De Miguel, 2005; USEPA, 2009; Gabarrón et al., 2017; Tan et al., 2021; USEPA, 2021