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Health Risk Assessment of Selected Heavy Metals in Vegetables Grown along River Kabuthi, Nairobi County

Kimani Ignatius[*], Nawiri Mildred, Nyambaka Hudson

Department of Chemistry, Kenyatta University, Nairobi, Kenya
Email: *ignahkimani@gmail.com

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Abstract

The increased advocacy for the consumption of vegetables such as spinach, kale and African nightshade to promote good health has led to the use of irrigation water polluted with industrial and household waste. Use of such water results in the vegetables being contaminated with PTEs like lead, cadmium, copper, and zinc. This study investigated the health risk assessment (HRA) of heavy metals (HMs), Cu, Zn, Pb and Cd from consuming vegetables grown along River Kabuthi in Nairobi City County, where irrigation is practised during the dry season. Samples of vegetables were collected in five different blocks along River Kabuthi during the dry and wet periods, in February and May, respectively. Levels of heavy metals (HMs) determined using atomic absorption spectroscopy (AAS) procedure were used to calculate the daily intake of metals (DIM), incremental lifetime cancer risk (ILCR) and target hazard quotient (THQ) in both adults and children. The results indicated that the levels of HM in the dry season were generally higher than the levels in the wet season and were significantly different ($p < 0.001$) in the five blocks. The DIM for all the HMs was within the FAO/WHO limits for adults and children. THQ was above 1 ($THQ > 1$), implying that there is a possible health risk. ILCR for Cd was noted to be above the tolerable limits of 10^{-4} and 10^{-6} in adults in the dry season for kale and spinach in B1 and in the wet season in spinach in B1. In children, the ILCR for Cd was above the recommended limits in kale and spinach in B1 in the dry season and high in spinach in B1 in the wet season. The implication is that ingestion of the vegetables cultivated along the River Kabuthi may pose a health risk associated with Cu, Zn and Cd, such as liver and kidney problems as well as cancer.

Subject Areas

Biochemistry

Keywords

Daily Intake of Metals (DIM), Incremental Lifetime Cancer Risk (ILCR), Target Hazard Quotient (THQ), Health Risk Assessment (HRA), Heavy Metals (HMs), Potentially Toxic Elements (PTEs)

1. Introduction

Food safety is a global concern that has attracted scientific investigations, including studies on vegetables being contaminated with Potentially Toxic Elements (PTEs) such as cadmium (Cd), lead (Pb), Copper (Cu), and Zinc (Zn) [1] [2]. Vegetables, including spinach, kale, and African nightshade, contribute significantly to health and human nutrition by providing nutrients such as niacin, vitamin C, minerals, folic acid, thiamine, pyridoxine, and dietary fibre [3]. Therefore, there has been advocacy for increased consumption of vegetables to improve and maintain good health. The presence of heavy metals such as Cd, Pb, Cu, and Zn in vegetables may have both beneficial and harmful effects on adults and children if ingested in large quantities and at a higher frequency [4]. The dietary patterns and a person's age dictate the exposure levels to the PTEs [5]. These heavy metals, Zn, Pb, Cd, and Cu, are harmful due to their extended half-lives, ability to accumulate in various human body organs, and their limited biodegradability [6] [7]. The consumption of vegetables like kale, spinach and African nightshade containing unsafe levels of heavy metals of Zn, Pb, Cd and Cu over time leads to the accumulation of the HMs to their chronic levels in human organs like the liver and kidney [8] [9]. Accumulation of Zn and Cu in the body tissues causes nervous and cardiac diseases, while Pb and Cd lead to bone, kidney, and various types of cancer [10] [11].

According to World Bank projections, 9 billion people will need to be fed by the year 2050, meaning there will be a 60% increase in food consumption above current levels [12]. The Food and Agriculture Organization of the United Nations (FAO) encourages peri-urban farming in Latin America and the Caribbean countries during the 31st FAO Regional Conference [13]. In Eastern African countries where approximately 10.7 million people are in need of humanitarian food relief, about 2.4 million people are in Kenya [12]. This is due to the population's constant growth, especially people moving into metropolitan areas [13].

In Nairobi, Kenya, some areas, such as Dagorreti, where the Kabuthi River is located, have approximately 57,827 people experiencing food shortages. As a result, the cultivation of vegetables along the Kabuthi River is being encouraged to address the food scarcity and promote healthier living [14]. The river is suspected to contain PTEs due to the municipal and industrial wastes channelled into the river. Wastewater irrigation is a common practice within Nairobi County. Studies have shown that the physicochemical properties of water are the primary soil-vegetable pathways. Studies have revealed that soils within the Nairobi river catchment are acidic (pH < 6.5) and this significantly increases the solubility and mobility of metals like Cd, Pb, and Zn, leading to higher uptake. Irrigation of the vegetables using untreated municipal and industrial wastewater introduces PTEs like Cu, Zn, Pb and Cd that accumulate in soil over time and get absorbed by the vegetables. Various physicochemical parameters such as high total dissolved solids (TDS) and high electrical conductivity (EC) often correlate with high content of PTEs like Cd, Cu, Pb and Zn. In addition, proximity to the sources of pollution, like industrial and municipal wastes, contributes to the pollution of water, soil and subsequently vegetables. Soil Organic Matter (SOM) acts as a dual-action factor. While high organic matter can immobilize heavy metals through adsorption and chelation, reducing their bioavailability, decaying organic matter can also release organic acids that make metals more soluble. Based on similar studies, River Kabuthi may be contaminated with heavy metals such as Zn, Cu, Pb, and Cd from industrial and domestic effluents channelled into the river [14]. The area is in proximity to pollution sources like Dagoretti slaughterhouse, petrol stations, garages and metal processing industries, making it ideal for the study. Studies have shown that domestic and industrial effluents are the major sources of potentially toxic elements in urban rivers [14]. Farms located on the upper side of R. Kabuthi are at greater risk of PTE pollution due to their proximity to municipal and domestic waste discharge points. Water used for irrigation is the major source of PTEs that contaminate the soils, altering the soil properties like pH, cation exchange capacity, and organic matter content [15]. Subsequently, soil properties determine the mobility and availability of heavy metals for plant roots to absorb, as in the case along River Kabuthi. During the dry season, water from the river is used for irrigation, hence polluting the soil, which can lead to contamination with heavy metals. However, ingesting large quantities of vegetables contaminated with heavy metals does not necessarily pose a significant health risk. Therefore, an evaluation of the health risks associated with the levels of Zn, Cu, Pb, and Cd in spinach (*Spinacia oleracea*), kale (*Brassica oleracea var. acephala*) and African nightshade (*Solanum nigrum*) vegetables grown along the River Kabuthi in Nairobi County is needed [15]. Spinach, kale, and African nightshade vegetables were chosen for this research since they are the commonly grown vegetables and consumed vegetables in the study area. Studies in Nairobi County have revealed that these vegetables also tend to accumulate heavy metals [15].

The process of assessing the health risks for both adults and children involves determining if harmful effects occur upon consuming food containing heavy metals over a defined period [16] uses Target Hazard Quotient (THQ), Daily Intake of Metals (DIM), and Incremental Lifetime Cancer Risk (ILCR) indices [17]. The health risk assessment is important because levels of elements in the vegetables do not necessarily lead to a health risk [18]. In studies where there was continuous use of wastewater for irrigation of vegetables, the levels of heavy metals were within the safe levels and a human health risk assessment indicated that Daily Metal Intake (DIM) and Target Hazard Quotient (THQ) were higher than the recommended levels [18] [19]. According to USEPA, 10^{-6} (1 in 1,000,000) to 10^{-4} (1 in 10,000) represent a range of permissible predicted lifetime risks for carcinogens [20]. In Kenya, the adults and children daily intake of vegetables are 345 g and 232 g (0.345 and 0.232 kg/person/day) respectively against the WHO recommendation of 400 grams of fruits and Vegetable intake. In a study in the Ilesha gold mine in southern Nigeria, the ILCR result showed that 2% of the 0.21 million people both adults and children were likely to develop cancer due to arsenic that exceeded the acceptable carcinogenic risk [21]. In Kenya, a study on the threat to health risk associated with the consumption of foods contaminated with elements found DIM levels were all below FAO/WHO provision, although the health risk assessment pointed out that lead alone could potentially lead to cancer risk to approximately 0.043% of the population (73 out of 0.17M) [22]. Although the levels of the HMs may be within acceptable levels, biochemical accumulation over several years to some of the heavy metals like Pb and Cd would be a health risk [22]. This study investigated the health risk associated with the consumption of kale, spinach and African nightshade vegetables grown along River Kabuthi, Kenya.

2. Materials and Methods

2.1. Research Design

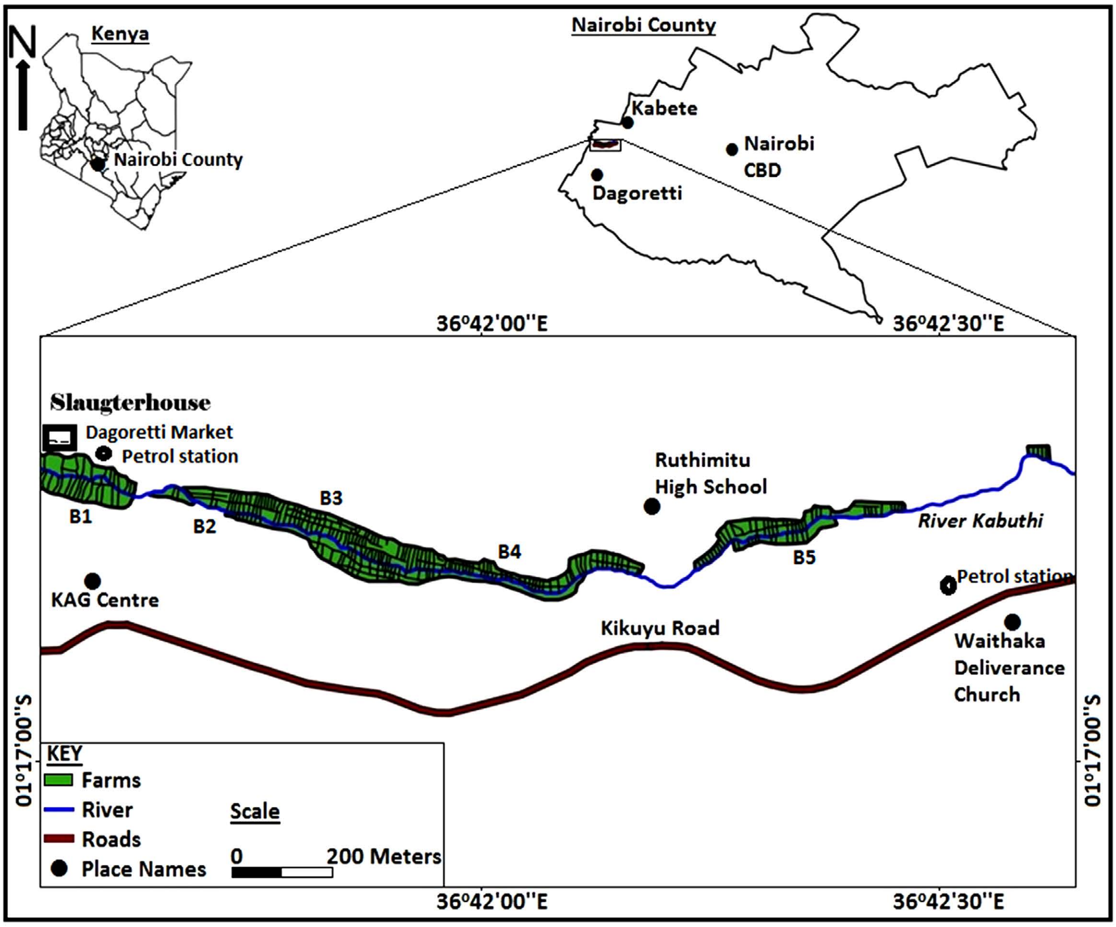
The study focused on analyzing samples from farms along River Kabuthi in one dry and wet seasons. A randomized block design was used to divide the study area into blocks labeled B1-B5, from which 3 farms containing vegetables from each block were sampled [23]. The levels of the heavy metals from the collected samples were used to assess the health risk using the DIM, ILCR, and THQ indices.

2.2. Study Area

Farming of vegetables like spinach (*Spinacia oleracea*), kale (*Brassica oleracea var. acephala*) and African nightshade (*Solanum nigru*m) is common along River Kabuthi, making it suitable to carry out the study. The area's geographical coordinates are 1˚17'41" South, 36˚42'25" East. According to the 2009 Kenya Population and Housing Census Report, the area has approximately 57,827 people, with the adult population being 22,964 [24]. The area receives rainfall averaging 1356 mm annually. The dry season is between January and early March, while April to June is considered as the period of long rains. Agricultural activities are sustained by both rainfall and irrigation water from River Kabuthi (See **Figure 1**).

2.3. Chemicals and Reagents

The reagents were 99.9% pure analytical grade obtained from Sigma Aldrich Company and supplied by Kobian Kenya Limited, Nairobi. The reagents were lead nitrate, copper sulphate, zinc granules, cadmium nitrate, 68% concentrated nitric (v) acid, and 70% perchloric acid.



Map source: https://www.scribblemaps.com.

Figure 1. Map showing farms in B1 to B5 along River Kabuthi in Dagoretti, Nairobi County.

2.4. Instrumentation

The Atomic absorption spectrometer (AAS) was used in the analysis of the samples (Shimadzu AAS-6300). An air-acetylene flame was used to analyze the metals. The operating conditions of the AAS are illustrated in Table 1.

Table 1. The operating conditions for the AAS (Shimadzu AA-6300).

Heavy metals	Wavelength (nm)	Path length (nm)	Burner Height (mm)	Lamp current (mA)	Flow (L/min)
Zn	213.9	0.7	7	5	2
Pb	283.3	0.7	7	5	2
Cd	228.8	1.2	7	2	2.8
Cu	324.8	0.5	7	4	2

2.5. Sample Collection and Pretreatment

Vegetable leaf samples of spinach (*Spinacia oleracea*), kale (*Brassica oleracea var. acephala*) and African nightshade (*Solanum nigru*m) were collected during one dry and one wet season in 2023, with the dry season in February and the wet season in May. This covered the study period of one dry and one wet season [25]. The three vegetables were chosen for the study because they are commonly grown in the area, fast-maturing, commonly consumed and sold locally.

The sampling sites were divided into blocks, coded B1-B5, and three farms containing each vegetable were marked for sampling. To obtain a representative sample of the farms, the study employed a simple random sampling design across the two sides of the river within the five blocks. Sampling entailed apportioning each sampled garden into four divisions, after which the two sides opposite each other and the middle of the farm were systematically sampled. Five mature, edible leaves from each vegetable were collected in one dry season and another five samples were collected in the wet season from each farm. Five samples from each farm were put together to form a composite sample. 90 samples of the vegetables were collected from the sampling sites. A composite sample is relatively efficient because it is cost-effective, representative of the average and enables sampling over a large area [25].

The collected leaf samples of kale, spinach, and African nightshade were washed with distilled water. The surfaces of the vegetables were dried using blotting paper, midribs removed, and cut into small pieces before being dried at 60˚C - 70˚C in an oven until a constant weight was achieved. The dried samples were grounded and then sieved (<0.5 mm). Finally, the samples were preserved at room temperature awaiting AAS instrumental analysis [25].

2.6. Preparation of Standard Solutions

By the use of metals of analytical grade (99.9% pure), element standard solutions (1000 mg/L) were prepared using a standard protocol [25]. Exactly 40 mL of 1:1 hydrochloric acid and nitric (V) acid mixture was used to dissolve 1.0 gram of zinc in analytical grade in a 1-litre volumetric flask to prepare the Zinc standard.

Distilled water was then added to the solution to dilute to the mark and prepare a 1000 mg/L stock solution. 1.598 g of pure lead nitrate in 10ml nitric (V) acid diluted to 1% (v/v) and topped up to 1 litre using distilled water. Copper standard was prepared by dissolving 1.965g of copper sulphate in 0.1M hydrochloric acid then diluting with distilled water to produce 1000 ml. To prepare a 1000 ppm (mg/L) cadmium (Cd) standard stock solution from cadmium nitrate tetrahydrate, $Cd(NO_3)_2 \cdot 4H_2O$, 2.7444 grams of the salt was weighed accurately and dissolved in a 1-litre volumetric flask using 10 ml of 2.0 M dilute nitric acid solution and distilled water added to the mark [26]. Calibration curves for the standard solutions for all the heavy metals were prepared by serial dilution of the standards per 1000 ppm [27] [28]. Serial dilution was used in obtaining the working solutions containing 1000 mg/L stock solution and preparing the metal standards of Cu, Pb, and Cd to 0.2 ppm, 0.4 ppm, 0.6 ppm, 0.8 ppm, and 1.0 ppm [29].

2.7. Acid Digestion of Vegetable Samples

Acid digestion of the samples was done according to the protocol by Bankaji *et al.* Exactly 1.00 g of each vegetable samples was weighed accurately, grounded to a fine powder and then placed in a 500 mL Kjeldahl digestion flask [30]. To this was added 10 mL of acid mixture containing 65% concentrated HNO_3- 37% HCl-H_2O_2 (8:1:1; v/v/v) and the mixture was heated in an oven digestion at 120˚C for about 15 - 30 minutes until no more brown fumes were seen. The mixture was allowed to cool for about 15 minutes. Exactly 5.00 mL of 70% perchloric acid was then added to the mixture, which was then heated until the solution became clear and white fumes were produced. This was allowed to cool, then it was filtered using Whatman no.42 filter paper. A 5.00 ml amount of filtrate was transferred into a volumetric flask of 50 mL capacity and topped to the mark using distilled water. The solution was then preserved in a deep freezer maintained at 4˚C in an acid-cleaned and sealed plastic bottle.

2.8. Method Validation Procedures and Quality Assurance

The performance characteristics of sensitivity, linearity and LOD were obtained from calibration curves of the standards. For quality assurance purposes, precision was assessed through the coefficient of variation and matrix-matched certified reference materials [31]. The Percentage Coefficient variation (CV) was determined by performing the measurement in triplicate with a given amount of the sample and determining the standard deviation (S) and the mean ($\bar{X}$) and the standard deviation (S). The percent CV was then calculated using Equation (1) [32].

$$\text{Percentage coefficient of variation } (\text{CV}) = \text{S}/(\text{X}) \times 100 \qquad (1)$$

In the recovery of Zn, Cu, Pb and Cd samples were spiked with the standards, then added to the samples in triplicate and extraction procedure followed. The amount of spiked samples in the digests were used to determine percentage recovery using Equation (2) below [33];

$$R = \frac{(C_s - C)}{S} \times 100 \tag{2}$$

C_s = is the concentration of the metal in the spiked sample;

C = concentration of metal in the non-spiked sample;

S = concentration equivalent for the analyte added to the sample.

The quality control from the standard solutions of Zn, Cd, Cu and Pb was analysed in triplicate and standard stock solutions from certified reference materials and blank standard samples were examined after every ten samples to set the instrument's baseline, and checking for solvent purity and instrumental drift. The limit of detection (LOD) was calculated as the sample concentration, which provides a signal equal to the signal of the blank (yB) plus three standard deviations of the blank, sB [34]. The three variations are expressed in Equation (3).

$$y - yB = 3sB \tag{3}$$

The LOD of the elements was calculated using Equation (4)

$$LOD = 3.3sB/slope \tag{4}$$

2.9. Methods for Health Risk Assessment

The health risk assessment linked with the ingestion of PTEs metals in the vegetables was performed using the DIM, THQ and ILCR indices.

The DIM is calculated using Equation (5) [35];

$$DIM = C_{metal} \times K_{factor} \times I_{average\ daily} / BW \tag{5}$$

C_{metal} is the heavy metal concentration in the vegetables ($mg \cdot kg^{-1}$),

K_{factor} is the conversion factor is 0.085. It is the conversion factor of fresh vegetable weight to dry weight [35].

$I_{average\ daily\ intake}$ equals the mean intake of vegetables among adults daily - considered to be 0.345 kg/person/day per adult and 0.232 kg/person/day in children

BW represents the average body weight [35].

THQ was calculated using Equation (6)

$$THQ = \frac{EF \times FD \times DIM}{R_f D_o \times W \times T} \tag{6}$$

where R_fD_o will be the oral dose of reference (mg/kg/day). The R_fD_o numerals for Cu, Pb, Cd, and Zn are 0.04, 0.004, 0.001, and 0.30 (mg/kg/bw/day), respectively

DIM is the daily intake of metals

EF is 183.5 days per year

FD represents the frequency of encounters (67.5 years in adults and 12 years in children).

W is the average body weight (67.5 kg in adults and 35 kg in children).

T refers to the mean time for all the non-carcinogenic elements.

ILCR was determined as follows [35];

$$\text{ILCR} = \text{CDI} \times \text{CSF} \tag{7}$$

CDI represents the chronic heavy metal daily intake in mg/kg BW/day and is the lifetime mean daily exposure to the carcinogen.

CSF is the cancer slope factor.

$$\text{CDI} = \frac{\text{EDI} \times \text{EF}_r \times \text{ED}_{tot}}{\text{AT}} \tag{8}$$

EDI represents the heavy metal daily intake

EF_r represents the frequency of exposure (365 days/year).

ED_{tot} represents an exposure duration of 67.5 years (Kenyan average lifespan) and 12 years in children.

AT is the average time for non-carcinogens.

EDI was performed using Equation (9);

$$\text{EDI} = \frac{C_{metal} \times W_{food}}{B_w} \tag{9}$$

C_{metal} refers to metal concentration for dry weight (mg/kg).

W_{food} is mean vegetables ingested daily.

B_w is the average weight (67.5 kg in adults and 35 kg in children).

Cancer slope factor (CSF) for Pb is 0.0085 and Cd is 0.38 mg/Kg/Day [35].

Incremental Lifetime Cancer Risk (ILCR) is not computed for Copper (Cu) and Zinc (Zn) because they are considered non-carcinogenic elements.

2.10. Data Analysis

Data analysis was performed using SPSS software version 21 for the parameters such as the mean, standard deviation, standard error and one-way ANOVA. A post hoc test using the Student-Newman-Keuls test (SNK-test) was also performed to determine the significance difference in the means.

3. Results and Discussions

3.1. Method Performance Characteristics

The detection limit was in the range 0.0367-0.86 ppm for heavy metals (**Table 2**). All the analytical blanks were lower than the limit of detection. The precision of the method was evaluated using the coefficient of variation, which ranged from 46% to 79.6%, indicating good method performance. Based on the graph, the positive slope values in the regression equation indicated that as the levels increase, there is a corresponding rise in the absorbance observed for each standard solution [36]. The Y-intercept fell in the range of 0.00001 and 0.0096, indicating that the matrix's effect was negligible. The least correlation coefficient was 0.9813, implying that over 98.13% correlated with the concentration. The percent recoveries ranged from 92% to 97%, demonstrating that the analytical method exhibited adequate accuracy [37]. Hence, the process was considered appropriate for assessing the quantities of the PTEs in the sampled vegetables. **Figure 2** illustrates a calibration curve of zinc with the calibration points and R^2.

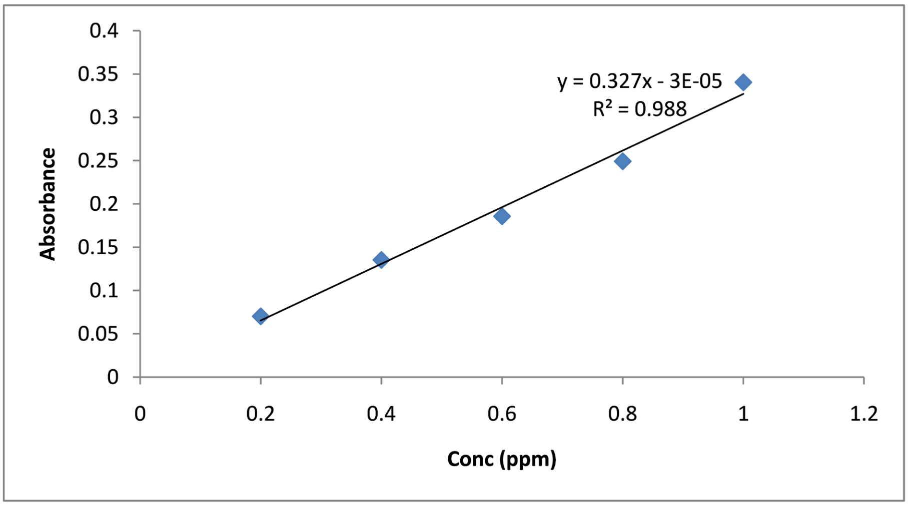


Figure 2. Calibration curve of zinc.

Table 2. Method performance characteristics evaluated during the method validation process.

Metals	Correlation coefficient (R^2)	Regression equation	% Recoveries	%CV	LOD (ppm)
Zn	0.9888	y = 0.3272x − 3E−05	92.4	46	0.13
Cu	0.9813	y = 0.0403x + 0.0002	99.4	48	0.86
Pb	0.9999	y = 0.0046x + 1E−05	98.9	79.6	0.044
Cd	0.9992	y = 0.2413x + 0.0096	99.6	49	0.0367

3.2. Levels of Heavy Metals in Vegetables

Table 3 shows the levels of heavy metals in kale, spinach, and African nightshade in five blocks based on their dry weights. In the dry season, the levels of the heavy metals (HMs) in the vegetables ranged as follows: Zn 0.87 ± 0.09 - 66.89 ± 0.71, Cu 0.86 ± 0.18 - 38.53 ± 1.33, Pb 0.97 ± 0.08 - 12.10 ± 0.59, and Cd 0.06 ± 0.01 - 1.95 ± 0.19 (mg/kg). In the wet season, the levels were Zn 0.13 ± 0.01 - 41.80 ± 0.33, Cu 0.86 ± 0.01 - 29.17 ± 0.76, Pb 0.21 ± 0.05 - 9.03 ± 0.37, Cd L.O.D - 1.47 ± 0.06 (mg/kg). The levels of Cu vegetables kale, African nightshade, and spinach in the dry and wet seasons were below the WHO/FAO limits. The levels of Zn were above the recommended limits in kale (B1 in dry and wet seasons), spinach (B1 in dry and wet seasons) and in African nightshade vegetables (B1 in the dry season). The levels of Pb were above the WHO limits in the vegetables except in African nightshade vegetables in the wet season in B5. The levels of Cd in the vegetables were above the WHO/FAO regulations except in the African nightshade in B5 in the dry season and B3 in the wet season, and kale in B5 in the dry season [38].

In the wet season, there is increased precipitation that subsequently leads to leaching of the HMs as well as dilution of river water used for irrigation compared to the dry season. In addition, there is less use of river water to irrigate the vegetables in the wet season. These factors contribute to the accumulation of the PTEs and, therefore the higher levels of HMs in the vegetables in the dry season compared to the wet season. Irrigation water contaminated with PTEs contributes to the higher levels of the elements in the dry season compared to the wet season [2]. The ANOVA results showed that the levels in the five blocks were significantly different from one another ($p < 0.001$). Farms in B1 are located near the pollution source compared to farms in the other blocks. This explains the variations in the levels of the heavy metals from B1 to B5. Blocks 1 and 2 are located near Dagoretti market, where municipal and some industrial effluents are released into the river. Human and domestic waste released into River Kabuthi contributes to pollution of the river and research has shown that human waste as well as municipal wastes contains heavy metals like Pb, Cu, Zn and Cd [39]. Petrol stations and motor vehicle garages located near the river release effluents into the river, which also contribute to the pollution of the river with PTEs [40].

Table 3. Mean levels (mg/kg) of heavy metals in kale, spinach, and African nightshade.

Sample (n = 3)	**Block**	**Zn**		**Cu**		**Pb**		**Cd**	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Kale	B1	66.89 ± 0.71^{h}	40.44 ± 1.10^{g}	29.49 ± 2.09^{d}	26.98 ± 1.68^{d}	10.24 ± 0.22^{g}	7.28 ± 0.16^{f}	1.53 ± 0.03^{e}	1.01 ± 0.39^{a}
	B2	36.96 ± 0.36^{f}	13.76 ± 0.32^{d}	3.39 ± 0.05^{a}	6.58 ± 0.31^{b}	6.55 ± 0.08^{e}	5.09 ± 0.48^{d}	1.09 ± 0.07^{d}	0.45 ± 0.01^{a}
	B3	15.86 ± 0.12^{e}	15.83 ± 0.30^{e}	14.53 ± 0.45^{c}	2.64 ± 0.20^{a}	4.79 ± 0.11^{d}	2.20 ± 0.12^{c}	0.48 ± 0.06^{c}	0.39 ± 0.05^{a}
	B4	4.56 ± 0.58^{c}	2.61 ± 0.05^{b}	0.98 ± 0.03^{a}	1.08 ± 0.08^{a}	1.58 ± 0.16^{b}	1.30 ± 0.05^{b}	0.83 ± 0.03^{b}	<L.O.D
	B5	0.97 ± 0.03^{a}	0.51 ± 0.09^{a}	0.86 ± 0.18^{a}	0.86 ± 0.04^{a}	0.97 ± 0.08^{b}	0.33 ± 0.05^{a}	0.16 ± 0.02^{a}	<L.O.D
p value ($\alpha = 0.05$)		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Spinach	B1	70.01 ± 1.45^{g}	41.80 ± 0.33^{g}	38.53 ± 1.33^{f}	29.17 ± 0.76^{e}	12.10 ± 0.59^{g}	9.03 ± 0.37^{f}	1.95 ± 0.19^{d}	1.37 ± 0.06^{c}
	B2	40.03 ± 0.40^{f}	15.24 ± 0.45^{d}	3.98 ± 0.05^{b}	9.55 ± 0.06^{c}	7.89 ± 0.36^{e}	6.65 ± 0.11^{d}	1.25 ± 0.09^{c}	0.82 ± 0.03^{b}
	B3	17.47 ± 0.44^{c}	13.46 ± 0.26^{c}	16.55 ± 0.69^{d}	2.64 ± 0.20^{b}	6.19 ± 0.08^{d}	2.86 ± 0.11^{c}	1.37 ± 0.15^{c}	0.58 ± 0.14^{b}
	B4	4.99 ± 0.17^{b}	3.98 ± 0.12^{b}	1.94 ± 0.09^{a}	0.88 ± 0.09^{a}	3.01 ± 0.07^{c}	1.64 ± 0.03^{b}	1.11 ± 0.05^{c}	<L.O.D
	B5	1.31 ± 0.04^{a}	0.92 ± 0.03^{a}	1.02 ± 0.15^{a}	0.87 ± 0.07^{a}	2.10 ± 0.11^{c}	0.81 ± 0.05^{a}	0.31 ± 0.01^{a}	<L.O.D
p value ($\alpha = 0.05$)		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
African Nightshade	B1	62.86 ± 1.94^{g}	36.87 ± 0.08^{f}	28.31 ± 1.41^{e}	19.26 ± 1.40^{d}	10.49 ± 0.23^{g}	6.45 ± 0.08^{f}	1.10 ± 0.04^{f}	0.59 ± 0.12^{b}
	B2	32.44 ± 0.69^{e}	13.45 ± 0.85^{d}	1.91 ± 0.08^{a}	6.58 ± 0.57^{b}	4.96 ± 0.15^{e}	3.62 ± 0.37^{d}	0.68 ± 0.03^{e}	0.42 ± 0.09^{cd}
	B3	6.52 ± 0.22^{c}	5.89 ± 0.09^{c}	13.26 ± 0.24^{c}	1.73 ± 0.04^{a}	3.09 ± 0.19^{c}	1.50 ± 0.05^{b}	0.35 ± 0.05^{cd}	0.19 ± 0.01^{b}
	B4	2.51 ± 0.06^{b}	1.85 ± 0.09^{ab}	1.54 ± 0.08^{a}	0.92 ± 0.09^{a}	1.46 ± 0.07^{b}	1.21 ± 0.02^{b}	0.29 ± 0.02^{bc}	<L.O.D
	B5	0.87 ± 0.09^{b}	0.13 ± 0.01^{a}	0.99 ± 0.01^{a}	0.87 ± 0.01^{a}	1.30 ± 0.10^{b}	0.21 ± 0.05^{a}	0.06 ± 0.01^{a}	<L.O.D
p value ($\alpha = 0.05$)		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
WHO/FAO, 2013 (mg/kg)		60		40		0.3		0.2	

Mean values followed by the same small superscript letter(s) within the same column do not differ significantly from one another (SNK-test, $\alpha = 0.05$). Where n is the number of replicates and LOD is below detection limit.

3.3. Health Risk Assessment for Adults and Children

3.3.1. Daily Intake of Metals (DIM)

The levels of the heavy metals in the selected vegetables were used to calculate the DIM, and the results are represented in Table 4. The DIM values for the heavy metals in the dry seasons were Zn 3.78×10^{-04} - 3.04×10^{-02}, Cu 3.65×10^{-04} - 1.67×10^{-02}, Pb 4.2×10^{-04} - 5.26×10^{-03}, and Cd 1.26×10^{-04} - 8.47×10^{-04} (µg/g/day) in adults and Zn 4.90×10^{-04} 3.94×10^{-02}, Cu 4.73×10^{-04} 2.17×10^{-02}, Pb 5.47×10^{-04} 6.82×10^{-03}, and Cd 3.38×10^{-05} 1.10×10^{-03} (µg/g/day) for children. During the wet season, the DIM values for adults and children were: Zn, 2.22×10^{-04} - 2.36×10^{-02}; Cu, 3.04×10^{-05} - 1.64×10^{-02}; Pb, 9.12×10^{-05} - 5.09×10^{-03}; and Cd, ND -7.72×10^{-04} (µg/g/day). The FAO/WHO recommended DIM for Zn, Cu, Pb, and Cd are 11, 0.3, 0.5, and 0.06 (µg/g/day), respectively [13]. From the table, the DIM values were below the permissible FAO/WHO levels, indicating that the levels in the selected vegetables were within safe limits for both adults and children [13]. In comparison with the provisional dietary intakes, the DIM of children was relatively higher than the DIM in adults in all the vegetables. The results are similar to the results from the study by Shao *et al.* [41], whose assessment of the heavy metal contamination and health risk in various vegetables found that the dietary intake of As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn among the local population was higher in the children than in adults [42]. In their research, they explain that children have a greater body mass index compared to adults and therefore, they are more exposed to the studied PTEs in their body tissues.

Table 4. The results of Daily intake of metals (DIM).

		Adults								Children							
	Block	Zn		Cu		Pb		Cd		Zn		Cu		Pb		Cd	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Kales	B1	2.91×10^{-02}	1.76×10^{-02}	1.28×10^{-02}	1.17×10^{-02}	4.45×10^{-03}	3.16×10^{-03}	6.65×10^{-04}	4.39×10^{-04}	3.77×10^{-02}	2.28×10^{-02}	1.66×10^{-02}	1.52×10^{-02}	5.77×10^{-03}	4.10×10^{-03}	8.62×10^{-04}	5.69×10^{-04}
	B2	1.61×10^{-02}	5.98×10^{-03}	1.47×10^{-03}	2.86×10^{-03}	2.85×10^{-03}	2.21×10^{-03}	4.74×10^{-04}	1.96×10^{-04}	2.08×10^{-02}	7.75×10^{-03}	1.91×10^{-03}	3.71×10^{-03}	3.69×10^{-03}	2.87×10^{-03}	6.14×10^{-04}	2.54×10^{-04}
	B3	6.89×10^{-03}	6.88×10^{-03}	6.31×10^{-03}	1.15×10^{-03}	2.08×10^{-03}	9.56×10^{-04}	2.09×10^{-04}	1.69×10^{-04}	8.94×10^{-03}	8.92×10^{-03}	8.19×10^{-03}	1.49×10^{-03}	2.70×10^{-03}	1.24×10^{-03}	2.70×10^{-04}	2.20×10^{-04}
	B4	1.98×10^{-03}	1.13×10^{-03}	4.26×10^{-04}	4.69×10^{-04}	6.86×10^{-04}	5.65×10^{-04}	3.61×10^{-04}	-	2.57×10^{-03}	1.47×10^{-03}	5.52×10^{-04}	6.09×10^{-04}	8.90×10^{-04}	7.32×10^{-04}	4.68×10^{-04}	-
	B5	4.21×10^{-04}	2.22×10^{-04}	3.65×10^{-04}	2.39×10^{-04}	4.2×10^{-04}	1.43×10^{-04}	6.95×10^{-04}	-	5.47×10^{-04}	2.87×10^{-04}	4.73×10^{-04}	3.10×10^{-04}	5.47×10^{-04}	1.86×10^{-04}	9.01×10^{-05}	-
Spinach	B1	3.04×10^{-02}	1.82×10^{-02}	1.67×10^{-02}	1.27×10^{-02}	5.26×10^{-03}	3.92×10^{-03}	8.47×10^{-04}	5.95×10^{-04}	3.94×10^{-02}	2.36×10^{-02}	2.17×10^{-02}	1.64×10^{-02}	6.82×10^{-03}	5.09×10^{-03}	1.10×10^{-03}	7.72×10^{-04}
	B2	1.74×10^{-02}	6.62×10^{-03}	1.73×10^{-03}	4.15×10^{-03}	3.43×10^{-03}	2.89×10^{-03}	5.43×10^{-04}	3.56×10^{-04}	2.26×10^{-02}	8.59×10^{-03}	2.24×10^{-03}	5.38×10^{-03}	4.45×10^{-03}	3.75×10^{-03}	7.04×10^{-04}	4.62×10^{-04}
	B3	7.59×10^{-03}	5.85×10^{-03}	7.19×10^{-03}	1.15×10^{-03}	2.69×10^{-03}	1.24×10^{-03}	5.95×10^{-04}	2.52×10^{-04}	9.84×10^{-03}	7.58×10^{-03}	9.33×10^{-03}	1.49×10^{-03}	3.49×10^{-03}	1.61×10^{-03}	7.72×10^{-04}	3.27×10^{-04}

Continued

	B4	2.17×10^{-03}	1.73×10^{-03}	8.43×10^{-04}	3.61×10^{-04}	1.31×10^{-03}	7.12×10^{-04}	4.82×10^{-04}	–	2.81×10^{-03}	2.24×10^{-03}	1.09×10^{-03}	4.68×10^{-04}	1.70×10^{-03}	9.24×10^{-04}	6.25×10^{-04}	–
	B5	5.69×10^{-04}	4.00×10^{-04}	4.43×10^{-04}	3.56×10^{-04}	9.12×10^{-04}	3.52×10^{-04}	1.35×10^{-04}	–	7.38×10^{-04}	5.18×10^{-04}	5.75×10^{-04}	4.62×10^{-04}	1.18×10^{-03}	4.56×10^{-04}	1.75×10^{-04}	–
African nightshade	B1	2.73×10^{-02}	1.60×10^{-02}	1.23×10^{-02}	8.37×10^{-03}	4.56×10^{-03}	2.80×10^{-03}	4.78×10^{-04}	2.56×10^{-04}	3.54×10^{-02}	2.08×10^{-02}	1.60×10^{-02}	1.09×10^{-02}	5.91×10^{-03}	3.63×10^{-03}	$6. \times 10^{-04}$	3.32×10^{-04}
	B2	1.41×10^{-02}	5.84×10^{-03}	8.30×10^{-04}	2.86×10^{-03}	2.16×10^{-03}	1.57×10^{-03}	2.95×10^{-04}	1.83×10^{-04}	1.83×10^{-02}	7.58×10^{-03}	1.08×10^{-03}	3.71×10^{-03}	2.80×10^{-03}	2.04×10^{-03}	3.83×10^{-04}	2.37×10^{-04}
	B3	2.83×10^{-03}	2.56×10^{-03}	5.76×10^{-03}	7.52×10^{-04}	1.34×10^{-03}	6.52×10^{-04}	1.52×10^{-04}	8.25×10^{-05}	3.67×10^{-03}	3.32×10^{-03}	7.47×10^{-03}	9.75×10^{-04}	1.74×10^{-03}	8.45×10^{-04}	1.97×10^{-04}	1.07×10^{-04}
	B4	1.09×10^{-03}	8.04×10^{-04}	6.69×10^{-04}	1.26×10^{-04}	6.34×10^{-04}	5.26×10^{-04}	1.26×10^{-04}	–	1.41×10^{-03}	1.04×10^{-03}	8.68×10^{-04}	1.63×10^{-04}	8.23×10^{-04}	6.82×10^{-04}	1.63×10^{-04}	–
	B5	3.78×10^{-04}	4.78×10^{-04}	4.30×10^{-04}	3.04×10^{-05}	5.65×10^{-04}	9.12×10^{-05}	2.61×10^{-04}	–	4.90×10^{-04}	6.20×10^{-05}	5.58×10^{-04}	3.94×10^{-05}	7.32×10^{-04}	1.18×10^{-04}	3.38×10^{-05}	–
WHO, 2013		11		0.3		0.5		0.06		11		0.3		0.5		0.06	

3.3.2. Target Hazard Quotient (THQ)

The THQ for adults in the dry season was in the ranges of Zn 2.05×10^{-5} - 1.12×10^{1} and Cu 1.15×10^{-4} - 1.19×10^{1}, and in the wet season the THQ were: Zn 1.47×10^{-6} - 1.6×10^{-1} and Cu 1.85×10^{-5} - 8.91×10^{-1}. In children, the THQ for the dry season was Zn 3.89×10^{-5} - 1.14×10^{1} and Cu 4.73×10^{-4} - 1.37×10^{1}, and in the wet season, Zn 5.01×10^{-7} - 1.62×10^{-1} and Cu 6.30×10^{-6} - 1.24×10^{1}. FAO/WHO recommends a THQ of heavy metals to be less than 1 [13]. In adults, the target hazard quotient (THQ) was above 1 (THQ > 1) for Zn in the dry season in kales B1 and spinach B1, and for Cu in kales B1, spinach B1, and African nightshade vegetables B1. In children, the target hazard quotient was above 1 (THQ > 10^{1}) in Zn the dry season for kales B1, spinach B1 and Cu in kales B1, spinach B2, African nightshade B1 and in the wet season the level of Cu was above 1 in kales B1 and spinach B1.

The results project a possible health hazard when the vegetables with THQ above 1 are consumed [34]. The calculated THQ was generally higher in children than in adults. Islam *et al.* in their THQ analysis noted similar results in adults and children [19]. In their study they explain that a higher THQ value in Children is because they have a relatively small body weight relative to the amount of food they ingest over time, leading to a higher THQ compared to adults [19] [42]. Ihienacho *et al.* noted that the bioaccumulation of these HMs in the food chain causes drastic health problems to humans. This is due to the accumulation of the PTEs in plant parts having secondary metabolites, which is responsible for a particular subsequent pharmacological activity when consumed by children, leading to adverse health effects [10]. The possible health risks associated with excess intake of zinc and copper in humans include severe illness such as anemia, damage to the pancreas, and renal and liver damage. Therefore, the consumption of the vegetables with THQ greater than 1 could lead to the disorders in adults and children [11] [19] (See **Table 5**).

Table 5. Target hazard quotient for adults and children.

		Adults				Children			
	Block	Zn		Cu		Zn		Cu	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Kales	B1	1.03×10^{1}	3.56×10^{-2}	1.16×10^{1}	1.09×10^{-1}	1.12×10^{1}	6.77×10^{-2}	1.34×10^{1}	1.21×10^{1}
	B2	2.97×10^{-2}	4.12×10^{-3}	1.88×10^{-3}	7.07×10^{-3}	5.65×10^{-2}	7.83×10^{-3}	3.57×10^{-3}	1.34×10^{-2}
	B3	5.48×10^{-3}	5.46×10^{-3}	3.45×10^{-2}	2.84×10^{-3}	1.04×10^{-2}	1.04×10^{-2}	6.55×10^{-2}	5.39×10^{-3}
	B4	4.53×10^{-4}	1.48×10^{-4}	1.57×10^{-4}	1.16×10^{-3}	8.60×10^{-4}	2.82×10^{-4}	2.98×10^{-4}	2.21×10^{-3}
	B5	2.05×10^{-5}	5.66×10^{-6}	1.15×10^{-4}	5.91×10^{-4}	3.89×10^{-5}	1.08×10^{-5}	2.19×10^{-4}	1.12×10^{-3}
Spinach	B1	1.12×10^{1}	3.80×10^{-2}	1.19×10^{1}	8.91×10^{-1}	1.14×10^{1}	7.23×10^{-2}	1.37×10^{1}	1.24×10^{1}
	B2	3.49×10^{-2}	5.06×10^{-3}	2.59×10^{-3}	1.49×10^{-2}	6.63×10^{-2}	9.61×10^{-3}	4.92×10^{-3}	2.83×10^{-2}
	B3	6.65×10^{-3}	3.95×10^{-3}	4.47×10^{-2}	1.14×10^{-3}	1.26×10^{-2}	7.50×10^{-3}	8.50×10^{-2}	2.16×10^{-3}
	B4	5.42×10^{-4}	3.45×10^{-4}	6.15×10^{-4}	1.13×10^{-4}	1.03×10^{-3}	6.55×10^{-4}	1.17×10^{-3}	2.14×10^{-4}
	B5	3.74×10^{-5}	1.84×10^{-5}	1.70×10^{-4}	1.10×10^{-4}	7.10×10^{-5}	3.50×10^{-5}	3.23×10^{-4}	2.09×10^{-4}
African nightshade	B1	4.80×10^{-1}	1.6×10^{-1}	1.09×10^{1}	1.16×10^{-1}	1.63×10^{-1}	1.62×10^{-1}	1.01×10^{1}	3.93×10^{-2}
	B2	1.28×10^{-1}	2.20×10^{-2}	4.93×10^{-2}	1.16×10^{-1}	4.35×10^{-2}	7.49×10^{-3}	1.68×10^{-2}	3.93×10^{-2}
	B3	5.17×10^{-3}	4.22×10^{-3}	2.31×10^{-2}	1.04×10^{-2}	1.76×10^{-3}	1.44×10^{-3}	7.86×10^{-3}	3.53×10^{-3}
	B4	7.66×10^{-4}	4.16×10^{-4}	1.86×10^{-2}	4.57×10^{-4}	2.61×10^{-4}	1.42×10^{-4}	6.34×10^{-3}	1.56×10^{-4}
	B5	9.20×10^{-5}	1.47×10^{-6}	1.39×10^{-3}	1.85×10^{-5}	3.13×10^{-5}	5.01×10^{-7}	4.73×10^{-4}	6.30×10^{-6}

3.3.3. Incremental Lifetime Cancer Risk (ILCR)

In adults, the ILCR were 2.12×10^{-04} - 1.70×10^{-05} for Pb and 1.53×10^{-03} -<LOD for Cd during the dry season. In children, the ILCR were Pb 1.92×10^{-04} - 1.54×10^{-05} and Cd 1.38×10^{-03} - 4.26×10^{-05}. In the wet season, the ILCR were Pb 1.58×10^{-04} - 5.77×10^{-06} and Cd 1.15×10^{-03} - -<LOD in adults. In children the ILCR during the wet season were Pb 1.43×10^{-04} - 4.26×10^{-05} and Cd 1.04×10^{-03} - <LOD. From the results, the ILCR of the vegetables in the gardens from the blocks were within the safe limits of 10^{-4} and 10^{-6} for Pb. The recommended ILCR limit is in the range of 10^{-4} and 10^{-6} therefore the consumption of the vegetables is free from any risk of cancer for Pb [13] [21]. In contrast, several studies within Nairobi County have linked carcinogenic effects of Pb in food with ILCR levels higher than 10^{-4} leading to cancer. For instance, a study by Nyabuti *et al.* [22] revealed that Pb alone could potentially lead to cancer risk to approximately 0.043% of the population (73 out of 0.17M) that represents an ILCR above 10^{-4} [22]. Another study by Islam *et al.* noted that the ILCR values of Pb in children were above the set limits (ILCR > 10^{-4}), indicating possible carcinogenic effects from the lifetime consumption of the vegetables [19]. However, the ILCR for Cd was noted to be above the tolerable limits of 10^{-4} and 10^{-6} in adults in the dry season for kale and spinach in B1 and in the wet season in spinach in B1. In children, the ILCR for Cd in the dry season was above the recommended limits in kale and spinach in B1and in the wet season, it was high in spinach in B1. Therefore, the consumption of these vegetables with elevated levels of Cd has a high risk of carcinogenic health risk [21]. Children as opposed to adults have a greater body mass index to the food ingested making them more vulnerable to the toxic effects of Cd (See **Table 6**).

Table 6. Incremental lifetime cancer risk (ILCR) of adults and children.

		Adults				Children			
	Garden	Pb		Cd		Pb		Cd	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Kales	B1	1.79×10^{-4}	1.27×10^{-4}	1.20×10^{-3}	7.90×10^{-4}	1.63×10^{-4}	1.16×10^{-4}	1.09×10^{-3}	7.17×10^{-4}
	B2	1.15×10^{-4}	8.91×10^{-4}	8.53×10^{-4}	3.52×10^{-4}	1.04×10^{-4}	8.08×10^{-5}	7.73×10^{-4}	3.19×10^{-4}
	B3	8.38×10^{-5}	3.85×10^{-5}	3.75×10^{-4}	3.05×10^{-4}	7.60×10^{-5}	3.49×10^{-5}	3.41×10^{-4}	2.77×10^{-4}
	B4	2.76×10^{-5}	2.27×10^{-5}	6.49×10^{-4}	–	2.51×10^{-5}	2.06×10^{-5}	5.89×10^{-4}	–
	B5	1.70×10^{-5}	5.77×10^{-6}	1.25×10^{-4}	–	1.54×10^{-5}	5.24×10^{-6}	1.14×10^{-4}	–
Spinach	B1	2.12×10^{-4}	1.58×10^{-4}	1.53E−03	1.15×10^{-3}	1.92×10^{-4}	1.43×10^{-4}	1.38×10^{-3}	1.04×10^{-3}
	B2	1.38×10^{-4}	1.16×10^{-4}	9.78×10^{-4}	6.41×10^{-4}	1.25×10^{-4}	1.06×10^{-4}	8.87×10^{-4}	5.82×10^{-4}
	B3	1.08×10^{-4}	5.00×10^{-5}	1.07×10^{-3}	5.55×10^{-4}	9.82×10^{-5}	4.54×10^{-5}	9.72×10^{-4}	5.04×10^{-4}
	B4	5.27×10^{-4}	2.87×10^{-5}	8.68×10^{-4}	–	4.78×10^{-5}	2.60×10^{-5}	7.88×10^{-4}	–
	B5	3.67×10^{-4}	1.42×10^{-5}	2.42×10^{-4}	–	3.33×10^{-5}	1.29×10^{-5}	2.20×10^{-4}	–
African Nightshade	B1	1.84×10^{-4}	1.13×10^{-4}	8.60×10^{-4}	4.62×10^{-4}	1.66×10^{-4}	1.02×10^{-4}	2.81×10^{-4}	2.19×10^{-4}
	B2	8.68×10^{-5}	6.33×10^{-5}	5.32×10^{-4}	3.29×10^{-4}	7.87×10^{-5}	5.75×10^{-5}	2.83×10^{-4}	2.98×10^{-4}
	B3	5.41×10^{-5}	2.62×10^{-5}	2.74×10^{-4}	1.49×10^{-4}	4.90×10^{-5}	2.38×10^{-5}	2.48×10^{-4}	1.35×10^{-4}
	B4	2.55×10^{-5}	2.12×10^{-5}	2.27×10^{-4}	–	2.32×10^{-5}	1.92×10^{-5}	2.06×10^{-4}	_
	B5	2.27×10^{-5}	3.67×10^{-6}	4.69×10^{-5}	–	2.06×10^{-5}	3.33×10^{-6}	4.26×10^{-5}	_

4. Conclusion

The DIM values for the HMs in the dry seasons for Zn and Cu were within acceptable WHO regulations in the dry and wet seasons. The levels of Pb were above the WHO limits in the vegetables except in African nightshade vegetables in the wet season in B5. The levels of Cd in the vegetables were above the WHO/FAO regulations except in the African nightshade in B5 in the dry season and B3 in the wet season, and kale in B5 in the dry season. The THQ for Cu and Zn was more than 1 (THQ > 1) in all the vegetables in the gardens from Block 1 in the dry season, except Zn in the African nightshade vegetable. The ILCR for Cd was noted to be above the tolerable limits of 10^{-4} and 10^{-6} in adults in the dry season for kale and spinach in B1 and in the wet season in spinach in B1. In children, the ILCR for Cd in the dry season was above the recommended limits in kale and spinach in B1 and in the wet season, it was high in spinach in B1. The results indicate that consuming vegetables irrigated with wastewater from River Kabuthi poses health risks to adults and children in both the dry and wet seasons. While this study specifically measured heavy metal concentrations in vegetable samples to evaluate consumption risks, the associated contamination of soil and irrigation water is inferred based on the geographical proximity of the farms to industrial and commercial zones and supported by findings from previous literature. The authors suggest regular monitoring of the levels of heavy metals in soils, irrigation water, and vegetables to advise on heavy metal accumulation levels in vegetables and thereby means of reducing such as phytoremediation of soil and creating awareness on safe farming methods will help mitigate the health risks.

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Conflicts of Interest

The authors declare no conflict of interest.

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