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Nwachukwu, Joseph Ikechukwu, Clarke, Leon ORCID logoORCID:
<https://orcid.org/0000-0002-2278-4139>, Symeonakis, Elias and Brearley,
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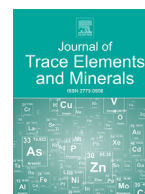
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Assessment of human exposure to food crops contaminated with lead and cadmium in Owerri, South-eastern Nigeria

Joseph Ikechukwu Nwachukwu^{a,b,*}, Leon J. Clarke^b, Elias Symeonakis^b, Francis Q. Brearley^b

^a Department of Environmental Management, Federal University of Technology, Owerri, Imo, Nigeria

^b Department of Natural Sciences, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, United Kingdom



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ABSTRACT

Background: Food safety and security have remained an emerging global challenge amidst increasing human activities that potentially contaminate the food chain. With the rapid population growth, urbanisation and unrestrained emission of toxic substances, urban-dwelling Nigerians are particularly vulnerable to consuming contaminated food crops.

Materials and method: This study presents a framework for critical analysis of human exposure patterns to potentially contaminated food crops using the city of Owerri (Nigeria) as case study. It systematically assessed the metal burden of soil and staple food crops and the potential health risk associated with dietary exposure of humans to contaminated food crops. Samples of soil, cassava (*Manihot esculenta*) tubers and fluted pumpkin (*Telfairia occidentalis*) leaves were collected from household gardens and analysed for concentration of selected metals (Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn) using ICP-OES. A risk assessment of human exposure to Pb contamination using both the Target Hazard Quotient (THQ) and Hazard Index (HI) was estimated.

Results: The majority of metals measured below the respective health-based maximum concentration limits of the Nigerian Department of Petroleum Resources target value, except for Pb in soil, which was above the limit of $85 \mu\text{g g}^{-1}$ in 0.9 % of sampled soils. However, Pb measured above the threshold of $0.3 \mu\text{g g}^{-1}$ stipulated by the FAO/WHO Codex Alimentarius in 46 % of sampled pumpkin leaves with no correlation established with soil Pb concentrations. This suggests possible Pb contamination via atmospheric deposition, and that human ingestion of pumpkin leaves presents the greatest health risks.

Conclusion: The findings revealed that children and toddlers are more prone to Pb contamination via food crop ingestion than adults based on the THQ and HI evaluations; hence need for relevant policies to ensure food safety. This study provides background data for epidemiological investigation of relationships between contaminated food crop ingestion and blood Pb.

1. Introduction

Urban expansion amplifies anthropogenic activities and modifies urban biogeochemistry, including through toxic trace metal contamination [1,2]. More than 54 % of the global population now inhabits urban areas [3]. Consequently, soil structures and processes are altered, increasing their vulnerability to surface contaminants, thereby exposing humans to contaminated food crops [2,4]. Increased emission rates caused by the unrestrained use of end-of-life vehicles promote deposition of toxic metals on soils and food plants. Ingestion of food crops, especially vegetables that comprise 70 % of the dietary intake of metals, can lead to significant public health concerns [2,5,6].

Despite its relative abundance within the earth's crust, lead (Pb) is often released into the atmosphere via anthropogenic activities, ac-

counting for about 0.6 % of the world's disease prevalence especially in the developing countries [7]. Accumulation of metals in soil and food plants, (especially those that are not essential for plant growth such as cadmium (Cd) and Pb), above the Food and Agricultural Organization (FAO)/World Health Organisation (WHO), threshold can result in cases of nervous, cardiovascular, renal, bone and neurological damage among other health conditions [8]. Exposure to automobile-emitted Pb, especially among children has been associated with the unrestrained use of leaded petrol in major Nigerian cities [9]. It is particularly dangerous due to its neurotoxic potential which hinders brain development among children, and leads to seizures, coma, or death at high concentrations [10,11]. Plant adsorption of atmospheric Pb and other trace metals is often influenced by proximity to roads (emissions from vehicles using tetraethyl lead (TEL) leaded petrol as an antiknock agent), or point sources such as soils and household dust (containing Pb-based paints) [8,12,13]. In addition to Pb, Cd is also a potentially toxic metal that can cause kidney and blood diseases, respiratory and reproduction disorders, as well as cancer, among other health impacts [14–16].

* Corresponding author.

E-mail address: joseph.nwachukwu@futo.edu.ng (J.I. Nwachukwu).

Cadmium is often released into the environment as a by-product of industrial processes such as mining, smelting, and refining, posing toxicity to exposed food crops and human beings. Significantly, waste incineration, which is a common waste management technique in most developing urban cities presents another pathway for Cd toxicity to both plants and humans [16,17].

Previous studies have shown that oral ingestion of contaminated food crops is the common pathway toxic substances enter the human body, compared with inhalation and dermal contact [2,5,18]. Techniques such as the estimated daily intake of metals (EDI) and probabilistic risk assessment models have been applied in the evaluation of source of exposure risk and toxic concentrations of metals in humans [2,5]. Nonetheless, little work has focused on human exposure patterns and public health risks associated with ingestion of staple African food crops such as cassava (*Manihot esculenta*; Euphorbiaceae) or fluted pumpkin leaves (*Telfairia occidentalis*; Cucurbitaceae). Research to fill such a knowledge gap becomes important amidst human-induced air pollution, climate change and eventual human exposure to toxic metals (through the food chain) within major Nigerian cities.

This study argues that urban traffic congestion, other anthropogenic activities, such as solid waste incineration and petrol-powered electricity generating sets, can contaminate the food chain and pose significant health risks using the city of Owerri, South-east Nigeria, as a case study. The objectives of this study are to: (i) assess the concentration of toxic metals with potential hazardous effect on human health (especially Pb and Cd) in soil and susceptible common edible food crops (i.e cassava and fluted pumpkin leaves) harvested from domestic gardens; (ii) place observed metal concentrations in soils and food crops in the context of local and international guideline values on food safety; and (iii) quantify the health risks associated with the consumption of contaminated food crops across different human age groups.

2. Materials and methods

2.1. Physical geography, population and land use

Owerri is situated in South-eastern Nigeria (05°21' to 05°30' N; 06°57' to 07°03' E). It has a population of approximately four hundred thousand (400,000) [19] and a population density of approximately one thousand, four hundred (1,400) persons km⁻² [20] (Figure 1), with most urban gardens used for subsistence farming. Soils are generally sandy (>90 %), with low soil organic matter (2.5 to 4.0 %), illustrating their typically poor metal adsorption capacity [21–23]. Vehicular traffic, indiscriminate waste dumping and incineration across the study area release trace metals into the atmosphere, which potentially settle on both soil and plants, especially in the rainy season.

2.2. Soil and plant sample collection and preparation

Soil samples across household gardens, as well as samples of the two commonest food crops, cassava (*Manihot esculenta*) tubers and fluted pumpkin (*Telfaira occidentalis*) leaves in Owerri, were collected during the 2015 rainy season (Figure 1) and analysed for elemental concentrations. Dry season sampling was not conducted due to poor availability of samples. Site coordinates were recorded with a hand-held GPS Map 62 (Garmin International, Inc.). Criteria for site selection and their categorisation were based on the urban density gradient, i.e., city centre>suburban>peri-urban. These categories were based on a semi-quantitative classification of the city centre as characterised by impervious surfaces such as asphalted roads and concrete drainage channels, with suburban and peri-urban categories referring to satellite areas. Whilst the suburban areas are currently undergoing expansion, resettlement and land surface modification, peri-urban areas are typified by minimally modified agricultural land surfaces.

One-hundred-and-eighty-six composite soil samples were collected from a 5 m × 5 m quadrat in each of the urban gardens, whereby five

topsoil (<15 cm depth) samples were randomly collected and mixed. Five grams of each fresh soil sample was combined with 12.5 ml of deionized water, stirred and then allowed to equilibrate for one hour, before soil pH was measured using a Hanna Instrument 9828 Multiparameter meter with a 769828 probe. The remaining soil was air-dried in an air-conditioned room for three days, ground, passed through a 2 mm plastic sieve and retained for further analysis. Soil carbon was determined using a Leco TruSpec CN analyser on samples of c. 0.2 g. A total of 96 and 86 samples of fluted pumpkin leaves and cassava tubers, respectively, were collected from the Owerri gardens. Edible parts of the fluted pumpkin leaves were collected, washed with distilled water and dried at 60 °C for 18 hours. The periderm and cortex of cassava tubers were peeled-off and about 10 cm³ removed from the centre of the tuber and oven-dried at 80 °C for 24 hours. All plant samples were pulverised using a plastic pestle and mortar and sieved through a 2 mm plastic sieve prior to metal determination.

2.3. Determination of elemental concentrations

Sample preparation for metal determination followed the US EPA 3051A standard method, using microwave digestion with nitric acid [24]. Approximately 0.5 g of each soil sample, 0.4 g of cassava tuber, or 0.25 g of fluted pumpkin leaf, were weighed into pre-cleaned PTFE microwave digestion tubes. One ml of 18.2 MΩ de-ionised water was added to each tube, followed by 10 ml (soil) or 5 ml (plants) of Aristar grade nitric acid. Metranal QCM32 Light Sandy Soil and LGC7162 Strawberry Leaves certified reference materials (CRMs) were prepared using identical procedures, and digested alongside samples using a Mars 5 version microwave oven (CEM-Mars Xpress, CEM Corporation, USA) at 1200 W power, with 40 minutes hold time [25] and maximum temperature of 210 °C. Both the relevant CRM and a method blank were included after every 10 samples. Solutions then were cooled, filtered through Whatman No. 1 qualitative filter papers and made up to 100 ml with 18.2 MΩ deionised water. Solutions were measured for elemental concentrations using a Thermo Scientific iCAP6300 Duo Inductively Coupled Plasma - Optical Emission Spectrophotometer (ICP-OES) for Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn. Metal concentrations were quantified using a 4-point calibration curve (R²>0.998 for all elements), whereas quality control was assessed using the two CRMs that showed recoveries of >80% for most elements (Supplementary Tables 1a & b). Lead and Cd, whose concentrations exceeded their respective maximum concentration limits (0.3 µg g⁻¹ and 0.2 µg g⁻¹) in pumpkin leaves and 0.1 µg g⁻¹ for cassava tubers, recorded CRM recoveries of 82 % (Pb) and 102 % (Cd); and 93 % (Pb) and 104 % (Cd) respectively. In order to convert metal concentrations on a dry weight basis to a wet weight basis for comparison with the FAO/WHO Codex Alimentarius [26], samples of leaves and tubers were dried at 30 °C for at least 72 hours to determine their moisture content.

2.4. Quantification of human health risk of exposure to contaminated food crops

This approach involved evaluation of the nature and potential for adverse human health effects due to exposure to toxic metal concentrations above health-based tolerable limits in the analysed samples. This study's assessments were limited to Pb and Cd since their concentrations in the analysed samples posed the most imminent health risks to exposed individuals. Overall median concentrations for fluted pumpkin leaves (Pb = 0.85 µg g⁻¹; Cd = 0.03 µg g⁻¹) and cassava tubers (Pb = 0.13 µg g⁻¹; Cd = 0.01 µg g⁻¹) across the study area were used to calculate risk assessment parameters, such as the estimated daily intake (EDI), target hazard quotient (THQ), and hazard index (HI), as proposed by the US Environmental Protection Agency (USEPA) [27]. Additionally, target hazard quotients (THQ) in the three urbanisation categories were estimated using median concentrations of Pb in fluted pumpkin leaves (City centre = 0.91 µg g⁻¹, Suburban = 0.86 µg g⁻¹, Peri-urban = 1.06 µg

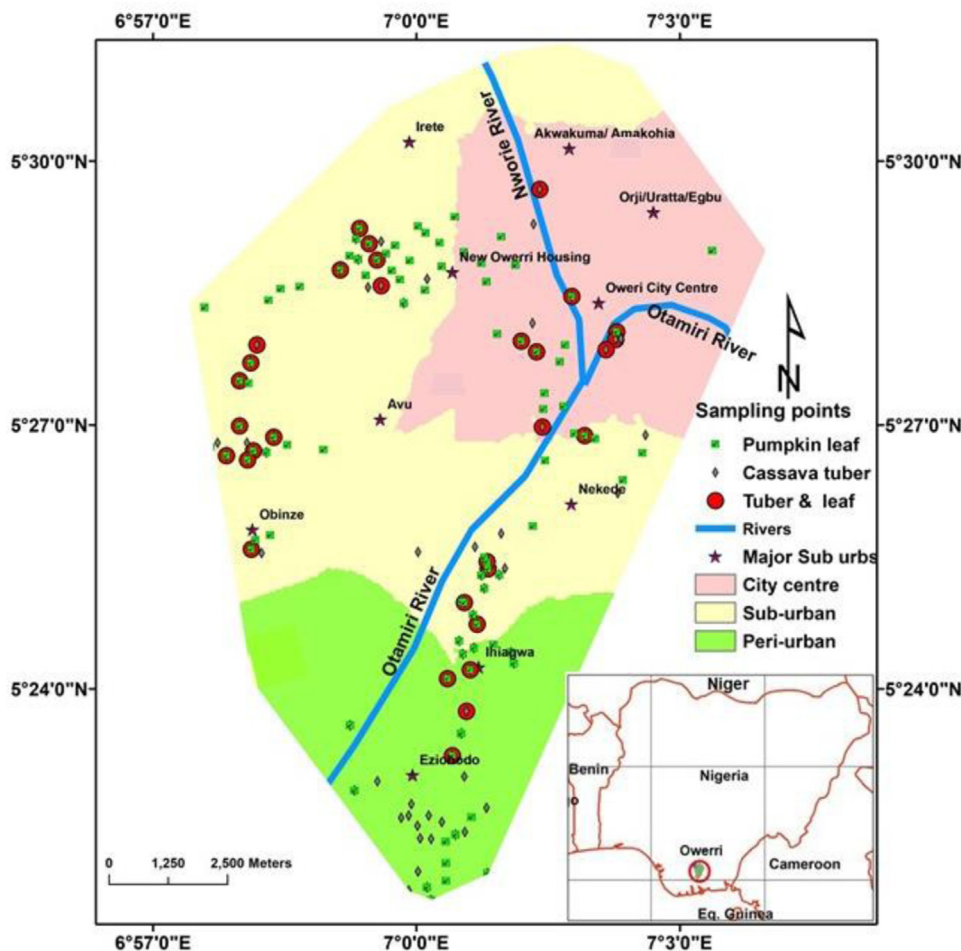


Fig. 1. Owerri, south-eastern Nigeria (inset), sample collection sites: fluted pumpkin leaves (light green symbols) and cassava tubers (grey symbols) were collected during the 2015 rainy season. Red symbols indicate sites where both food plants were collected. The study area map was cropped to reflect the shape of the sampled areas only.

g^{-1}). Risk assessment focused on four age categories, viz. Adult (20-47.6 yr; an average life expectancy of adults in Nigeria as adopted from [28], Teen (T = 12-19 yr), Child (C = 5-11 yr) and Toddler (Tod = 7 mo-4 yr).

2.4.1. Estimated daily intake (EDI) of metals

Estimated daily intake (EDI), as has been used in previous studies [29–31], was calculated using the equation:

$$EDI = C_m \times IR / BW \tag{1}$$

where C_m is the metal concentration in plants ($\mu g g^{-1}$), IR is the ingestion rate ($g person^{-1} day^{-1}$), taken from [32] due to a dearth of food intake diaries that monitor metal intake in Nigeria, as Adult = 130, Teen = 120, Child = 98, Toddler = 67. Such data was adapted because of the explained food consumption rates and patterns in the neighbouring cities of Igwuruta and Port Harcourt where leafy vegetables were frequently consumed at least four times per week [32] consistent with that of the current study area. This study also assumed equal consumption rate for the two food crops (often served together as a meal) by all age categories. Body weights (BW) of Nigerian Adult (70 kg) and Child (24 kg) were as previously estimated [33], whilst values for Teen (59.7 kg) and Toddler (16.5 kg) were as per the Guidance on Human Health Preliminary Quantitative Risk Assessment [34]. RfDo is the oral reference dose ($\mu g g^{-1} day^{-1}$) of 3.5×10^{-3} and 3.6×10^{-3} for Pb and Cd, respectively, indicating the maximum tolerable daily intake of these two toxic metals [2]. EDI/RfDo indicates the degree of health risk, thus $EDI \leq RfDo$ (minimum risk), $EDI > 1-5 \times RfDo$ (low risk), $EDI > 5-10 \times RfDo$ (moderate risk) and $EDI > 10 \times RfDo$ (high risk) [35].

2.4.2. Target hazard quotient (THQ)

This risk evaluation model is based on the ratio of the average daily metal dosage of an individual to a safe reference dose [36], indicating public health threat at values > 1.0 [31,37]. Its calculation is based on the USEPA standard recommendation [27] and the equation:

$$THQ = \frac{EFr \times ED \times IR \times C}{RfDo \times BW \times AT} \times 10^{-3} \tag{2}$$

where, EFr is the exposure frequency ($365 days year^{-1}$), ED is exposure duration (47.6 years) equivalent to Nigerian life expectancy [28], IR is the ingestion rate (as above), C is the metal concentration in analysed plant material ($\mu g g^{-1}$), RfDo is the reference dose, BW is body weight as above, and AT is the average exposure time for non-carcinogens ($ED \times 365 days year^{-1}$). This study assumes that all ingested metals are equally absorbed by the body at any given time and that metal toxicity is not influenced by cooking [31,38].

2.4.3. Hazard index (HI)

Hazard index assesses the overall probable health risk of the two metals and is calculated by summation of their respective THQs, i.e.:

$$HI = \sum THQPb + \sum THQCd \tag{3}$$

2.5. Data analysis

2.5.1. Spatial distribution of contaminants

Concentrations of Pb and Cd in fluted pumpkin leaves and cassava tubers across the study area were displayed using graduated symbols within the layer properties of ArcGIS version 10.2.

2.5.2. Statistical analysis

The descriptive statistical software incorporated in Origin Lab version 2017 was used to present data as experimental quartiles. Data are presented as median \pm interquartile ranges (soil) and mean \pm standard deviation (plants) but analysed using ANOVA with Tukey's post-hoc test on log-transformed data to determine differences between urbanisation categories and plant species. Correlations (Spearman's) were applied to determine relationships between Pb in leafy vegetables and soil parameters using Minitab v. 19.

2.5.3. Bioconcentration factor (BCF)

BCF of the two toxic metals (Pb and Cd) was calculated to evaluate possible plant metal uptake from soil:

$$BCF = \frac{Cm(plant)}{Cm(soil)} \quad (4)$$

where Cm (plant) and Cm (soil) are the concentrations of metals in plants (fluted pumpkin leaves and cassava tubers) and in soil, respectively.

3. Results and discussion

3.1. Trace metal concentrations in soil

Median concentrations of metals in the soil samples broadly assumed the following decreasing pattern: Fe>Al>Ca>Mg>K>Mn>Cr>Pb>Cu>Ni>As>Co>Cd>As, ranging between 0.9 % for Fe to 0.5 $\mu\text{g g}^{-1}$ for As (with about 45 % of samples less than the lowest limit of detection for As). Broadly, as could be expected, there was increased metal pollution in the city centre, likely due to greater traffic volume and congestion and emissions from other pollution sources as previously outlined. However, there was a decline in soil metal concentrations from the very dense to less dense regions, statistically significant for As, Co and Ni but not for Cr, Cu, Pb or Zn (Table 1).

Conversely, Cd and Mn exhibited statistically significant increases in concentration away from the city centre (Table 1). Earth surface modification and removal of soil organic matter and amorphous Mn oxides during urbanisation may lead to desorption of previously adsorbed Cd and Mn [39], hence the observed City centre<Suburban<Peri-urban concentration trend of these two metals.

Although most measured concentrations fell within the maximum allowable limit for metals in Nigerian soil, as stipulated by the Department of Petroleum Resources [40,41] (Supplementary Table 2), concentrations of Cd, Cu, Pb and Zn in a few samples, exceeded the limit values at specific sites. One sample exceeded the Pb limit of 85 $\mu\text{g g}^{-1}$ up to three-fold (Figure 2a), three samples exceeded the Cd limit of 0.8 $\mu\text{g g}^{-1}$ by up to 18 % (Figure 2b), five samples exceeded the Cu limit of 36 $\mu\text{g g}^{-1}$ up to six-fold (Figure 2c) and 11 % of the samples exceeded the Zn limit of 140 $\mu\text{g g}^{-1}$ up to three-fold (Figure 2d).

3.2. Soil pH

Soil pH values mostly fell between 5.5 and 6.5 and were less acidic in the city centre and suburban regions by about 0.5 units on the pH scale compared to the peri-urban region (Table 1). Studies have shown that increasing pH is commonly associated with urbanisation owing to the prevalence of Ca-rich construction materials [42,43], which is also supported by the significantly greater Ca concentrations in the city centre locations (Table 1).

3.3. Metals of public health concern in food plants

All the elements measured in cassava tubers were at lower concentrations, i.e., ranging from 4 % (Mn) to around 50 % (As), of those in the fluted pumpkin leaves (Table 2). The majority of metal concentrations within the food plants were within safe limits of the joint FAO/WHO

Table 1

Chemical characteristics of soils sampled across an urbanisation gradient in Owerri, Nigeria. All values are $\mu\text{g g}^{-1}$, except pH and C, and are shown as median (lower quartile – upper quartile) and <LLD = less than lower limit of detection. Letters indicate significant ($p < 0.05$) differences between urbanisation categories according to a Tukey's test with bold letters indicating significant differences between categories.

Parameter ($\mu\text{g g}^{-1}$)	Urbanisation Category		
	City centre	Suburban	Peri-urban
	N = 62	N = 94	N = 51
pH	6.03 (5.72-6.42) a	6.04 (5.30-6.35) a	5.51 (5.00-6.02) b
C (%)	0.94 (0.64-1.33) a	1.30 (1.13-1.56) b	1.43 (1.07-1.87) b
Al	5010 (3650-6630) b	5700 (4820-7550) a	4990 (4130-5810) b
As	0.42 (<LLD-0.64) a	<LLD (<LLD-0.58) b	<LLD (<LLD-0.27) b
Ca	1200 (697-1960) a	921 (503-1750) b	793 (451-1420) b
Cd	0.13 (0.06-0.18) b	0.16 (0.12-0.26) a	0.18 (0.12-0.26) a
Co	0.45 (0.34-0.69) a	0.43 (0.35-0.59) a	0.39 (0.29-0.51) b
Cr	14.8 (11.6-18.3) a	14.6 (12.8-17.1) a	14.2 (12.7-16.9) a
Cu	4.18 (2.96-8.36) a	3.27 (2.43-5.75) a	3.69 (2.77-6.34) a
Fe	8880 (7360-10900) a	9380 (8220-11100) a	8820 (7450-10300) a
K	71.8 (51.8-106) a	88.3 (62.6-121) a	76.3 (56.1-110) a
Mg	155 (104-283) a	138 (100-193) a	133 (99-186) a
Mn	42.9 (31.1-56.0) c	52.9 (39.0-69.7) b	66.3 (47.6-84.5) a
Ni	2.24 (1.65-2.94) ab	2.26 (1.71-3.06) a	1.89 (1.53-2.50) b
Pb	6.40 (4.91-10.27) a	5.84 (4.56-9.01) a	4.76 (3.72-6.74) b
Zn	34.8 (18.0-91.0) a	33.2 (12.0-76.0) a	21.3 (8.5-73.6) a

Codex Alimentarius health based maximum concentration limit (MCL) [26], except for Pb and Cd (Supplementary Table 3), hence we focus on the potential toxicity of these two metals hereon.

There were few statistically significant differences noted in plant metal concentrations across the different urbanisation categories, except Fe that was greater in the city centre in both leaves and tubers, while Mn was at greater concentrations in the city centre for tubers only (Table 2).

Lead concentrations in fluted pumpkin leaves posed the greatest potential public health risk, having exceeded the joint Codex Alimentarius maximum concentration limit of 0.30 $\mu\text{g g}^{-1}$ in 46 % of the samples measured (99 % if considered on a dry weight basis) (Figure 3a).

Several studies have acknowledged that plants can absorb and accumulate metals either passively with the mass flow of water into the roots, or through active transport across the plasma membrane of root epidermal cells [44–46]. However, correlation between Pb in leaves and associated soil samples in this study showed no relationship ($R^2 = -0.02$), indicating that Pb in leaves was not strongly related to soil Pb and was thus most likely deposited from the atmosphere, e.g., having origins from waste incinerators, and emissions from increased use of generator exhaust and/or end-of-life vehicles. This is additionally supported by a principal components analysis that found eigenvectors for Pb to be similar to that for Al and Fe that are both dominant in soils (Supplementary Table 4).

Similar patterns of a lack of correlation between plant and soil Pb has been reported in recent related studies [47–50]. Studies have also shown that plant leaves are vulnerable to aerial pollutants attached to atmo-

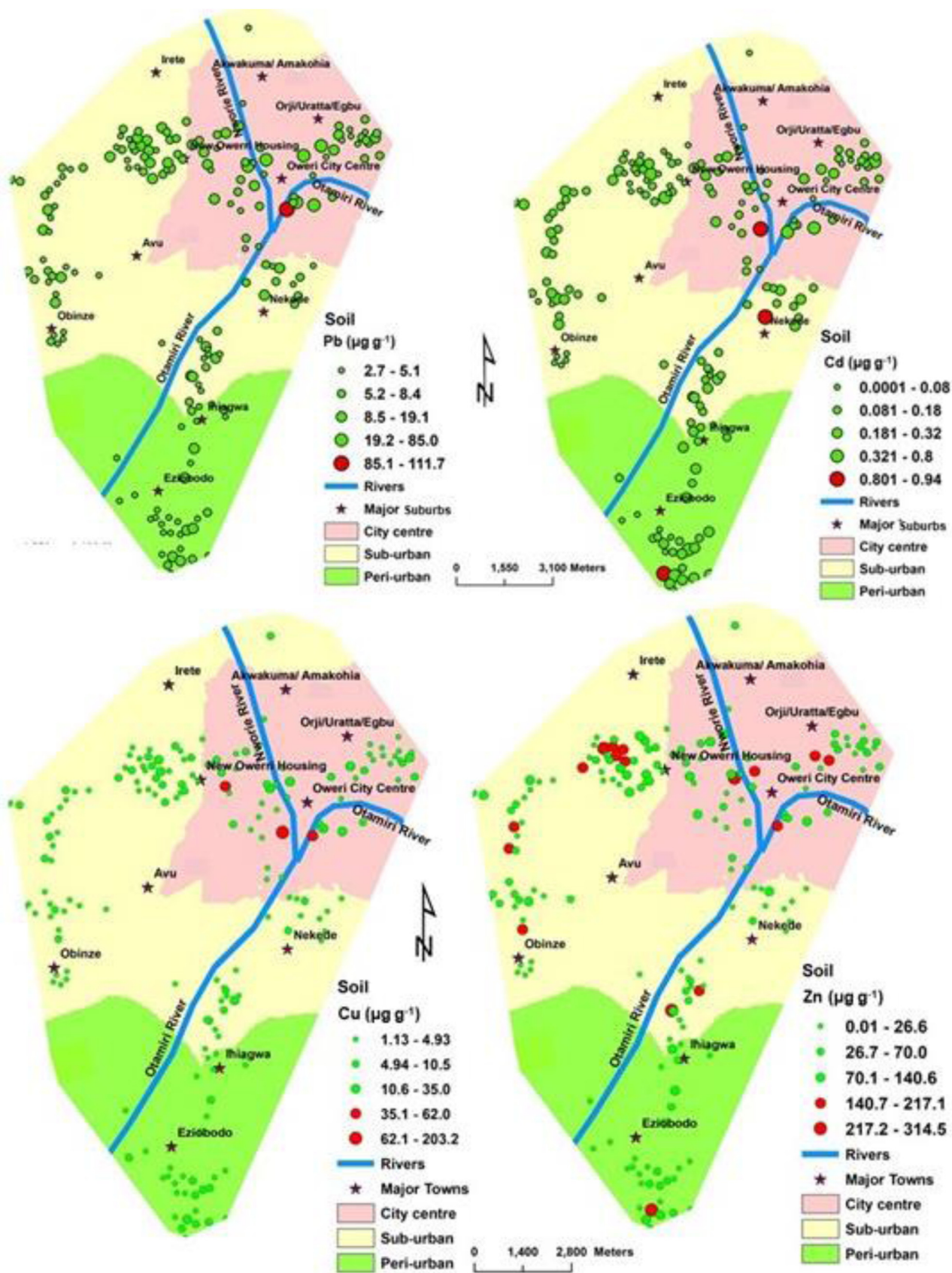


Fig. 2. (a) Lead (Pb), (b) cadmium (Cd), (c) copper (Cu) and (d) zinc (Zn) concentrations in soils sampled across the study area of Owerri, Nigeria. Red symbols indicate locations where metal concentration exceeded intervention values for metals in soil as stipulated by the Department of Petroleum Resources, Nigeria.

Table 2

Chemical characteristics of fluted pumpkin (*Telfairia occidentalis*) leaves and cassava (*Manihot esculenta*) tubers sampled across an urbanisation gradient in Owerri, Nigeria. All values are $\mu\text{g g}^{-1}$ and are shown as mean (\pm standard deviation); <LLD = less than lower limit of detection. The Statistics columns indicate significant differences between species (S), urbanisation categories (U) and their interaction (SxU) with $p < 0.05 = *$, $p < 0.01 = **$, $p < 0.001 = ***$ and ns = not significant.

	Fluted pumpkin leaves			Cassava tubers			Statistics		
	City centre	Suburban	Peri-urban	City centre	Suburban	Peri-urban	S	U	SxU
Al	284 (± 215)	155 (± 173)	198 (± 201)	18.0 (± 14.1)	13.3 (± 12.4)	12.6 (± 14.0)	***	ns	ns
As	0.44 (± 0.21)	0.63 (± 0.99)	0.43 (± 0.13)	0.12 (± 0.10)	0.12 (± 0.09)	0.54 (± 1.07)	***	ns	ns
Ca	14200 (± 7470)	13500 (± 9800)	13000 (± 540)	1270 (± 766)	995 (± 556)	913 (± 735)	***	ns	ns
Cd	0.12 (± 0.27)	0.07 (± 0.09)	0.07 (± 0.07)	0.03 (± 0.02)	0.03 (± 0.02)	0.07 (± 0.18)	**	ns	ns
Co	0.11 (± 0.13)	0.16 (± 0.29)	0.10 (± 0.08)	<LLD	<LLD	<LLD	***	ns	ns
Cr	0.95 (± 0.33)	0.99 (± 0.67)	1.26 (± 0.98)	0.37 (± 0.16)	0.15 (± 0.14)	0.36 (± 0.34)	***	ns	ns
Cu	12.0 (± 3.58)	11.8 (± 5.71)	11.0 (± 5.13)	1.89 (± 0.88)	2.07 (± 0.85)	1.82 (± 0.87)	***	ns	ns
Fe	322 (± 148)	224 (± 156)	226 (± 133)	22.3 (± 13.7)	21.3 (± 18.3)	17.6 (± 12.1)	***	*	ns
K	29700 (± 1530)	27600 (± 14000)	25700 (± 6900)	6290 (± 3170)	7850 (± 2720)	7540 (± 3090)	***	ns	ns
Mg	4050 (± 1530)	4620 (± 1460)	3920 (± 1160)	573 (± 181)	657 (± 350)	552 (± 206)	***	ns	ns
Mn	65.2 (± 37)	219 (± 355)	89.3 (± 44)	3.00 (± 1.27)	3.23 (± 2.11)	3.63 (± 2.63)	***	*	*
Ni	2.29 (± 1.92)	2.96 (± 4.79)	2.42 (± 1.71)	1.12 (± 0.76)	1.50 (± 1.41)	1.04 (± 0.41)	***	ns	ns
Pb	0.84 (± 0.34)	1.02 (± 0.56)	0.89 (± 0.43)	0.15 (± 0.09)	0.15 (± 0.14)	0.12 (± 0.18)	***	ns	ns
Zn	51.0 (± 21)	250 (± 466)	34.9 (± 13)	5.74 (± 4.95)	9.10 (± 11.3)	7.23 (± 3.73)	***	ns	ns

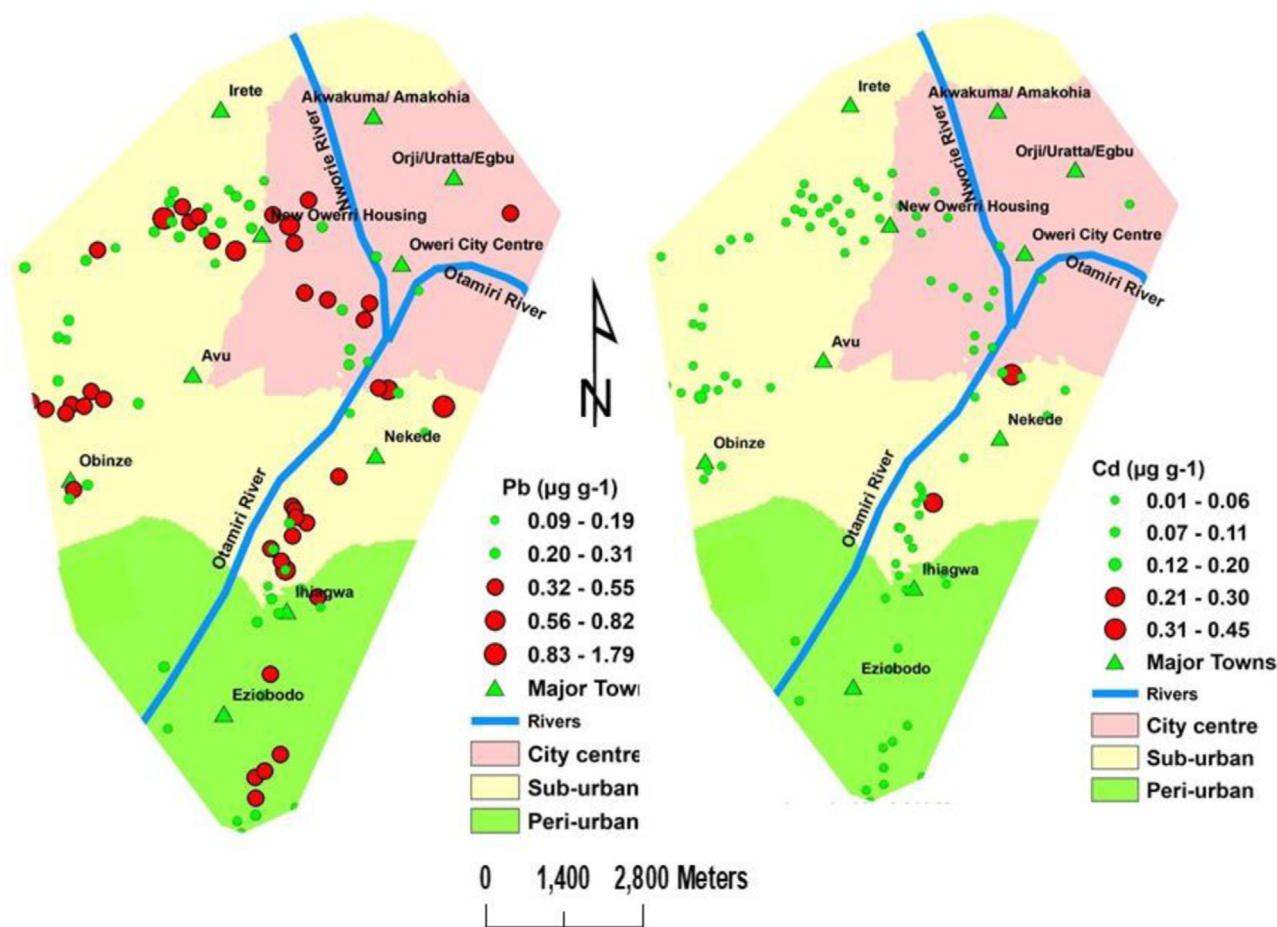


Fig. 3. (a) Lead (Pb) and (b) cadmium (Cd) concentrations in fluted pumpkin leaves in the city of Owerri, Nigeria. Green and red graduated symbols represent values above the WHO/FAO Codex Alimentarius tolerable limit for Pb ($< 0.3 \mu\text{g g}^{-1}$) and Cd ($< 0.2 \mu\text{g g}^{-1}$) in leafy vegetables.

spheric particles often deposited by rain or dust on leaves' surface and subsequently absorbed [51–53]. Previous studies of rainwater across the study area showed a high Pb concentration of $0.44 \pm 0.36 \text{ mg l}^{-1}$ [54]. Leaves of younger plants have greater capacity to accumulate foliar metals than older plants due to their thinner cuticles that allow greater penetration of metals [52,55,56]. Thus, fluted pumpkin as an annual crop remains vulnerable to absorption of Pb emitted into the atmosphere. Similar analysis of vegetable leaves in Northern Greece suggested that

the prevailing pathway for most trace metals, such as Pb, Cr and Cd is from atmospheric emissions [57], with related studies coming to the same conclusion for urban garden vegetables in other cities such as New York and New Jersey, USA [4,58].

Cadmium concentrations in two gardens' pumpkin leaves measured up to $0.45 \mu\text{g g}^{-1}$ exceeding the FAO/WHO Codex Alimentarius health based maximum concentration limit (MCL) [26] of $0.2 \mu\text{g g}^{-1}$ for leafy vegetables (Figure 3b). Bioconcentration factor (BCF) results further re-

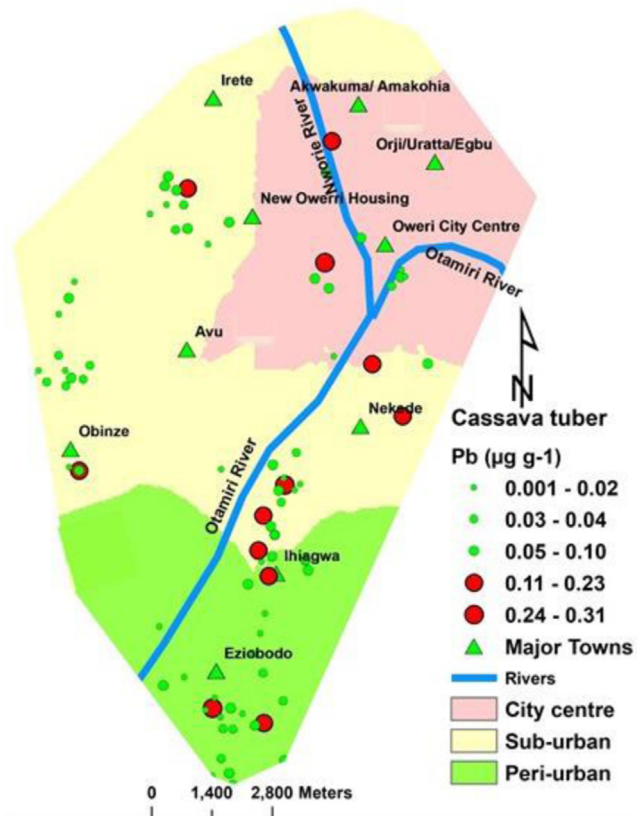


Fig. 4. Lead (Pb) concentration in cassava tubers in the city of Owerri, Nigeria. Green and red graduated symbols represent values above the WHO/FAO Codex Alimentarius tolerable limit for Pb (<0.10 µg g⁻¹) in tuber crops.

vealed accumulation of Cd in pumpkin leaves with values >1 (BCF<8.3) in approximately 15 % of sampled leaves. This observation might be explained by the gardens' location in an area formally used for municipal waste dumping or be attributed to the unrestrained emissions from exhaust of vehicles or sand dredging machines at nearby locations, thus possible sourcing from contaminated soil or atmospheric deposition. Equally, cassava tuber Pb also measured above the joint WHO/FAO 0.1 µg g⁻¹ MCL in 14 % of the samples (Figure 4), while Cd concentrations were within the limit in all the samples. Atmospheric Pb could be deposited on surfaces in the form of dissolved ions, leached into soil pore water during the rainy season and directly adsorbed by cassava tubers via the periderm or tuber roots. Background concentrations of soil Pb and Cd in Owerri were reported as 0.103±0.015 µg g⁻¹ and 0.323 ± 0.015 µg g⁻¹, respectively [59]. Comparatively therefore, the two metals measured above the background concentrations at all sampled locations in our study.

3.4. Exposure assessment and potential health risks

Estimated daily intake (EDI; µg g⁻¹ BW day⁻¹) for Pb in fluted pumpkin leaves for all age categories ranged from 1.66 × 10⁻³ (Adult) to 3.45 × 10⁻³ (Toddler); all exceeded >5 times the RfDo of Pb, hence portend a 'moderate' to 'high' health risk to consumers. Highest values of the estimated daily intake (EDI; µg g⁻¹ BW day⁻¹) for the respective metals (Cd and Pb) in fluted pumpkin leaves was recorded for the Child category (Figure 5). Studies have shown that children easily absorb Pb [33], and that such exposure could lead to reduction in IQ and behavioral problems [29,30]. Excepting the Cd EDI of the child age category for fluted pumpkin leaf consumption, at 3.42 × 10⁻¹ suggesting a low health risk, the Cd EDI for other age categories showed no health risk.

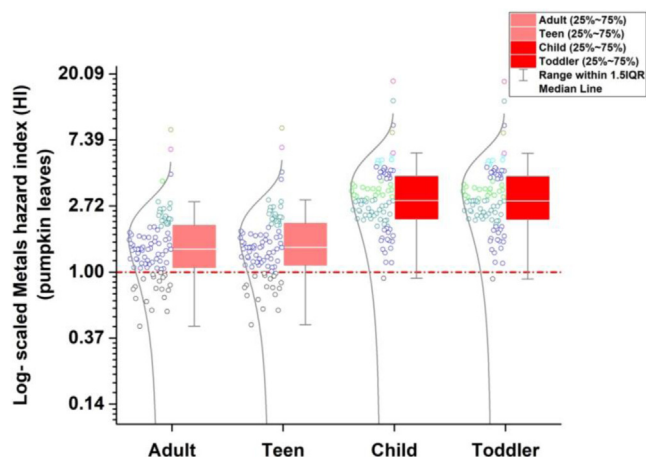


Fig. 5. Estimated Hazard Index in pumpkin leaves for the respective age categories in the study area of Owerri, Nigeria. Red dotted horizontal line indicates the HI threshold of 1.0, suggesting potential health hazard to all consumers of pumpkin leaves.

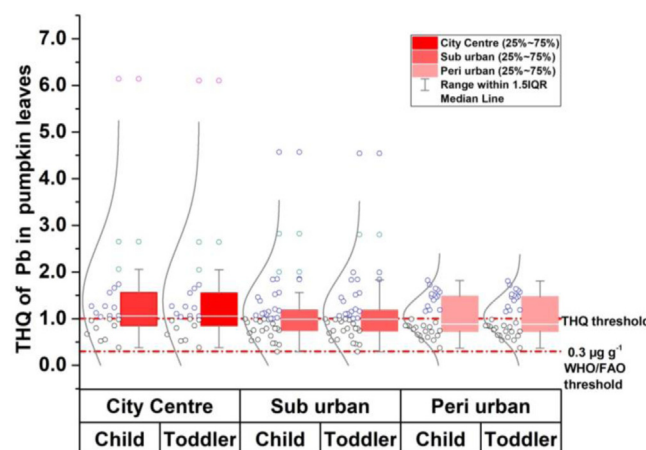


Fig. 6. Target Hazard Quotient (THQ) for Pb among the child and toddler age brackets in the study area of Owerri, Nigeria. Red dotted lines indicate the respective THQ (1.0) and WHO/FAO thresholds for Pb in leafy vegetables, revealing susceptibility of children to Pb poisoning via pumpkin leaf consumption.

EDI values for both Cd and Pb via cassava tuber consumption are less than their respective RfDo, inferring minimum health risk.

Additionally, estimated THQ values of >1.0 implies that all age brackets are exposed to Pb-contaminated fluted pumpkin leaves, signalling a potential health hazard particularly among children whose immunological systems are less well developed than adults [31,33,37] (Figure 6). THQ values for cassava tuber were all <1.0.

However, the THQ and HI of metal consumption (Figures 5 and 6) for all the age categories present public health risks associated with continuous consumption of fluted pumpkin leaves. The data suggest greater risks among children, which could also be attributed to their low body weight ensuing higher food consumption rate. This observation suggests that: (i) children are more exposed to toxic metals for their body weight as they consume more food than adults; (ii) children's metabolic pathways are still developing thus lack necessary enzymes to naturally eliminate toxic substances from the body; (iii) children are more susceptible to chronic infections due to early exposure to toxic chemicals in the environment [59]. Significantly, the THQ predictions associated with consumption of pumpkin leaves are consistent with the urban density trend in the study area, implying anthropogenic influence on metal con-

tamination of food crops in terms of urban emissions, which can most easily be associated with the persistent use of leaded petrol in Nigeria.

Conclusions

Urban modification, due to increasing population density, significantly impacts on the concentrations of toxic metals, with potential deleterious effect on the exposed Owerri (Nigeria) residents via a contaminated food chain. This study identified Pb as critical contaminant in the population's staple food plants, namely fluted pumpkin leaf (*Telfairia occidentalis*) and cassava tuber (*Manihot esculenta*), albeit with no correlation between soil and plant Pb concentrations. Nevertheless, BCF has shown some relationships between soil Cd and plant Cd at few sites situated within closed solid waste dumpsites, demonstrating long term toxic impacts of open solid waste dumpsites on agricultural activities and human health. Human exposure to chemical contaminants in staple food varied with the urban density pattern in the study area, providing a guide for safe household farming to town planners and policy makers especially within heavily congested cities of sub-Saharan Africa. Elevated THQ and HI were found to be above the safe limits for children and toddlers which is a cause for public health concern. Hence, there is urgent need for further verification of the metal burden of individuals across the study area, for example via measurement of human tissue (e.g. blood or scalp hair) Pb concentrations and/or conducting risk management activities to avert imminent health hazards. However, given that Pb was likely from atmospheric sources often deposited via water droplets retained on leaves, simple washing of leaves prior to consumption should be promoted. This assessment becomes expedient considering the high consumption rate of these crops by residents in major cities of Nigeria thereby increasing risk of Pb accumulation and toxicity within the local population.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary material.

Ethical approval and consent to participate

Not Applicable.

Consent for publication

Not Applicable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. We also declare that our manuscript has not been submitted to any other journal for simultaneous consideration.

CRedit authorship contribution statement

Joseph Ikechukwu Nwachukwu: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration, Funding acquisition. **Leon J. Clarke:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration. **Elias Symeonakis:** Conceptualization, Methodology, Software, Resources, Writing – review & editing, Supervision. **Francis Q. Brearley:** Conceptualization, Methodology, Formal analysis, Resources, Writing – original draft, Writing – review & editing, Supervision.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtemin.2022.100037.

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