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Heavy metal contamination and health risk assessment of horticultural crops in two sub-cities of Addis Ababa, Ethiopia

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ABSTRACT

This particular study was aimed to establish the level of heavy metals in different horticultural crops cultivated by irrigation and the soil in two sub-cities of Addis Ababa, Ethiopia, and quantitatively assess the health treat they pose for the consumer. A total of 151 vegetable samples comprised of lettuce *(Lactuca sativa)*, cabbage *(Brassica oleracea var. capitate)*, cucumber *(Cucumis sativus)*, potato *(Solanum tuberosum)*, parsley *(Petroselinum crispum)*, Swiss chard (Beta vulgaris subsp. vulgaris), beetroot *(Beta vulgaris)*, green onion *(Allium porrum L.)* and 28 soil samples were collected for this study. Six toxic elements were analyzed using microwave plasma atomic emission spectroscopy (MP-AES) after microwave assisted digestion of the samples. The concentrations of examined trace elements in vegetables (mg/kg) were found in the range of 5.50–93.00 for zinc; below detection limit (BDL)– 18.50 for copper; BDL-2.50 for nickel; BDL-17.00 for lead; 5.00–4256.50 for manganese and 22.00–8708.00 for iron. Considering the mean Pb content values, all vegetables exceeded the maximum permissible level set by the joint FAO/WHO commission in both irrigation sites. In case of Mn parsley, swiss chard, and green onion all from site two exceeded the maximum allowable values. With the exception of potato from irrigation site one, all vegetables exceeded the maximum permissible limit set for Fe concentration and out of which parsley, swiss chard, and green onion, all from site two, exceeded by more than double amount. The same trend is observed for the concentration of Mn and Fe in the soil samples. In fact, in both irrigation sites their concentration exceeded the allowable limits set by United Nation Environment Program (UNEP) for agricultural soils. The metal pollution load index revealed that in most of the vegetables studied the overall pollution load of trace metals were higher in Kolfe Keranyo irrigation site. The risk assessment study using indices like estimation of daily/weekly dietary exposure, hazard quotient and metal pollution load index all suggested consumption of the studied vegetables poses a significant health risk for the consumer. For adults the calculated target hazard quotient for the trace element Pb is higher than 1 (one) for all of studied vegetables ranging from 11.086 (cucumber) to 17.881 (beetroot) with a 98.216% and 98.464% contribution to the hazard indices, respectively. For a child consumer, Mn showed a higher target hazard quotient vales ranged from 0.0107 (cucumber) to 0.0495 (green onion) with a 70.86% and 88.85% contribution to the total hazard indices, respectively. The soil pollution indices also indicated that the degree of metal enrichment in soils and sediments are higher than the allowable limits. Therefore, a prompt action is required to curb the problem and ensure the public safety along the food system line.

1. Introduction

There has been an increasing ecological and global public health concern associated with environmental contamination by trace metals. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications [1]. And it is an important task of nutritionists, environmentalists and scientists to demonstrate and determine these metals in food. Trace metals can be classified as potentially toxic (lead, mercury, cadmium, etc.), probably essential

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(cobalt, nickel, vanadium, etc.) and essential (zinc, selenium, iron, etc.). Those toxic metals can be very harmful even at low concentration when ingested over a long period of time [1,2]. Vegetable crops constituent a vital component of the human diet since they are reach source of vitamins, minerals and also take on dependable anti-oxidative effects. Due to an improved awareness on the food value of vegetables, their consumption is increasing gradually. And one of the most significant aspects of food quality is trace metal contamination of food [2, 3 and 4]. Contamination of vegetables by trace metals may be related to irrigation with contaminated water, addition of fertilizers and metal-based pesticides, and industrial emissions [5]. Irrigation by contaminated water may not only result in soil contamination, but also affect food quality and safety [6].

Trace metals can be classified as potentially toxic (lead, mercury, cadmium, etc.), probably essential (cobalt, nickel, vanadium, etc.) and essential (zinc, selenium, iron, etc.). Those toxic metals can be very harmful even at low concentration when ingested over a long period of time [7,8]. They ultimately induce generation of reactive oxygen species which produces oxidative stress that may lead toward different kind of cancers, neurological disorders, damage of kidney function, and other endocrine abnormalities [9]. The essential metals may also create toxic effects when metal intake is getting too high [10–14].

Literatures have been widely reported on the levels of trace elements in vegetables (Table 1) and soils (Table 2). However, the data on the trace metals in soil and vegetable samples cultivated on irrigation by the potentially polluted river in the capital Addis Ababa, Ethiopia, is very limited and insufficient. In addition those few works have not employed microwave digestion for sample preparation. In the contrary, the current study does employ microwave digestion as part of the analytical procedure. In two sub cities of Addis Ababab (Nifas Silk-Lafto and Kolfe-Keranyo) vegetable crops are highly produced using irrigation water. Due to unorganized industrialization and urbanization the water bodies in the sub cities are highly contaminated. Particularly the contaminated Small Akakai and Jemo rivers are the water sources which have been used for irrigation purposes in the sub cities. In the present study, the cultivated vegetable and soil samples from both sub cities were collected and analyzed for metal contents of Zn, Cu, Ni, Pb, Mn and Fe. Microwave assisted digestion of the samples followed by microwave plasma atomic emission spectrometer (MP-AES) were employed for the determination. And therefore, the objective of this study is to determine the level of toxic metals in commonly consumed vegetables cultivated by irrigation and in the soil they are grown at. Furthermore the present study planned to investigate the health consequences of those metals to the consumer based on the dietary consumption.

2. Experimental

2.1. Area of the study

The study area includes Nifas Silk-Lafto (S1) and Kolfe-Keranyo (S2) irrigation sites. Nifas Silk-Lafto (S1) is located between latitudes 08°53’36"N and 09°00’27"N, and, longitudes 38°41’21"E and 38°46’39"E whereas Kolfe-Keranyo (S2) is located between latitudes 08°57’01"N and 09°05’39"N, and, longitudes 38°43’10"E and 38°39’06"E. The Nifas Silk-Lafto irrigation sites spread along the sides of the river Jaja, Small Akakai and Jemo and that of Kolfe-Keranyo is

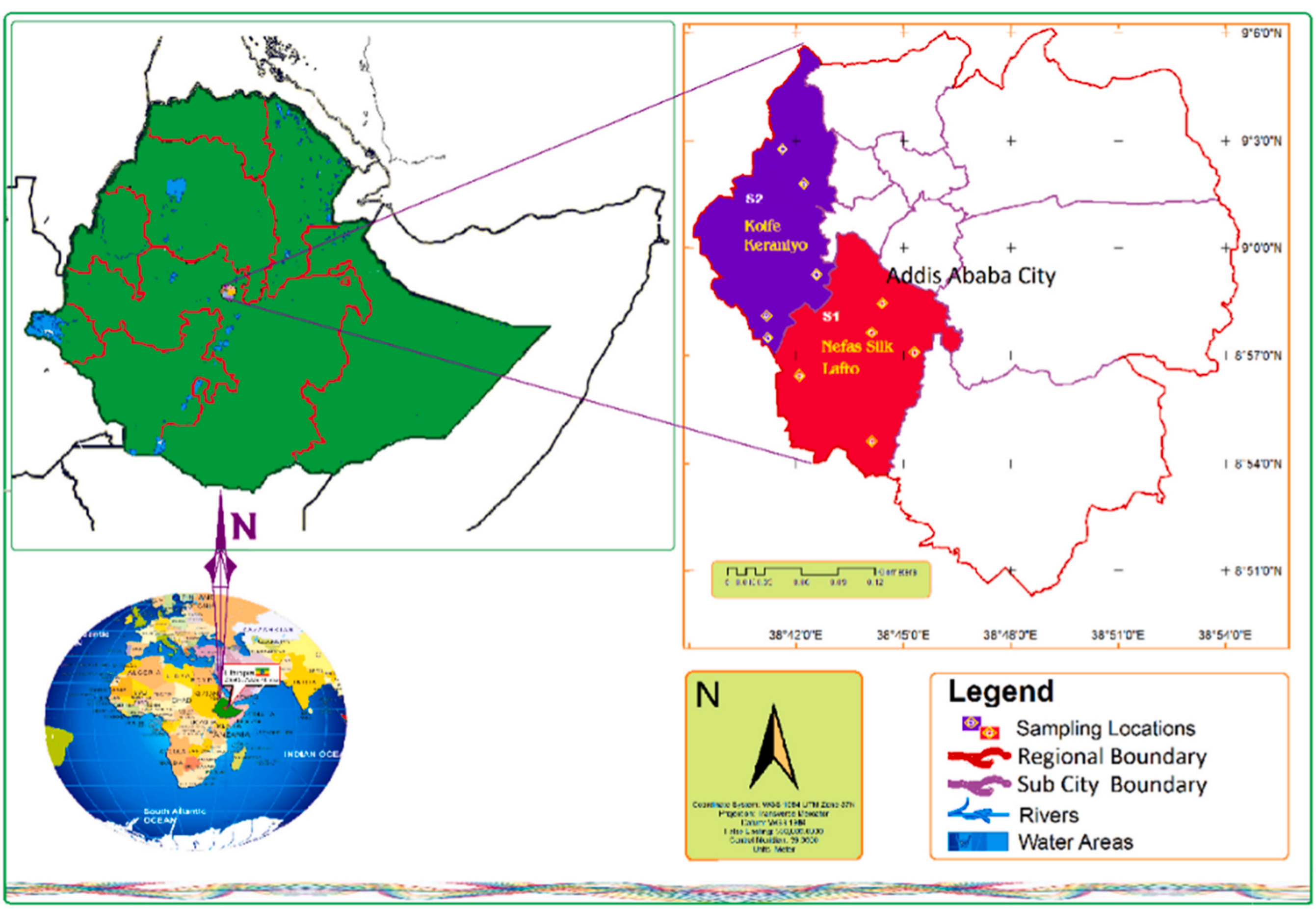
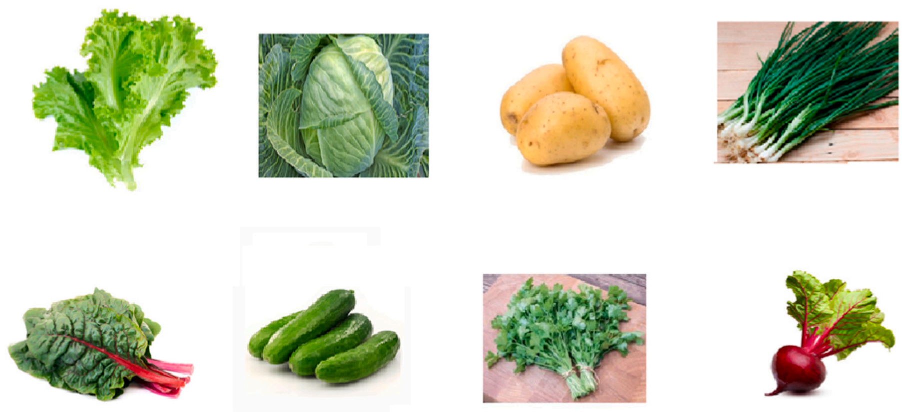


Fig. 1. Study areas from Addis Ababa, Ethiopia.



Pic 1. Pictures of vegetable samples cultivated and collected from both irrigation sites in Addis Ababa, Ethiopia (
Source: Google internet).

spread along Anjeso, Small Akaki and Jemo Rivers. Complex effluents are disposed of to the rivers from multi-industries located within and around the sub cities. The two sub-cities are selected as they produce a relatively larger amount of vegetable crops by irrigation. .

2.2. Sample collection

A total of 151 vegetable samples containing commonly cultivated crops of lettuce *(Lactuca sativa*), cabbage *(Brassica oleracea var. capitate),* cucumber *(Cucumis sativus*), potato *(Solanum tuberosum),* parsley *(Petroselinum crispum)*, swiss chard *(Beta vulgaris subsp. vulgaris)*, beetroot *(Beta vulgaris)*, green onion *(Allium porrum L.)* and 28 soil samples were collected in polyethylene bags from the irrigation sites in the dry season of 2017–2018. For cucumber and green onion the tuber part and for potato and beetroot the root parts are employed fort the analysis. And the leafy part of lettuce, cabbage and parsley are used for the analysis.

2.3. Reagents and chemicals

Analytical reagent-grade concentrated nitric acid (HNO_3, 70%), hydrogen peroxide (H_2O_2, 30–32%) and hydrofluoric acid (HF, 70%) were obtained from Dong Woo Fine-Chem Iksan, Korea. Ultrapure deionized water (18.2 MΩ.cm) obtained from a Milli-Q plus water purification system (Millipore, Bedford, MA, USA) was used. A 10 mg/L multi-elemental standard solution from Anapure Kriat, Daejeon, Korea was used for preparing standards for calibration curves. A certified reference material (CRM), spinach leaves, (NIST-1570a) was obtained from National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA. And the soil CRM (GBM399–5) was obtained from GEOSTATS PTY LTD, Mining Industry Consultants Reference Material Manufacture and Sales, O′Connor, Western Australia. All laboratory plastic/glassware was decontaminated by soaking in 10% solutions of purified HNO_3 for 24 h.

2.4. Instrumentation

A Multiwave 3000 microwave system (Anton Paar, Graz, Austria) programmable for time and power between 600 and 1400 W and equipped with 16 high-pressure polytetrafluoroethylene vessels (MF 100) was used for samples digestion. A 4100 MP-AES (Agilent, California, US) was used for the analysis of investigated elements. The instrument was used with a high-efficiency sample introduction desolvating system equipped with a quartz cyclonic double pass spray chamber and an additional mixing peristaltic pump. The operating conditions of the instrument were forward plasma power 1.0 kW, nitrogen gas (spectral purity, 99.95%), flow rate 16.0 L/min (plasma), 1.2 L/min (auxiliary), and 1.0 L/min (nebulizer). The instrument was tuned for daily performance using Elan 6100 DRC sensitivity detection limit solution (PerkinElmer Pure, USA). All other instrumental operating conditions were set according to manufacturer guidelines.

2.5. Sample pretreatment and microwave digestion

The collected vegetable samples were washed with deionized water, dried between layers of clean scientific tissue paper, and the known quantity of edible portion of the samples were sliced with stainless steel knife. For determination of moisture, each vegetable sample was dried at 60 °C (HB-502 M, Han Back, Korea) until constant weight was achieved [15]. The dried samples were then homogenized and powdered in a grinder with titanium blades (MR 350 CA, Braun, Spain). The powdered samples were properly labeled and stored in plastic bags at − 20 °C (Micom CFD-0622, Samsung, Korea) until analysis. The soil samples went through the same moisture determination procedures, labeled and stored.

For digestion, 0.5 g of each sample, vegetable and soil, in triplicate was accurately weighed directly into separate digestion vessels. For vegetable samples it was followed by the addition of 7.0 mL of concentrated HNO_3 and 2.0 mL of H_2O_2 [16]. As for the soil samples it was followed by the addition of concentrated 9.0 mL of HNO_3 and 3.0 mL of HF, using with slight modification of the method followed by [17]. The combustion procedure was 1000 W at 80 °C for 5 min, 1000 W at 50 °C for 5 min, 1000 W at 190 °C for 20 min, and 0 W for 30 min for cooling. After cooling, the contents of the tubes were diluted to 50 mL with ultrapure deionized water. Repeated analyses of certified reference materials, spinach leaves (NIST-1570a) for vegetables & GBM399–5 for soil, was also included as samples during digestion and passed through the same dissolution procedure. Several analytical blanks taken through the same digestion and dissolution procedure were also included and analyzed to characterize instrumental drift.

2.6. Analysis and quality assurance

The concentrations of Zn (wavelength = 213.857 nm), Cu (324.754 nm), Ni (352.454 nm), Pb (405.781 nm), Mn (403.076 nm), and Fe (259.940 nm), were determined by MP-AES. Quantitative analysis of the samples was performed by external calibration. Standard solutions were prepared in the same concentration of acids present in digested samples, for both vegetable and soil, by diluting a multi-elemental standard containing the analytes. Under the optimized conditions, eight concentrations within the linear dynamic range were measured, and calibration curves of the standards for each analyte were plotted from the limits of detection. To avoid error, a slight instrumental drift monitored by analyzing calibration standards at regular intervals during analysis alongside samples was taken into account. All measurements were performed using the full quantitative analysis mode. To ensure the reliability of the analytical methods, appropriate quality assurance procedures such as plant (CRM-1570a, spinach leaves) and soil (GBM399–5) certified reference materials were determined. The validity of the method was further verified through spike recovery measurements and replicate analysis.

2.7. Health risk assessment

The health risks of trace elements by consumption of lettuce, cabbage, cucumber, potato, parsley, Swiss chard, beetroot, and green onion were assessed by estimated dietary exposure, target hazard quotient and hazard index, and metal pollution load index.

2.7.1. Estimated dietary exposure (EDI)

The dietary intake values of trace elements were calculated by [18];.

$$EDI = [C_{metal} \text{ x } D_{food\ intake}] / BW_{average} \quad (1)$$

Where; C is the concentration (mg/kg) of the trace metals present in the vegetables, D is the daily intake of food in kg per person and BW represents the average body weight in kg person^{-1} of a consumer, an adult (60 kg) and a child (12 kg). The calculated values were compared with the recommended dietary values, tolerable upper intake levels, and provisional tolerable daily intake values of the elements established by the Joint World Health Organization and Food and Agriculture Organization Expert Committee on Food Additives [19, 20 and 21], United States Environmental Protection Agency [22], European Food Safety Authority [23] and Food and Nutrition Board of the United States [24] for both adults and children. Daily intake of vegetables was taken as 0.100 kg for adults, as this is the minimum vegetable requirement for a balanced diet, [25]. Also, a survey conducted by USDA has suggested that people from developing countries like Ethiopia consume 100 g per capita per day of vegetables [26]. Daily intake of vegetables for children below 3 years was taken as 0.05 kg [25]. Average body weight for adult male was taken as 60 kg and average body weight of female as 45 kg and of children (below 3 years) is 12 kg [27].

2.7.2. Target hazard quotient (THQ) and hazard index (HI)

To estimate the human health risk from consuming those vegetables with trace elements, target hazard quotient which is the ratio between exposure and the reference oral dose was calculated. It is set forward by the United States Environmental Protection Agency [28] and later on employed by [29];.

$$THQ = [EF \text{ x } ED \text{ x } FIR \text{ x } C / RfD \text{ x } BW \text{ x } AT] \text{ x } 10^{-3} \quad (2)$$

where EF is exposure frequency (365 days/year); ED is exposure duration, equivalent to the average lifetime where according to World Health Organization life expectancy at birth [30] the average life time of Ethiopian men is 64 years and women is 67 and for estimation of a child health risk 6 year is considered [31]; FIR is the food ingestion rate, 100 and 50 g/day for an adult and children, respectively [26,32]; C is the concentration (mg/kg) of the trace elements present in the vegetable; RfD stands for the reference oral dose, an estimation of the daily exposure of a contaminant to which the human population may be continually exposed over a lifetime without an appreciable risk of harmful effects; BW represents the body weight of an adult (60 kg) and a child (12 kg, below 3 years) consumer [27] and AT is the average exposure time (365 days/year x number of exposure years).

To assess the overall potential risk to human health posed by more than one metal, THQ of every metal is summed up and is known as hazard index. The HI can be determined by exposure factors handbook, intake of fruits and vegetables [33];.

$$HI = {}_{i}THQ_{i} = THQ_{Zn} + THQ_{Cu} + THQ_{Ni} + THQ_{Pb} + THQ_{Mn} + THQ_{Fe} \quad (3)$$

2.7.3. Metal pollution load index (MPI)

Assessment of overall load of metals in each vegetable growing at each site was computed as the geometric mean of concentration of all metals in edible part of the plant (mg/kg) [32,34].

$$MPI = (C_1 \text{ x } C_2 \ldots \cdot\text{x } C_n)^{1/n} \quad (4)$$

Where; C_n represents concentration of metal n in sample.

2.8. Soil pollution indices

To quantify the degree of metal enrichment or pollution in soils of the two sites indices like pollution load index, integrated pollution load index, and enrichment factors were considered.

2.8.1. Pollution load index (PI)

The pollution load of trace metals concentration in the soil samples as compared to the geometric means of the natural background concentration of the corresponding metal was determined using; [35,36].

$$PI = C_i / S_i \quad (5)$$

Where; PI is the evaluation score corresponding to each sample, C_i is the measured concentration of the examined metals in the soils, and S_i is the geochemical background concentration of the metals. The PI value of each metal is classified as a low contamination ($PI \le 1.0$), a moderate contamination ($1.0 < PI \le 3.0$) or a high contamination ($PI > 3.0$).

2.8.2. Integrated pollution load index (IPI)

The mean of all pollution load index values of all of the considered metals was established based on the method used by different researchers [35,37–39]. IPI is classified as a low contamination ($IPI \le 1.0$), a moderate contamination ($1.0 < IPI \le 2.0$), a high contamination ($2.0 < IPI \le 5$), and extremely high level of contamination ($IPI > 5$).

2.8.3. Enrichment factor (EF)

The level of pollution and the potential anthropogenic effects in the sampled soils was quantified using the method proposed by [40] and later used by [41];.

$$EF_x = [C_x/C_{ref}]_{Sample} / [B_x/B_{ref}]_{Background} \quad (6)$$

Where; Cx is the concentration of the element of interest, Cref is the concentration of reference element for normalization (world average), Bx is the concentration of the element in the crust, and Bref is the concentration of the reference element used for normalization in the crust. In this investigation Aluminum (Al) is used as a reference element [42, 43]. Five contamination categories are assigned on the basis of the enrichment factor [44,45]: EF < 2 indicates deficiency to minimal enrichment, EF = 2–5 suggests moderate enrichment/pollution, EF = 5–20 shows significant enrichment/pollution, EF = 20–40 signifies very high enrichment/pollution, and EF > 40 implies extremely high enrichment/pollution.

2.9. Soil-vegetable transfer coefficient (TF)

The transfer factor which quantifies the relative differences in bioavailability of metals to plants was analyzed by [46].

$$TF = C_{Plant} / C_{Soil} \quad (7)$$

Where; C_{plant} is metal concentration in vegetable and C_{soil} stands for metal concentration in soil. Higher transfer coefficient represents relatively poor retention in soils or greater efficiency of plants to absorb metals. Low coefficient demonstrates the strong sorption of metals to the soil colloids [47].

2.10. Statistical analysis

The results were evaluated using the Statistical Package for Social Sciences, Software Version 20 (IBM, New York, USA). The results were reported as the mean ± standard deviation. Significant differences ($p < 0.05$) within the means of same elements among the vegetable varieties and soil samples were analyzed by one-way analysis of variance.

3. Result and discussion

The average concentrations after incorporation of the moisture content of all vegetables and soil (mean ± standard deviation) for the trace elements are reported on a fresh weight basis [48]. Tables 1 and 2 tabulates the average concentrations of vegetables and soil respectively in the present study with literatures. Table 3 shows analysis of elements both in the certified reference materials, vegetable (NIST-1570a) and soil (GBM399–5), and spick recovery results as validation parameters of the analytical method. Table 4 lists the concentrations (mg/kg) of trace elements in the cultivated vegetables and soil samples collected from the two irrigation sites (S1- Nifassilk Lafto and S2-Kolfe Keranyo) in comparison with maximum allowable limits established by standard regulatory bodies such as the Joint FAO/WHO [49–52] and United Nation Environment Program; UNEP [53]. Tables 5 and 6 presents the calculated dietary intake (daily/weekly) of trace metals obtained through consumption of lettuce, cabbage, cucumber, potato, parsley, Swiss chard, beetroot, and green onion with comparison and the contribution

Table 1
Comparison of the mean concentrations (mg/kg) of the vegetables analytes in the current study with previously reported values.

Element	Current Study	[46]	[55]	[58]	[57]	[59]	[56]	[64]
Swiss chard								
Zn	45.49	-	-	-	-	1.87	-	-
Cu	9.57	-	-	-	-	3.65	-	-
Ni	0.24	-	-	-	-	0.68	-	-
Pb	8.06	-	-	-	-	2.52	-	-
Mn	531.00	-				317.54	-	-
Fe	860.01	-	-	-	-	132.21	-	-
Cabbage								
Zn	42.84	2.97	-	21.55	-	0.92	14.90	-
Cu	8.60	0.36	-	4.33	-	3.38	0.43	-
Ni	0.06	-	-	-	-	0.57	0.29	-
Pb	8.44	0.02	-	3.84	-	3.31	BDL	-
Mn	249.84	-	-	21.19	-	5.94	21.71	-
Fe	705.77	-	-	88.40	-	51.55	76.90	-
Lettuce								
Zn	45.63	3.21	1.73	-	39.50	4.82	42.00	-
Cu	7.84	0.37	0.20	-	59.93	5.30	0.90	-
Ni	0.17	-	0.03	-	6.30	0.70	0.70	-
Pb	8.43	0.62	0.03	-	9.70	1.55	3.70	-
Mn	312.02	-	-	-	-	118.65	20.37	-
Fe	694.30	-	-	-	-	112.95	323.90	-
Parsley								
Zn	46.50	-	-	-	38.69	-	21.00	-
Cu	9.75	-	-	-	53.12	-	3.34	-
Ni	BDL	-	-	-	3.47	-	0.60	-
Pb	9.35	-	-	-	9.90	-	3.29	-
Mn	363.60	-	-	-	-	-	13.09	-
Fe	977.05	-	-	-	-	-	182.8	-
Potato								
Zn	50.17	-	2.60	15.83		1.40	4.50	-
Cu	9.73	-	0.54	4.21		2.52	0.88	-
Ni	0.45	-	0.05	-		0.25	10.74	-
Pb	8.58	-	0.02	4.01		2.58	2.81	-
Mn	250.00	-	-	7.56		2.62	5.67	-
Fe	458.59	-	-	62.28		40.49	48.20	-
Green onion								
Zn	44.23	-	-	-		-	-	30.25
Cu	9.23	-	-	-		-	-	6.21
Ni	0.18	-	-	-		-	-	0.90
Pb	7.68	-	-	-		-	-	5.62
Mn	659.59	-	-	-		-	-	16.24
Fe	1034.27	-	-	-		-	-	167.00
Beetroot								
Zn	47.75	3.55	-	-		-	-	-
Cu	9.75	0.95	-	-		-	-	-
Ni	BDL	-	-	-		-	-	-
Pb	10.00	0.02	-	-		-	-	-
Mn	257.88	-	-	-		-	-	-
Fe	538.50	-	-	-		-	-	-
Cucumber								
Zn	57.50	-	-	22.67	20.08	-	32.30	-
Cu	8.00	-	-	5.00	37.10	-	2.47	-
Ni	BDL	-	-	-	13.45	-	10.88	-
Pb	6.17	-	-	5.37	6.90	-	4.26	-
Mn	142.83	-	-	15.47	-	-	8.02	-
Fe	518.50	-	-	107.73	-	-	83.50	-

Lactuca sativa (lettuce), Brassica oleracea var. capitate (cabbage), *Cucumis sativus* (cucumber), Solanum tuberosum (potato), Petroselinum crispum (parsley), Beta vulgaris subsp. vulgaris (swiss chard), Beta vulgaris (beetroot), Allium porrum L. (green onion).

Table 2
Average concentrations of trace metals (mg/Kg) in soil compared with data compiled from international literatures & regulatory standards.

Literature/Standard	Zn	Cu	Ni	Pb	Mn	Fe	Reference
Literature							
NL&KK (Addis A.)	190.87	51.02	12.42	111.63	3486.41	53847.41	Present Study
Accra (Ghana)	37.33	202.99	72.00	183.66	*N/A	N/A	[41]
Guangzhou (China)	277.00	11.00	11.10	65.4	N/A	N/A	[65]
Beijing (China)	92.90	17.73	24.00	23.30	N/A	N/A	[66]
Islamabad (Pakistan)	1638.97	101.00	92.47	212.34	N/A	N/A	[67]
Wien (Austria)	75.00	56.35	N/A	54.00	N/A	N/A	[68]
Kurdistan (Iran)	77.20	42.60	47.90	25.40	N/A	N/A	[69]
Havana (Cuba)	240.00	29.70	66.00	101.00	N/A	N/A	[70]
13 Provinces (Cuba)	90.70	83.70	294.20	34.6	1446.8	43317.80	[71]
Andhra Pradesh (India)	77.10	35.36	27.30	28.30	N/A	N/A	[72]
Fallujah (Iraq)	5.50	2.01	8.96	3.820	N/A	N/A	[73]
Baghdad (Iraq)	33.06	5.25	46.31	8.34	N/A	N/A	[74]
Tuscany (Italy)	127.65	16.41	59.03	218.58	N/A	N/A	[75]
Eastern Cape (SA)	34.95	5.92	N/A	9.72	440.00	N/A	[76]
Standard							
EEA	300.00	140.00	75.00	300.00	N/A	N/A	[77]
US EPA	110.00	270.00	72.00	200.00	N/A	N/A	[78]
Canada	500.00	150.00	100.00	200.00	N/A	N/A	[79]
China	300.00	125.00	50.00	80.00	N/A	N/A	[80]
Australia	200.00	100.00	60.00	300.00	N/A	N/A	[81]
Tanzania	150.00	200.00	100.00	200.00	N/A	N/A	[82]

EEA- European Environment Agency; US EPA- United States Environmental Protection Agency; CME- Canadian Ministry of the Environment; EPMC- Environmental Protection Ministry of China; EPAA- Environment Protection Authority of Australia; TMS- Tanzania Ministry of State.
[*] N/A- Not available

Table 3
Method validation of the elements and analysis of certified reference materials (vegetable [ng/g] and soil [μg/g]) by MP-AES ($n = 5$).

Element	Linearity correlation coefficient (R^2)	Precision coefficient of variation (%)	Certified reference material						Spike recovery	
			Vegetable (NIST −1570a)			Soil (GBM399-5)			Vegetable (%)	Soil (%)
			Certified value	Obtained value	Recovery (%)	Certified value	Obtained value	Recovery (%)		
Zn[a]	1.0000	0.74	82.0 ± 3	79.0 ± 0.61	96.3	9493 ± 504	9401 ± 413	99.0	94.0	95.7
Cu[a]	0.9992	2.61	12.2 ± 0.6	11.9 ± 0.32	97.5	29,424 ± 1446	28,811 ± 1074	97.9	105.6	102.3
Ni[a]	0.9995	2.93	2.14 ± 0.10	2.05 ± 0.04	95.8	24,412 ± 1248	22,991 ± 1010	94.2	92.1	94.9
Pb	0.9991	2.95	0.2	0.18 ± 0.06	90.0	21,173 ± 1402	20,164 ± 1265	95.2	97.3	93.4
Mn[a]	0.9997	1.89	75.9 ± 1.9	74.1 ± 0.11	97.6	nr	-	-	96.4	98.6
Fe	0.9994	2.36	nr	-	-	4.47	4.25 ± 1.23	95.1	98.2	105.8

nr – not reported
[a] Elements fortified at 1000 μg/kg; others at 100 μg/kg for spike recovery study

to the recommended standards and tolerable intake values for an adult and a child consumer, respectively. Tables 7 and 8 describes target hazard quotients and hazard indices, and the contribution of each trace element to the calculated hazard indices of the vegetable. Pollution load index, integrated pollution load index, and enrichment factor of the soil samples from the two sites are tabulated in Table 9. And transfer factors of trace metals from the soil into the vegetable samples are contained in Table 10.

3.1. Validation of analytical methods

For the validation of analytical methods, the correlation coefficient (R^2) values calculated from the calibration curves of each analyte element were at least 0.9991 (Table 3). These values ensured the linearity of the calibration curves. The coefficient of variance (%) for the analytes was from 0.74 (Zn) to 2.95 (Pb), confirming the precision of the methods. The recoveries (%) for certified reference materials, spinach leaves (CRM-1570a) and soil (GBM399–5), were from 90.0 (Pb) to 97.6 (Mn) and 94.2 (Ni) to 99.0 (Zn), respectively. The recoveries (%) of fortification for vegetables and soil were 92.1 (Ni) to 105.6 (Cu) and 93.4 (Pb) to 105.8 (Fe), respectively. Both recovery studies in Table 3 confirmed that there were no significant losses or contamination during the procedures. Therefore, based on the determination of linearity, precision, accuracy, and recovery the methods satisfied the criteria set by [54].

3.2. Analysis of trace metals

The concentrations of examined trace elements in vegetables (mg/kg) were found to be in the range of 5.50–93.00 for zinck (Zn); below detection limit (BDL)− 18.50 for copper (Cu); BDL-2.50 for nickel (Ni); BDL-17.00 for lead (Pb); 5.00–4256.50 for manganese (Mn); and 22.00–8708.00 for iron (Fe). Considering the mean Pb content values, all vegetables exceeded the maximum permissible level set by the joint

Table 4
Concentration (mg/kg) of trace metals (mean ± SD) in cultivated vegetables (N = 151) and Soil (N = 28) in the two irrigation sites, Nifas Silk-Lafto (S1) and Kolfe-Keranyo (S2).

Sample	Area	Zn	Cu	Ni	Pb	Mn	Fe
Vegetable							
Lettuce	S1	37.4 ± 15.0	7.0 ± 2.5	BDL[††]	9.9 ± 2.0	174.3 ± 121.3	664.9 ± 437.4
	S2	53.8 ± 30.3	8.7 ± 2.7	0.2 ± 0.3	6.9 ± 2.9	449.8 ± 530.3	723.7 ± 627.4
Cabbage	S1	42.7 ± 20.6	8.4 ± 3.4	0.1 ± 0.2	9.3 ± 2.2	172.3 ± 148.4	652.3 ± 349.5
	S2	43.0 ± 17.1	8.8 ± 3.7	0.1 ± 0.2	7.6 ± 2.9	327.4 ± 419.1	759.2 ± 746.1
Cucumber	S1	57.5 ± 19.1	8.0 ± 2.0	BDL	6.2 ± 1.6	142.8 ± 45.2	518.5 ± 68.9
	S2	-	-	-	-	-	-
Potato	S1	55.5 ± 22.5	10.7 ± 2.3	0.7 ± 1.2	8.3 ± 2.9	232.7 ± 241.2	337.0 ± 222.5
	S2	44.8 ± 22.5	8.8 ± 3.8	0.2 ± 0.6	8.8 ± 2.4	267.3 ± 244.0	580.2 ± 537.5
Parsley	S1	51.6 ± 11.4	9.1 ± 2.4	BDL	10.1 ± 1.9	178.2 ± 63.8	566.8 ± 215.4
	S2	41.4 ± 9.8	10.4 ± 3.1	BDL	8.6 ± 4.5	549.0 ± 525.2	1087.3 ± 465.7
Swiss chard	S1	46.8 ± 11.3	9.5 ± 2.2	0.3 ± 0.7	8.8 ± 3.1	398.6 ± 583.2	622.5 ± 372.3
	S2	44.2 ± 23.6	9.7 ± 4.1	0.2 ± 0.5	7.3 ± 3.9	663.4 ± 691.7	1097.5 ± 1030.7
Beetroot	S1	-	-	-	-	-	-
	S2	47.8 ± 9.0	9.8 ± 3.2	BDL	10.0 ± 1.8	254.9 ± 143.0	538.5 ± 309.3
Green onion	S1	-	-	-	-	-	-
	S2	44.2 ± 17.9	9.2 ± 2.8	0.2 ± 0.6	7.7 ± 4.6	659.6 ± 579.4	1034.3 ± 1044.1
Range		5.50–93.00	BDL-18.50	BDL-2.50	BDL-17.00	5.00–4256.50	22.00–8708.00
Maximum Permissible Limit (mg/Kg)		60[a]	40[b]	1.5[c]	0.3[d]	500[d]	425[d]
Soil							
Soil	S1	236.8 ± 51.5	36.9 ± 12.6	1.1 ± 4.4	133.2 ± 55.7	3597.1 ± 1564.7	54015.8 ± 13587.7
	S2	144.9 ± 31.2	65.1 ± 29.5	23.8 ± 16.9	7.7 ± 4.6	3375.8 ± 1339.4	53679.0 ± 12003.6
Range		100.5–315.0	10.0–100.0	BDL- 60.0	40.0–227.5	1780.0–6640.0	34402.5–74482.5
[†] Maximum Permissible Limit (mg/Kg)		400	200	150	750	2000	50,000

[a-d]represents references for maximum permissible limit for vegetables:
[†] represents references for maximum permissible limit for agricultural soil: UNEP (united nation environment program, 2013).
[††] Below detection limit
[a] WHO/FAO (codex alimentarius commission. Joint FAO/WHO, 1991);
[b] WHO/FAO (FAO/ WHO, codex general standard for contamination and toxin in foods, 1996);
[c] WHO/FAO (Codex Alimentarius Commission. Joint FAO/WHO, 2007);
[d] WHO/FAO (Codex Alimentarius Commission, Joint FAO/WHO, 2001).

Table 5
Estimated daily/weekly intake (EDI/EWI in mg/day, fresh weight basis) values of trace elements by an adult (60-kg) consumer with the percentage contribution to the recommended dietary intake and tolerable upper intake levels (UL).

	Lettuce			Cabbage			Cucumber			Potato			mg/day/person	
Element	EDI	(EWI)	RDI, %	EDI	(EWI)	RDI, %	EDI	(EWI)	RDI, %	EDI	(EWI)	RDI, %	RDI	UL
Zn	0.076	(0.532)	0.69	0.071	(0.450)	0.65	0.095	(0.007)	0.86	0.084	(0.585)	0.76	8–11	25
Cu	0.013	(0.091)	0.43	0.001	(0.007)	0.03	0.013	(0.093)	0.43	0.016	(0.114)	0.53	0.9–3.0	5
Ni	0.0002	(0.002)	-	0.0001	(0.0007)	-	Not detected		-	0.001	(0.005)	-	0.3 (2.1)[a]	1
Pb	0.014	(0.098)	-	0.014	(0.098)	-	0.010	(0.072)	-	0.014	(0.100)	-	0.02–3[b]	NE
Mn	0.520	(3.640)	10.40	0.491	(3.440)	9.82	0.238	(1.665)	4.76	0.417	(2.917)	8.34	2.5–5.0	11
Fe	1.157	(8.100)	6.43	1.176	(8.234)	6.53	0.863	(6.038)	4.79	0.764	(5.350)	4.24	8–18	45
	Parsley			Swiss chard			Beetroot			Green onion			mg/day/person	
Element	EDI	(EWI)	RDI, %	EDI	(EWI)	RDI, %	EDI	(EWI)	RDI, %	EDI	(EWI)	RDI, %	RDI	UL
Zn	0.065	(0.457)	0.59	0.076	(0.531)	0.69	0.080	(0.557)	0.73	0.074	(0.516)	0.67	8–11	25
Cu	0.015	(0.102)	0.50	0.016	(0.112)	0.53	0.016	(0.114)	0.53	0.015	(0.108)	0.50	0.9–3.0	5
Ni	Not detected		-	0.0004	(0.0028)	-	Not detected		-	0.0003	(0.0021)	-	0.3 (2.1)[a]	1
Pb	0.014	(0.097)	-	0.013	(0.094)	-	0.017	(0.117)	-	0.013	(0.090)	-	0.02–3[b]	NE
Mn	0.547	(3.830)	10.94	0.585	(4.095)	11.7	0.430	(3.009)	8.60	1.099	(7.695)	21.98	2.5–5.0	11
Fe	1.628	(11.340)	9.04	1.433	(10.033)	7.96	0.900	(6.283)	5.00	1.724	(12.066)	9.58	8–18	45

NE- Not established
[a] represents the provisional tolerable daily/weekly intake (PTDI/PTWI) value of Ni (mg/day).
[b] represents the provisional tolerable daily intake (PTDI) value of Pb (μg/day).

FAO/WHO commission (Table 4) in both irrigation sites. In case of Mn parsley, swiss chard, and green onion all from site two exceeded the maximum allowable values (Table 4). With the exception of potato from irrigation site one, all vegetables exceeded the maximum permissible limit set for Fe concentration and out of which parsley, swiss chard, and green onion, all from site two, exceeded by more than double amount (Table 4). Irrigation site two (Kolfe-keranyo sub city) is more densely populated than irrigation site one (Nifasseilk-Lafto) and therefore in addition to the industrial west, which is the major contributor, the house hold west might have contributed to the higher amount of trace metals in the studied vegetables in that particular site. The same trend is observed for the concentration of Mn and Fe in the soil samples, in fact in both irrigation sites their concentration exceeded the allowable limits set by United Nation Environment Program (UNEP) for agricultural soils (Table 4). The mean values of Zn, Cu, & Ni in the studied vegetables as well as soil are well within the maximum permissible limits. In opposite

Table 6
Estimated daily/weekly intake (EDI/EWI in mg/day, fresh weight basis) values of trace elements by a child (12 kg, 1–3 year) consumer with the percentage contribution to the recommended dietary allowance (RDA) & tolerable upper intake levels (UL).

	Lettuce			Cabbage			Cucumber			Potato			mg/day/child	
Element	EDI	(EWI)	RDA, %	EDI	(EWI)	RDA, %	EDI	(EWI)	RDA, %	EDI	(EWI)	RDA, %	RDA	UL
Zn	0.190	(1.331)	5.14	0.179	(1.250)	4.84	0.238	(1.668)	6.43	0.209	(1.463)	5.65	3.70	7.0
Cu	0.033	(0.229)	9.71	0.036	(0.251)	10.59	0.033	(0.233)	9.71	0.041	(0.284)	12.06	0.34	1.0
Ni	0.0007	(0.005)	-	0.0003	(0.0018)	-	Not detected		-	0.002	(0.013)	-	NE	0.2
Pb	0.035	(0.246)	-	0.035	(0.246)	-	0.026	(1.180)	-	0.036	(0.250)	-	0.03–9[a]	NE
Mn	1.300	(9.101)	108.3	1.041	(7.287)	86.75	0.595	(4.166)	49.58	1.042	(7.292)	86.83	1.20[b]	2.0
Fe	2.893	(20.250)	41.33	2.941	(20.585)	42.01	2.156	(15.094)	30.80	1.911	(13.376)	27.30	7.00	40
	Parsley			Swiss chard			Beetroot			Green onion			mg/day/child	
Element	EDI	(EWI)	RDA, %	EDI	(EWI)	RDA, %	EDI	(EWI)	RDA, %	EDI	(EWI)	RDA, %	RDA	UL
Zn	0.163	(1.143)	4.40	0.120	(1.327)	3.24	0.120	(1.393)	3.24	0.184	(1.290)	4.97	3.70	7.0
Cu	0.036	(0.254)	10.59	0.040	(0.279)	11.76	0.041	(0.284)	12.09	0.038	(0.269)	11.17	0.34	1.0
Ni	Not detected		-	0.001	(0.007)	-	Not detected		-	0.0008	(0.0053)	-	NE	0.2
Pb	0.035	(0.242)	-	0.034	(0.235)	-	0.042	(0.292)	-	0.032	(0.224)	-	0.03–9[a]	NE
Mn	1.368	(9.574)	114.0	2.212	(15.488)	184.3	1.075	(7.522)	89.58	2.748	(19.238)	229.0	1.20[a]	2.0
Fe	4.071	(28.497)	58.16	3.583	(25.084)	51.19	2.244	(15.706)	32.06	4.309	(30.166)	61.56	7.00	40

NE- Not established
[a] represents the provisional tolerable daily intake (PTDI) value of Pb (μg/day).
[b] represents adequate intake value of Mn

Table 7
Target hazard quotients (THQ), hazard indices (HI), and percentage contribution of trace elements (fresh weight basis) in the studied vegetables by an adult (60-kg) consumer.

	Lettuce		Cabbage		Cucumber		Potato	
Element	THQ	Contribution to HI, %	THQ	Contribution to HI, %	THQ	Contribution to HI, %	THQ	Contribution to HI, %
Zn	0.0130	0.0846	0.0123	0.0798	0.0165	0.1462	0.0143	0.0919
Cu	0.0112	0.0729	0.0123	0.0798	0.0097	0.0859	0.0139	0.0894
Ni	0.0014	0.0091	0.0007	0.0045	Not detected	-	0.0032	0.0206
Pb	15.020	97.795	15.110	98.054	11.086	98.216	15.289	98.285
Mn	0.2028	1.3204	0.1624	1.0539	0.0928	0.8222	0.1625	1.0446
Fe	0.1103	0.7182	0.1121	0.7275	0.0824	0.7300	0.0729	0.4686
HI	15.3587		15.4098		11.2874		15.5558	
	Parsley		Swiss chard		Beetroot		Green onion	
Element	THQ	Contribution to HI_{total}, %	THQ	Contribution to HI_{total}, %	THQ	Contribution to HI_{total}, %	THQ	Contribution to HI_{total}, %
Zn	0.0133	0.0776	0.0130	0.0872	0.0137	0.0754	0.0126	0.0876
Cu	0.0139	0.0811	0.0137	0.0919	0.0140	0.0771	0.0132	0.0917
Ni	Not detected	-	0.0018	0.0121	Not detected	-	0.0014	0.0097
Pb	16.719	97.554	14.395	96.576	17.881	98.464	13.769	95.689
Mn	0.2364	1.3794	0.3452	2.3159	0.1657	0.9124	0.4288	2.9800
Fe	0.1556	0.9079	0.1367	0.9171	0.0856	0.4714	0.1643	1.1418
HI	17.1382		14.9054		18.1600		14.3893	

Table 8
Target hazard quotients (THQ), hazard indices (HI), and percentage contribution of trace elements (fresh weight basis) in the studied vegetables by a child (12-kg) consumer.

	Lettuce		Cabbage		Cucumber		Potato	
Element	THQ	Contribution to HI, %	THQ	Contribution to HI, %	THQ	Contribution to HI, %	THQ	Contribution to HI, %
Zn	9.77×10^{-4}	3.452	9.18×10^{-4}	3.890	1.23×10^{-3}	8.146	1.07×10^{-3}	4.573
Cu	1.18×10^{-3}	4.170	1.29×10^{-3}	5.466	1.20×10^{-3}	7.947	1.46×10^{-3}	6.239
Ni	1.50×10^{-4}	0.530	7.50×10^{-5}	0.318	Not detected	-	3.38×10^{-4}	1.444
Pb	-	-	-	-	-	-	-	-
Mn	0.0234	82.69	0.0187	79.24	0.0107	70.86	0.0188	80.34
Fe	2.60×10^{-3}	9.187	2.61×10^{-3}	11.06	1.94×10^{-3}	12.85	1.72×10^{-3}	7.350
HI	0.0283		0.0236		0.0151		0.0234	
	Parsley		Swiss chard		Beetroot		Green onion	
Element	THQ	Contribution to HI_{total}, %	THQ	Contribution to HI_{total}, %	THQ	Contribution to HI_{total}, %	THQ	Contribution to HI_{total}, %
Zn	9.96×10^{-4}	2.982	9.75×10^{-4}	2.138	1.02×10^{-3}	4.322	9.47×10^{-4}	1.694
Cu	1.46×10^{-3}	4.371	1.44×10^{-3}	3.158	1.47×10^{-3}	6.299	1.38×10^{-3}	2.469
Ni	Not detected	-	1.88×10^{-4}	0.412	Not detected	-	1.5×10^{-4}	0.268
Pb	-	-	-	-	-	-	-	-
Mn	0.0273	81.74	0.0398	87.28	0.0191	80.93	0.0495	88.55
Fe	3.66×10^{-3}	10.96	3.23×10^{-3}	7.083	2.02×10^{-3}	8.559	3.88×10^{-3}	6.941
HI	0.0334		0.0456		0.0236		0.0559	

Table 9
Pollution Load Index (PI), Integrated Pollution Load Index (IPI) and Enrichment Factor (EF) of the Soil Sample.

Heavy	Background	Mean Conc. (mg/Kg)		PI		EF	
Metal	(mg/kg)	NLSC	KKSC	NLSC	KKSC	NLSC	KKSC
Zn	95	236.81	144.92	2.49	1.53	30.04	18.38
Cu	45	36.91	65.13	0.82	1.45	9.88	17.43
Ni	68	1.09	23.75	0.02	0.35	0.19	4.20
Pb	20	133.22	90.04	6.66	4.50	80.25	54.24
Mn	850	3597.06	3375.75	4.23	3.97	50.99	47.85
Fe	47200	54015.81	53679.00	1.14	1.14	13.79	13.70
IPI				2.56	2.16		

NLSC – Nifasesilk Lafto Sub City; KKSC – Kolfe Keranyo Sub City

Table 10
Transfer factors of trace metals from the soil into the vegetable samples.

Vegetable	Zn	Cu	Ni	Pb	Mn	Fe	Min.	Max.	Mean
Swiss chard	0.238	0.188	0.019	0.072	0.152	0.016	0.016	0.188	0.114
Cabbage	0.224	0.169	0.005	0.077	0.072	0.013	0.005	0.224	0.093
Lettuce	0.239	0.154	0.015	0.076	0.089	0.013	0.013	0.239	0.098
Seden	0.205	0.171	BDL	0.074	0.094	0.018	0.018	0.205	0.112
Potato	0.263	0.191	0.036	0.077	0.072	0.009	0.009	0.263	0.108
Green onion	0.232	0.181	0.014	0.069	0.189	0.019	0.014	0.232	0.117
Beetroot	0.250	0.191	BDL	0.090	0.074	0.010	0.010	0.250	0.123
Cucumber	0.300	0.157	BDL	0.055	0.041	0.010	0.010	0.300	0.113
Min.	0.205	0.154	BDL	0.055	0.041	0.009			
Max.	0.300	0.191	0.036	0.090	0.189	0.019			
Mean	0.244	0.175	0.019	0.074	0.099	0.014			

to Pb concentration in the soil which is all samples are within the allowable limits, it exhibited higher concentrations in all vegetable samples when compared from permissible limits (Table 4).

The concentration and maximum permissible limits of trace elements is found in Table 4. And Table 1 compares the mean concentration of those elements with literatures. The concentration range of Zn was found to be from 37.4 (lettuce) to 57.5 (cucumber) mg/kg, both from irrigation site one (Table 4). In the literatures the minimum and maximum amount of zinc in lettuce was found to be 1.73 and 42.0 mg/kg [55,56], respectively and in cucumber it was 20.08 and 32.30 mg/kg [56,57], respectively (Table 1). So in this study zinc was found to be higher in cucumber in comparison with literature values but still within maximum permissible limits (60 mg/kg) set by [49].

The obtained mean concentration range of Cu was 7.0 (lettuce) to 10.7 (potato) mg/kg again both from site one. When compared with literature values, lettuce recorded 0.20 and 59.93 mg/kg as minimum and maximum [55,57], respectively whereas in potato it was 0.54 and 4.21 [55,58], respectively. The present study result of copper is therefore comparable with most of the literature values and is well within the maximum permissible limit (40 mg/kg) established by the joint FAO/WHO [50] (Table 4).

Nickel recorded below detection limit as a minimum mean concentration for parsley in both irrigation sites while beetroot, cucumber and lettuce showed a value of below detection limit in one of the two irrigation sites. Potato registered the highest Ni content (0.7 mg/kg) in irrigation site one. Considering literatures, the minimum value was recorded in lettuce (0.03 mg/kg) by [55] and the maximum was in potato (10.74 mg/kg) by [56]. Both the present study and some literature values suggested that potato tends to accumulate more Ni than the studied vegetables (Table 1). However, the concentration of Ni in the present study was found below the maximum permissible limit (1.5 mg/kg) put forward by [52].

The lowest and highest mean concentration of Pb was 6.2 (cucumber) and 10.1 (parsley) mg/kg, both from irrigation site one. In literatures, parsley was found to contain the highest amount (9.9 mg/kg) studied by [57] and cabbage was the lowest (0.02 mg/kg) put forward by [46]. With regard to the lowest amount of Pb, the present study results were comparable with some of the literature values. However, considering the highest amount of Pb in literature and its maximum permissible limit (0.3 mg/kg) which is set by [51] all the vegetables under the present study were found to contain significantly higher concentration of lead.

Obtained mean concentration of Mn ranges from 142.8 (cucumber) to 663.4 (swiss chard) mg/kg. In contrast to literatures in which the minimum and maximum amount was 2.62 (potato) and 317.54 (cabbage), both reported by [59], the highest and lowest values of the present study were found to be higher (Table 1). In the present study parsley, Swiss chard and green onion, all from irrigation site two, showed even bigger concentration of Mn compared to the maximum permissible limits (500 mg/kg) allowed by [51].

Iron mean concentration of the studied vegetables ranks from 337.0 (potato, site one) to 1387.3 (parsley, site two) mg/kg. And when these compared with literatures which states 40.49 mg/kg (potato) as minimum [59] and 323.9 mg/kg (lettuce) [56] as maximum, the present study result revels much higher concentration of Fe (Table 1). It is also noted that with the exception of potato from irrigation site one, all the studied vegetables exhibited higher concentration of Fe in comparison with the maximum allowable limit (425 mg/kg) seat by [51] (Table 4). Both literature and present study results suggested that potato tends to accumulate lower amount of Fe among the studied vegetables.

In both irrigation sites Mn and Fe showed elevated concentration in the sampled soils when compared with permissible limits while the remaining elements were found to be within the allowable limits (Table 4). The mean concentration level of metals in the soil decreased in the order of Fe > Mn > Zn > Pb > Cu > Ni. Considering literatures, varying concentration of trace elements were observed in different parts of the world (Table 2). Zinc for example showed a concentration range as little as 5.50 (Fallujah, Iraq) to 1638.97 mg/kg (Islamabad, Pakistan) while in the present study a mean concentration of 190.87 mg/kg was obtained. As that of Zn, a similar trend is observed for Cu, Ni, and Pb when compared with literature values of soil concentration. However, the current study result revealed that higher concentration for Mn and Fe in the sampled soils in comparison with the literatures obtained (Table 2).

Overall, Zn and Ni showed higher mean concentration in potato (50.15 and 0.45 mg/kg, respectively), Cu and Pb mean concentrations were superior in beetroot (9.8 and 10.0 mg/kg, respectively), and Mn and Fe exhibited higher mean content in green onion (659.6 and 1034.3 mg/kg, respectively) when compared with literature values (Table 1). From Table 4 it is deduced that in irrigation site one the mean concentration of trace metals in the studied vegetables decreased in the order of Swiss chard > lettuce > parsley > cabbage > cucumber > potato. Similarly, in irrigation site two the mean trace metals in vegetables exhibited the following order; parsley > Swiss chard > green onion > lettuce > cabbage > beetroot > potato.

3.3. Estimated dietary (Daily/Weekly) intake

Among the approaches for the estimation of human health risk for metals in food, the most widely used is the calculation of estimated dietary intake values and their comparison with the standard recommended dietary and tolerable upper intake values. Those values are established by Joint World Health Organization and Food and Agriculture Organization Expert Committee on Food Additives, [19, 20 and 21], United States Environmental Protection Agency [22], and European Food Safety Authority [23] and Food and Nutrition Board of the United States [24] for both adults and children. The estimated daily intake values of elements depend on the element concentrations in the food and the consumption of the food. In this study, the daily intake was considered for each vegetable. The recommended dietary intakes (RDI) for Zn, Cu, Mn, and Fe for a 60-kg-adult consumer are 8–11, 0.9–3.0, 2.5–5.0, and 8–18 mg/day [19,20]. Similarly, the provisional tolerable daily intake (PTDI) value for Ni is 0.3 mg/day [22] and for Pb 0.02–3 μg/day for a 60 kg adult [21]. And for a child (12 kg, 1–3 year) consumer the recommended dietary allowance for Zn, Cu, Mn, and Fe are 3.7, 0.34, 1.2, and 7.0 [48,49]. The provisional tolerable daily intake (PTDI) value of Pb for a child is 0.03–9 μg/day [21] and for Ni it is not established. Nickel and Pb are non-essential elements, and hence their percentage contribution to the recommended dietary intake value could not be calculated. However, it is possible to compare and appreciate their estimated daily intake (EDI) values against the provisionally tolerable daily intake (PTDI) values.

The calculated dietary values of the elements through consumption of the analyzed vegetables, and their comparison and contribution to standard recommended and tolerable upper intake values and provisional tolerable daily intake values for adults and children are provided in Tables 5 and 6, respectively. The result of calculated dietary intake for adults in Table 5 show that the trace element Mn contributed the most to the RDI value in all of the vegetables, exhibiting a range of 0.238–1.099 mg/day with a contribution of 4.76 (cucumber) to 21.98 (green onion)%. However, the dietary exposure level of Pb was found well above the provisionally tolerable daily intake values for all of the vegetables studied for both adults (PTDI = 0.02–3 μg/day) and children (PTDI = 0.03–9 μg/day) Tables 5 and 6. For children in Table 6 the calculated dietary contribution of lettuce and parsley were found more than the adequate intake value of Mn per day. Swiss chard (2.212) and green onion (2.748) even offered greater than not only the adequate intake value per day but also the established standard upper tolerable dietary intake value of Mn per day.

3.4. Target hazard quotient and hazard index

The target hazard quotient is an integrated risk index that compares the ingested amount of a contaminant with a standard reference dose (upper tolerable intake). The hazard index is the sum of the target hazard quotients of all analyzed elements. The magnitude of adverse effects of toxic metals in a given sample is proportional to the sum of multiple metal exposures. Hence, it is necessary to determine the health risk arising from multiple metals. The target hazard quotient and hazard index values less than one signify that the level of exposure is lower than the reference dose, which assumes that a daily exposure at this level does not pose any threat to the consumer during his/her lifetime.

The target hazard quotients for trace elements ingested through lettuce, cabbage, cucumber, potato, parsley, Swiss chard, beetroot, and green onion in Table 7 for adults shows that the calculated target hazard quotient for the trace element Pb is higher than one for all of studied vegetables ranging from 11.086 (cucumber) to 17.881 (beetroot) with a 98.216% and 98.464% contribution to the hazard indices, respectively. And consequently the total hazard indices on the same table for all vegetables become higher than one. Therefore, both the target hazard quotient and total hazard indices result suggested that the daily consumption of the studied vegetables by adults does indeed pose a threat to the consumer in his /her lifetime. In Table 8 for children, with the exception of lead for which we do not have the standard reference does established to help calculate target hazard quotient, the remaining trace elements calculated result suggested that the daily exposure does not pose a health threat for a child consumer. However, in comparison with other trace elements, Mn showed a higher target hazard quotient vales ranged from 0.0107 (cucumber) to 0.0495 (green onion) with a 70.86% and 88.85% contribution to the total hazard indices, respectively (Table 8).

These results for adults show that all target hazard quotients of Pb and the total hazard indices for all vegetables are well above one. As these values are exceeded one, there is a significant concern for potential health effects as exposure to more contaminant may produce an additive effect on the consumers [60,61]. Though we lacked standard reference does for lead for a child, by considering figures from target hazard quotient of adults similar scenarios can be drawn for a child consumer with potential health effects by consuming the studied vegetables.

3.5. Metal pollution load index

As shown in Fig. 2 the overall load of metals in each vegetable growing at each irrigation site, Kolfe Keranyo and Nifasesilk Lafto sub city were computed and assessed. It is observed that in most of the vegetables studied the overall pollution load of trace metals were higher in Kolfe Keranyo irrigation site. And the reasons could be the number of pollutants (eg. industries and garages) which damp there unregulated wastes to the nearby streams which ultimately end up for irrigation use. Other additional reason could be the population density in Kolfe Keranyo sub city which contributed higher house hold wastes than Nifasesilk Lafto sub city.

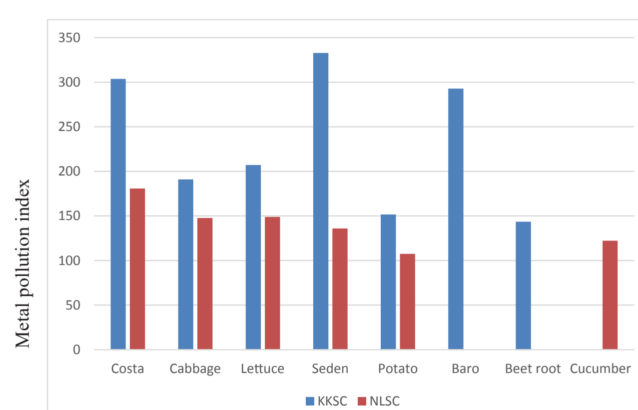


Fig. 2. Metal pollution indexes of vegetables from the two sites; Kolfe Keranyo (KK) and Nifasesilk Lafto (NL) sub city.

3.6. Soil pollution indices

The degree of metal enrichment or pollution in soils of the two irrigation sites were assessed using indices like pollution load index, integrated pollution load index, and enrichment factors. The pollution load index (PI) of trace metals concentration in the soil samples as compared to the geometric means of the natural background concentration of the corresponding metal was determined as given in Table 9. It was only Ni that showed lower contamination of the soil in both irrigation sites as the PI is less than one. Cu showed lower contamination in the NLSC site but moderate contamination in the KKSC site with the PI value of 1.45. Both Zn and Fe showed moderate contamination of the soil in both irrigation sites with the PI vale ranges between 1 and 3.

Higher contamination of the soil in both irrigation sites were registered by the trace elements Mn and Pb with the PI vales above three.

The integrated pollution load index (IPI), mean of all pollution load index, values of all of the considered metals were also tabulated in Table 9. In both NLSC and KKSC irrigation sites the IPI value suggested higher contamination of the soils with the IPI number 2.56 and 2.16, respectively. In Table 9 the level of pollution and potential anthropogenic effects which is termed as enrichment factor (EF) was quantified for the sampled soils. The trace element Pb and Mn showed extremely high enrichment/pollution in the sampled soils of both irrigation sites, as the EF vales are above 40 whereas Cu and Fe in both sites exhibited significant enrichment/pollution with an EF values in between 5 and 20. Very high and significant enrichment/pollution was obtained in both irrigation sites by the element Zn with a calculated EF values from 20 to 40. However, deficiency to minimal and moderate enrichment/pollution was recorded by Ni in both irrigation sites (Table 9).

3.7. Soil-vegetable transfer coefficient

Transfer factor (TF) or plant concentration factor (PCF) is a parameter used to describe the transfer of trace toxic elements from soil to plant body and it is also a function of both soil and vegetable properties. Table 10 lists the transfer coefficient which quantifies the relative differences in bioavailability of metals to the vegetables studied. The trend of TF for trace metals in to vegetable samples were in order of: Zn>Cu>Mn>Pb>Ni>Fe. That means Zn is relatively poorly retained in the soil or greater efficiency of plants to absorb it and Fe has the strong sorption to the soil colloids. The trend is consistent with a study made by [62]. From the calculated TF again in terms of vegetables the trends which intend to accumulate more trace metals were found to be in order of: beetroot>green onion>Swiss chard>cucumber>parsley >poteto>lettuce>cabbage. It means that beetroot was found to have greater efficiency to adsorb the metals and cabbage is the least efficient [63].

4. Conclusion

It is very important to assess and monitor the concentrations of potentially toxic heavy metals and metalloids in different environmental segments and in the resident biota. In the current study toxic trace metals which can cause tremendous amount of health problems are investigated in terms of their quantity present in the commonly consumed vegetables and in terms of their health significance based on the daily/weekly dietary consumption. The findings showed that the levels of metals such as Pb, Mn and Fe in most of the vegetables studied are way above the maximum permissible limits set by WHO/FAO guideline. More or less the same trend of toxic metals pollution level was observed within the soil. And their health significance, which was calculated based on the dietary intake of an adult and a child consumer, suggested that the dietary exposure level Pb and Mn was found well above the provisionally tolerable daily intake values for most of the vegetables studied for both adults and children. Some of the vegetables even offered more than the established standard upper tolerable dietary intake value of Mn per day.

Both the target hazard quotient and total hazard indices result suggested that the daily consumption of the studied vegetables by adults does pose a threat to the consumer in his/her lifetime. Though we lacked standard reference does for lead for a child, by considering figures from target hazard quotient of adults similar scenarios can be drawn for a child consumer with potential health consequences by consuming the studied vegetables. In both irrigation sites the integrated pollution load index value suggested higher contamination of the soils by the studied metals. The trace element Pb and Mn showed even extremely high enrichment/pollution in the sampled soils in both irrigation sites. Therefore, concrete steps, such as policy measures, should be taken to minimize the dire consequence of these and other hazardous heavy metals on the human-ecological systems.

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.

Data availability

The data that has been used is confidential.

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