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# **ASSESSING THE CARCINOGENIC AND NON-CARCINOGENIC HEALTH RISK OF HEAVY METAL CONTAMINATION IN SOILS FROM RATCON QUARRY SITE IN IBADAN, SW NIGERIA**

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## **ABSTRACT**

This study estimates the health risks due to the concentration of heavy metals in the soil samples around a quarry near Ibadan, Nigeria. Soil samples were collected in triplicates (three samples collected per sampling point) from ten sampling points in the quarry site and control.

The soil samples were digested for 17 heavy metals (Al, As, Co, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Pb, Sb, Se, Sn, V, and Zn) and quantified using Inductively Coupled Plasma- Optical Emission Spectrometry)- (ICP-OES). Health risk was assessed for metals including hazard quotient (HQ), hazard index (HI) and cancer risk (CR). Data obtained were subjected to descriptive (Mean ±SD) and inferential (Anova) statistics. Results showed that 16 heavy metals were detected, Fe had highest concentration (4354±17.4 mg/kg), followed by Al (1678 ±0.15 mg/kg) and Mn (192±1.29 mg/kg), Cd was not detected. The estimation of non-carcinogenic risks in this study indicated that all identified heavy metals in soils do not pose a non-carcinogenic risk to the health of children and adults. Hazard quotient (HQ) and hazard index (HI) values consistently were less than one (< 1). Also, this study revealed that values of most metals assessed were below 1  $\times$  10<sup>-6</sup> lower limit for CR, except for chromium (1.97 X 10<sup>-1</sup>), which poses a cancer risk in adults.

**KEYWORD:** Carcinogenic, Non-carcinogenic, Heavy Metals, Quarry, Human Health.

#### **INTRODUCTION**

A quarry is a surface mine that generates large amounts of building materials such as limestone and gravel for industrial use, (Majid *et al.,* 2015). Quarrying usually alters landscape drastically: Clearing of vegetation disrupts the ecosystem by diminishing surface hydrology, groundwater levels, and flow paths (Oyinloye and Olofinyo, 2017). The blasting, crushing, and emission of harmful substances usually have severe effect on human health and well-being. Doubtlessly, the most controversial environmental impact on the people living near quarries is caused by blasting. The most common method of mining in Nigeria is quarry as a result of granite and limestone due to the abundance and the clarity of recovering these materials compared to other available minerals.

Ratcon quarry site was specifically chosen due to the persistent and continuous blasting of rocks, resulting in the release of radionuclides and heavy metals that contaminate the surrounding environment. For the extraction of granite, Ratcon quarry employs the openpit mining method. Initially, the rocks undergo drilling, followed by blasting using explosives. The resultant stones are then crushed into various sizes before being transported out of the quarry. This extraction process leads to the destruction of parent vegetation and the removal of topsoil. Consequently, environmental health is negatively impacted by the generation of particulate matter, noise, and vibrations. The inhabitants of the area primarily engage in farming, with secondary occupations including trading, fabrication, artisanship, civil service, and food processing.

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The periodic table comprises dense, high-atomicweight heavy metals, predominantly distributed in the biosphere which is made up of water, soils, and rocks. The hazardous properties of heavy metals have been recognized for decades, heavy metals exert detrimental environmental effects, such as the conversion of mercury into highly toxic methylmercury in aquatic sediments. However, recent experimental investigations propose essential roles for certain heavy metals, such as nickel, copper, and zinc, in human physiology (Azeh-Engwa *et al.,* 2019).

Heavy metals present in soil can enter the human body through various exposure routes, including ingestion, dermal contact, and inhalation. This entry into the body has significant implications for human health, giving rise to both carcinogenic and noncarcinogenic risks associated with the exposure pathways (USEPA,2011).

The benefits of heavy metals are often overshadowed by their hazards, with high exposures to antimony and chromium promoting carcinogenicity, and lead poisoning causing cognitive abnormalities in children (Hou *et al.,* 2013). The term "heavy metal" refers to metallic elements with relatively higher density compared to water. It encompasses potentially phytotoxic elements (As, Cd, Hg, Pb, or Se) lacking physiological roles in plant growth. Conversely, essential metals (Cu, Zn, Mn, Mo, Ni) are vital for plant metabolic processes and normal growth. Heavy metals, located at the lower end of the periodic table with high densities, pose intrinsic hazards even at low concentrations. Certain heavy metals exhibit distinct indicators of toxicity. In many workplaces and

residential settings, heavy metals can enter the human body through ingestion (via food, water) or inhalation (via air) or absorption (via skin). For youngsters, feeding has been the most common entry point (CI, 2015).

Due to possible health effects of heavy metals contamination such as nephrotoxicity, neurotoxicity, hepatotoxicity, skin toxicity cardiovascular toxicity and cancer this study therefore estimate the health risks due to the concentration of heavy metals in the soil samples.

from the quarry sites in Oluyole area of Ibadan.

#### **MATERIALS AND METHODS Description of Study Area**

Ratcon Quarry is located at Oluyole Local Government area of Oyo state, Nigeria. Oluyole Local Government was established in 1976, and the Council occupies about 629 square kilometers. Based on the 2006 population Census, its population was 202,725 (Chukwu and Olajuyigbe, 2017). The Agricultural products in the area include cocoa, citrus, cassava, and maize. It is located approximately on Latitudes 7º 3′ 0′′ to 7º 3′ 21′′ N and Longitudes 3º 42′ 0′′ to 4º 3′ 0′′ E. Oluyole is within the forest savannah eco-climatic zone with an average annual rainfall of about 1225mm and an average annual maximum and minimum temperature of  $34.80^{\circ}$ C and  $24.30^{\circ}$ C respectively (Chukwu and Olajuyigbe, 2017). The rainy season commences around the end of March and ends around the first week of November. The area is mainly drained by the Ona River, which has the characteristic of dry valleys that are usually covered by floods during periods of high rainfall. Fig 1 is the map of the study area showing sampling points.



Fig 1: Map of the Ratcon quarry site showing sampling points

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**Experimental Design and Soil Sample Collection** Top Soil samples (0-15cm) were collected from 10 different points (A-J) at 300m intervals from the blasting point to loading point in the quarry site. The samples were collected in triplicates, each making thirty (30) samples (i.e. three samples per point for ten sampling points). The control sample was collected in an undeveloped location in Oluyole LGA with no history of quarrying pollution. Samples of soil were airdried at room temperature for several days, and stones, organic debris, and pebbles were removed before sieving. The samples were crushed, homogenized, and sieved through a 2mm mesh sieve to obtain a smaller fraction, which was then ground into a fine powder and kept in a glass jar before analysis.

**Digestion of Soil Sample for Heavy Metal Analysis** The USEPA (1996) method was used to digest the soil samples. The ground soil sample was digested with aqua-regia solution to extract metal ions. For digestion, 4mL concentrated nitric acid and 2mL concentrated hydrochloric acid was added to 1g soil sample in a 50mL volumetric flask. The sample was kept overnight in the flask and heated in the fume cupboard to boiling for two hours and allowed to cool. Afterward, distilled water was added up to the 50mL graduation mark.

The contents of the flask were stirred for 5minutes, then cooled and filtered using a filter paper (0.45 microns). The resulting filtrate was stored in a plastic bottle for analysis using an ICP-OES (Inductively Coupled Plasma- Optical Emission Spectrometry) at Nigeria Institute of Medical Research (NIOMR). ICP-OES is a technique in which the composition of elements (mostly water-dissolved) samples can be determined using plasma and a spectrometer. The solution is conducted by a peristaltic pump though a nebulizer into a spray chamber.

#### **Statistical analysis**

The data was subjected to descriptive (mean  $\pm$ SD) and inferential (Anova) statistics. The mean was separated using Duncan's multiple range test (DMRT) and statistical package for Social Science version 20. **Health Risk Assessment of Heavy Metals.**

The health risk evaluation method recommended by the US Environmental Protection Agency (EPA, 2011) was used in calculating by using the following equations 1-5:

ADDsoil−dermal contact = Cs × CF × EF × SA × AF ×  $ABS \times ED / BW \times AT$  (1)

ADDsoil−inhalation = C s × IR 2 × EF × ED/ BW × PEF  $\times$  AT (2)

ADDsoil-Ingestion =  $Cs \times IngR \times EF \times ED \times CF/BW \times$  $AT$  (3)



 $CR = ADD \times SF$ (5)

Where ADD is the long-term average daily exposure dose (mg/kg/d) of heavy metal; HQ is the noncarcinogenic risk entropy of each heavy metal; RfD is the reference dose (mg/kg/d) of heavy metals following different exposure pathways; R is the heavy metal carcinogenic risk index; SFi is the slope of carcinogenic risk of heavy metal I; HI is the noncarcinogenic risk index, and CS is the content of soil heavy metals (mg/kg). The US EPA recommended standard parameters that indicate that the noncarcinogenic risk is negligible when the  $HQ < 1$ , and there is a non-carcinogenic risk when the  $HQ > 1$ . The carcinogenic risk is insignificant when  $CR < 10^{-6}$ . CR of  $10^{-6}$  to  $10^{-4}$  indicates some carcinogenic risk to humans, and when  $CR > 10^{-4}$ , there is a carcinogenic risk. The values and significance of the specific parameters are shown in Tables 2 and 3





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Heavy metals	<b>RfD</b> Ingestion	<b>Dermal</b> <b>RfD</b> contact	<b>RfD</b> <b>Inhalation</b>	<b>SF</b> Ingestion	<b>SF</b> <b>Dermal</b> contact	<b>SF</b> <b>Inhalation</b> 42		
Cr	$3 \times 10^{-3}$	$7.5 \times 10^{-5}$	$2.55 \times 10^{-5}$	0.5	20			
Mn	NA	NA	<b>NA</b>	NA	<b>NA</b>	<b>NA</b>		
Ni	$2 \times 10^{-2}$	$5.4 \times 10^{-3}$	$2.06 \times 10^{-2}$	NA	<b>NA</b>	<b>NA</b>		
Cu	$4.02 \times 10^{-2}$	$4.00 \times 10^{-2}$	$1.20 \times 10^{-2}$	NA	<b>NA</b>	<b>NA</b>		
Zn	0.3	$6 \times 10^{-2}$	0.3	NA	<b>NA</b>	<b>NA</b>		
Sb	$4.00 \times 10^{-4}$	<b>NA</b>	<b>NA</b>	NA	<b>NA</b>	<b>NA</b>		
As	$3.00 \times 10^{-4}$	$1.23 \times 10^{-4}$	$3.00 \times 10^{-4}$	1.5	3.66	1.51		
Cd	$1.00 \times 10^{-3}$	$1.00 \times 10^{-5}$	$1.00 \times 10^{-3}$	6.10	6.10	<b>NA</b>		
Pb	$3.50 \times 10^{-2}$	$3.50 \times 10^{-3}$	$5.30 \times 10^{-4}$	NA	<b>NA</b>	<b>NA</b>		



NA- Not Available

## **Results and Discussion**

Tables 4 show the concentrations of heavy metals in soils. Al, As, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, and Zn were detected except Cd. Results showed that in all the metals studied, Fe had highest concentration (4354±17.4 mg/kg), followed by Al  $(1678 \pm 0.15 \text{ mg/kg})$  and Mn  $(192 \pm 1.29 \text{ mg/kg})$  (Table 4). This agreed with the report of Azizi *et al*. (2023) that mining waste materials near natural soils are composed of high concentrations of Fe, Pb, Al, Zn, and Mn.

The average concentration of manganese (Mn) was recorded as (192±1.29 mg/kg). Manganese is known to form various minerals, including todorokite, clinochlore, pyrolusite, and serandite, and is abundantly present in igneous rocks such as gabbros and basalts. Significantly, due to its similarity in size to  $Mg^{2+}$  and Fe<sup>2+</sup>, manganese often substitutes for these ions in oxides and silicates. This substitution can enhance the specific surface area, ultimately contributing to the flux control of several heavy metals like Co, Ni, Cu, and Zn (Queiroz *et al*., 2021). The result showed that the mean concentration of Fe was  $(4354.0 \pm 20.49)$ . It was suggested that the sample location be composed of high amounts of Fe, Al, and Mn related to the parent materials. The crystalline rocks of Ibadan are chiefly divided into a series of units, which include: gneiss-migmatite complex, quartz, pegmatite, amphibolites, xenoliths, and aplites, amphibolites are mainly rich in Fe, & Mn (Ganiu *et al.***,** 2018).

The result of this study showed that the mean concentration of As, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sn, V and Zn were (1.59±1.11, 3.81±0.26, 8.44±0.26, 13.03±0.15, 1.51±1.84, 0.69±0.49, 1.59±0.75, 10.16±2.57, 5.51 ±1.29, 11.60±2.30, 3.60  $\pm 0.95$ , 24.72 $\pm 0.74$ , and 10.16 $\pm 0.25$  mg/kg) respectively. Chromium is quite abundant in most soils as chromite (FeCr<sub>2</sub>O<sub>4</sub>) and Crocoite (PbCrO<sub>4</sub>), the most common Cr-minerals, which usually are associated with pyroxenes, amphibolites, and micas are heavy metals such as Ni and Co.<br>Nickel predominantly forms

Nickel predominantly forms sulphides and sulfarsenides in conjunction with iron (Fe) and cobalt (Co) and is commonly associated with various iron minerals. Following weathering, nickel co-precipitates with iron and manganese oxides and can also be found in association with carbonates, phosphates, and silicate minerals (Ahmady-Birgani *et al.,* 2019). Serving as the central atom in bacterial enzymes, nickel plays a crucial role in urea degradation. Beyond its geological roles, nickel is a micronutrient

essential for the proper functioning of the human body; it enhances hormonal activity and is involved in lipid metabolism. Exposure to nickel occurs through inhalation, ingestion, and skin contact. However, excessive doses or prolonged contact with nickel can lead to various adverse effects. These harmful effects encompass genotoxicity, hepatotoxicity, teratogenicity, immunotoxicity, and carcinogenicity (Fabiano *et al.,* 2015).

<b>Sampling</b> Locations	A	As	Co	Cr	Cu	<b>Fe</b>	Hq	Mn	<b>Mo</b>		<b>Pb</b>	lSb	Sе	<b>Sn</b>		ΙZη
$\mathsf{A}$	18476±20.	$0.11 \pm 0.16$	12.87±0.06	16.65±0.13	17.12±0.37	6945±31.64	1.36±0.89	557±5.11	$1.05 \pm 0.67$	$3.72 \pm 2.94$	14.57±3.85 4.68±2.30		$13.77 + 4.73$	$32+0.73$	29.18±0.12	19.65+0.30
B	2320±8.42°	.19±1.55	$5.58 + 0.44$	14.19±0.27	16.83±0.21	7407±24.12 <sup>ª</sup>	4.86±11.04	$560 + 2.12$	$0.97 + 0.55$	$0.68 \pm 0.69$	8.17±3.86	$4.06 + 2.39$	10.57±0.94	5.72±0.74 21.65±0.17		12.35±0.41
C	1892+9.62	$1.99 + 0.19$	$3.18 \pm 0.33$	$5.91 \pm 0.12$	$16.51 \pm 0.05$	$4231 \pm 25.59$	$1.69 + 0.70$	$118 + 0.53$	<b>BDL</b>	$0.34 + 0.44$	$7.74 \pm 4.00$	$13.30 \pm 1.00$	9.44±2.75	3.86±1.14	10.33±0.15	13.19±0.30
D	753±9.02	2.58±0.72	1.58±0.51	$8.04 \pm 0.42$	$805 \pm 0.10$ <sup>cc</sup>	1583±5.12	$0.59 + 0.29$	76.87±0.36	1.19±0.70	$1.13 \pm 0.17$	<b>BDL</b>	$5.21 \pm 0.50$	10.92±0.65	$2.11 \pm 0.01$	13.15±0.06	6.90±0.12
E	1500±7.21	1.17±2.66	$2.13 \pm 0.10$	$5.39 \pm 0.13$	$11.18 \pm 0.35$ <sup>tr</sup>	3432±33.60	$0.67 + 0.57$	86.46±0.73	0.12±0.45 3.31±0.19		<b>BDL</b>	$3.00 + 0.60$	12.54±0.23	$3.52 \pm 1.68$	18.65±0.31	$11.77 + 0.22$
	2033±27.85	2.70±0.87	$2.73 \pm 0.19$	$5.84 \pm 0.43$	$9.03 + 0.11$	4320±9.84	1.28±0.83	101±0.30	1.09±0.40	2.23±0.68	<b>BDL</b>	$3.67 \pm 0.00$	$16.42 \pm 1.80$		2.95+0.55 20.82+0.14	12.97±0.11
G	2565±0.19	$1.22 + 0.55$	$3.05 \pm 0.22$	$9,29+0.14$	12.23±0.03	6166±21.48	2.09+0.31	$126 + 1.24$	$0.47 + 0.37$	$1.66 + 0.35$	<b>BDL</b>	$5.73 \pm 1.50$	11.99±2.64		2.55±0.19 23.48±0.13	13.88±0.49
H	1386±9.70	1.70±1.69	$2.03 \pm 0.27$	$5.45 \pm 0.56$	$11.61 \pm 0.08$ <sup>tc</sup>	2781±8.11	$1.13 \pm 1.12$	92.10±0.91 <sup>c</sup>	0.70±0.61	$1.00 \pm 1.70$	<b>BDL</b>	$8.30 \pm 1.90$	$10.33 + 2.70$	$5.17 \pm 2.26$	26.03.16.03	$8.05 + 0.18$
	1025±5.78	$0.39 + 0.78$	$1.61 + 0.20$	$5.05 \pm 0.06$	10.95±0.03	1787±12.66 <sup>e</sup>	$0.86 \pm 1.49$	75.83±0.59°	0.39±0.45	$1.31 \pm 0.07$	<b>BDL</b>	8.56±0.41	7.59±3.77	$3.52 \pm 1.66$	42.16.17	$3.44 \pm 0.15$
	2482+55.44	$2.81 \pm 2.00$	$3.36 + 0.26$	$8.62 + 0.37$	10.18±0.19	4889.±31.93	$0.61 \pm 1.13$	$126 \pm 1.04$	$0.87 + 0.65$ $0.53 + 0.26$		<b>RDL</b>	$8.63 + 2.34$	12.68±2.83	$3.30 + 0.55$	41.79±0.08	$1261 + 0.21$
Mean	1678±0.15	$1.59 + 1.12$	$3.81 + 0.26$	$0.84 + 0.26$	12.37±0.01	4354±17.41	$1.51 \pm 1.84$	192±1.29	$0.69 + 0.48$	1.60±0.60	$3.05 + 1.17$	$5.52 + 1.29$	11.63±2.30		3.60±0.95 24.72±0.74	11.48±0.25
K(Control)	584±3.09	$0.13 + 0.05$	$1.02 + 0.03$	3.45±0.48	6.58±0.11	1750±3.77	$0.09 + 0.44$	258±2.40	0.31±0.25	1.30±0.50	<b>BDL</b>	1.58±0.64	14.21±3.12	1.60±0.35 7.38±0.13		10.29±0.13

**Table 4: Concentration of Heavy Metals in 10 Soil Samples (mg/kg)**

Mean values with same superscript along the same column are not significantly different (P>0.05); <BDL= Below Detection Limit

The non-carcinogenic assessment of soil heavy metals for both adults and children, considering ingestion, dermal contact, and inhalation exposure pathways, is presented in Table 5. The non-carcinogenic risk was found to be negligible for individuals of both age groups within the study area. The Hazard quotient (HQ) values for ingestion in adults ranged from 8.01 x 10<sup>-5</sup> to 1.25 x 10<sup>-</sup> <sup>3</sup>, while in children, it varied between 8.73 x 10<sup>-5</sup> and 1.63 x 10<sup>-3</sup>. The HQ values for dermal ranged from 8.86 x 10<sup>-3</sup> to 1.12 x 10<sup>-1</sup> (adults) and 9.02 x 10<sup>-2</sup> to 1.20 x 10-1 (children). The HQ values for inhalation varied between 9.09 x 10-15 and 1.09

 $x$  10<sup>-13</sup> (adults) and 6.37 x 10<sup>-15</sup> to 1.04 x 10<sup>-13</sup> (children). All HQ values were less than 1.0, which sum of HQs for three exposure pathways ( $\overline{Z}$  HQs = HI) for both adults and children were also less than 1.0 indicating non-carcinogenic adverse effect. The results derived from the estimation of non-carcinogenic risks in this study indicated that all identified heavy metals in soils do not pose a noncarcinogenic risk to the health of children and adults, as evidenced by hazard quotient (HQ) and hazard index (HI) values consistently were less than  $1$  (< 1)

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**Table 5: Non- Carcinogenic Risk (Hazard Quotient and Hazard Index (HI))**

The carcinogenic evaluation of heavy metals in soil for adults and children following ingestion, dermal, and inhalation pathways of exposure in this study is shown in Table 6. The ingestion rate cancer risk (CR) for adults and children ranged from  $1.17 \times 10^{-6}$  to 1.97 x 10<sup>-1</sup> and 2.25 x 10<sup>-5</sup> to 1.27 x 10<sup>-5</sup>, respectively. In adults, the CR value of Cr indicated cancer risk because the values were higher than the USEPA acceptable upper limit of  $1 \times 10^{-4}$ . But CR values in children were within the limit. CR values for dermal and inhalation pathways for both adults and children were far below acceptable limit.

This study showed that values of most metals assessed were below 1  $\times$  10<sup>-6</sup> lower limit of USEPA. Also, the cancer risk of lead, cadmium, and mercury can be considered insignificant except for chromium  $(1.97 \times 10^{-1})$ , which poses a cancer risk in adults. This finding agreed with the report of Aliakbar *et al* (2019) and Urbain *et al.,* (2021) where a similar work was done in Iran. Carcinogenic risk of some of the metals could not be calculated because their slope factors was not available

## **Table 6: Carcinogenic Risk.**



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#### **CONCLUSION**

The study concludes that Al, As, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, and Zn were detected except Cd. Fe had the highest concentration in the sampled soils. Also, the CR ingestion rate in adults for Cr was  $(1.97x10^{-1})$  which is higher than the USEPA limit, and can pose a health risk of cancer. Also, ingestion CR for adults and children was slightly higher than the lower limit of USEPA (1×10<sup>-6</sup>.) Noncarcinogenic risk estimation showed that the heavy metals assessed have no adverse health effects for adults and children.

## **RECOMMENDATIONS**

Following the outcome of this study, the following recommendations are made:

• Awareness and sensitization on health risks posed by contaminated quarry soil to residents must be done regularly.

Quarry workers should always use personal protective equipment (PPE) masks to reduce the risk of inhaling quarry dust, which could have long-term effects.

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