Pollution, 7(1): 205-216, Winter 2021 *Research Paper*
DOI: 10.22059/poll.2020.308766.877
Print ISSN: 2383-451X Online ISSN: 2383-4501
Web Page: https://jpoll.ut.ac.ir, Email: jpoll@ut.ac.ir

Analysis of heavy metal concentration in some vegetables using atomic absorption spectroscopy

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Received: 23.08.2020 Revised: 20.10.2020 Accepted: 21.11.2020

ABSTRACT: This study assesses heavy metal levels in water, soil, and vegetables (swiss chard, lettuce, cabbage, collard green, tomato, green pepper and carrot) irrigated with waste water in Gamo, Ethiopia. The samples of soils, water, and vegetables were randomly collected, processed, and analyzed for heavy metals using atomic absorption spectrophotometry. The results obtained show that the irrigational water is profoundly contaminated with heavy metals Cd, Cr and Ni and Pb, Zn and Cu had the lowest concentration in irrigation water. The levels of Cd in Kulfo river area and Chamo Lake area and Ni in most of the farm soils were also found to be higher than the guideline values. The study also revealed that the mean levels of Cd in most vegetables and Cr and Pb in some vegetables were higher than the maximum recommended limits set by WHO/FAO. In general the results show that the highest concentration of the heavy metals was obtained from Kulfo river area compared to the Arbaminch textile share company area, Abaya Lake area, and Chamo Lake area. Cabbage was maximally contaminated with potential toxic elements followed by Swiss-chard, carrot, tomato, collard green, green pepper and lettuce. Hence, from kulfo river area frequent consumption of cabbage and Swiss chard may cause serious health risks to consumers. The levels of many elements were found to vary with location, suggesting localized inputs of the various contaminants related to industrial and other activities that generate wastewater. This study recommends regular monitoring of heavy metals in soils, waters, and foodstuffs to prevent excessive accrual in food chain.

KEYWORDS: Pollution, Vegetables, Waste Waters, Soils, food safety.

INTRODUCTION

Vegetables are common diet taken by populations throughout the world, being sources of essential nutrients, antioxidants and metabolites (Thompson *et al.,* 1990). They also act as buffering agents for acid substance obtained during the digestion process. However, both essential and toxic elements are present in vegetables over a wide range of concentrations as they are said to be good absorber of metals from the soil (Lokeshwari and Chandrappa, 2006; Eslami et *al.,* 2007; Karbassi et *al.,* 2014). Reports have shown that, vegetables grown in heavy metal-rich soils are also contaminated (Kawatra and Bakhetia , 2008 ; Sharma *et al.,* 2007). Vegetables absorb these metals from contaminated soils as well as from polluted environmental deposits through the roots and incorporate

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them into the edible part of plant tissues or deposit on the surface of vegetables (Haiyan and Stuanes ,2003; Nwajei, 2009). Some heavy metals such as Cr, Mn, Ni, Zn, Cu, and Fe are considered essential components for biological activities in the body; however, their presence in elevated levels is reported to cause problems to humans (Lokeshwari and Chandrappa, 2006). On the other hand, Pb, Cd, Hg and As are non essential and play toxic role to living organism and hence are considered as toxic elements. A number of factors influence the concentration of heavy metals on and within plants. These factors include climate, atmospheric deposition, the nature of soil on which the plant is grown, application of fertilizers and irrigation with wastewater (Anyanwu *et al.,* 2004; Khairiah *et al.*, 2004). The water of rivers can be polluted by heavy metals such as Pb, Cu, Zn, Fe, Cr, Cd, Hg etc. The major sources of heavy metals are industrial effluents and indiscriminate disposal of domestic or sewage drainage directed to the rivers untreated or partially treated (Itanna, 2002; Nasrabadi e*t al.,* 2015; Nasrabadi e*t al.*, 2018). Currently, in Gamo, Ethiopia there is no regulatory criterion of heavy metals in irrigation water, soils and vegetables. However, due to businesses economic, industrial and other development activities, the levels of heavy metals are increasing in the irrigation water, agricultural soils, vegetables and crops grown in and outside the city. The farmlands along the bank of the river areas are extensively used for crops and vegetable production for the city, but still very little information exists regarding the levels of heavy metals in irrigation waters, soils and vegetables. Therefore, the study aimed to investigate the concentrations of Cd, Pb, Ni, Zn, Cu and Cr in the most frequently consumed vegetables of the Gamo, Ethiopia to compare them with the permissible limits established by World Health Organization/Food and Agriculture Organization (WHO/FAO) guidelines. The results will provide invaluable baseline data for further investigation of heavy metal accumulation in foodstuffs, thereby improving food safety and the health of the inhabitants.

MATERIALS AND METHODS

Arba Minch located at 6°2′N 37°33′E is one of a town in Gamo Gofa Zone, Southern Nations Nationalities and Peoples Region (SNNPR) regional state in Ethiopia found around 500 km away from Addis Ababa, Ethiopia's capital city. The town got its present name Arba Minch, meaning '40 springs' since it has 40 natural springs which is major tourist attraction. Kulfo River, Abaya Lake and Chamo Lake are the water source for many inhabitants in Arba Minch area for farm lands, for domestic activities, etc. The river and lakes have their source from the high lands of Gamo region which have experienced high levels of agricultural development. The farmlands where these lakes and river water were used for irrigation were selected for this study.

The common apparatuses Microwave system, Digit-heat dry oven, flame atomic absorption spectrometry (FAAS, model nov AA 400P, Germany), 25-100 mL volumetric flask, Whatman filter paper No.42, Erlenmeyer flask, conical flask, beakers, measuring cylinder, polyethylene sample bottles and watch glass were used in the experimental work.

Analytical-reagent grade chemicals and deionized water were used to prepare all solutions. The reagents Nitric acid (HNO_3), Perchloric acid ($HClO_4$), & Hydrogen Peroxide (H_2O_2) were used for cleaning glassware and digesting samples throughout the work. The other graphical calibration standard solutions for Pb, Cd, Cr, Zn, Cu & Ni were prepared by sequential dilution of stock standards of 1000 ppm.

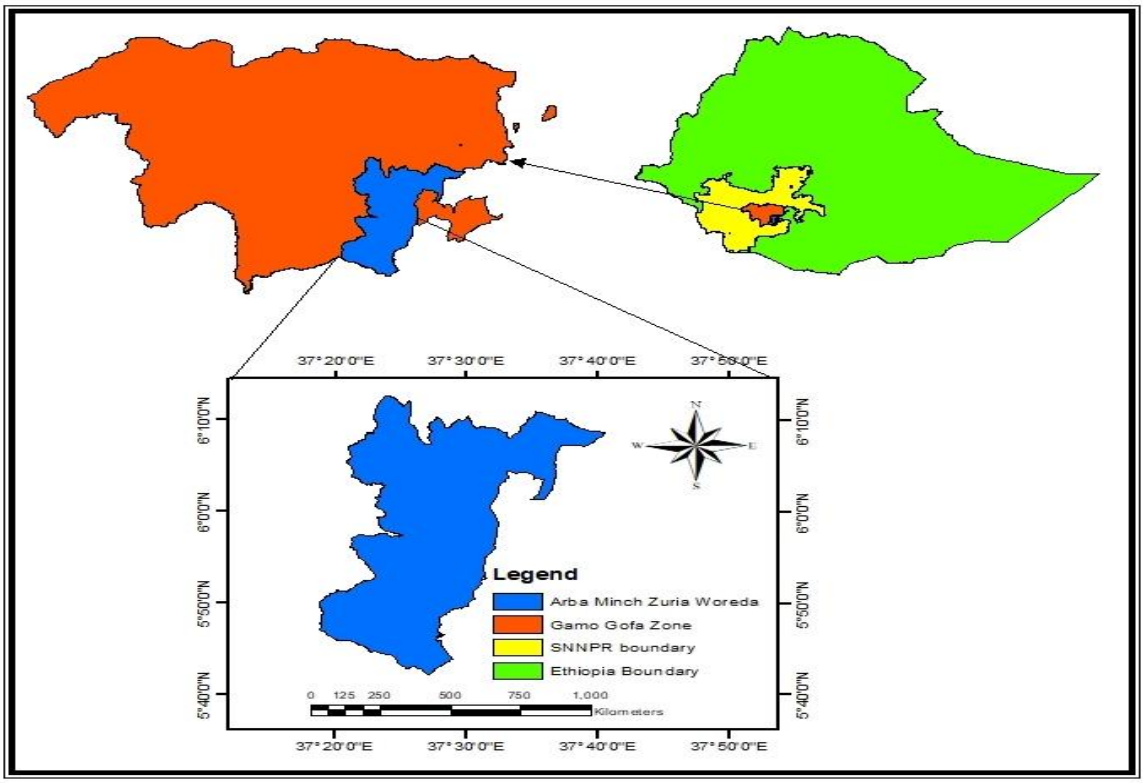

Fig. 1. Location map of Arba Minch Zuriya district

The vegetable samples were collected from four irrigational sites in Gamo, Ethiopia and washed thoroughly with tap water followed by distilled water to remove adsorbed elements. The samples were cut into small pieces and then dried using the oven dry method at 105 °C for 24 hr (Memmert UF 260 plus 230V Sunon model) to obtain (remove) the moisture content. The dry samples were ground to powder and then passed through a 1 mm sift. 0.5 g of sample was taken in reference vessels, 6 ml of 65% HNO_3, 3 ml of 70% $HClO_4$ and 1 ml of 30% H_2O_2 were added and carousel was positioned into microwave unit. The mixture was heated at 80 °C over 3 hr on block digester (microwave digester). After digestion was completed, the clear and colorless solution was filtered using Whatman filter paper No.42 and diluted with deionized water to raise the volume of the solution up to 50 mL (United State Environmental Protection Agency (USEPA) method: 3005A, 1998) and finally stored in plastic bottles for analysis.

Water samples were collected at four sampling sites from diversion points of irrigation in Gamo, Ethiopia in pre-cleaned 100 ml polythene bottles and 2 ml of nitric acid was add as preservative. The collected water samples were brought to the laboratory. 15 ml of water sample was taken in Teflon tubes and 5 ml con. HNO_3 and 1 ml con. H_2O_2 were added. The vessels were closed with a valve and tightened. The mixture was heated at 120 °C over 3 hr on block digester (microwave digester). After digestion was completed, the clear and colorless solution was filtered using Whatman filter paper No. 42 and diluted with deionized water to raise the volume of the solution up to 50 mL (USEPA method: 3005A, 1998) and finally stored in plastic bottles for analysis.

The soil samples (0-20 cm depth) were collected randomly from various localities of the waste water irrigated sites. The 500 g soil sample was placed in polythene bag, dried in an oven and ground to a fine powder which was passed through a 2-mm

mesh sieve. The 1.0 g of soil sample was digested in tri-acid mixture of 65% of HNO_3: 70% of $HClO_4$: 30% of H_2O_2 with 6:4:1 ratio at the ratio 6:4:1 respectively. The solution was heated to 200 ℃ over 3 hr until the cessation of brown fumes from the solution. The solution was filtered through Whatman filter paper no 42. The solution was diluted with deionized distilled water to raise the volume of the solution up to 50 mL (USEPA method: 3005A, 1998). The prepared samples were analyzed the level of heavy metals (Pb, Cd, Cr, Zn, Cu & Ni) by flame atomic absorption spectroscopy (model nov AA 400P, Germany). The details of the samples of vegetables, soils & waters collected from four sites in Ethiopia are illustrated in Table 1.

The prepared samples were analyzed the concentration of heavy metals using flame atomic absorption spectrometry (model nov AA 400P, Germany).

Atomic absorption spectrometry (AAS) is a quantitative method of metal analysis suitable for the determination of approximately 70 elements. This method measures the concentration of the element by passing light of a specific wave length emitted by a radiation source of a particular element through clouds of atoms from a sample. Atoms will absorb light from an energy source known as hollow cathode lamp (HCL). The reduction in the amount of light intensity reaching the detector is seen as a measure for the concentration of a particular element in the original sample. A typical AA spectrometer consists of an energy (light) source, a sample compartment (atomizer) monochromator, a detector, and a data process system (Fig. 2).

Table 1. Samples of vegetables, soils & waters taken from four sites in Ethiopia.

	Sampled	Waste water irrigated site			
		KRA	**ATSHCA**	**ALA**	**CHLA**
Vegetables	Swiss chard	✓	✓	✓	✓
	lettuce	✓	✓	✓	✓
	cabbage	✓	✓	✓	✓
	Collard Greens	✓	✓	✓	✓
	tomato	✓	✓	✓	✓
	Green pepper	✓	✓	✓	✓
	carrot	✓	✓	✓	✓
	Soil	✓	✓	✓	✓
	Irrigation water	✓	✓	✓	✓

Where KRA = kulfo river area, ATSHCA = Arbaminch textile share company area, ALA = Abaya lake area, CHLA = chamo lake area, Right mark (✓) indicates samples collected

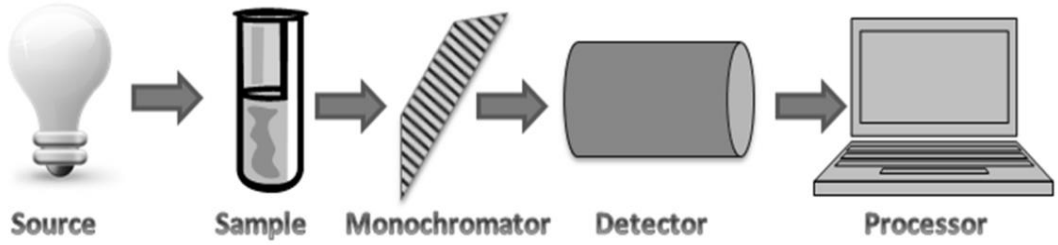

Fig. 2. Basic illustration of atomic absorption spectrometer.

The radiation source is usually a hollow cathode lamp (HCL) or electrode-less discharge lamp (EDL), while different atomizers are used in various AAS techniques, such as flame, a graphite furnace, or a quartz tube. In effect, a monochromator produces monochromatic light by removing lights of unwanted wavelengths from the source light beam. The function of the monochromator is to isolate a single atomic resonance line from the spectrum of lines emitted by the hollow cathode lamp (Helaluddin *et al.*, 2016).

Flame atomic absorption spectrometer (FAAS) is a suitable technique for determining metals at parts per million (ppm) concentration levels with good precision. FAAS requires an oxidant gas in addition to fuel gas to support combustion. Samples are introduced into the atomizer as an aerosol by the nebulizer. FAAS technique provides fast analysis of 10-15s per sample, with very good precision (repeatability), moderate interferences that can be easily corrected, and relatively low cost. FAAS was successfully applied for the determination of heavy metals in various matrices (Helaluddin *et al.*, 2016). The instrumental operating conditions for the determination of heavy metals using FAAS are illustrated in Table 2.

Table 2. Instrumental operating conditions for the determination of heavy metals in wastewater, soil and vegetable samples by FAAS (Dagne, 2017; Deribachew *et al.*, 2015).

Elements	Wave length (nm)	Lamp Current (mA)	Slit Width (nm)	Flame Type
Cd	228.8	2.0	1.2	Air - acetylene
Cr	357.9	6.0	0.7	Air - acetylene
Pb	283.3	5.0	0.7	Air - acetylene
Zn	213.9	5.0	0.7	Air - acetylene
Cu	324.7	4.0	0.5	Air - acetylene
Ni	232.0	7.0	0.6	Air - acetylene

nm : Nano Meter , mA = milli ampere

In order to validate the analytical method, the following method validation parameters such as linearity, precision, accuracy, instrumental detection limit (IDL), limit of detection (LOD), and limit of quantification (LOQ) studies were carried out . The validation method followed the protocol guidelines on International Conference on Harmonization (ICH, 1994).

Analytical grade (Merck, Germany) reagents were used in all the experimental procedures of the research study. All the glass ware and plastic ware used in the experimental work of the research were thoroughly rinsed with 10% HNO_3 solution followed by washing with de-ionized water. To ensure the quality data of samples of research work, each sample was analyzed in triplicate (USEPA method: 3005A, 1998).

RESULTS AND DISCUSSION

As can be seen from Table 3, Calibration curves for the various concentration ranges showed good correlation coefficients ranged between 0.9987and 0.9999, which were all greater than the required limit (0.995) for trace element analysis (USEPA, 2007 ; Christian ,2003). This showed that there was good correlation (or relationship) between concentration and absorbance indicating good calibration of the instrument.

The instrumental detection limits (IDL) ranged between 0.0005 and 0.01 mg/kg which were below the limit of detection (LOD) indicating good sensitivity of the measuring instrument for analysis. The limit of detection (LOD) ranged from 0.075 to 0.372 mg/kg. The limit of quantification (LOQ), value lied in range 0.227 - 1.127 mg/kg the result shows both the LOD and LOQ values were greater

than the IDL; hence, the results of the analysis could be reliable (Temminghoff and Houba, 2004).

The percentage recovery (accuracy) and precision test of samples are given in Table 3. The table shows that the recovery results lie within the acceptable range of 80 – 120% for metal analysis (USEPA, 2008). The precision of the method was expressed as relative standard deviation (RSD) of the three replicate readings. The RSD values obtained in the ranged from 2.110 to 8.543 %, which was under the required control limits ≤ 15% (Csuros and Csuros, 2002). These results indicate that the proposed method was precise and accurate.

The mean concentrations of heavy metals found in the soil, effluent and vegetable samples from four sites of Ethiopia are summarized in Tables 4-6.

Table 3. Validation Parameters

Metals	IDL (mg/kg)[a]	LOD (mg/kg)	LOQ (mg/kg)	Regression Equation	Correlation Coefficient (R^2)	Recovery (%)[b]	RSD (%)
Cd	0.0005	0.153	0.465	y = 0.1247x - 0.003	0.9998	101.294 ± 3.398	3.355
Cr	0.002	0.184	0.558	y = 0.0112x + 0.002	0.9997	98.905 ± 3.578	3.618
Pd	0.01	0.372	1.127	y = 0.0044x + 0.0009	0.9987	99.436 ± 8.495	8.543
Zn	0.0008	0.075	0.227	y = 0.1429x + 0.0277	0.9999	99.265 ± 2.095	2.110
Cu	0.001	0.200	0.606	y = 0.063x - 0.0013	0.9996	98.273 ± 5.608	5.706
Ni	0.002	0.211	0.638	y = 0.0243x + 0.0019	0.9996	98.974 ± 4.515	4.562

[a]Source (Persons & Forster ,1983) for FAAS; [b]Mean ± SD , n = 7 , SD = standard devation , mg/kg : milligram per kilogram , RSD : relative standard deviation

Table 4. Average concentration of heavy metals found in soil farmlands and irrigation water.

Heavy Metals	KRA		ATSHCA		ALA		CHLA		Guidelines for max. levels in	
	water (mg/L)	Soil (mg/kg)	water (mg/L)	Soil (mg/kg)	water (mg/L)	Soil (mg/kg)	water (mg/L)	Soil (mg/kg)	water (mg/L)[a]	Soil (mg/kg)[b]
Cd	0.2605	3.9096	0.185	1.8261	0.1634	1.7512	0.245	3.2113	0.01	3
Cr	0.8402	19.897	0.2567	13.0664	0.4738	16.2893	0.6701	8.2187	0.1	50
Pb	0.0094	13.8313	0.0038	10.4406	0.0024	12.5333	0.0056	11.7341	0.015 [c]	100
Zn	0.3488	52.2735	1.3954	42.5626	0.1461	53.0685	0.0770	68.5274	2	300
Cu	0.4643	48.8125	0.6743	40.8878	1.2759	57.1213	0.366	51.2222	2 [d]	50 [c]
Ni	0.8767	42.1764	0.5609	31.3822	0.3953	19.5129	0.6811	31.3866	0.07 [d]	80 [c]

[a]WHO/FAO (2007), [b]WHO/FAO (2001), [c] USEPA (2010) , [d] WHO (2008) **,** mg/kg : milligram per kilogram, mg/L : milligram per litter

The heavy metals in soil are associated with various chemical forms that relate to their solubility which directly bear on their mobility and biological availability. Heavy metals in soluble form have high relation to their uptake by plants.

As shown in Table 4, the experimental results showed that Cd concentration in soil samples occurred in the range of 1.7512 and 3.9096 mg/kg. The KRA soil was observed to have the highest level (3.9096 mg/kg) of Cd, while the ALA soil had the smallest level (1.7512 mg/kg) of Cd. Being a non-essential metal, it can be considered very toxic. The cadmium level in the farms were in the order of KRA > CHLA > ATSHCA > ALA. The Cd levels from the soils were not significantly different between all the vegetable farms. These indicate that except KRA and CHLA the concentration of Cd in soil samples were below the permissible limit set by FAO/WHO (2001).

The concentration of Cr in soil varied from the range of 8.2187 to 19.897 mg/kg dry weight. The highest mean concentration of the metal was obtained from KRA (19.897 mg/kg) followed by ALA farm (16.2893 mg/kg) and the lowest concentrations were recorded from CHLA

(8.2187 mg/kg). All the average results of the current analysis of Cr were found to be lower than the recommended maximum limits for soils by FAO/WHO (2001).

The Pb contents in the soil samples were found to be within the range of 10.4406 and 13.8313 mg/kg. The highest (13.8313 mg/kg) and lowest (10.4406 mg/kg) contents of Pb occurred in the soils of KRA and ATSHCA, respectively. These indicate that all samples obtained were found to be within the stipulated limit of Pb stated by FAO/WHO which is 99.40 mg/kg.

The other heavy metal determined in the soil samples was Zn. Its concentrations in the soil samples at ATSHCA, CHLA, ALA and KRA sites were 42.5626, 68.5274, 53.0685 and 52.2735 mg/kg, respectively. The sample at CHLA recorded the highest concentration than that of samples at ATSHCA, ALA and KRA. Finally the concentration of Zn in all soil samples was below the permissible limit set by FAO/WHO.

Table 5. Concentration of heavy metals (mg/kg) in vegetables taken from four sites.

Sites	KRA						ATSHCA					
Vegetables	**Cd**	**Cr**	**Pb**	**Zn**	**Cu**	**Ni**	**Cd**	**Cr**	**Pb**	**Zn**	**Cu**	**Ni**
Swiss Chard	0.4524	1.4062	0.4564	27.2354	11.2354	13.8213	0.3313	1.1245	0.1987	23.4859	9.5894	9.4152
Lettuce	0.2537	1.8213	0.3125	22.4562	16.4235	17.7014	0.1897	1.4526	0.1595	18.5642	13.8976	15.8631
Cabbage	0.4185	2.7801	0.4562	14.2563	16.5426	19.8916	0.3281	2.8456	0.2895	10.4586	14.5642	18.6542
Collard Green	0.2304	2.9945	0.2901	10.4568	13.9648	24.9745	0.1887	2.7589	0.1693	8.5642	9.5689	23.3456
Tomato	0.4324	1.8452	0.2812	13.6548	24.2345	26.8945	0.2791	1.5243	0.1623	10.2365	19.5642	24.4538
Green Pepper	0.2394	1.9452	0.2945	9.9865	21.4563	21.8916	0.1714	1.5624	0.1915	5.4568	16.5894	20.6542
Carrot	0.3515	2.0145	0.3912	12.4568	25.2345	25.7865	0.2988	1.7451	0.3056	9.4758	20.5642	21.5917
FAO/WHO (2001)	0.2	2.3	0.3	99.4	73.3	67	0.2	2.3	0.3	99.4	73.3	67

Sites	ALA						CHLA					
Vegetables	**Cd**	**Cr**	**Pb**	**Zn**	**Cu**	**Ni**	**Cd**	**Cr**	**Pb**	**Zn**	**Cu**	**Ni**
Swiss Chard	0.3041	1.2345	0.2956	28.3793	11.5564	5.3914	0.4194	1.0292	0.3477	31.4526	9.9524	11.3121
Lettuce	0.1797	1.5462	0.1895	24.3427	18.5462	9.8756	0.2165	1.6271	0.3009	27.4589	17.4371	16.8123
Cabbage	0.2973	2.0461	0.3125	16.4024	20.6542	11.9517	0.3685	2.1686	0.4218	21.5643	18.4682	17.9453
Collard Green	0.191	2.2451	0.1885	12.2014	16.2457	17.8501	0.2155	2.6527	0.2189	16.8956	14.3566	22.7254
Tomato	0.3152	1.4452	0.1812	15.0882	32.4568	15.3968	0.4057	1.6977	0.2101	19.5641	26.3741	25.8745
Green Pepper	0.1885	1.7854	0.2282	10.6628	29.5463	16.7969	0.2051	1.6362	0.2586	14.5623	23.1016	19.9453
Carrot	0.292	1.6123	0.3156	14.5447	31.4568	15.8259	0.3421	1.9557	0.3524	17.5659	26.0377	23.6895
FAO/WHO (2001)	0.2	2.3	0.3	99.4	73.3	67	0.2	2.3	0.3	99.4	73.3	67

Table 6. Average concentration of heavy metals found in vegetables of all farms (mg/kg).

Heavy Metals	Swiss Chard	Lettuce	Cabbage	Collard Green	Tomato	Green Pepper	Carrot	Guideline value (mg/kg)[a]
Cd	0.38 ± 0.07	0.21 ± 0.03	0.35 ± 0.05	0.21 ± 0.02	0.36 ± 0.07	0.20 ± 0.03	0.32 ± 0.03	0.2
Cr	1.20 ± 0.16	1.61 ± 0.16	2.46 ± 0.41	2.66 ± 0.31	1.63 ± 0.18	1.73 ± 0.17	1.83 ± 0.19	2.3
Pb	0.32 ± 0.11	0.24 ± 0.08	0.37 ± 0.08	0.22 ± 0.05	0.21 ± 0.05	0.24 ± 0.04	0.34 ± 0.04	0.3
Zn	27.64 ± 3.29	23.21 ± 3.72	15.67 ± 4.63	12.03 ± 3.57	14.64 ± 3.86	10.17 ± 3.73	13.51 ± 3.41	99.4
Cu	10.58 ± 0.96	16.58 ± 1.98	17.56 ± 2.61	13.53 ± 2.82	25.66 ± 5.35	22.67 ± 5.35	25.82 ± 4.46	73.3
Ni	9.99 ± 3.55	15.06 ± 3.54	17.11 ± 3.53	22.22 ± 3.07	23.15 ± 5.27	19.82 ± 2.17	21.72 ± 4.29	67

[a] FAO/WHO-codex alimentarius commission (2001). Results are expressed as mean ± SD (n = 4) .

As shown in Table 4 above, the highest level (57.1213 mg/kg) of Cu was found in ALA soil and the soil of ATSHCA had the smallest level (40.8878 mg/kg) of Cu. The USEPA (2010) permissible limit of copper in soil is 50 mg/kg. Hence Cu content in ALA soil (57.1213 mg/kg) and CHLA soil (51.2222 mg/kg) samples were found above safe permissible levels recommended by USEPA (2010). But the content of Cu in soil from irrigational sites of ATSHCA and KRA that contain 40.8878 and 48.8125 mg/kg respectively were below the permissible level.

The soil samples contained Ni in the concentration range of 19.5129 and 42.1764 mg/kg. The highest mean concentration of the Ni metal was obtained from the KRA (42.1764 mg/kg) followed by CHLA farm (31.3866 mg/kg) and the lowest concentrations were recorded from ALA (19.5129 mg/kg). All the average

results of the current analysis of Ni are found to be lower than the recommended upper limits for soils by USEPA (2010).

Water contamination by heavy metals in some areas is practically inevitable due to natural process (weathering of rocks) and anthropogenic activities (industrial, agricultural and domestic effluents). Waste water from the industries of mining, electroplating, paint or chemical laboratories often contains high concentrations of heavy metals, including cadmium (Cd), copper (Cu) and lead (Pb). Heavy metal contamination of agricultural soils from wastewater irrigation is of serious concern since it has implications on human health. A study carried out by Mensah *et al.* (2008) in Ghana using water to which Cd and Pb had been added to irrigate cabbage, carrots and lettuce revealed that Cd and Pb concentrations increased with irrigation water concentrations significantly. In many developing countries it is a common practice to grow vegetables along banks of rivers passing through urban centers. Waters of such rivers have often been reported to be polluted by heavy metals (Othman, 2001). The extent of absorption of the elements by the plant depends on among other things, the nature of the plant, and chemical constitution of the pollutant, concentration of the element in the soil, pH and the interaction with other metals. Water pollution by heavy metals is mainly caused by point source emissions from mining activities and a wide variety of industries (Nazif *et al.*, 2006).

The data presented in Table 4 show that high concentrations (mg/L) of toxic heavy metals were found in the effluent samples from some of the sites. The concentration of Cd in the effluent was found to be the lowest (0.1634 mg/L) in the samples collected from ALA and the highest (0.2605 mg/L) in the samples collected from KRA. The concentration of the same metal was found to be 0.1850 mg/L in the effluent collected from ATSHCA site. The concentration of Cr in the effluents varied from 0.2567 mg/L for the sample collected from ATSHCA site to 0.8402 mg/L for the sample collected from KRA. The highest concentration of the metal (0.8402 mg/L) was observed in the effluent sampled from KRA site. However, the highest concentration in the effluent sample was found to be that of Pb, which ranged from 0.0024 mg/L for the sample collected from ALA to 0.0056 mg/L for the sample collected from CHLA and 0.0094 mg/L for the sample obtained from KRA. The highest concentration (0.0094 mg/L) of this heavy metal was detected in the effluent collected from KRA. The concentration of Cu in the effluent ranged from 0.3660 mg/L for the sample collected from CHLA and 0.4643 mg/L for the sample collected from KRA to 0.6743 mg/L for the sample collected from ATSHCA and 1.2759 mg/L for the sample collected from ALA. The concentrations of Ni in wastewater samples were found in the range of 0.3953 to 0.8767 mg/L. These values were found to be higher than the recommended limit of Ni for irrigation water set by WHO (2008). The concentration of Zn in water samples collected from irrigational sites ranged from 0.0770 to 1.3954 mg/L. The maximum concentration of Zn is observed in ATSHCA and the minimum in CHLA sample. The results indicate that the mean concentration of Zn obtained from the effluent water samples which is used to irrigate the vegetable farms was lower than the recommended maximum level for irrigation water set by WHO/FAO (2007). In general, the results obtained show that the effluent samples are profoundly contaminated with these heavy metals. Therefore, attention should be focused on regular monitoring and control of wastewater used for irrigation.

Table 5 & 6 are shown the concentration of heavy metals investigated in some vegetables i.e. Swiss chard, lettuce, cabbage, collard green, tomato, green pepper and carrot from four vegetable irrigational and

farming sites of Ethiopia, namely Kulfo River Area (KRA), Arbaminch Textile Share Company Area (ATSHCA), Abaya Lake Area (ALA) and Chamo Lake Area (CHLA). The results are expressed as mean ± SD of the three replicate analyses**.** The heavy metal levels determined were based on plants' dry weight. Vegetables can absorb metals from soil as well as from deposits on the parts of the vegetables exposed to the air from polluted environments (Haiyan and Stuanes, 2003). Toxicity from heavy metals can directly affect physiology of plant structure and plant growth, and many cases of toxicity from heavy metals have been reported. A study carried out by Jorgensen *et al.* (2005) show that, intensive horticultural systems in urban areas may be threatened by soil toxicity through trace elements such as Zn, Cu, As & Pb.

The Cd content was highest in Swiss chard from CHLA (0.4194 mg/kg) and KRA (0.4524 mg/kg) farms and the lowest in green pepper (0.1714 mg/kg) collected from ATSHCA farm. The Cd content in all vegetables from all farms, except lettuce, collard green and green pepper from ATSHCA and ALA farms surpassed the maximum permissible limit as shown in Table 5. The high concentration of Cd in the vegetables might be due to the use of untreated industrial effluent. Applications of untreated industrial effluent build up the concentration of metal in the soil (Chary *et al.,* 2008). From the soil, metals can transfer to the vegetables and accumulate in the tissues of vegetables. Several compounds of Cadmium are used in chemical industries and in the manufacture of pesticides, and herbicides used in agriculture (Ogundele *et al.,* 2015). Cd is more soluble as compared to other metals and hence it can accumulate more into the vegetables tissues (Farid *et al.,* 2015). The permissible limit of Cd proposed by FAO/WHO (2001) in the plant tissue is 0.20 mg/kg. The efficiency of plants to absorb metals can be evaluated by their metal uptake ability or soil to plant transfer factor (Farid *et al.,* 2015).

Exposure of humans to chromium may occur through breathing, drinking, or eating food containing chromium or even through skin contact. Exposure to elevated levels of chromium leads to skin irritation, ulceration, damage to circulatory and nerve tissues which cause health problems. However, daily uptake of it within a certain range of concentrations (up to 200 μg/day) by human beings and animals is considered to be essential for carbohydrate and lipid metabolism (Girmaye, 2012).

The concentration of chromium at different vegetable farms were distributed as follows: Lettuce from 1.4526 mg/kg in ATSHCA to 1.8213 mg/kg in KRA; Swiss chard from 1.0292 mg/kg in CHLA to 1.4062 mg/kg in KRA; cabbage from 2.0461 mg/kg in ALA to 2.8456 mg/kg in ATSHCA; collard green from 2.2451 mg/kg in ALA to 2.9945 mg/kg in KRA; tomato from 1.4452 mg/kg in ALA to 1.8452 mg/kg in KRA; green pepper from 1.5624 mg/kg in ATSHCA to 1.9452 mg/kg in KRA and Carrot from 1.6123 mg/kg at ALA farm to 2.0145 mg/kg in KRA. Chromium concentrations were not significantly higher in Lettuce, collard green, tomato, green pepper and Carrot between the farms. The result Cr content in cabbage and collard green from four irrigational sites, Ethiopia were higher than permissibility level set by FAO/WHO (2001) is 2.3 mg/kg.

Table 5 shows Pb concentrations in vegetables at various farms. The Pb concentration ranges between 0.1595 mg/kg in Lettuce at ATSHCA and 0.4564 mg/kg in Swiss chard at KRA. The Swiss chard had the highest mean concentration of Pb from KRA followed by cabbage from KRA and again cabbage from CHLA farms. The results indicate that the Pb levels in some of the vegetables obtained from KRA & CHLA farms surpassed the maximum permissible limit of FAO/WHO

(2001) but Pb contents in vegetables from the other two sites were on the safe limit as shown in Table 5.

In this study, results show that the levels of zinc in the vegetables studied had a range from 5.4568 mg/kg in green pepper from ATSHCA to 31.4526 mg/kg in Swiss chard from CHLA and the FAO/WHO permissible limit is 99.4 mg/kg. All the vegetables exhibited very low concentration compared to the permissible limit set by FAO/WHO (2001). The concentration of Zn in vegetables was found to be in the order of Swiss chard > lettuce > cabbage > tomato > carrot > collard green > green pepper.

Copper is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation (Martinez and Motto 2000). Copper showed maximum concentration in tomato (32.4568 mg/kg) and the minimum in Swiss chard (11.5564 mg/kg) in samples collected from ALA. In samples collected from CHLA the highest concentration of Cu was found in tomato (26.3741 mg/kg) and the lowest in Swiss chard (9.9524 mg/kg). And also Cu showed maximum concentration in carrot (25.2345 mg/kg) and the minimum in Swiss chard (11.2354 mg/kg) in samples collected from KRA. In samples collected from ATSHCA the highest concentration of Cu was found in carrot (20.5642 mg/kg) and the lowest in collard green (9.5689 mg/kg). The FAO/WHO (2001) maximum limit for Cu concentration in vegetables is 73.3 mg/kg. The results obtained in this study were lower than the recommended limit.

Nickel is required in minute quantity for body as it is mostly present in the pancreas and hence plays an important role in the production of insulin whose deficiency results in the disorder of the liver (Khan *et al.*, 2008). As can be from Table 5, the concentration of Ni ranged from 5.3914 to 26.8945 mg/kg in vegetable samples collected from the four irrigational sites of Gamo, Ethiopia. The highest concentration of Ni was found in tomato: 26.8945 mg/kg from KRA followed by again tomato: 25.8745 mg/kg from CHLA and lowest concentration of 5.3914 mg/kg was recorded in Swiss chard sample from ALA. The results obtained in this study were lower than the recommended maximum limit set by WHO/FAO (2001).

The high concentration of trace heavy metals present in the parts of the vegetables may be due to the absorption ability of the plants to get the trace heavy metals from the polluted soils. In general the results show that the highest concentration of the heavy metals was obtained from Kulfo river area as compared to Abaya Lake area, Chamo Lake area and Arbaminch textile share company area. Higher concentration of heavy metals in the KRA farms were probably due to industrial wastes from textile industry, fertilizers, pesticides, sewage sludge, cement waste, and metal production waste which dispose its effluent directly into the river.

CONCLUSION

The concentration of elements varied greatly among vegetables species and sampling locations which may be attributed to a differential absorption capacity of vegetables for different toxic elements. In general the results show that the highest concentration of the heavy metals in soils, waters and vegetables were obtained from Kulfo river area as compared to the Chamo lake area, Arbaminch textile share company area and Abaya lake area. These results obtained well similar with previous published works (Tsade, 2016). The high levels of heavy metals found in KRA might be closely related to the pollutants found in irrigation water and farm soil contaminated by metal production waste, cement waste, sewage sludge and stone crashing waste or due to pollution from the highway traffic. Furthermore, agronomic practices such as

the application of fertilizer, pesticides and water managements on growing these vegetables could be affecting the accumulation of these heavy metals. Thus regular monitoring of these toxic heavy metals from effluents and sewage in foods is essential to prevent their excessive build-up in the food chain.

ACKNOWLEDGMENT

The authors are thankful to physics department of Addis Ababa University (AAU) and chemistry department of Arba Minch University (AMU) for laboratory facilities.

GRANT SUPPORT DETAILS

The present research has been financially supported by Arba Minch University (AMU) & Addis Ababa University (AAU).

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

REFERENCES

Anyanwu, E.C., Ijeoma Kanu, E.J.E. and Saleh, M.A. (2004). Bioavailable of lead concentration in vegetable plants grown in soil from a reclaimed industrial site: Health implications. Int.J.Food Saf.,6, 31-34 .

Chary, N.S., Kamala, C.T. and Raj, D.S.S. (2008). Assessing Risk of Heavy Metals from Consuming Food Grown on Sewage Irrigated Soils and Food Chain Transfer. Ecotox. Environ. Safe., 69, 513-524.

Christian, G.D. (2003). Analytical Chemistry sixth Edition, John Wiley and Sons, New York.

Csuros, M., Csuros, C. (2002). Environmental sampling and analysis for metals. CRC Press, USA.

Dagne,B.B. (2017). Levels of Some Toxic Heavy Metals in Selected Vegetables, Soil and wastewater Around Eastern Industry Zone, Central Ethiopia, MSc. Graduate project, Haramaya University, Haramaya, Ethiopia.

Deribachew, B., Made, M., Nigussie-Dechassa,R. and Abi,M. T. (2015). Selected heavy metals in some vegetables produced through wastewater irrigation and their toxicological implications in eastern Ethiopia . Afr. J. Food Agric. Nutr. Dev., 15,10013-10032 .

Eslami, A., Khaniki, Gh.R.J., Nurani, M., Meharasbi, M., Peyda, M. and Azimi, R. (2007). Heavy metals in edible green vegetables grown along the sites of the Zanjan roads Iran. J. Biol. Sci., 7, 943-948 .

FAO/WHO. (2001). Codex Alimentarius Commission. Food additive and contaminants, Joint FAO/ WHO Food Standards Programme, ALINORM 01/12A.

Farid, G., Sarwar, N., Saifullah ,U., Ahmad, A., Ghafoor, A. and Rehman, M. (2015). Heavy Metals (Cd, Ni and Pb) Contamination of Soils, Plants and Waters in Madina Town of Faisalabad Metropolitan and Preparation of GIS Based Maps. Adv. Crop Sci. Tech., 4(1), 1-7.

Girmaye, B. R. (2012). Heavy metal and microbial contaminants of some vegetables irrigated with

wastewater in selected farms around Adama town, Ethiopia. MSc. Graduate project, Haramaya University, Haramaya, Ethiopia.

Haiyan, W. and Stuanes, A. (2003). Heavy Metal Pollution in Air-Water-Soil-Plant System of Zhuzhou City, Hunan Province, China. Water Air Soil Pollut., 147, 79-107 .

Helaluddin, A.B.M., Reem,S.K., Mohamed,A. and Syed, A.A. (2016). Main Analytical Techniques Used for Elemental Analysis in Various Matrices. Trop. J. Pharm. Res., 15 (2) , 427-434 .

International Conference on Harmonization (ICH). (1994). Validation of Analytical Procedures: Text and Methodology. Downloaded from: http://www. *ich.org/fileadmin/Public/Web_Site/ICH_Products/ Guidelines/Quality/Q2_R1/Step4/Q2_R1_Guideline . pdf., 19/04/2011*.

Itanna, F. (2002). Metals in leafy vegetables grown in Addis Ababa and toxicological implications. Ethiop. J. Health Dev., 6, 295- 302 .

Jorgensen, N., Laursen, J., Viksna, A., Pind, N. and Holm, P.E. (2005). Multi-elemental EDXRF mapping of polluted soil from former horticultural land. Environ. Int., 31(1) , 43-52 .

Karbassi, A., Nasrabadi, T., Rezai, M., & Modabberi, S. (2014). Pollution with metals (As, Sb, Hg, Zn) in

agricultural soil located close to Zarshuran gold mine, Iran. Environmental Engineering & Management Journal, 13(1):115-122.

Kawatra, B.L. and Bakhetia P. (2008). Consumption of heavy metal and minerals by adult women through food in sewage and tube-well irrigated area around Ludhiana city (Punjab, India). J. Hum. Ecol., 23, 351-354 .

Khairiah, J., Zalifah, M.K., Yin, Y.H. and Aminha, A. (2004). The Uptake of Heavy Metals by Fruit Type Vegetables Grown in Selected Agricultural Areas. Pak. J. Biol. Sci., 7,1438-1442 .

Khan, S.A., Khan, L., Hussain, I., Marwat,K.B. and Akhtar, N. (2008). Profile of heavy metals in selected medicinal plants. Pak. J. Weed Sci. Res., 14(1– 2): 101–110 .

Lokeshwari, H. and Chandrappa, G.T. (2006). Impact of heavy metal contamination of Bellandur Lake on soil and cultivated vegetation. Curr. Sci., 91, 622-627 .

Martinez, C. E. and Motto, H. L. (2000). Solubility of lead, zinc and copper added to mineral soils. Environ. Pollut., 107(1), 153–158 .

Mensah, E., Allen, H.E., Shoji, R., Odai, S.N., Kyei-Baffour, N., Ofori, E. and Mezler, D. (2008). Cadmium (Cd) and Lead (Pb) Concentrations Effects on Yields of Some Vegetables Due to Uptake from Irrigation Water in Ghana. Int. J. Agric. Res., 3, 243-251 .

Nasrabadi, T., Maedeh, P. A., Sirdari, Z. Z., Bidabadi, N. S., Solgi, S., & Tajik, M. (2015). Analyzing the quantitative risk and hazard of different waterborne arsenic exposures: case study of Haraz River, Iran. Environmental earth sciences, 74(1), 521-532.

Nasrabadi, T., Ruegner, H., Schwientek, M., Bennett, J., Fazel Valipour, S., & Grathwohl, P. (2018). Bulk metal concentrations versus total suspended solids in rivers: Time-invariant & catchment-specific relationships. PloS one, 13(1), e0191314.

Nazif, W., Perveen, S. and Shah, S.A. (2006). Evaluation of irrigation water for heavy metals of Akbarpura area. J. Agric. Biol. Sci., 1(1),51-54 .

Nwajei, G.E. (2009).Trace elements in soils and vegetations in the vicinity of shell Petroleum Development Company operating area in Ughelli, delta state of Nigeria. Am.-Eurasian J. Sustain. Agric., 3, 574-578 .

Ogundele, D.T., Adio, A.A. and Oludele, O.E. (2015). Heavy Metal Concentrations in Plants and Soil along Heavy Traffic Roads in North Central Nigeria. J. Environ. Anal. Toxicol., 5(6), 1-5 .

Othman, O.C. (2001). Physicochemical characteristics of some locally manufactured edible vegetable oils marketed in Dar es Salaam. Tanz. J. Sci., 27, 1-10 .

Parsons, M.L. and Forster, A.L. (1983). Applied Spectroscopy, 37, 411-418.

Sharma, R.K., Agrawal, M. and Marshall, F.M. (2007). Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. Ecotoxicol. Environ. Saf., 66, 258-266 .

Temminghoff, E..J., Houba, V.J. (2004). Plant Analysis Procedures Second Edition. Kluwer Academic Publishers, Netherlands.

Thompson, H.C. and Kelly, W.C. (1990). Vegetable Crops, 5th Edn., McGraw Hill Publishing Company Ltd., New Delhi.

Tsade, H.K. (2016). Atomic absorption spectroscopic determination of heavy metal concentrations in kulufo river, arbaminch, gamo gofa, Ethiopia. J Environ Anal Chem 2016, 3:1. DOI: 10.4172/2380-2391.1000177

United State Environmental Protection Agency (USEPA) Method 3005A. (1998), Acid digestion of water for total recoverable or dissolved metals for analysis by FLAA or ICP-Spectroscopy.

USEPA. (2007). Solutions to Analytical Chemistry Problems with Clean Water Act Methods. EPA 821-R-07-002, Washington, DC.

USEPA. (2008). National Functional Guidelines for Superfund Organic Methods Data Review. USEPA-540- R08-01, Washington, DC.

USEPA. (2010). Risk-based concentration table. United State Environmental Protection Agency,

Washington, DC, USA.

WHO. (2008). Guidelines for Drinking Water Quality, 3rd edition.

WHO/FAO. (2007). Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission 13th Session. Report of the Thirty Eight Session of the Codex Committee on Food Hygiene, Houston, United States of America, ALINORM 07/ 30/13.