

Assessment of Potentially Toxic Elements in Vegetables Grown along Akaki River in Addis Ababa and Potential Health Implications

Minbale Aschale[1*] Yilma Sileshi[2] Mary Kelly-Quinn[3] Dereje Hailu[1]
1.Ethiopian Institute of Water Resources, Addis Ababa University, Ethiopia
2.School of Civil and Environmental Engineering, Institute of Technology, Addis Ababa University
3.School of Biology and Environmental Science, University College Dublin, Belfield, Dublin 4, Ireland
*Corresponding author email: minsinas@yahoo.com

Abstract
The present study was carried out to assess contamination of vegetables from five farmlands in Addis Ababa with toxic and potentially toxic elements (Cd, Pb, As, Cu, Zn, Cr, Co, Ni, Ba, B, Sr, V, Fe and Mn) and health risk concerns to consumers of these vegetables as well as farm soils and water used to irrigate the vegetables. Pollution levels were varied with metals and vegetable types. The average total metal accumulation (mg kg-1) in the vegetables was potato (245.54) > carrot (202.20) > Swiss chard (52.42) > lettuce (47.43) > cabbage (38.04) > Ethiopian kale (30.17). Results also revealed that the average concentrations (mg kg-1) of all elements in the vegetables were found in order of Pb (744.10) > Fe (288.5) > Mn (51.66) > Sr (50.12) > Zn (38.81) > Ba (35.51) > B (21.65) > Cu (7.95) > Cr (1.97) > Ni (1.14) > V (0.54) > Co (0.20) > As (0.08) > Cd (0.08). Many of the concentrations were higher than previously reported. The average metal concentration (mg kg-1) of vegetables by farm was Burayu (136.58) > Akaki (125.00) > Kolfea (54.19) > Goffa (37.11) > Kera (29.40). The concentration of Cr, Cd, Pb and Fe in most vegetables surpassed the maximum recommended levels. From health standpoint consuming lettuce, Swiss chard, carrot and potato may cause serious health risk to consumers than cabbage and Ethiopia kale due to the high level of toxic metal accumulation. Elevated levels of some heavy metals were detected in the soil and irrigation water (Cd, Pb, As, Cu, Zn, Cr, Co, Ni, Ba, B, Sr, V, Fe and Mn) suggesting contamination from various the industrial and municipal discharges to the local river network. The present study highlights the immediate need for proper treatment and disposal of wide range of effluents and waste materials that currently enter the Akaki River and its tributary and farmlands as well as regular monitoring of potential contaminants in soil, water and vegetables and enforcement of standards.
Keywords: Potentially toxic elements, contamination, plant uptake, health risk

1. Introduction

Potentially harmful metal in soils may come not only from the bedrock but also from anthropogenic sources like solid or liquid wastes, atmospheric sources, surface runoff, mining of coal and ore, agricultural inputs, landfill leachate and fallout of industrial and urban emissions (Zarazua *et al*., 2006; Wilson and Pyatt, 2007; Fernando, 2012). In developing country, rapid urbanization and industrialization releases wastewater to rivers which also are increasingly utilized as sources of water for irrigation. Long term irrigation of agricultural land with sewage and industrial wastewater may cause toxic pollutants such as heavy metals to be accumulated in the soil and food crops (Sharma *et al*., 2009; Anita *et al*., 2010). The application of contaminated water can change the physicochemical nature of soils (Anita *et al*., 2010). Excessive accumulation in agricultural soils may result not only in soil contamination but has also consequences for food quality and safety. It is thus essential to analyze and monitor the quality of food given that plant uptake is one of the main pathways through which toxic pollutants enter the food chain (Wang *et al*., 2011; Harmanescu *et al*., 2011; Fernando., 2012). Vegetables take up heavy metals and accumulate them in their edible and non-edible parts at quantities high enough to cause clinical problems to human beings (Aktar *et al*., 2010). The uptake and accumulation by vegetables depend on the concentrations of available metals in soils and on the vegetable species. Trace element contamination is therefore of concern due to potential toxicity to the environment and human beings (Kar *et al*., 2008*)*. The contamination of vegetable by heavy metals is a serious ecological problem as many heavy metals such as Hg, As, Pb, Sb, Ni, Sr and Cd are toxic even at low concentrations. They are non-degradable and can accumulate in the human body causing damage to the nervous system and internal organs (Lee *et al*., 2007; Lohani *et al*., 2008; Minable *et al*., 2015). Though some metals such as Cu, Fe, Mn and Zn are essential as micronutrients for living organisms, they can be detrimental to their physiology at higher concentrations (Kar *et al.,* 2008; Nair *et al.,* 2010).

The city of Addis Ababa with approximately 5 million people hosts large numbers of industries whose wastewaters are discharged into the small river network, most often untreated despite the Addis Ababa Environmental Authority insistent to treat any water before disposal and the commitment of the industries concerned to do so. Accordingly, old as well as new factories, commercial, public and domestic utilities in Addis

Ababa release untreated wastes into any aquatic receiving environment found nearby. The streams and rivers in the Addis Ababa are also a receptacle for a variety of wastes released by the residents. At the same time the river is used for irrigating vegetables and crops, livestock watering, washing cattle, and other domestic needs for the rural people living outside Addis Ababa and Akaki (Alemayehu, 2001; Itanna, 2002; Weldegebriel *et al*., 2012; Minbale *et al*., 2015). The Little Akaki River, locally known as Tinishu Akaki River, and its tributaries receives the major portion of the waste released in the western part of the city where most of the industries such as tanneries, breweries, wineries, distilleries, pharmaceutical and national alcohol liquor factories are established along the course of the river. Irrigation with water from these rivers could contaminate the soil with toxic elements such as Cd, Pb, As, Cu, Zn, Cr, Co, Ni, Fe and Mn and hence the plants grown in these soils could be a potential health concern to consumers (Itanna, 1998; Weldegebriel *et al*., 2012; Minbale *et al*., 2015). Moreover, an increasing awareness in terms of the importance of vegetables and fruits to human diet suggests that monitoring of heavy metals in food crops should be carried out frequently. However this is rarely undertaken in Ethiopia.

In Addis Ababa, to date there have been limited studies and knowledge on the concentrations of potentially toxic elements in vegetables. Studies on trace elements in vegetables and farmlands of Addis Ababa by Itanna (1998, 2002) to assess their toxicological implications reported higher concentrations of trace metals in the more industrial sites of the river catchment and gradual increases in soils over time. This study also reported tolerable levels of As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in vegetables except As in Swiss chard, Cr in lettuce, Pb and Fe in Swiss chard and lettuce in one farm, all of which surpassed maximum permitted concentrations. Later Weldegebriel *et al* (2012) determined the concentrations of Cd, Co, Cr, Cu, Pb, Mn, Ni and Zn in vegetables grown in soils irrigated with Akaki river water in Addis Ababa and the result indicated that Ethiopian kale, Swiss chard, lettuce and cauliflower grown in four farms showed Cd and Pb at levels that could cause health risk concerns to consumers. The present study aimed to further investigate the potential contamination by Cd, Pb, As, Cu, Zn, Cr, Co, Ni, Ba, B, Sr, V, Fe and Mn in the most frequently consumed vegetables from five farms, river water used for irrigation and farm soils irrigated with these waters in Addis Ababa with a view to addressing potential health risk implications to consumers. The findings of this study will inform concerned authorities in evaluating the environmental impacts on agriculture farmland and human health for further intervention.

2. Materials and Methods

2.1 Study Area

Addis Ababa, the nation's capital and largest city lies high in the foothills of Mount Entoto in central Ethiopia. It is geographically located at 9°N and 38°E between 2200 and 2500 meters above sea level. It is the country's commercial, manufacturing and cultural center. Five vegetable farms namely Burayu, Kolfea, Kera, Gofa and Akaki irrigated with water from the Little Akaki River and its tributaries in Addis Ababa were selected to study the level of potentially toxic element contamination (Figure 1). The five farms are typical vegetable growing areas in the western-central part of Addis Ababa. Burayu farm is irrigated from the Burayu River located in the upstream of the Little Akaki River. Kolfea and Gofa farms are irrigated from the Little Akaki River, which flow in the south westerly direction. The Kera farm is situated in the southern part of the city nearer to Kera Abattoir and is irrigated from the Kera River while Akaki farm is located in the south western part of Addis Ababa near Lake Aba Samuel in Genda Jersa village and irrigated from the Little Akaki River.

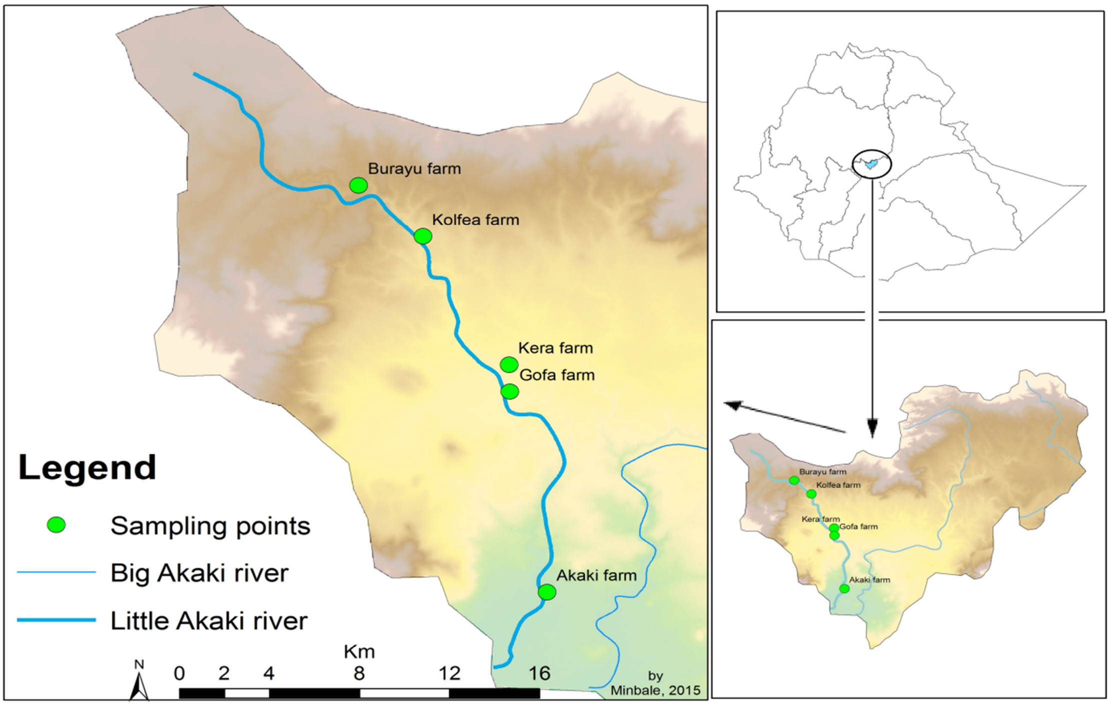

Figure 1: Sampling sites of study vegetable farms in Addis Ababa

2.2 Reagents and Standard Solutions

All chemicals used were of analytical grade. High-purity water (18.2 MΩ cm^{-1}) from a Milli-Q water purification system (Millipore, France), concentrated nitric acid (BDH, England), 30% H_2O_2 (BDH, France) and argon of 99.999% purity were used. Analytical multi-element standard solutions were prepared by appropriate dilution of single and multi-element standard solutions containing the metal ions of interest supplied commercially for ICP-MS. Multi-element standard for Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, Ba, V, As, Sr and Co and internal standard solutions for Ge, Sc and Bi were purchased from VLG labs (Manchester, USA). The matrix of all samples, standards, wash solutions and quality control standards was made in a 0.5% HNO_3. Vegetable certified reference materials (CRM), spinach leaves (SRM 1570a), and soil certified reference materials, San Joaquin soil (SRM, 2709a) obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA) were used. The analysis on the soil, vegetable and water samples was carried out using inductively coupled plasma mass spectrometry/ICP-MS (ELAN DRC-e ICP Mass Spectrometer Axial Field Technology, PerkinElmer SCIEX, Concord, Ontario, Canada) in the Inland Fisheries Ireland (IFI) laboratory and the Irish Environmental Protection Agency laboratory, both in Dublin, Ireland. All polyethylene bottles were washed with detergent, followed by repeated rinsing with distilled water and soaked overnight in 10% HNO_3 for 24 hr and finally rinsed three times with doubly deionized water.

2.3 Collection, Preparation and Preservation of Samples

2.3.1 Vegetable samples

Composite samples of mature vegetables namely Ethiopian kale (*Brassica carinata A. Br.*), Swiss chard (*Beta vulgaris L. var. cicla*), lettuce (*Lactuca sativa L.*), cabbage (*Brassica oleracea L. var. capitata*), carrot (*Daucus carota L.*) and potato (*Solanum tuberosum L.*) were collected randomly from a minimum of twenty five vegetables per sample from Burayu, Kolfea, Kera, Gofa and Akaki farms depending on their availability. Samples were collected between February and May, 2014. A total of 19 samples were collected, packed, labeled and transported to the laboratory and washed with tap water and then rinsed with distilled deionized water to remove dust and extraneous matter and air dried. Hand gloves were used to process the samples to avoid any contamination. The air dried edible portions of the samples were grounded, homogenized and placed in a clean polyethylene container and stored in a desiccator until analysis.

2.3.2 Soil samples

Composite soil samples were collected randomly from distributed sampling points within the five study farms (Figure 1) using a stainless steel auger in the same periods as the vegetable samples. The grass on the top of the soil was removed. Each soil sample was collected by removing the surface soil and sampling vertically from a 0 to 20 cm borehole. The collected soil was put inside a plastic bag, and labeled to include the sample point, date of collection and the site where it was collected. During sampling, handling and preparation polyethylene gloves were worn. The soil samples were collected from nearly the same slopes, at each site, to minimize the effects of topographical differences on soil properties (Hunde *et al*., 2011). During each sampling program, ten to twenty samples were collected and thoroughly mixed in the field, from which composite samples weighing about 1 kg each were brought to the laboratory packed in plastic bags. All samples were well mixed again in the laboratory and one fourth of each sample was air dried. The dried samples were then ground and homogenized using a porcelain pestle and mortar and kept packed in clean and dry containers until digestion.

2.3.3 Water samples

Water samples were collected at five sampling sites from diversion points of irrigation. At each sampling station 500 mL of water sample was collected by lowering pre cleaned polyethylene bottles into the upper surface of the river, 30-50 cm deep, and allowing them to over flow before withdrawing. Before taking the final water samples, the bottles were rinsed three times with the river water to be collected. Sampling took place twice between February and June, 2014. The collected river water samples were brought to the laboratory and filtered using Whatman 42 pore size filter paper and preserved with 1 ml of 69% HNO_3 in 200 ml polyethylene bottles. The filtered samples were stored in a refrigerator to minimize volatilization and biodegradation between sampling and analysis periods.

2.4 Digestion Procedure for Total Metal Analysis.

Vegetable and soil samples were digested according to the EPA 3050B acid digestion method (Hagedorn, 2008; Dowdell and Thompson, 2014). The resulting mixture was finally analyzed by ICP-MS for the metal contents. The digests were stored at 4°C until analysis.

2.5 Sample Analysis

The instrument was conditioned for a minimum of 30 minutes and optimized by running the daily performance check solution. The daily performance was checked based on the recommended optimization values of Mg > 50,000 counts per second (cps), In > 250,000 cps, U > 200,000 cps, CeO/Ce < 3%, Ba^{++}/Ba < 3% and autolens 0.5% < slope < 2%. On verifying configuration of the various operating parameters such as the nebulizer flow rate, the position of the torch and RF power and the interference corrections, analysis of samples was preceded. The analysis of sequence was: blank, working standard solution, blank, certified calibration blank, samples of the interest and at the end of the sequence the standard. The selected trace elements in vegetable, soil and water samples were quantified using a calibration curve. Each sample was analyzed in triplicate and the concentrations were determined as average of replicates. Duplicate samples were tested after every 10 samples. For ICP-MS measurements, 1 mL of sample was pipetted into a 10 mL polyethylene tube. Then the volume was adjusted to 10 mL with 0.5% HNO_3. Where sample dilutions were necessary, they were performed by pipetting the required volume of sample into a sample tube and pipetting the required volume of 0.5% HNO_3 i.e. a 5x dilution is made by combining 1 ml sample and 4 ml 0.5% HNO_3 in a 10 ml sample tube, capping and inverting several times in order to avoid signals that were too high for the detector to measure adequately.

2.6 Analytical Performances

Sensitivity, limit of quantification, precision, linear dynamic range and interference corrections were established for each individual target analyte. Hence, for validation of the analytical procedure, standard reference materials and spiking experiment were included in every batch of sample digestion and analysis as a part of the quality control. A vegetable certified reference material, spinach leaves SRM 1570a**,** and soil certified reference material, San Joaquin soil SRM 2709a, with concentrations certified for the elements were analyzed using the method described for vegetable and soil analysis. A spiking experiment involving the addition of known amounts of standard solutions containing the elements of interest into the vegetable sample was also carried out employing the same procedure. The mean of measured certified concentrations were compared with the elements analyzed. The known concentrations of the spiked metals and the percentage recoveries were calculated (Table1). Analytical performance as accuracy was considerable high since the concentrations of all elements analyzed fell within in the range of given certified value. The percentage recoveries of the metals in the certified reference material (SRM 1570a) and the spiked vegetable samples ranged from 78.9% to 119.6% and in the soils from 77.5% to 108.5% were presented in Table 1. These values are within acceptable range for the analysis of environmental samples, which confirmed validity of the optimized digestion and extraction procedures used for the soil and vegetable analysis.

The careful choice of internal standard in ICP-MS is used to compensate for signal drift, and to correct for instrumental instability and non-spectral interferences. Since the analyte elements are spread over a wide range of atomic masses, to obtain optimal accuracy and precision results, the internal standard should closely match the analyte in terms of mass number and ionization potential of the analyte element. For this reason, in the present study, multi-element internal standard, containing Ge for As, Co, Cu, Sr, Cd, Ba, Ni and Zn; Sc for Fe, Cr, V and Mn; and Bi for Pb were used. When the element of interest had more than one isotope, careful selection of the isotopes of the given element is critical. The masses of at least two were monitored and the isotope with less interference and higher abundance was selected. And thus, ^{51}V, ^{52}Cr, ^{54}Fe, ^{55}Mn, ^{58}Ni, ^{59}Co, ^{65}Cu, ^{66}Zn, ^{75}As, ^{87}Sr, ^{114}Cd, ^{137}Ba, and ^{208}Pb isotopes were used for this analysis. Before conducting sample analysis, different concentrations of standards were analyzed and a linear calibration curve was prepared. The calibration curve was acceptable for all reported elements with correlation coefficient $R^2 > 0.999$ and that blank results were < limit of quantification in each case. For metals whose calibration extend above 2 million cps, the linearity between the pulse and analog measurements should be verified visually, that is data from the highest pulse measurement should lie on the same calibration line as the point from the highest analog measurement.

2.7 Determination of Limits of Detection (LOQ)

To determine the LOQ of the entire analytical methods, reagent blanks were prepared following the same procedures for the quantification of trace elements in the samples. The intensities of 10 blanks were measured. Standard deviations were calculated from the intensity readings of these 10 blanks. The LOQs for the species under study, based on three times the standard deviation (3σ) of the average of 10 individually prepared blank solutions, were calculated (Table 1).

Table 1: Method detection limits for the analysis procedures, percentage recoveries of metals in spiked vegetable samples and in the vegetable and soil certified reference material.

Element	Concentration in SRM 1570a (mg kg-1)			Concentration in soil 2709a (mg kg-1)			% recovery of spike		Detection limit (µg L-1)	
	Found	Certified	% recovery	Found	Certified	% recovery	Lettuce in Akaki	Lettuce in Kolfea	Vegetable/ soil	Water
V	0.449	0.568	79.05	42.13	48	87.77	100.50	96.31	0.9	1
Cr	-	-	-	49.21	53	92.85	99.98	95.21	0.1	1
B	34.751	37.7	92.18	-	-	-	97.15	89.82	0.2	10
Mn	67.132	76	88.33	410.45	420	97.73	106.39	104.11	0.05	0.25
Fe	-	-	-	23275	24000	96.98	119.55	102.12	20	10
Co	0.310	0.393	78.88	8.10	10	89.97	113.00	106.18	0.04	1
Ni	1.820	2.142	84.97	58.11	66	88.04	109.80	103.42	0.06	1
Cu	11.328	12.22	92.70	25.43	27	94.19	108.71	103.35	0.05	1
Zn	67.501	82.30	82.02	74.57	79	94.39	99.24	97.00	0.2	1
As	0.074	0.068	108.82	7.10	7.8	91.03	110.42	102.51	0.4	1
Sr	51.678	55.54	93.05	-	-	-	115.16	112.28	0.1	10
Cd	2.433	2.876	84.60	0.31	0.4	77.50	106.59	101.71	0.04	0.02
Ba	-	-	-	348.82	380	91.80	119.05	118.07	0.04	1
Pb	0.23	0.2	115	9.98	9.2	108.47	108.79	104.98	0.03	1

3. Results and Discussion

3.1 Concentrations of Metals in Soils and Irrigation Waters

The trace element concentrations found in soil and irrigation water samples collected from diversion points are summarized in Table 2. Among the elements, the concentrations of Cr and B in Kolfea, Mn in Kera, Kolfea and Akaki farms were higher than the maximum concentration limits given for irrigation waters (Ayers and Westcot, 1994). Previous reports also revealed that mean concentration of Cd (18 µg L^{-1}), Co (137 µg L^{-1}) and Cu (24 µg L^{-1}) in Akaki, Mn (1414 µg L^{-1}) in Gofa, Cd (33 µg L^{-1}), Co (219 µg L^{-1}), Cu (370 µg L^{-1}), Mn (804 µg L^{-1}) and of Zn (618 µg L^{-1}) in Kera farms (Weldegebriel *et al*., 2012); Cu (39µg L^{-1}) and Mn (1690 µg L^{-1}) in Kera River (Itanna, 1998) were beyond the maximum concentration limits given for irrigation waters. The presence of high amounts of these metals in irrigation waters may increase their concentration in soils, which in turn may boost metal uptake by plants ultimately leading to elevated concentrations in the vegetables. In all cases a high concentration of essential trace elements Mn, Fe, B, Zn and Cu and low concentrations of the toxic trace metals Cd and As were detected in the river water used for irrigation.

The mean concentrations (mg kg-1) of toxic elements in the irrigated farmland soil samples exhibited the following ranges for As (1.87-2.44), Ba (96.42-272.92), B (0.03-6.17), Cd (0.13-0.23), Cr (21.16-234.23), Co (14.63-24.89), Cu (18.34-33.46), Fe (26280-37011), Mn (844.21-1489.81), Pb (18.35-62.80), Ni (27.70-52.58), Sr (13.78-34.96), V (39.80-63.37) and Zn (52.38-81.82). Comparisons of the various metal concentrations from the five farms indicate higher concentrations of Zn and V in Burayu, Cr, Ni, V and Zn in Kolfea, Zn, Pb and Cr in Goffa, Pb and Zn in Kera, and Zn and Sr in Akaki farm. In all farms the concentration of essential metals was in the order of Fe > Mn > Zn > Cu. Average concentration of Fe, Mn and Ba were relatively high in all farms. The trend in the total concentrations of the metals by farm was Goffa > Kolfea > Kera > Burayu > Akaki farm. The average metal concentrations of the soils in Kolfea farm for Cr and Ni were found to be higher than the maximum permissible levels of metals given in the relevant guidelines (Ewers, 1991; Pendias and Pendias, 1992) (Table 2). Previous reports also revealed that concentration Ni in Akaki farm (Weldegebriel *et al*., 2012); Cr, Ni, Pb and Mn in Kera farm soil (Itanna, 1998) were beyond the maximum concentration limits given for arable soils. The high concentration of chromium in soil and water samples observed in Kolfea and Akaki irrigated farm could be due to the discharges from the tanneries.

Table 2: Concentrations of elements found in Burayu, Kolfea, Kera , Gofa and Akaki irrigation water and soil farmlands in Addis Ababa.

Element	Burayu		Kolfea		Kera		Gofa		Akaki		Guidelines for max. Levels in	
	river (µg/L)	soil (mg/kg)	river (µg/L)	soil (mg/kg)	river (µg/L)	soil (mg/kg	river (µg/L)	soil (mg/kg	river (µg/L)	soil (mg/kg	river (µg/L)[a]	soil (mg/kg)[b]
As	<1.0	2.44	1.3	2.21	1.1	2.41	1.2	2.09	1.9	1.87	100	20
Ba	55.5	96.42	125	128.48	102.5	272.92	130	175.14	145	187.64	-	-
B	11	0.10	**1000**	6.17	53.5	0.32	148	0.03	115	0.45	750	-
Cd	0.06	0.17	0.06	0.13	0.06	0.23	0.04	0.17	0.06	0.16	10	3
Cr	2.4	42.94	**255**	**234. 23**	2.35	42.25	3.85	49.87	46	21.16	100	100
Co	<1.0	21.72	2.05	24.89	2.65	21.05	2.1	21.49	2.15	14.63	50	50
Cu	5.75	23.64	3.3	33.46	5.55	21.16	6.55	22.42	6.35	18.34	200	100
Fe	974	35217	905	37011	945	35541	565	36595	555	26280	5000	50000[c]
Mn	38	1135	**2000**	894.48	**1150**	1489.81	**1300**	1224.97	**1400**	844.21	200	2000[c]
Pb	1.6	18.61	1.4	18.35	5.05	62.80	4.1	51.86	4.3	20.39	65	100
Ni	3.1	36.15	4.9	**52.58**	5.15	27.70	3.9	34.30	6.5	29.58	200	50
Sr	98.5	13.78	315	27.25	395	23.43	350	28.09	365	34.96	-	-
V	3.2	57.23	5.95	63.37	3.4	54.36	3	51.90	3.9	39.80	100	-
Zn	13	56.00	21	52.38	21.5	80.94	10.9	81.82	22.5	68.31	200	300

[a]Ayers and Westcot, 1994
[b]Ewers, 1991
[c] Pendias and Pendias, 1992
Exceedences of thresholds are in bold type

3.2. Metal Accumulations in Leafy Vegetables

Average concentrations of heavy metals (mg kg-1) in the edible parts of vegetables on a dry weight basis grown in water from the Little Akaki River and its tributaries along with the permissible limits set by Weight (1991) and FAO/WHO (2001) are presented in Table 3. The concentrations of elements varied greatly among vegetable species and sampling locations, which may be attributed to a differential absorption capacity of vegetables for different toxic elements. The average total metal accumulation (mg kg-1) in all the vegetables was potato (245.54) > carrot (202.20) > Swiss chard (52.42) > lettuce (47.43) > cabbage (38.04) > Ethiopian kale (30.17). Hence, the health risk due to metal accumulation was high for potato, carrot, Swiss chard and lettuce which are consumed vegetables in some part of the city. The average total metal concentration (mg kg-1) of vegetables by farm was Burayu (136.58) > Akaki (125.00) > Kolfea (54.19) > Gofa (37.11) > Kera (29.40). As shown in Table 2 the Kolfea, Akaki and Buryau farm sites had the highest amounts of metals in soils. This could provide a partial explanation for the highest average concentrations of metals observed in the vegetables. Vegetables irrigated in Kolfea, Gofa and Akaki farms are polluted with water from the Little Akaki River, Burayu farm from Burayu River and Kera farm is polluted with Kera River water. The ranked order of metal concentrations varied between vegetables (Table 4). All metals had the highest concentration in leafy vegetables except Pb which was highest in potato followed by carrot. Of the leafy vegetables Swiss chard topped the ranking for six of the ten metals and lettuce was the second. Potato was ranked lowest of the eight of the ten metals, cabbage was lowest in two metals and ranked the second lowest in three metals and kale was the second lowest in five of the ten metals as shown in Table 4. However, few of these exceeded thresholds.

Table 3: Average element accumulation in vegetables from five farms in Addis Ababa (mg kg-1, dry weight).

	Ethiopia kale					**Lettuce**				**Cabbage**	Guideline
Element	Buraya	Kolfea	Kera	Gofa	Akaki	Burayu	Kolfe	Kera	Akaki	Akaki	value[a]
Cr	1.52	1.60	1.78	1.39	1.73	1.99	**3.99**	1.39	**2.89**	1.66	2.3
Mn	31.13	22.01	30.55	29.60	27.65	51.65	43.94	23.23	51.31	29.31	500[c]
Fe	241.0	162.0	148.0	185.0	153.0	248.0	**712.0**	183.0	**795.0**	357.5	425.5
Cu	4.23	3.74	5.17	5.14	5.74	9.76	16.11	5.46	13.67	3.26	73.3
Zn	31.16	26.74	35.03	44.81	49.01	40.11	56.19	36.88	63.85	24.20	99.4
As	0.09	0.06	0.07	0.07	0.08	0.11	0.13	0.05	0.11	0.08	0.43
Sr	101.1	84.21	109.4	100.6	115.6	34.57	35.39	23.13	29.95	65.51	-
Cd	0.06	0.03	0.09	0.05	0.17	**0.12**	0.07	0.07	0.13	0.04	0.2[b]
Ba	57.80	41.33	43.92	30.86	59.66	20.76	19.20	13.26	19.05	31.65	-
Pb	0.23	0.21	**1.11**	**0.61**	**1.37**	**0.62**	**0.50**	**0.69**	**1.27**	**0.32**	0.3[b]
B	11.18	45.21	15.12	18.13	19.30	16.98	21.55	21.83	24.36	16.97	-
V	0.51	0.33	0.45	0.35	0.35	0.56	1.27	0.37	1.25	0.60	-
Co	0.05	0.05	0.07	0.03	0.08	0.25	0.43	0.07	0.41	0.21	50[c]
Ni	1.18	0.55	0.29	0.38	0.75	2.63	1.88	0.76	1.99	1.26	67

Table 3: Continued

	Swiss chard				Carrot			potato		Guideline
Element	Burayu	Kolfea	Kera	Gofa	Burayu	Kolfe	Akaki	Burayu	Akaki	value[a]
Cr	2.04	**2.46**	1.24	2.11	2.13	2.24	**2.32**	1.05	1.81	2.3
Mn	229.8	143.03	112.09	103.34	21.12	11.81	9.23	3.78	7.02	500[c]
Fe	**557.00**	369.00	209.00	315.00	291.00	178.0	174.5	75.50	128.00	425.5
Cu	14.31	11.58	10.35	10.10	5.94	6.56	9.50	3.19	7.28	73.3
Zn	83.27	47.11	58.07	42.62	21.92	21.22	25.96	7.54	21.72	99.4
As	0.13	0.12	0.08	0.14	0.06	0.05	0.04	0.03	0.03	0.43
Sr	60.99	48.66	33.65	40.12	26.57	16.67	20.71	3.017	2.40	-
Cd	**0.21**	0.05	0.09	0.06	0.05	0.02	0.07	0.01	0.06	0.2[b]
Ba	71.35	71.73	63.39	70.19	21.10	11.86	23.60	1.94	2.002	-
Pb	**0.38**	**0.85**	**0.76**	**3.99**	**4500**	**716**	**2314**	**2598**	**3997**	0.3[b]
B	22.84	51.25	28.02	32.74	12.64	19.80	21.25	5.20	6.99	-
V	0.99	0.64	0.48	0.65	0.51	0.33	0.34	0.16	0.12	-
Co	0.44	0.42	0.24	0.26	0.21	0.15	0.09	0.07	0.19	50[c]
Ni	2.76	1.47	0.93	0.73	1.42	0.74	0.84	0.53	0.57	67

[a]weight, 1991
[b]FAO/WHO-Codex alimentarius commission, 2001
[c]Pendias and Pendias, 1992
Exceedences of thresholds are in bold type

Table 4: Ranked order (highest to lowest) of metal concentrations in the various vegetables across all farms

Pb	Cr	Cd	Mn	Fe	Zn	Cu	Co	Ni	As
potato	lettuce	S. chard	S. chard	lettuce	S. chard	S. chard	S. chard	lettuce	S. chard
carrot	carrot	lettuce	lettuce	S. chard	lettuce	lettuce	lettuce	S. chard	lettuce
S. chard	S. chard	kale	kale	cabbage	kale	carrot	cabbage	kale	cabbage
lettuce	cabbage	carrot	carrot	carrot	cabbage	potato	carrot	carrot	kale
kale	kale	cabbage	cabbage	kale	carrot	kale	kale	cabbage	carrot
cabbage	potato	potato	potato	potato	potato	cabbage	potato	potato	potato

On average, Pb content was highest in carrot (4500 mg kg-1) and potato (3997 mg kg-1) collected from Burayu and Akaki farms and the lowest in Ethiopian Kale (0.21 mg kg-1) collected from Kolfea farm. Pb in all of the vegetables from all farms, except Ethiopia kale from Burayu and Kolfea farms, surpassed the maximum permissible limit as shown in Table 3. The values for potato and carrot were extremely high and may pose a threat for the consumers. This could be due to the fact that they are root vegetables and thus more susceptible to Pb contamination from the surrounding soils. In the other studies in contaminated areas high concentration of Pb was also recorded in carrot and potato (Radu and Anca-Rovena, 2008; Mohamed and Khairia, 2012). Pb concentrations in Swiss chard, cabbage and lettuce from Kera, Goffa and Akaki farms except lettuce in Goffa and cabbage in Akaki farm, surpassing the maximum limit were also reported by Weldegebriel *et al* (2012). Previous studies also indicated elevated Pb concentration (mg kg-1) in lettuce (1.59) and Swiss chard (1.79) from Kera farm by Itanna (1998), lettuce (1.24), Swiss chard (0.43), Ethiopian kale (0.73) and carrot (0.40) from Burayu farm by Tamiru *et al* (2011). The source of the lead is unclear but could arise from wastewater, industries such as textile, metal works or from vehicle emissions and direct atmospheric deposition. The average Cd concentration was highest in Swiss chard (0.21 mg kg-1) and lowest in potato (0.01 mg kg-1), again both from Burayu farm. The Swiss chard from Burayu farm was the only vegetable that had Cd exceeding the maximum limit recommended by FAO/WHO. Mean concentrations of Cd above permissible level (0.2 mg kg-1) in Swiss chard (0.32 mg kg-1), Ethiopian kale (1.02 mg kg-1) and lettuce (0.46 mg kg-1) from Kera, Gofa and Akaki farms were also reported by Weldegebriel *et al* (2012). The relatively high levels of cadmium in vegetables from Addis Ababa are probably due to the use of agrochemicals and industrial wastes such as textile and metal works.

The highest concentrations of Cr was in lettuce (3.99 mg kg-1)) from Kolfea while the lowest was for potato (1.05 mg kg-1) from Burayu farm. The average concentrations of Cr in lettuce and Swiss chard from Kolfea farm, carrot and lettuce from Akaki farm were higher than the maximum limit recommended by FAO/WHO. Above permissible level of Cr concentration in lettuce (9.47 mg kg-1) from Kera farm was also reported by Itanna (1998, 2002). Cr concentrations recorded in this study were also higher in lettuce (0.81 mg kg-1), Swiss chard (0.57 mg kg-1), Ethiopian kale (0.76 mg kg-1) and carrot (0.52 mg kg-1) from Burayu farm than reported by Tamiru *et al* (2011) and in Swiss chard, cabbage and lettuce from Kera, Goffa and Akaki farms than reported by Weldegebriel *et al* (2012). Higher concentration of Cr in the Kolfea and Akaki farms is probably due to industrial wastes from textile, Addis Ababa and Batu tannery which dispose its effluent directly into the river. In terms of Mn Swiss chard recorded the highest (229.8 mg kg-1) and potato was the lowest concentrations (3.78 mg kg-1), both from Burayu farm. The Mn concentrations in this study, although below the permissible levels, were higher in cabbage and Swiss chard from Kera farm than those reported by Itanna (1998, 2002); and in Swiss chard, cabbage and lettuce from Kera, Gofa and Akaki farms than reported by Weldegebriel *et al* (2012).

The average concentration of Fe ranged from 75.5 to 795 mg kg-1. Concentrations in lettuce from Kolfea and Akaki farm, and Swiss chard from Burayu farm were higher than the maximum limit recommended by FAO/WHO. In the previous study Itanna (1998, 2002) reported that Fe concentrations in lettuce (1345 mg kg-1) and Swiss chard (527 mg kg-1) from Kera farm that were higher than the maximum permissible limits. The average Zn concentrations (mg kg-1) by farm was Gofa (43.72) > Kera (43.33) > Kolfea (37.82) > Akaki (36.95) > Burayu (36.8). This trend could be attributed to the high Zn concentration present in the studied vegetables. The concentrations in the present study were higher than the average of those (mg kg-1) in Swiss chard (22.37), Ethiopia kale (23.45) and lettuce (11.69) from Kera, Goffa and Akaki farms reported by Weldegebriel *et al* (2012). Zn concentration (mg kg-1) in cabbage (31.80), lettuce (48.63) and Swiss chard (56.19) from Kera farm was also reported by Itanna (1998). The average Cu concentration ranged from 3.19-16.11 mg kg-1 in vegetables and across farms from 18.34-33.46 mg kg-1. The high level of Cu in vegetables from Kolfea corresponded to the high soil Cu found there (Table 2). Cu concentrations (mg kg-1) recorded in this study were higher than reported for cabbage (3.03), lettuce (6.62) and Swiss chard (8.06) from Kera farm reported by Itanna (1998)) and Swiss chard, cabbage and lettuce from Kera, Gofa and Akaki farms by Weldegebriel et al. (2012).

The average As concentration was highest (0.14 mg kg-1) in Swiss chard from Gofa farm and lowest (0.03 mg kg-1) in potato from Burayu farm. The values recorded in this study were lower than the threshold levels (0.43 mg kg-1) set by FAO/WHO. Concentrations were also lower than values for lettuce (1.04 mg kg-1) and Swiss chard (1.21 mg kg-1) from Kera farm reported by Itanna (1998). The average concentrations of Co in all the vegetables were below the maximum limit recommended by FAO/WHO. Co concentrations (mg kg-1) in the present study were also lower than reported for lettuce (0.76) and Swiss chard (0.68) from Kera farm reported by Itanna (1998). Average Co concentration (mg kg-1) in Swiss chard (0.82), Ethiopia kale (1.46), lettuce (0.42) and cabbage (0.05) from Kera, Goffa and Akaki farms were also reported by Weldegebriel *et al* (2012). The average concentrations of Ni in all the vegetables were below the maximum limit recommended by FAO/WHO. Swiss chard was the highest (2.76 mg kg-1) accumulators from Burayu farm and Ethiopia Kale was the lowest (0.29 mg kg-1) from Kera farm. Ni concentration (mg kg-1) in the present study was lower in the figures reported for lettuce (1.86) and Swiss chard (2.10) from Kera farm by Itanna (1998).

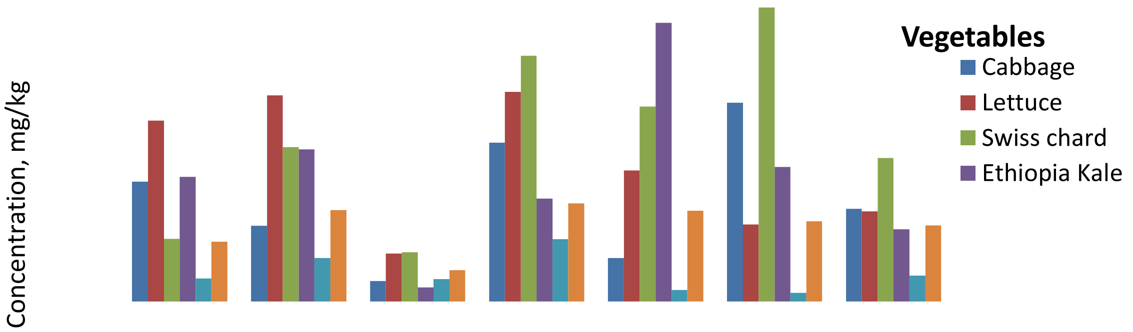

Figure 2: Average concentrations of metals in leafy vegetables. Fe concentrations in all vegetables, Mn in Swiss chard and Sr in cabbage are scaled down by a factor of 10.

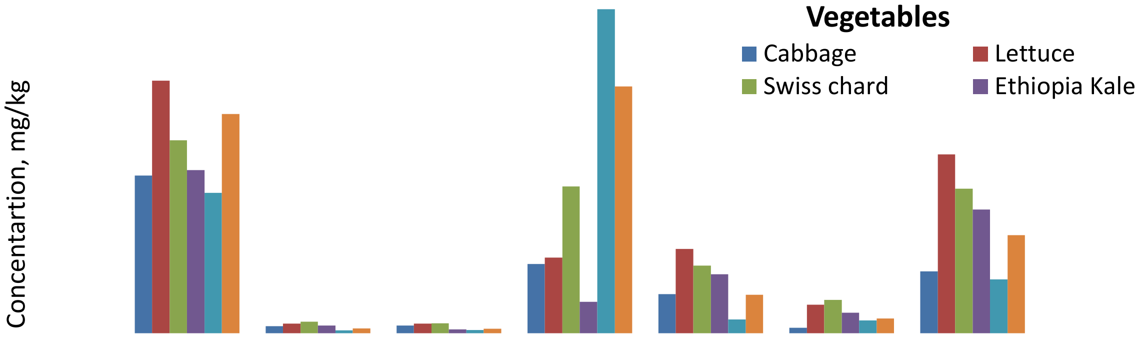

Figure 3: Average concentrations of metals in leafy vegetables. Pb concentrations in potato and carrot are scaled down by a factor of 1000.

There are no thresholds set for Sr, Ba, B and V by international organizations (weight, 1991; Pendias and Pendias, 1992; FAO/WHO-Codex alimentarius commission, 2001). This is probably due to the assumption that their concentrations normally observed in vegetables are not a health concern. As shown in Figure 2 the average concentration of Sr were highest in Ethiopia kale (102.19 mg kg-1) followed by cabbage (65.51 mg kg-1), Swiss chard (45.86 mg kg-1), lettuce (30.76 mg kg-1), carrot (21.32 mg kg-1) and potato (2.71 mg kg-1). The average values of B recorded in the present study were highest in Swiss chard (33.71 mg kg-1) and lowest in potato (6.10 mg kg-1). The uptake capacity of V in all vegetables in the present study was relatively low. The highest average concentration of Ba was detected in in Swiss chard (69.17 mg kg-1) followed by Ethiopia kale (46.71 mg kg-1) and was lowest in potato (1.97 mg kg-1)(Figure 2).

Pearson correlation coefficients were calculated to investigate the relationship between the toxic and potentially toxic elements in soil, irrigation water and concentrations in the various vegetables. The relationships between the average metal concentrations in the three media were relatively weak. However, a strong correlation ($r=0.99$, $P<0.01$) was detected between Burayu irrigation water and soil. Significant but relatively moderate correlations was found between Kera irrigation water and average soil metal content ($r=0.60$, $P<0.01$). The other relationships tested were also relatively weak but suggest that the sources of these metals is to some extent linked in the three media but would need to be further verified, perhaps through experimental cultivation of vegetables using contaminated river water. Relationship between contaminant in the soil, irrigation water and vegetables are complex and dependent on the particular metals and genetic nature of the plant.

The accumulation of toxic metals in the edible parts of vegetables with high concentrations could have a direct impact on the health risks of consumers. They are non-degradable, long biological half-life, less visible, not metabolized and can accumulate in the human body causing damage to the nervous system, dysfunction of kidney, liver, lung, bladder, high blood pressure, prevalence cancer, skin disorders and reproductive system (Kar *et al*., 2008, Lee *et al*., 2007; Lohani *et al*., 2008; Minable *et al*., 2015). Therefore, the concentrations of toxic and potentially toxic element contaminants in vegetables are of concern as vegetables produced from these farms are mostly consumed by residents of the city. Prolonged and frequent human consumption of vegetable contaminated by heavy metals such As, Pb, Ni, Sr and Cd, even at low levels, presents potential human health risk.

4. Conclusion

In Burayu, Kolfea, Kera, Goffa and Akaki vegetable farms in Addis Ababa that were irrigated with contaminated waters displayed increased concentrations of potentially toxic trace element concentrations in the vegetables grown on them. This study shows that there is a correlation between metals in irrigation water, soil and vegetables, indicating potential transfer of heavy metals into the food chain. Since accumulation potential is varied from metal to metal and vegetable to vegetable, the impact on health needs to be evaluated based on the trace element available in the particular vegetable. Cr concentration in lettuce and Swiss chard at Kolfea, carrot and lettuce at Akaki farm, Cd concentration in Swiss chard at Burayu farm, Fe in lettuce at Kolfea and Akaki farm, and Swiss chard from Burayu farm, Pb at all farms except Ethiopia kale at Burayu farm surpassed the maximum limit. These vegetables are supplied to local markets. In these cases, from a health standpoint, consuming lettuce, Swiss chard, carrot, potato and Ethiopia kale may cause serious health risk to consumers. Although the concentrations of some metals established for the vegetables are lower than those permissible limits, in the long run the health risk is depending on the quantities consumed and the frequency of intake.

It may be less risky to eat cabbage and Ethiopian kale than lettuce, Swiss chard, potato and carrot since they contain the lowest concentrations of potentially toxic trace elements. However, the health risk related to these toxic metals depends on the dietary pattern of the consumers. With increase in vegetable consumption the health risk could worsen. Therefore, treatment of wastes from the various factories, analysis of the effluent before being released into nearby environment, together with proper management of municipal, domestic and medical wastes should be a priority in any future remediation program to prevent potential health risks to the inhabitants of Addis Ababa. It is also vital to utilize low cost and globally acceptable wastewater treatment technology (such as constructed wetlands and phytoremediation) to remove toxic elements at the sources. Regular monitoring of the concentration of toxic heavy metals in vegetables consumed is required. In summary, a three pronged approach is required to safeguard human and environment health; waste treatment and disposal, monitoring of potential contaminants in soil, water and vegetables and enforcement of standards.

Acknowledgements

Financial support by the Irish Environmental Protection Agency, Ireland and University of Connecticut-Addis Ababa University project are greatly appreciated. Use of analyses facilities in the laboratory of Inland Fisheries Ireland is duly acknowledged and thanks are due to Dr. Diarmiud Ryan for his expert guidance on chemical analysis. Dr. Mary Kelly Quinn, Dr. Yilma Sileshi and Dr. Dereje Hailu are gratefully acknowledged for their valuable comments and guidance.

References

1. Aktar M., Paramasiva M., Anguly M., Purka S. and Sengupta D., 2010. Assessment and occurrence of various heavy metals in surface water of Ganga River around Kolkata: a study for toxicity and ecological impact. Environmental Monitoring and Assessment, 160 (4) : 207-213
2. Alemayehu, T., 2001. The impact of uncontrolled waste disposal on surface water quality in Addis Ababa, Ethiopia. SINET: Ethiop. J. Sci. 24: 93-104.
3. Anita S., Rajesh K., Madhoolika A. and Fiona M., 2010. Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. Food and Chemical Toxicology 48 : 611–619.
4. Ayers R. S. and Westcot D. W. (1994). Water Quality for Agriculture: FAO Irrigation and Drainage. Paper 29 Rev. 1, FAO, Italy
5. Dowdell C. and Thompson M., 2014. Hot Block Digestion of Soil, Sediment, Waste and Tissue Samples for Total Recoverable Metals. MT-069-1.3.
6. Ewers, U., 1991. Standards, guidelines and legislative regulations concerning metals and their compounds. In metals and their compounds in the environment: occurrence, analysis and biological relevance (Merian, E. ed.), VCH, Weinheim, pp. 458–468.
7. FAO/WHO, 2001. Codex Alimentarius Commission. Food additive and contaminants. Joint FAO/ WHO Food Standards Programme, ALINORM 01/ 12A. pp 1–289.
8. Fernando G., Anderson R., Takashi M., Nericlenes C., and Solange G., 2012. Heavy metals in vegetables and potential risk for human health. Sci. Agric. 69 (1): 54-60.
9. Hagedorn, B. 2008. Acid Digestion of Sediments, sludge and Soil (EPA 3050), Applied Science, Engineering and Technology Laboratory, University of Alaska, Anchorage.
10. Harmanescu M., Alda L., Bordean D., Gogoasa I. and Gergen I., 2011. Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; a case study: Banat County. Romania. Chem. Cent. J. 5 : 64.
11. Hunde D., Njoka J., Asfaw Z. and Nyangito M., 2011. Physico-chemical soil properties of semiarid Ethiopia in two land use systems: Implications to crop production. Int. J.Agric. Res. 6: 840-847.

12. Itanna F., 1998. Metal Concentrations of Some Vegetables Irrigated with Industrial Liquid Waste at Akaki, Ethiopia. Ethiopian Journal of Science 21 (1): 133-44.
13. Itanna F., 2002. Metals in Leafy Vegetables Grown in Addis Ababa and Toxicological Implications. The Ethiopian Journal of Health Development 16 (3): 295-302.
14. Kar D., Sur P., Mandal S., Saha T. and Kole R., 2008. Assessment of heavy metal pollution in surface water. Int. J. Environ. Sci. Tech., 5(1):119-124.
15. Lee C. L., Li X. D., Zhang G., Li J., Ding A. J. and Wang T., 2007. Heavy metals and Pb isotopic composition of aerosols in urban and suburban areas of Hong Kong and Guangzhou, South China Evidence of the long-range transport of air contaminants. Environ. Pollut., 41(2): 43 2-44 7.
16. Lohani M. B., Singh S., Rupainwa D. and Dhar D. N., 2008. Seasonal variations of heavy metal contamination in river Gomti of Lucknow city region. Environ. Monitor. Assess., 147 (1): 253-263.
17. Minbale A., Yilma S., Mary K.Q. and Dereje H., 2015. Potentially Toxic Trace Element Contamination of the Little Akaki River of Addis Ababa, Ethiopia. Journal of Natural Sciences Research, www.iiste.org . 5(1): 1-13**.**
18. Mohamed A. and Khairia M., 2012. Assessment of some heavy metals in vegetables, cereals and fruits in Saudi Arabian markets. Egyptian Journal of Aquatic Research 38: 31–37
19. Nair I., Singh K., Arumugam M., Gangadhar K. and Clarson D., 2010. Trace metal quality of Meenachil River at Kottayam, Kerala by principal component analysis. World Appl. Sci. J., 9(10):1100-1107
20. Pendias A. K. and Pendias H. 1992. Elements of Group VIII. In: Trace Elements in Soils and Plants. CRC Press, Boca Raton, pp.271–276.
21. Radu L. & Anca-Rovena l., 2008. Vegetable and Fruits Quality within Heavy Metals Polluted Areas in Romania. Carpth. J. of Earth and Environmental Sciences, 3(2):115-129
22. Sharma R.K., Agrawal M. and Marshall F., 2009. Heavy metal in vegetables collected from production and market sites of tropical urban area of India. Food Chem. Toxicol. 47: 583–591.
23. Wang Z., Chen J., Chai L., Yang Z., Huang S. and Heng Y., 2011. Environmental impact and site-specific human health risks of chromium in the vicinity of a Ferro-alloy manufactory, China. J. Hazard. Mater. 190: 980-985.
24. Weigert P., 1991. Metal loads of food of vegetable origin including mushroooms. In: Merian E, ed. Metals and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance. Weinheim: VCH, 458-68.
25. Weldegebriel Y., Chandravanshi B. S. and Wondimu T., 2012. Concentration Levels of Metals in Vegetables Grown in Soils Irrigated with River Water in Addis Ababa, Ethiopia. Ecotoxicology and Environmental Safety 77 (1): 57-63.
26. Wilson B. and Pyatt, F., 2007. Heavy metal dispersion, persistence, and bioaccumulation around an ancient copper mine situated in Anglesey, UK. Ecotoxicology and Environmental Safety 66: 224-231.
27. Zarazua G., Avila-Perez P., Tejeda S., Barcelo I. and Martinez T., 2006. Analysis of total and dissolved heavy metals in surface water of a Mexican polluted river by Total reflection X-ray Fluorescence Spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy, 61: 1180-1184.