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Health Risk Assessment of Selected Heavy Metals in Cocoyam from Three Quarry Sites in Old Netim, Cross River State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

This study assessed health risk assessment of heavy metals in cocoyam from three quarry sites in Akamkpa LGA, Cross River State, Nigeria. Cocoyam tubers were obtained from three quarry sites in Oban Okoroba, each 4.5 kilometers apart and 20 kilometers from the control site. Cocoyam tubers were obtained from 0km, 0.2km, 0.4km, and 0.6km. Atomic Absorption Spectrophotometry (AAS) was used to determine the content of Lead (Pb), Cadmium (Cd), Copper (Cu), Arsenic (As) and Manganese (Mn), showing relative abundance across all sites and samples in the sequence Mn > Cu > Pb > As > Cd. Quarry site D had highest levels of Mn, As and Cu (50.003 ± 5.478 mgkg-1, 0.207 ± 0.184 and 4.522 ± 1.204mgkg-1). Quarry site C and B respectively had the highest levels of Pb and Cd (1.136 ± 0.267 mgkg-1 and 0.041 ± 0.028 mgkg-1). Results of Estimated Daily Intake (EDI), Target Hazard Quotient (THQ) and Life Carcinogenic Risk (LCR) showed ingestion of cocoyam tubers from Old Netim is safe and devoid of non-carcinogenic and carcinogenic risks. THI on the other hand revealed non-carcinogenic threat may result from prolonged ingestion of cocoyam tubers cultivated within quarry sites in Old Netim.

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1. INTRODUCTION

Quarry operations are sources of heavy metals in the ecosystem. Plants grown in quarry areas are likely to accumulate these metals from the soil through the roots or from atmospheric pollutants through the leaves [1]. Plants absorb heavy metals from polluted soil without any physical signs resulting in a possible risk to humans and animals consuming these plants [2]. Both active and abandoned quarry sites suffer heavy metal pollution. Heavy metal pollution within quarry environments increases from year to year [3]. Globally, heavy metal emissions even at low levels have long-term cumulative health consequences such as development of skin lesions, lung disease, neurological disorders, peripheral vascular disease, diabetes mellitus, hypertension and cardiovascular disease [4]. Heavy metals which are non-biodegradable and remain in both marine and terrestrial habitats for a long duration may be transferred from soil to groundwater or taken up by plants like farm crops such as Cocoyam [1]. Cocoyam, a starch-rich food and inexpensive root crop is cultivated by natives of southern Nigeria for its tuber. However, the fact that cocoyam is cultivated within many quarry sites sparked concerns that it may bioaccumulate heavy metals to levels dangerous to man when consumed. Heavy metals are reported to be the most prevalent of all metabolic toxins, with their cations interacting with ligands in enzymes like thiols, causing harmful consequences by displacing key metals from their usual binding sites or attaching to proteins and nucleic acids, causing conformational changes [5].

When the environmental heavy metal concentrations increase because of elevated quarrying activities, the quantity of heavy metals in soil, plants, bodies of surface water, tubers and fruit also increase over time within the quarry and its environment. Given the variety of activities conducted in quarries which increases the environmental heavy metal concentration, there is need to investigate the negative impact of quarry on plants and humans around such areas. This study aimed at investigating heavy metal concentration and health risk assessment associated with consumption of cocoyam from three quarry sites in Old Netim, Cross River State, Nigeria.

2. MATERIALS AND METHODS

2.1 Study Area

The location of the research area is within latitudes 5°10"N - 5° 25"N and longitude 8°20"E - 8°35"E in the southern senatorial district of Cross River State (Fig. 1). It is a typical rainforest vegetation that has been disturbed by quarrying activities with an undulating topography. It has a secondary forest commonly occupied by oil palms, umbrella tree, cabbage tree, silk cotton trees and walnut.

2.2 Sample Collection

Cocoyam Samples were obtained from three independent quarry industries (B, C and D) polluted with heavy metals at 4.5km apart in Old Netim and 20km away from control (A) not polluted with heavy metals in Oban Okoroba, all in Akamkpa L.G.A of Cross River State for heavy metals investigation. At each of the quarry sites, samples of cocoyam were harvested at various distances; 0km, 0.3km, 0.6km and 0.9km.

2.3 Sample Preparation

The cocoyam tubers were peeled, cleaned in deionized water, sliced and dried in a dust free environment for one week. The cocoyam was blended into powder and digested by wet digestion method. An overall quantity of 100ml H_2SO_4, HNO_3, and HClO was prepared in ratio 2:2:1. 1g of powdered cocoyam tuber was poured into a conical flask, 2ml of the acid mixture was added to the sample and digested on a hot plate in fume hood till whitish fumes appeared. The digested sample was cooled, filtered into 100 ml flask and deionized water used to make it up to mark.

2.4 Determination of Heavy Metal Concentration

Heavy metal concentrations in the samples were determined using an Atomic Absorption Spectrophotometer [6].

2.5 Health Risk Assessment

Estimated Daily Intake (EDI), Target Hazard Quotient (THQ) and Life Carcinogenic Risk (CR) were used to assess the potential risk of heavy metals in cassava and cocoyam from Old

Netim and Urban Okoroba. The calculations were based on USEPA [7] standards (Table 1).

Estimated Daily Intake (EDI): EDI of heavy metals was determined as described by USEPA [7].

$$\text{Estimated Daily Intake (EDI)} = \frac{\text{CHM} \times \text{Cf} \times \text{DFI}}{\text{ABW}}$$

Where: CHM = Concentration of Heavy Metal in $mgkg^{-1}$, Cf = Conversion Factor, DFI = Daily Food Intake in $kgperson^{-1}$ and ABW = Average Body Weight in $kgperson^{-1}$ [1,7,8].

Target Hazard Quotient (THQ): The target hazard quotient (non-carcinogenic risk) that may result from consumption of cocoyam tuber from Old Netim and Urban Okoroba was determined as described by USEPA [7].

$$\text{Target Hazard Quotient (THQ)} = \frac{\text{EDI}}{\text{RFD}}$$

Where: EDI = Estimated Daily Intake of Metal in $mgkg^{-1}day^{-1}$ and RFD = Oral reference dose in $mgkg^{-1}day^{-1}$ [1,7,8].

Target Hazard Index (THI): Target Hazard Index (THI) was calculated by summation of the overall Target Hazard Quotient (THQ) [8].

Target Hazard Index (THI) = Sum of THQ (THQ_{Pb}+ THQ_{Cd}+ THQ_{Cu}+ THQ_{As} + THQ_{Mn})

Where: THQ = Target Hazard Quotient, THQ_{Pb} = Target Hazard Quotient of Lead, THQ_{Cd} = Target Hazard Quotient of Cadmium, THQ_{Cu} = Target Hazard Quotient of Copper, THQ_{As} = Target Hazard Quotient of Arsenic and THQ_{Mn} = Target Hazard Quotient of Manganese [8].

Life Carcinogenic Risk (CR): Lifetime likelihood of getting cancer as a result of heavy metal concentration was obtained by calculating the Carcinogenic Risk [8] as shown below.

$$\text{Life Carcinogenic Risk (CR)} = \text{EDI} \times CSF_{ing}$$

Where: EDI = Estimated Daily Intake in heavy metals in $mgkg^{-1}day^{-1}$ and CSF_{ing} = Ingestion Cancer Slope Factor in $mgkg^{-1}day^{-1}$ [1,8].

2.6 Statistical Analysis

Statistical Package for Social Sciences (SPSS) (Version 23) was used to analyze the data. The significant difference ($p \leq 0.05$) was determined using one-way ANOVA, and the LSD Post Hoc test was utilized to discover where these differences lay. Microsoft Excel was used for other statistical analyses and calculations.

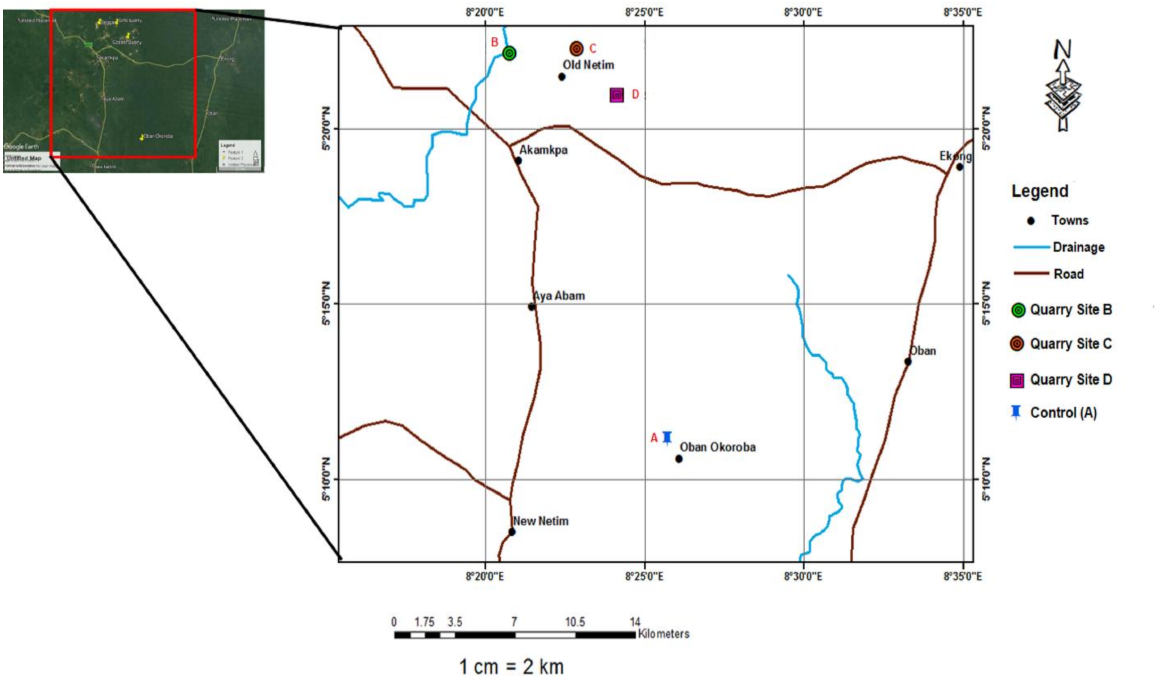

Fig. 1. Sample location and accessibility map

Table 1. Toxicological characteristics ($mgkg^{-1}day^{-1}$) of investigated metals [7,8]

Metals	Ingestion reference dose (RFDing)	Ingestion cancer slope factor (CSFing)
Pb	0.0035	0.0085
Cd	0.001	0.38
Cu	0.04	0.00
As	0.003	1.5
Mn	0.14	0.00

Table 2. Recommended standard values for health risk assessment in cocoyam tubers [8]

	Average Body Weight (ABW) (kg)	Daily Food Intake (DFI) ($kgperson^{-1}day^{-1}$)	Conversion Factor (CF)
Adult	60	0.418	0.085
Children	3.2	0.209	0.085

3. RESULTS

3.1 Heavy Metals Concentration ($MgKg^{-1}$ dry weight) in Soils and Cocoyam Tubers

Table 3 presents the heavy metals concentration ($mgkg^{-1}$ dry weight) in Soil from Quarry Sites B, C, D and Control Site A. Results show that mean concentration of Pb ranges from 2.831 ± 0.001 $mgkg^{-1}$ to 12.289 ± 2.882 $mgkg^{-1}$, Cd from 0.201 ± 0.001 $mgkg^{-1}$ to 2.157 ± 1.230 $mgkg^{-1}$, Cu from 4.92 ± 0.013 $mgkg^{-1}$ to 26.580 ± 6.181 $mgkg^{-1}$, As ranged from 0.813 ± 0.001 $mgkg^{-1}$ to 3.076 ± 1.650 $mgkg^{-1}$ and Mn ranges from 5.94 ± 0.013 $mgkg^{-1}$ to 47.166 ± 5.206 $mgkg^{-1}$. Table 4 presents heavy metals concentration ($mgkg^{-1}$ dry weight) in Cocoyam tubers from Quarry Sites B, C, D and Control Site A. Result show that mean concentration ranges from 0.051 ± 0.001 $mgkg^{-1}$ to 1.136 ± 0.267 $mgkg^{-1}$ for Pb, 0.019 ± 0.005 $mgkg^{-1}$ to 0.041 ± 0.028 $mgkg^{-1}$ for Cd, 1.150 ± 0.001 $mgkg^{-1}$ to 4.522 ± 1.204 $mgkg^{-1}$ for Cu, 0.008 ± 0.001 $mgkg^{-1}$ to 0.207 ± 0.184 $mgkg^{-1}$ for As and 7.812 ± 0.001 $mgkg^{-1}$ to 50.003 ± 5.478 $mgkg^{-1}$ for Mn.

3.2 Estimated Daily Intake (EDI) of Metals in Cocoyam ($Mgkg^{-1}person^{-1}day^{-1}$)

Table 5 shows the Estimated Daily Intake (EDI) of metals in cocoyam tubers for adults. The EDI for Pb was between 3.02E-05 $mgkg^{-1}person^{-1}day^{-1}$ and 6.73E-04 $mgkg^{-1}person^{-1}day^{-1}$, Cd was between 1.13E-05 $mgkg^{-1}person^{-1}day^{-1}$ and 2.43E-05 $mgkg^{-1}person^{-1}day^{-1}$, Cu was between 6.81E-04 $mgkg^{-1}person^{-1}day^{-1}$ and 2.68E-03 $mgkg^{-1}person^{-1}day^{-1}$, As was between 4.74E-06 $mgkg^{-1}person^{-1}day^{-1}$ and 1.23E-04 $mgkg^{-1}person^{-1}day^{-1}$ and Mn was between 4.63E-03 $mgkg^{-1}person^{-1}day^{-1}$ and 2.96E-02 $mgkg^{-1}person^{-1}day^{-1}$. Table 6 shows the EDI of metals in cocoyam tubers for children. The EDI for Pb was between 2.77E-05 $mgkg^{-1}person^{-1}day^{-1}$ and 6.17E-04 $mgkg^{-1}person^{-1}day^{-1}$, Cd was between 1.03E-05 $mgkg^{-1}person^{-1}day^{-1}$ and 2.23E-05 $mgkg^{-1}person^{-1}day^{-1}$, Cu was between 4.35E-06 $mgkg^{-1}person^{-1}day^{-1}$ and 2.46E-03 $mgkg^{-1}person^{-1}day^{-1}$, As was between 4.35E-06 $mgkg^{-1}person^{-1}day^{-1}$ and 1.12E-04 $mgkg^{-1}person^{-1}day^{-1}$ and Mn was between 4.24E-03 $mgkg^{-1}person^{-1}day^{-1}$ and 2.72E-02 $mgkg^{-1}person^{-1}day^{-1}$.

3.3 Targeted Hazard Quotient (THQ) and Targeted Hazard Index (THI) of metals in Cocoyam tubers ($Person^{-1}$)

The non-carcinogenic risk assessment of heavy metals in cocoyam samples from quarry site B, C, D and control site A for adults is presented in Table 7. Results show that the THQ of Pb was between 8.60E-03 $Person^{-1}$ and 1.92E-01 $Person^{-1}$, Cd was between 1.13E-02 $Person^{-1}$ and 2.43E-02 $Person^{-1}$, Cu was between 1.70E-02 $Person^{-1}$ and 6.69E-02 $Person^{-1}$, As was between 1.58E-02 $Person^{-1}$ and 7.50E-02 $Person^{-1}$ and Mn was between 3.30E-02 $Person^{-1}$ and 2.12E-01 $Person^{-1}$. THI for site A, B, C and D were 9.76E-02 $Person^{-1}$, 4.66E-01 $Person^{-1}$, 4.70E-01 $Person^{-1}$ and 7.92E-01 $Person^{-1}$ respectively. Table 8 shows the non-carcinogenic risk assessment of heavy metals in cocoyam samples from quarry site B, C, D and control site A for children. Results show that the THQ of Pb was between 7.90E-03 $Person^{-1}$ and 1.76E-01 $Person^{-1}$, Cd was between 1.03E-02 $Person^{-1}$ and 2.23E-02 $Person^{-1}$, Cu was between 1.56E-02 $Person^{-1}$ and 6.14E-02 $Person^{-1}$, As was between 1.45E-02 $Person^{-1}$ and 3.75E-01 $Person^{-1}$, Mn was between 3.03E-02 $Person^{-1}$

and 1.94E-01 $Person^{-1}$. THI for site A, B, C and D were 8.95E-02 $Person^{-1}$, 4.27E-01 $Person^{-1}$, 4.31E-01 $Person^{-1}$ and 7.26E-01 $Person^{-1}$ respectively.

3.4 Carcinogenic Risk (CR) of Metals in Cocoyam Tubers ($mgkg^{-1}day^{-1}$)

The Carcinogenic Risk (CR) of heavy metals in cocoyam samples from quarry site B, C, D and control site A for adults is shown in Table 9. Results show that the CR for Pb was between 2.57E-07 $mgkg^{-1}day^{-1}$ and 5.72E-06 $mgkg^{-1}day^{-1}$, Cd was between 4.28E-06 $mgkg^{-1}day^{-1}$ and 9.23E-06 $mgkg^{-1}day^{-1}$, Cu was 0.00 $mgkg^{-1}day^{-1}$, As was between 7.11E-06 $mgkg^{-1}day^{-1}$ and 1.84E-04 $mgkg^{-1}day^{-1}$ and Mn was 0.00 $mgkg^{-1}day^{-1}$. TLCR for site A, B, C and D were 1.61E-05 $mgkg^{-1}day^{-1}$, 4.66E-05 $mgkg^{-1}day^{-1}$, 3.40E-05 $mgkg^{-1}day^{-1}$ and 1.91E-04 $mgkg^{-1}day^{-1}$ respectively. Table 10 shows the Carcinogenic Risk (CR) of heavy metals in cassava samples from quarry site B, C, D and control site A for children. Results showed that CR for Pb was between 2.36E-07 $mgkg^{-1}day^{-1}$ and 5.25E-06 $mgkg^{-1}day^{-1}$, Cd was between 3.92E-06 $mgkg^{-1}day^{-1}$ and 8.46E-06 $mgkg^{-1}day^{-1}$, Cu was 0.00 $mgkg^{-1}day^{-1}$, As was between 6.52E-06 $mgkg^{-1}day^{-1}$ and 1.69E-04 $mgkg^{-1}day^{-1}$ and Mn was 0.00 $mgkg^{-1}day^{-1}$. TLCR for site A, B, C and D were 1.48E-05 $mgkg^{-1}day^{-1}$, 4.28E-05 $mgkg^{-1}day^{-1}$, 3.12E-05 $mgkg^{-1}day^{-1}$ and 1.76E-04 $mgkg^{-1}day^{-1}$ respectively.

4. DISCUSSION

Results in Tables 3 and 4 show the heavy metals concentration ($mgkg^{-1}$ dry weight) in Soil and Cocoyam tubers from Old Netim (polluted region) and Oban Okoroba (control region) of Akamkpa Local Government Area of Cross River State. Heavy metal toxicity test for this study was performed using Lead (Pb), Cadmium (Cd), Copper (Cu), Arsenic (As) and Manganese (Mn). The abundances of under sought toxic metals were Mn > Cu > Pb > As > Cd throughout all sites and samples. Results also show that quarry operations had a considerable impact on the level of heavy metals studied which is in consonance with the study of Zhuang et al. [11] who reported mining activities resulted in elevated heavy metal levels in soils and food crops around Dabaoshan mine in Guangdong China. Also, Ebrahimi et al. [12] showed that pollution of soil, plants and groundwater resulted from industrial practices, while Onyedikachi et al. [1] found out that there was an elevated levels of Heavy metals in soil and consumable crops cultivated within quarry industries in Ebonyi State of Nigeria.

Pb concentrations of cocoyam samples from quarry sites (B, C, D) were higher than that of control site A and WHO/FAO [9] set limit (0.100 $mgkg^{-1}$). Pb concentration in cocoyam tubers from Old Netim, Akamkpa (Table 4) fell beyond normal levels, making Pb a threat to life of indigenes living in Old Netim, Akamkpa and the neighboring LGAs in Cross River State. These results also corroborate those of Eteng et al. [13]. Acute exposure to Pb can contribute to loss of appetite, headache, hypertension, stomach discomfort, renal failure, nausea, insomnia, arthritis, hallucinations, and vertigo, while chronic exposure can lead to intellectual disability, birth defects, hysteria, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscle weakness, brain injury, kidney damage and even death [14]. Pb replaces Ca^{2+} and Mg^{2+} during metabolic processes in cell adhesion, intercellular/intra-cellular signaling, apoptosis, ionic transport, protein folding, enzyme control and neurotransmitter release [15].

Cd levels in cocoyam tubers from the quarry sites were below WHO/FAO [9] permissible limit (0.100 $mgkg^{-1}$), indicating that indigenes of Old Netim would not suffer Cd poisoning on consuming cocoyam cultivated within the stone quarry factories. Cd toxicity affects cell growth, apoptosis and cell differentiation. Cd interferes with DNA repair, apoptosis, cellular respiration and oxidative phosphorylation, triggering mutations and chromosomal deletions, leading to chromosomal aberrations, exchange of sister chromatids, breaks of DNA strands and crosslinks of DNA proteins in cell lines [16].

Cu concentration in cocoyam tubers from the three quarry sites were all higher than concentration of Cu in the control site, implicating quarry activities as a cause of elevated Cu levels in cocoyam tubers grown within the quarry factories. Cu levels in cocoyam from quarry sites B, C, and D together with control site A were above WHO/FAO permissible limit of 0.05 $mgkg^{-1}$ and this is in consonance with the study of Onyedikachi et al. [1] on concentration of Cu in edible crops cultivated proximal to quarry sites. While adequate copper intake protects man from lead poisoning, elevated lead absorption is attributed to increased Cu consumption [17]. Cu(I) and Cu (II) have a strong binding affinity for proteins with side chains of cysteine, methionine

Table 3. Mean concentration of heavy metals in soils from Quarry Sites A, B, C and D ($mgkg^{-1}$ dry weight)

SAMPLE	Pb	Cd	Cu	As	Mn
A_s	2.831 ± 0.001[a]	0.201 ± 0.001[ab]	4.92 ± 0.013[a]	0.813 ± 0.001[abd]	5.94 ± 0.013[a]
B_s	10.396 ± 2.541[bcd]	1.440 ± 0.582[abcd]	21.319 ± 5.130[bcd]	2.709 ± 1.094[abcd]	46.552 ± 7.931[bd]
C_s	9.089 ± 1.548[bc]	2.157 ± 1.230[bcd]	22.839 ± 7.696[bcd]	3.076 ± 1.650[bcd]	33.930 ± 6.653[c]
D_s	12.289 ± 2.882[bd]	1.649 ± 1.119[bcd]	26.580 ± 6.181[bcd]	2.076 ± 1.737[abcd]	47.166 ± 5.206[bd]
WHO/FAO	8.00	0.430	11.000	0.500	9.940

Values are presented as mean ± SD of quadruplet determination (n=4). Mean values with the same superscript letters are not statistically significant at $P \leq 0.05$. A_s - Soil sample from Control Area, B_s -Soil sample from Quarry B, C_s -Soil sample from quarry C, D_s -Soil sample from quarry D. WHO/FAO [9].

Table 4. Heavy Metals Concentration ($mgkg^{-1}$ dry weight) in Cocoyam Tubers

SAMPLE	Pb	Cd	Cu	As	Mn
A_{cy}	0.051 ± 0.001[ad]	0.039 ± 0.001[abcd]	1.150 ± 0.001[a]	0.008 ± 0.001[abc]	7.812 ± 0.001[a]
B_{cy}	0.712 ± 0.494[bcd]	0.041 ± 0.028[abcd]	2.378 ± 0.525[bc]	0.038 ± 0.025[abc]	49.852 ± 5.038[bd]
C_{cy}	1.136 ± 0.267[bc]	0.019 ± 0.005[abcd]	3.448 ± 0.830[bcd]	0.027 ± 0.012[abc]	38.372 ± 3.015[c]
D_{cy}	0.545 ± 0.360[abd]	0.021 ± 0.013[abcd]	4.522 ± 1.204[cd]	0.207 ± 0.184[d]	50.003 ± 5.478[bd]
*WHO/FAO	0.100	0.100	0.050	0.100	2.000

Values are presented as mean ± SD of quadruplet determination (n=4). Mean values with the same superscript letters are not statistically significant at $P \leq 0.05$. A_{cy} - Cocoyam sample from Control Area, B_{cy} - Cocoyam sample from quarry B, C_{cy} - Cocoyam sample from quarry C, D_{cy} - Cocoyam sample from quarry D. * WHO/FAO [9].

Table 5. Estimated Daily Intake (EDI) of Metals in Cocoyam Tubers for Adults ($Mgkg^{-1}person^{-1}day^{-1}$)

SAMPLE	Pb	Cd	Cu	As	Mn	Total
A_{cy}	$3.02x10^{-5}$	$2.31x10^{-5}$	$6.81x10^{-5}$	$4.74x10^{-6}$	$4.63x10^{-3}$	$5.37x10^{-3}$
B_{cy}	$4.22x10^{-4}$	$2.43x10^{-5}$	$1.41x10^{-3}$	$2.25x10^{-5}$	$2.95x10^{-2}$	$3.14x10^{-2}$
C_{cy}	$6.73x10^{-4}$	$1.13x10^{-5}$	$2.04x10^{-3}$	$1.60x10^{-5}$	$2.27x10^{-2}$	$2.55x10^{-2}$
D_{cy}	$3.23x10^{-4}$	$1.24x10^{-5}$	$2.68x10^{-3}$	$1.23x10^{-4}$	$2.96x10^{-2}$	$3.27x10^{-2}$
*UTDI	$2.4x10^{-1}$	$6.4x10^{-2}$	$1x10^{1}$	$2x10^{-2}$	$1.1x10^{1}$	

**UTDI - Upper Tolerable Daily Intake levels of heavy metals in foodstuffs* [8,10]

Table 6. Estimated Daily Intake of Metals (EDI) in Cocoyam Tubers for Children ($mgkg^{-1}person^{-1}day^{-1}$)

SAMPLE	Pb	Cd	Cu	As	Mn	Total
A_{cy}	$2.77x10^{-5}$	$2.12x10^{-5}$	$6.25x10^{-6}$	$4.35x10^{-6}$	$4.24x10^{-3}$	$4.92x10^{-3}$
B_{cy}	$3.87x10^{-4}$	$2.23x10^{-5}$	$1.29x10^{-3}$	$2.06x10^{-5}$	$2.71x10^{-2}$	$2.88x10^{-2}$
C_{cy}	$6.17x10^{-4}$	$1.03x10^{-5}$	$1.87x10^{-3}$	$1.47x10^{-5}$	$2.08x10^{-2}$	$2.34x10^{-2}$
D_{cy}	$2.96x10^{-4}$	$1.14x10^{-5}$	$2.46x10^{-3}$	$1.12x10^{-4}$	$2.72x10^{-2}$	$3.00x10^{-2}$
*UTDI	$2.4x10^{-1}$	$6.4x10^{-2}$	$1x10^{1}$	$2x10^{2}$	$1.1x10^{1}$	

**UTDI* [8,10]

Table 7. Targeted Hazard Quotient (THQ) and Targeted Hazard Index (THI) of metals in Cocoyam tubers for Adult ($Person^{-1}$)

SAMPLE	Pb	Cd	Cu	As	Mn	THI
A_{cy}	$8.60x10^{-3}$	$2.31x10^{-2}$	$1.70x10^{-2}$	$1.58x10^{-2}$	$3.30x10^{-2}$	$9.76x10^{-2}$
B_{cy}	$1.21x10^{-1}$	$2.43x10^{-2}$	$3.52x10^{-2}$	$7.50x10^{-2}$	$2.11x10^{-1}$	$4.66x10^{-1}$
C_{cy}	$1.92x10^{-1}$	$1.13x10^{-2}$	$5.10x10^{-2}$	$5.33x10^{-2}$	$1.62x10^{-1}$	$4.70x10^{-1}$
D_{cy}	$9.22x10^{-2}$	$1.24x10^{-2}$	$6.69x10^{-2}$	$4.09x10^{-1}$	$2.12x10^{-1}$	$7.92x10^{-1}$
*USEPA	1	1	1	1	1	1

**USEPA- United States Environmental Protection Agency [7]*

Table 8. Targeted Hazard Quotient (THQ) and Targeted Hazard Index (THI) of metals in Cocoyam tubers for Children ($Person^{-1}$)

SAMPLE	Pb	Cd	Cu	As	Mn	THI
A_{cy}	$7.90x10^{-3}$	$2.12x10^{-2}$	$1.56x10^{-2}$	$1.45x10^{-2}$	$3.03x10^{-2}$	$8.95x10^{-2}$
B_{cy}	$1.11x10^{-1}$	$2.23x10^{-2}$	$3.23x10^{-2}$	$6.88x10^{-2}$	$1.93x10^{-1}$	$4.27x10^{-2}$
C_{cy}	$1.76x10^{-1}$	$1.03x10^{-2}$	$4.68x10^{-2}$	$4.89x10^{-2}$	$1.49x10^{-1}$	$4.31x10^{-2}$
D_{cy}	$8.46x10^{-2}$	$1.14x10^{-2}$	$6.14x10^{-2}$	$3.75x10^{-1}$	$1.94x10^{-1}$	$7.26x10^{-2}$
*USEPA	1	1	1	1	1	1

**USEPA [7].*

Table 9. Life Carcinogenic Risk (CR) of metals in Cocoyam tubers for adults ($mgkg^{-1}day^{-1}$)

Sample	Pb	Cd	Cu	As	Mn	TLCR
A_{cy}	$2.57x10^{-7}$	$8.78x10^{-6}$		$7.11x10^{-6}$		$1.61x10^{-5}$
B_{cy}	$3.58x10^{-6}$	$9.23x10^{-6}$		$3.38x10^{-5}$		$4.66x10^{-5}$
C_{cy}	$5.72x10^{-6}$	$4.28x10^{-6}$		$2.40x10^{-5}$		$3.40x10^{-5}$
D_{cy}	$2.74x10^{-6}$	$4.73x10^{-6}$		$1.84x10^{-4}$		$1.91x10^{-5}$
*USEPA	10^{-6} - 10^{-4}	10^{-6} - 10^{-4}		10^{-6} - 10^{-4}		10^{-6} - 10^{-4}

**USEPA* [7]

Table 10. Life Carcinogenic Risk (CR) of metals in Cocoyam tubers for Children ($mgkg^{-1}day^{-1}$)

Sample	Pb	Cd	Cu	As	Mn	TLCR
A_{cy}	$2.36x10^{-7}$	$8.05x10^{-6}$		$6.52x10^{-6}$		$1.48x10^{-5}$
B_{cy}	$3.29x10^{-6}$	$8.46x10^{-6}$		$3.10x10^{-5}$		$4.28x10^{-5}$
C_{cy}	$5.25x10^{-6}$	$3.92x10^{-6}$		$2.20x10^{-5}$		$3.12x10^{-5}$
D_{cy}	$2.52x10^{-6}$	$4.34x10^{-6}$		$1.69x10^{-4}$		$1.76x10^{-4}$
*USEPA	10^{-6} - 10^{-4}	10^{-6} - 10^{-4}		10^{-6} - 10^{-4}		10^{-6} - 10^{-4}

**USEPA* [7]

and histidine. Cu concentration above the safe limit contributes to displaced key metal ions from their catalytic sites, thus causing protein misfolding. Excess amounts of Cu participate in development of Reactive Oxidative Species (ROS) and this is known to have a devastating effect on the cell, DNA protein and lipids [18].

As concentration in cocoyam tubers from the quarry sites in this study were all higher than As concentration of the control site, implicating quarry activities as a cause of elevated As levels in cocoyam tubers cultivated around the quarry factories. The findings of Ukpong [19] corroborates results in this study. Only site D had an As concentration above the WHO/FAO permissible limit of 0.100 $mgkg^{-1}$, suggesting that only residents consuming cocoyam planted within quarry site D were at risk of As toxicity. As is associated with a broad range of health problems such as skin, liver, kidney, lymphatic cancer and gastrointestinal disorders due to its toxicity [20]. Arsenic inhibits different cell signaling pathways. It interacts with biological macromolecules resulting in damage to DNA, peroxidation of lipids and modification of antioxidant enzyme concentration such as superoxide dismutase (SOD) and catalase (CAT) [20]. Exposure for a short period of time to minimal As reduces erythrocyte and leukocyte production, damages the blood vessels, causes nausea and vomiting, causes irregular heartbeat and feelings of prickling sensations in hands and legs, while exposure for a long period of time leads to skin lesions, peripheral vascular disease, pulmonary and cardiovascular disease, neurological disorders and diabetes [21].

Mn concentration in cocoyam tubers across all quarry sites B, C, D and control site A were above the WHO/FAO [9] permissible limit of 2.00 $mgkg^{-1}$. Mn concentration in cocoyam tubers from the quarry sites were all higher than that of the control site, implicating quarry activities as a cause of elevated Mn levels in cocoyam tubers cultivated within the stone quarry factories.

The health risk associated with consumption of cocoyam from the quarry sites were examined using toxicological indices such as EDI, THQ and CR for children and adults (Tables 4 - 9).

EDI for adults and children through the consumption of cocoyam tubers from quarry sites B, C, D and control site A (Tables 5 and 6). Respective EDI from quarry polluted sites were higher than their corresponding controls, except for Cd whose EDI for control site was slightly greater than that of quarry site C and D for both adults and children. EDI was dependent on the concentration of heavy metal, and the elevation of EDI levels for Pd, Cu, As and Mn in the quarry sites over that of the control site indicates quarry activities are impacting negatively on soil and tuber crops planted within the quarry factories as earlier reported by Onyedikachi et al*.* [1]. Cd levels in quarry sites C and D could be lower than that of the control sit A because of the relatively low or zero content of Cd in soil parent rocks of quarry sites C and D as reported by Onyedikachi et al*.* [1].

THQ and THI for adults and children in cocoyam tubers from quarry sites B, C, D and control site A (Tables 7 and 8). Levels of THQ in cocoyam from quarry sites were higher than that of their corresponding controls, indicating a negative impact of quarry activities on cocoyam cultivated within the quarry sites, and agreeing with the findings of Onyedokachi et al*.* [1]. However, levels of THQ in cocoyam tubers from these quarries for both adults and children were below the USEPA [7] standard, indicating indigenes of Old Netim who feed on cocoyam from farms within these sites are likely not to suffer noncarcinogenic risks.

LCR and TLCR ($mgkg^{-1}day^{-1}$) for adults and children in cocoyam tubers from quarry sites B, C, D and control site A (Tables 9 and 10). Levels of LCR in the quarry sites were higher than that of their corresponding controls, except for Cd whose control was slightly greater than that of quarry sites C and D for both adults and children which could be as a result of the fact that parent rocks material in quarry sites C and D may contain just a little or zero amount of Cd as reported by Onyedikachi et al. [1] who found out that high amounts of heavy metals in edible plants and top soil originated from parent rock materials. LCR and TLCR for both tubers and sites were within the permissible lifetime risk set by USEPA [7] for carcinogens.

5. CONCLUSION

Levels of Pb, Cd, Cu, As and Mn in cocoyam samples from quarry sites were above that of control site and WHO/FAO standard. This implies quarrying activities have tailing impact on levels of heavy metals in soil within quarry sites in Old Netim, Akamkpa of Cross River State. EDI was higher in cocoyam tubers cultivated within quarry sites than in tubers from control site, but below the UTDI. THQ for cocoyam tubers grown within quarry sites were above that of control site, implying quarry activities affected THQ levels of tubers cultivated within quarry sites in Old Netim. THI of cocoyam within quarry sites for adult and children were above that of control site, but all below USEPA standard (< 1 $Person^{-1}$). Meaning adult and children consuming cocoyam tubers cultivated within these quarry sites may not suffer noncarcinogenic risk, given that their THI was bellow USEPA standard. All LCR and TLCR for cocoyam tubers were within USEPA permissible lifetime risk for carcinogens.

DISCLAIMER

The products employed in this study is widely and often used in our field of study and in our country. There is no conflict of interest between the authors and suppliers of the products because we do not plan to use them as a means of pursuing legal action, but rather to further knowledge. Furthermore, the research was not supported by the production firm, but rather by the authors' own efforts.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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