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Hazardous Heavy Metals in Urban Cemetery Soils: Health Risk Assessment of Vegetable Cultivation in Benin City

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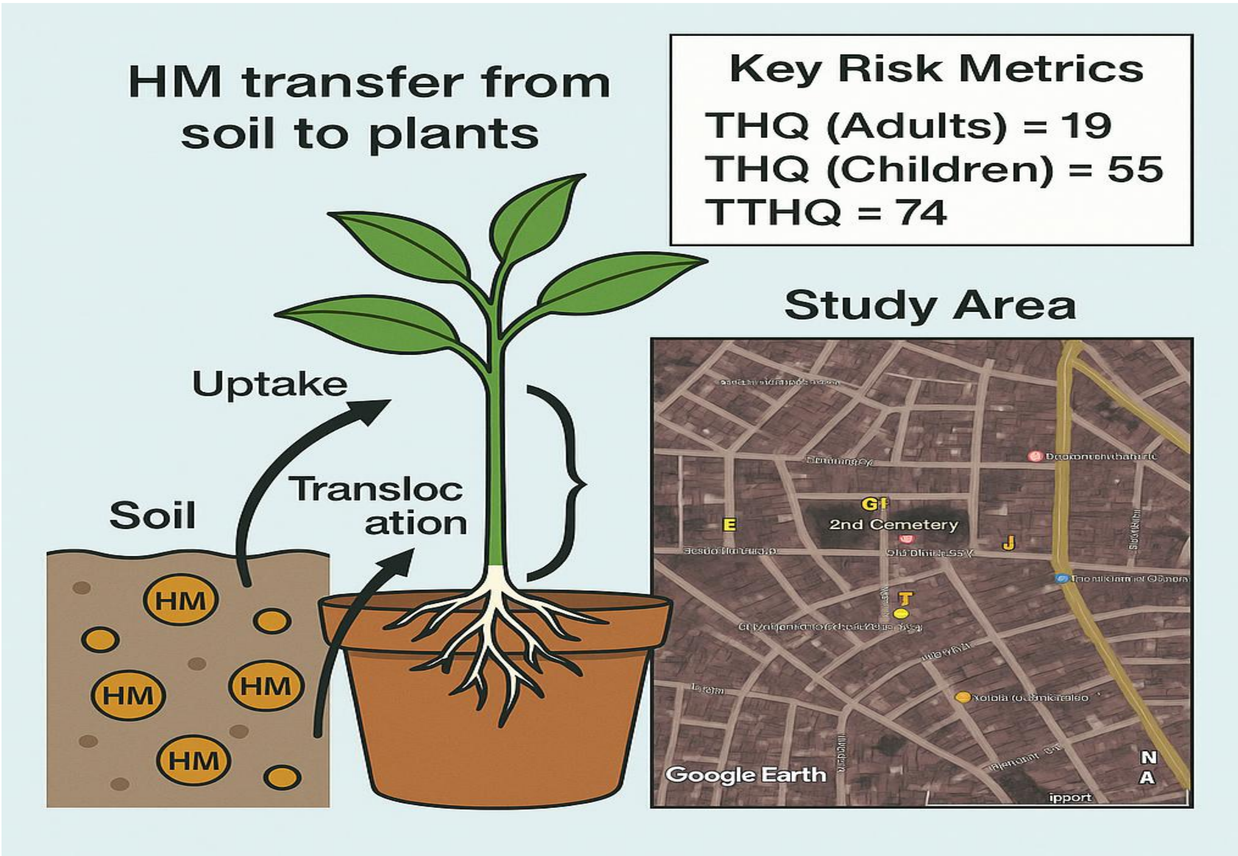
Abstract

In this research, we examined the amounts of heavy metals in both vegetables and soil samples, and the potential health risks associated with consuming vegetables sourced from the vicinity of Second cemetery, Benin City, Edo State, Nigeria. Soil samples, were collected using a hand auger from depths of 0 to 20cm, air-dried, crushed to powder and sieved to obtain fine particles. Simultaneously, four distinct vegetables (mango, orange, potato, and bitter-leaf) were randomly gathered from the areas surrounding the cemetery, and taken to the Civil Engineering Laboratory at the University of Benin, Benin City, Nigeria, for further preparation. After washing with distilled water to remove dirt, they were separated, air-dried, and further dried in an oven at 65°C for 72 hours until a constant weight of 5g was obtained. Subsequently, the dried leaves were pulverized with a mortar and pestle, converted to powder, and stored in a plastic bag for subsequent analysis. The analysis of the collected vegetable samples involved employing a wavelength-dispersive X-ray fluorescence spectrometer (SKYRAY INSTRUMENT EDX3600B). Health risk parameters such as Health Risk Index, and Target Health Quotient, were assessed. The results obtained disclosed that the soils and plants are contaminated with Sn, Sb, Fe, Pb, Cd, and Zn. The Target Health Quotient (THQ) values reached 74.606, surpassing the WHO-recommended limit of one, suggesting that the ingestion of these vegetables poses significant health risks to humans, with children being the most vulnerable due to their susceptibility to heavy metals toxicity.

Keywords: *Pollution; Heavy metals; Health risk; X-ray fluorescence spectrometer method.*

Graphical Abstract



1.0 INTRODUCTION

Soil and the consumable portions of vegetables worldwide are challenged by heavy metals contamination[1]. The presence of toxic concentrations of heavy metals in soils not only adversely impacts the soil and plant health but also poses risks to the well-being of individuals. Heavy metals are not biodegradable; therefore, they stay in the soil and are taken up by plants [2]. The attention given to agriculturally productive soils contaminated with heavy metals is crucial, as soil is a vital resource for life and necessitates protection from an excess buildup of these contaminants [3]. Also, there is a crucial need for the study of HMs in agricultural soils as children are particularly susceptible to the toxic health effects of ingestion of vegetables contaminated with them [4]. There has been a growing concern in assessing the quantities of HMs in public food supplies. However, their overall concentrations might not always match their concentration in a bioavailable condition [5]. This leads to challenges in waste management, such as clogged streams, auto shops and service stations pollution, inappropriate toxic waste disposal, and dump yards that pose health hazards to the environment.

Health hazards that arises from the ingestion of HMs into the body include conditions such as cancer, neurological disorders, fragile bones, and organ damage [6], [7], [8]. According to the USEPA (2000), antimony (Sb) causes inflammation of the lungs, chronic bronchitis, emphysema, skin and eye irritation. Excessive ingestion of antimony through foods contaminated with Sb can lead to cancer, liver, and cardiovascular diseases. Ingesting substantial amounts of inorganic tin (Sn) compounds can result in liver and kidney problems, anemia, and stomachaches (ASTDR 2005). The National Institute of Health (NIH) and Office of Dietary Supplements (ODS) warns that excessive iron (Fe) intake could cause constipation, abdominal pain, vomiting, diarrhea, stomach upset, convulsions, ulcers, and ultimately death. Regardless of zinc's importance to the body, excessive intake can lead to copper deficiency [9]. Excessive intake of cadmium (Cd) is linked to prostate and lung cancer, cardiovascular issues, and problems in the gastrointestinal and reproductive systems [10]. Children who are exposed to lead (Pb) may suffer harm

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to their kidneys, bone marrow, brains, and other organs [11].

[12] disclosed that the breakdown and decay of interred bodies in cemeteries result in substantial releases of HMs into the soil. The primary origin of heavy metals in Ehyaekpen, Benin City, Edo State, Nigeria, is due to the existence of the second cemetery. Notably, the study area lacks a reputation for intense agricultural activities, with most farming conducted on a small scale. Vegetables are typically grown in gardens and residential zones in proximity to the cemetery. Despite this scenario, there has been no prior assessment of the possible health hazards that arises from consuming crops grown in the study area. The current investigation aims to contribute valuable scientific insights into human health implications, and soil assessment in this context

2.0 MATERIALS AND METHODS

2.1 Study Area

The study area is located within latitude 6°20'29" North and longitude 5°36'28" East, in Ehyaekpen, Oredo Local Government Area, Edo State as shown in Figure 1&2 below.

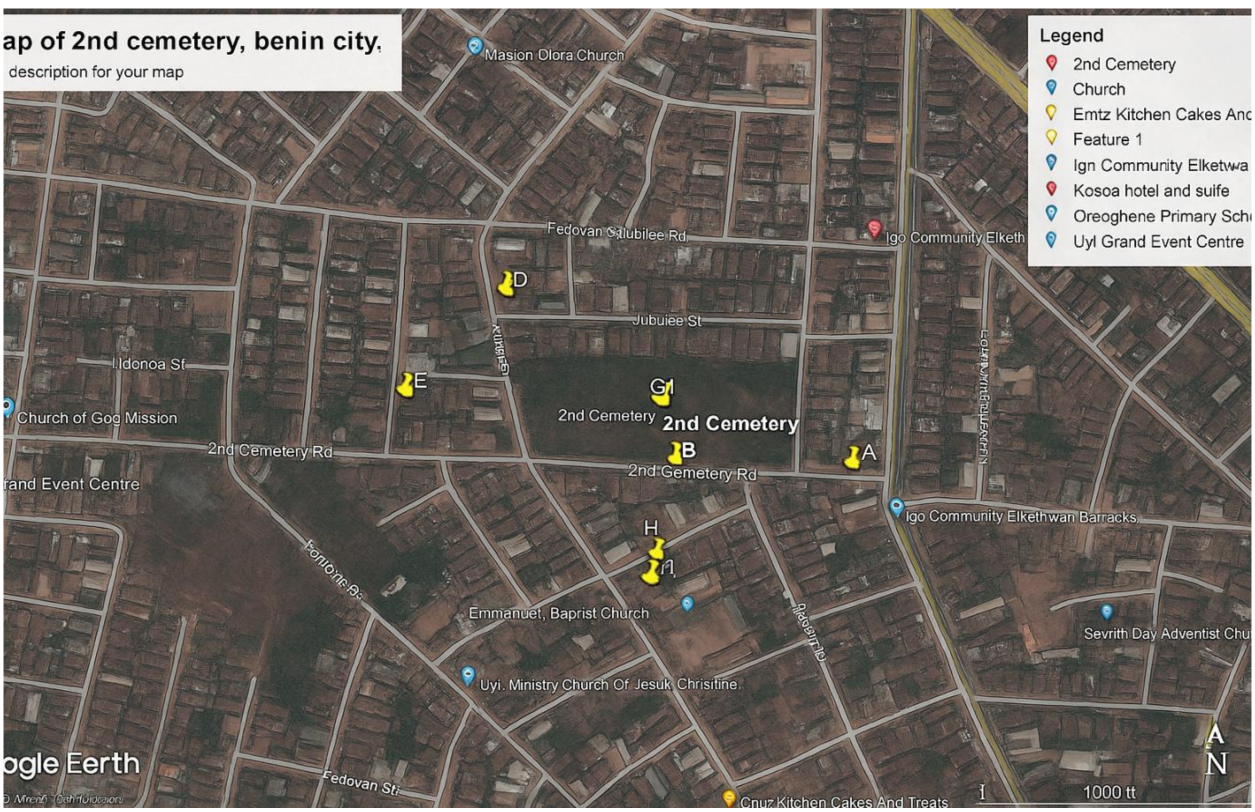

Figure 2. Location map of sample collection

2.2 Sample Collection

A methodical soil sampling process was carried out in the sample location as shown in Figure 2 above, to assess the concentrations of HMs and establish the health risk associated with them. Leafy vegetables, including Bitter leaf (Vernonia amygdalina), sweet potato (Ipomoea batatas), orange (Citrus sinensis), and mango (Mangifera indica), were systematically gathered from the vicinity of the cemetery and taken to the Civil Engineering laboratory at the University of Benin in Benin City, Nigeria, for

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meticulous sample preparation. The vegetables underwent a thorough cleaning with distilled water to eliminate any traces of dirt, while the soil samples were dried in open air, converted to powder and sieved. The washed vegetables were chopped, air-dried, and dried further in an oven for 72 hours at 65 °C. Subsequently, the dried leaves were pulverized using a mortar and pestle, converted into powder, and individually stored in plastic bags for subsequent analysis.

Table 1. Location of soil and vegetable samples.

Location	Latitude	Longitude	Elevation
A	6.340900	5.609597	95 yards
B	6.340983	5.608042	96 yards
C	6.341360	5.606835	93 yards
D	6.342380	5.606615	97yards
E	6.340983	5.605820	92 yards
F	6.339733	5.607698	93 yards
G	6.340108	5.607962	93 yards
H	6.339925	5.609052	72 yards
I	6.341767	5.609190	98 yards

2.3. Determination of Heavy Metals

The analysis of HMs in the collected samples was conducted at the Nanotechnology and Advanced Material Laboratory, affiliated with the National Agency for Science and Environmental Infrastructure (NASENI) on Ondo Road, Akure, Ondo State, Nigeria. A wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, specifically the SKYRAY INSTRUMENT EDX3600B, was employed for experimental investigations. This X-ray fluorescence spectrometer utilizes XRF technology to swiftly and accurately analyze intricate compositions. Preceding the analysis, the samples underwent drying in an oven at 80°C for 18-20 hours. The samples were meticulously ground to achieve a size smaller than a 50 µm sieve, weighed within the range of 100 to 200 mg, and then utilized to create pellets with a diameter of 2.5 cm using a pellet pressing machine under a pressure of 10 to 15 tons. The subsequent analysis of these pellets was carried out using XRF spectroscopic technology. Each pellet received primary radiation from a Cd-109 radioactive source for a total duration of 2500 seconds. Two irradiations were performed

for each pellet: one with the sample alone and the other with the sample and a molybdenum target on top. Absorption adjustments were calculated using data from these two irradiations.

Distinct X-rays emitted by the elements in the samples were captured by the NaI(Tl) detector. The measurements were conducted in a vacuum, incorporating various filters between the source and sample to optimize element detection. A 0.05-mm-thick Ti filter was positioned in front of the source with an applied voltage of 14 kV and an applied current of 900 mA for elements such as Cr, Mn, Fe, Co, Ni, Cu, and Zn. Higher Z elements like Pb, Bi, and Ag were analyzed using a 0.05-mm-thick Fe filter at a voltage of 37 kV and a current of 45 mA. Quantitative analysis of the X-ray fluorescence spectra was performed using the system's built-in "nEXt" software, operating on the Windows NTTM operating system. In both qualitative and quantitative analyses, acquiring spectra played a pivotal role, and acquisition parameters were carefully selected to enhance the counts for the essential elements.

2.4. Transfer Factor

The transfer factor (TF) or bio-accumulation factor, expressed as the ratio of Heavy Metal (HM) concentration in soil to that in plants was computed using Equation 3.

This formula has been previously employed in studies by [13], [14], and [15].

$$TF = \frac{C\ vegetable}{C\ soil} \qquad (1)$$

Where,

$C_{vegetable}$ = concentration of metals in vegetable (mg/kg)
C_{soil} = concentration of metals in soil (mg/kg)

3.0 RESULTS AND DISCUSSION

3.1 Geophysical Investigation

Resistivity data from transverse 1 were employed to generate the 2-D dipole-dipole profile maps presented in Figures 3 and 4

Indicators, including daily intake of metals (DIM), health risk index (HRI), target health quotient (THQ), and total target health quotient (TTHQ), were analyzed using Table 2 & 3, in order to assess the potential health

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hazards associated with consuming vegetables contaminated with heavy metals. DIM estimates the daily buildup of metals in the human bodies based on their body weight, is influenced by the relative phyto-availability of metals. While it provides an estimation of the potential ingestion rate of a specific metal, it doesn't account for the potential metabolic elimination of metals. DIM was estimated as referenced in [16].

$$DIM = \frac{Cm \times Cf \times Dvi}{Baw} \quad (2)$$

Where,

Cm = HM concentration in vegetables (mg/kg)
Dvi = Daily intake of vegetable
Baw = Average body weight (kg)

Furthermore, Cf denotes the conversion factor for vegetables from fresh weight to dry weight, a concept discussed by [17] In this investigation, the value of Cf, 0.085, [18] was employed. Additionally, Dvi values (205g/person/day) and Baw (70kg) applied to adults, and 150g/person/day and 20kg, respectively for children were consistent with those used in this study.

Table 2. Transfer factors of Sb, Sn, and Fe from soil to vegetables

	SL1	**SL2**	**SL3**	**SL4**	**SL5**	**SL6**	**SL7**	**SL8**	**SL9**
Sb									
Mango	0.8696	0.9191	0.7565	0.8840	0.9864	0.8671	0.8631	0.8890	0.8381
Potato	0.8295	0.8767	0.7216	0.8432	0.9408	0.8271	0.8232	0.8479	0.7994
Orange	0.8504	0.8988	0.7398	0.8645	0.9646	0.8480	0.8440	0.8693	0.8196
Bitter leaf	0.8787	0.9287	0.7664	0.8932	0.9967	0.8762	0.8721	0.8983	0.8469
Sn									
Mango	0.8596	0.9683	0.9508	0.8408	0.9858	0.8401	0.9081	0.9766	0.8565
Potato	0.8295	0.8767	0.7216	0.8432	0.9408	0.8271	0.8232	0.8479	0.7994
Orange	0.8504	0.8988	0.7398	0.8645	0.9646	0.8480	0.8440	0.8693	0.8196
Bitter leaf	0.8787	0.9287	0.7644	0.8932	0.9967	0.8762	0.8721	0.8983	0.8469
Fe									
Mango	0.5849	0.3043	4.6537	0.3540	0.9569	1.1331	0.4452	0.2731	0.8691
Potato	0.1380	0.0718	1.0980	0.0835	0.2258	0.2674	0.1050	0.0644	0.2051
Orange	0.1712	0.0891	1.3627	0.1037	0.2802	0.3318	0.1304	0.0800	0.2545
Bitter leaf	0.1344	0.0699	1.0690	0.0813	0.2198	0.2603	0.1023	0.0627	0.1996

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Table 3. transfer factor of Cd, Pb and Zn from soil to vegetables

	SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9
Cd									
Mango	ND	ND	ND	ND	ND	ND	ND	ND	ND
Potato	1.45	ND	ND	ND	ND	ND	1.45	ND	ND
Orange	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bitter leaf	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pb									
Mango	ND	ND	ND	ND	ND	ND	ND	ND	ND
Potato	ND	0.79	3.10	0.81	ND	0.54	ND	ND	0.52
Orange	ND	1.04	4.06	1.07	ND	0.70	ND	ND	0.68
Bitter leaf	ND	ND	ND	ND	ND	ND	ND	ND	ND
Zn									
Mango	1.06	1.04	ND	1.08	1.10	1.07	1.05	1.07	1.07
Potato	0.86	0.85	ND	0.88	0.90	0.87	0.85	0.88	0.87
Orange	0.92	0.91	ND	0.95	0.96	0.93	0.92	0.96	0.94
Bitter leaf	0.82	0.81	ND	0.84	0.85	0.83	0.81	0.83	0.83

ND; Not Detected

Table 4. DIM computation for heavy metals

Metals	Adults	Children
Zn	0.07	0.18
Pb	0.003	0.008
Cd	0.0003	0.0007
S b	1.5025	3.8482
Sn	1.7245	4.4163
Fe	0.2954	0.7565

Table 5. HRI computation for HM

Metals	Adults	Children
Zn	0.07	0.18
Pb	0.003	0.008
Cd	0.0003	0.0007
Sb	3756.5	9620.5
Sn	574.83	14721
Fe	0.422	1.08

Table 6. THQ and TTHQ computation

Meals	Adults	Children
Zn	0.007	0.03
Pb	0.59	2.74
Cd	2.05	9.59
Sb	7.045	18.49
Sn	9.39	24.66
Fe	0.004	0.01
	$\sum THQ = 19.086$	$\sum THQ = 55.52$

TTHQ = $\sum THQ$ (Adult + Children) = 74.606mg/kg

Table 7. Comparison between soil/vegetable HM and WHO/FAO standards

Metals	**Adults**	**Children**	**WHO/FAO maximum permissible values**
Zn	0.007	0.007	0.007
Pb	0.59	0.59	0.59
Cd	2.05	2.05	2.05
Sb	7.045	7.045	7.045
Sn	9.39	9.39	9.39
Fe	0.004	0.004	0.004

3.2. Discussions`

3.3. Health Risk Assessment

In farmlands around the study location, agricultural activities are limited, primarily involving small-scale cultivation for personal consumption. This study assessed health risks, employing indicators such as Daily Intake of Metals (DIM), Health Risk Index (HRI), and Target Health Quotient (THQ) for both adults and children.

The DIM of antimony (Sb) and tin (Sn) through vegetable consumption exceeded the recommended oral reference doses (RfDs) of 0.0004 mg/kg/day and 0.0003 mg/kg/day, respectively as shown in Tables 4 & 7. Conversely, iron's daily intake was lower than the RfDs for adults but higher for children.

For lead (Pb) and zinc (Zn), the daily intake values from vegetable ingestion surpassed the oral reference doses (RfDs) of 0.0035 mg/kg/day and 0.300 mg/kg/day, respectively. Notably, the Target Health Quotient (THQ) for cadmium (Cd) intake, recording 2.05 and 9.59 mg/kg/day for adults and children, stemmed from the consumption of mango, potato, orange, and bitter leaf. The DIM/HRI, (Tables 4 & 5) values of Cd were calculated using the concentrations obtained in potato.

The maximum and minimum daily intake of Cd fell below the oral reference doses RfD (0.001mg/kg/day), suggesting no adverse health effects from consistent consumption of vegetables contaminated with Cd. [4] emphasized the ingestion of leafy vegetables as a significant route for human exposure to Cd globally.

THQ results as shown in Table 6 for children consistently exceeded those for adults, with a Pb THQ of 0.59 mg/kg for adults and 2.74 mg/kg for children because children's and adults' daily vegetable intake and body weight differ. [15] reported similar results.

Zinc, an essential nutrient, poses lower health toxicity compared to Pb and Cd. Adequate concentrations are necessary to prevent health issues, but excessive intake can lead to adverse effects.

In contrast to a study conducted in Challawa, Kano, Nigeria by [18], which compared the maximum HRI values for zinc, children's consumption of tomatoes had greater HRI values than other vegetables consumed by both adults and children. The HRI values for Zn in a study carried out in India by [14] were likewise greater than those in our study

The study disclosed that the THQ values were in a descending order of Sn>Sb>Fe>Cd>Pb>Zn, indicating that Sn is the most significant pollutant. Similarly, HRI values for metals showed a descending order of Sn>Sb>Fe>Zn>Pb>Cd. Zhou et al.

3.4. Concentration of vegetables

The presence of tin (Sn), antimony (Sb), iron (Fe), lead (Pb), and cadmium (Cd) contamination deems

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vegetables from these areas unsuitable for human consumption. Including these vegetables in one's diet could lead to adverse health effects, as indicated by [6]. Additionally, cultivation on these soils should be strongly discouraged. HM absorption by plant tissues from the soil is dependent on many factors including the concentration of HM in the soil, plant species, and the plant growth stage [19]. [14] also observed this in India for different vegetable species, [13] in Pakistan for Pb and Cd in various species across selected regions, and [18] in Challawa, Kano, Nigeria for diverse species studied. The heightened concentration of magnesium could be attributed to the decomposition of corpses, converting them into nutrients in the soil, given that magnesium is an essential nutrient in the human body.

3.5. Transfer factor

The ratio of the concentrations of HMs in plants and their corresponding concentrations in the soil is termed the transfer factor, bio-concentration factor, or bio-accumulation factor [14], and [20]. It serves as a crucial tool for evaluating and elucidating the uptake of HMs from soils to plants and their presence in humans through food consumption. The transfer factor is determined by the characteristics of both plants and soils [21]

The identified transfer factors for heavy metals are presented in Table 4.3. In locations 1, 2, 4, 6, and 9, the transfer factor was less than one (1). However, in location 3, the transfer factor for iron exceeded one (1). Notably, in location 5, the transfer factor for magnesium was 1.60 in mango, for tin (Sn) it was 1.01 in orange, and 1.02 in bitter leaf. For location 7, the transfer factor for magnesium was 1.05 in mango. In location 8, the transfer factor for tin (Sn) was 1.00 in both orange and bitter leaves.

A high transfer factor indicates a significant capability to absorb soil metals or that the soil has a limited capacity to retain metals, in line with the observations by [19]The transfer factors follow the order of Cd > Pb > Zn. [22]reported an average metals transfer factor order of Pb > Cd > Cr > Zn for certain plant samples from a farm settlement in Agbabu, western Nigeria.

4.0CONCLUSION

This research has shown that the soils around the cemetery exhibit contamination with tin (Sn), antimony (Sb), iron (Fe), lead (Pb), cadmium (Cd), and zinc (Zn), with concentrations surpassing the corresponding WHO standards established for soils designated for crop cultivation. Consequently, plants and vegetables such as Vernonia amygdalina, Ipomoea batatas, Citrus sinensis, and Mangifera indica cultivated in these soils are tainted and unsuitable for consumption. The results obtained indicate soil pollution with Sn, Sb, Fe, Pb, Cd, and Zn as shown in Tables 4,5,6&7. The concentrations of Sn, Sb, and Fe were below the maximum recommended limits (200mg/kg, 36mg/kg, 20mg/kg), while Zn exceeded the maximum recommended limit (0.3 mg/kg) set for crop production soils. However, Pb and Cd concentrations were within the recommended limits (0.1mg/kg, 0.3mg/kg).

Daily intake results of Sb and Sn from these vegetables exceeded the recommended RfDs of 0.0004mg/kg/day and 0.0003mg/kg/day, respectively. In contrast, iron's daily intake was lower than the RfDs for adults but higher for children. Cd and Zn daily intakes were below the RfDs doses of 0.001 and 0.300mg/kg/day, while Pb intake exceeded the oral reference dose of 0.0035mg/kg/day. Both HRI and THQ values exceeded one, suggesting potential adverse health effects from ingesting these vegetables.

The transfer factor analysis revealed that Ipomoea batatas had the highest transfer factor for Cd, Citrus sinensis for Pb, and Mangifera indica for Zn. Although the respective results of Target Hazard Quotient (THQ) for Sn, Sb, Fe, Pb, and Cd in the studied vegetables surpassed one, the THQ value for Zn was less than one. However, the Total Target Hazard Quotient (TTHQ) for all the HMs investigated in the vegetables surpassed one. Consequently, the vegetables investigated should not be consumed due to the elevated health hazards associated with their ingestion. Children, in particular, are identified as being at a higher risk of health hazards from consuming vegetables sourced from these locations in the study area compared to adults.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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Authors' Contribution.

Udogwu, N.G. was responsible for the performance analysis of HM detection, documentation of the experimental procedures and results. Ilaboya R.I. provided technical guidance, and critically reviewed the manuscript for intellectual content.

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Author's Declaration
The authors affirm that the content of this manuscript has not been published elsewhere, is original, and is not under consideration for publication in any other journal. The authors accept full responsibility for the integrity and accuracy of all data and interpretations presented herein.

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