Research Article

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Heavy Metal Concentration And Health Risk Assessment In Soil, Vegetables, And Water Of Central Rift Valley, Ethiopia

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Abstract

Background

Several heavy metals are toxic to organisms including human and therefore their entry into food chain from polluted agricultural land is required to be controlled. The objective of this study was to investigate the impact of industrialization on the quality of agricultural products and environments in the area of the central rift valley, Ethiopia. The samples of soils, water, and vegetables were randomly collected, processed, and analyzed for heavy metals using microwave plasma atomic emission spectroscopy (MP-AES). Also, it examines potential health risks from the consumption of these vegetables.

Results

The result shown the average concentration gradient of metals in the soil, water, and vegetables (ppm) was Ni<Co< Cd<Pb<Cu<Cr<Zn<Mn<Fe. According to the statistics, Pearson cross-correlation analysis results for the element pairs of Co-Ni (0.879), Cr-Cu (0.582), Fe-Cr (0.597), Fe-Cu (0.581), Fe-Pb (0.587) and Fe-Cu (0.694) were showed the highest and positive. Metals with the highest positive correlations indicated that the same behavior in the environment, increasing or decreasing together in the environment. The correlations obtained between Cr-Mn, Cr-Zn, Cu-Mn, Cu-Zn, Mn-PB, and Ni-Zn was the moderately highest among the others. The moderately high correlations between these metals indicated that the pollutants possibly shared the same source, whereas the others may have arisen from individual sources in the region. Moreover, the soil concentrations of Fe, Mn, Zn, and Cr were also high and higher compared with the level of different countries' standards. The average daily intake for Pb(7.79), Fe(2755.38), Zn(55.83) and Cu(639.05) mg/person/day were above the permissible maximum tolerable daily intake of 0.21, 15, 15, 2.0mg/person/day endorsed by WHO/FAO. Hazard quotient of Pb, Fe, Zn, Zn, Mn and Cu as well as the hazard indices of selected vegetables were exceeded unity, signifying presence of health risks from consumption of the vegetables.

Conclusion

Based on the results of this study, heavy metals had a significant health risk (both non-carcinogenic and carcinogenic) effects to the consumer associated with the consumption of these vegetables grown within the study area. Consequently, we recommend a strict regulatory control on the safety of vegetables originated from the study area and food chain.

Keywords: Heavy Metals, Soil, Water, Vegetables, Assessment And Contamination

Introduction

Environmental pollution by the heavy metals and a direct result of human, social and industrial activities associated the food safety are a major global concern now adays. The incensement of urbanization has led to the pollution soil, water, vegetables and degradation of ecosystems, especially in municipal rivers in developing countries [1-3]. The impact of the industrialization process rank was higher among contributors to environmental pollution and degradation of the ecosystem. Among the industrialization, metal mining, smelting and meat processing, oil and gas exploration, petrochemical manufacturing and such other industrial activities have a severe impact on the fragile ecosystem. These negative impacts on the environment are from direct results of production activities or by the release of waste and by-products which often are toxic heavey metals in their untreated states [4, 5].

Heavy metals are among the major contaminants of food supply(soil, water and vegetables) and can be found on the surface. Its may be considered a major problem for our environment. The issue of heavy metals toxicity effect getting more serious all over the world especially in developing countries[6-9].Toxic heavy metals are not biodegradable, have long biological half-lives and potential for accumulation in the different body organs leading to unwanted side effects [10-12]. In Ethiopia, many researchers have been conducted on the waste discharging factors of the country showed high toxic heavy metals contaminants on the environments. The identified heavy metals(Cr, Cd, Pb, As, Hg,Ni, Zn, Cu) as a risk to human health through the consumption of vegetable crops[13, 14]. Different authors also reported the wasts of the cities and industries in Ethiopia is far from the prescribed limits and standards given by the EEPA and/or WHO [15-18].

Small and medium scale industries, which are established along the banks of the River discharge wastes into the environment and considered as amajor source of heavy pollution to the environment. These industries are working mainly on the food processing, beverages, textiles, chemicals, metal processing, and tanneries. Industrial effluents which discharged from the textile and tannery contain a higher amount of metals especially chromium, copper, and cadmium. These effluents released on the land as well as dumped into the surface water which ultimately leaches to groundwater and leads to contamination due to the accumulation of toxic metallic components and resulted in a series of well-documented problems in living beings because they cannot be completely degraded[19, 20].

The danger of this to human binges is bladder, skin, lung cancer, kidney failure, damage to the nervous system, especially in children, carcinogenic-accumulates in kidneys [21-24]. Hence, industrial effluents offer a wide scope of environmental problems and health hazards are becoming more complex and critical in Ethiopia. Furthermore, there is limited data available for most of these contaminants from the majority of the region in Ethiopia. The absence of detailed studies on heavy metal contaminates assessment and their mitigation practices initiated this study with the objectives of assessing and determining the accumulation of heavy metals on surface or irrigation water sources, soil, and agricultural fields. Therefore, this study attempts to assess the level of heavy metals contaminants in the central rift valley of Ethiopia in major vegetable productive areas and provide a recommendation based on information for best waste management and remediation techniques. In the present context of the study, particular emphasis is placed on the status of metals in different industries effluent, polluted water body, soils, and vegetables grown in contaminated areas.

Materials And Methods

Study Area

This study was conducted in the central rift valley of Ethiopia at Melkassa Agricultural Research Center. The Center located at adistance of about 117 km southeast of Addis Ababa in centeral rift valley of Oromia Regional State. It has a latitude of 8°24'N and longitude of 39°12'E with an elevation 1550-1650 meters above sea level. The area includes many small-and large-scale industrial facilities as well as agricultural land, with around 75 % of the area suitable for farming. The central rift valley areas are the home for many industries including medium-sized leather and textile factories, plastic factory, edible oil; factories and other related factories.

Study Design

A cross-sectional survey was conducted to assess the level of heavy metal contamination on the main study areas, vegetables, soil, and water found in the central rift valley. Based on the survey the specific sampling areas and times were identified. The samples (vegetables, soil, and water) were collected and analyzed the heavy metals such as cadmium (Cd), lead (Pb), chromium (Cr), iron (Fe), zinc (Zn), nickel (Ni), cobalt (Co) and copper (Cu) concentrations using microwave plasma atomic emission spectroscopy (MP-AES).

Sample Collection

The sampling areas used in this study were chosen based on the preliminary survey. Sixty-four (64) samples were taken mostly from the southern and south-southwestern parts of the central rift valley district(Figure 1) at intervals by taking into consideration the dominant pollution, stack emissions, pollution source areas, and particles. The fresh vegetables (cabbage, lettuce, tomato, and onion) were collected from central rift valley, Ethiopia vegetable farms using a random sampling technique method according to methods used by Fisseha (1998) [25]. All samples were collected in a sterilized universal container and plastic bags. Then, transported to Melkassa Agricultural research center food science and nutrition laboratory for laboratory processing. The detailed sample description is presented in Table 1.

Table 1: Description of samples collected

locations	Number of samples	Sample types
Bole(Bishola Awash)	7 3 2 4 3 1	Soil Water Cabbage(*Brassica oleracea,var.capitata*) Tomato (*Solanum Lycopersicum*) Onion (*Allium cepa*) Lettuce(*Lactuca sativa*)
Dufundufiye	5 1 3 2 2	Soil Water Lettuce(*Lactuca sativa*) Tomato (*Solanum Lycopersicum*) Cabbage(*Brassica oleracea,var.capitata*)
Edibesto	11 2 8	Soil Water Tomato (*Solanum Lycopersicum*)
Kela-59	4 3 2 1	Soil Onion (*Allium cepa*) Tomato (*Solanum Lycopersicum*) Cabbage(*Brassica oleracea,var.capitata*)

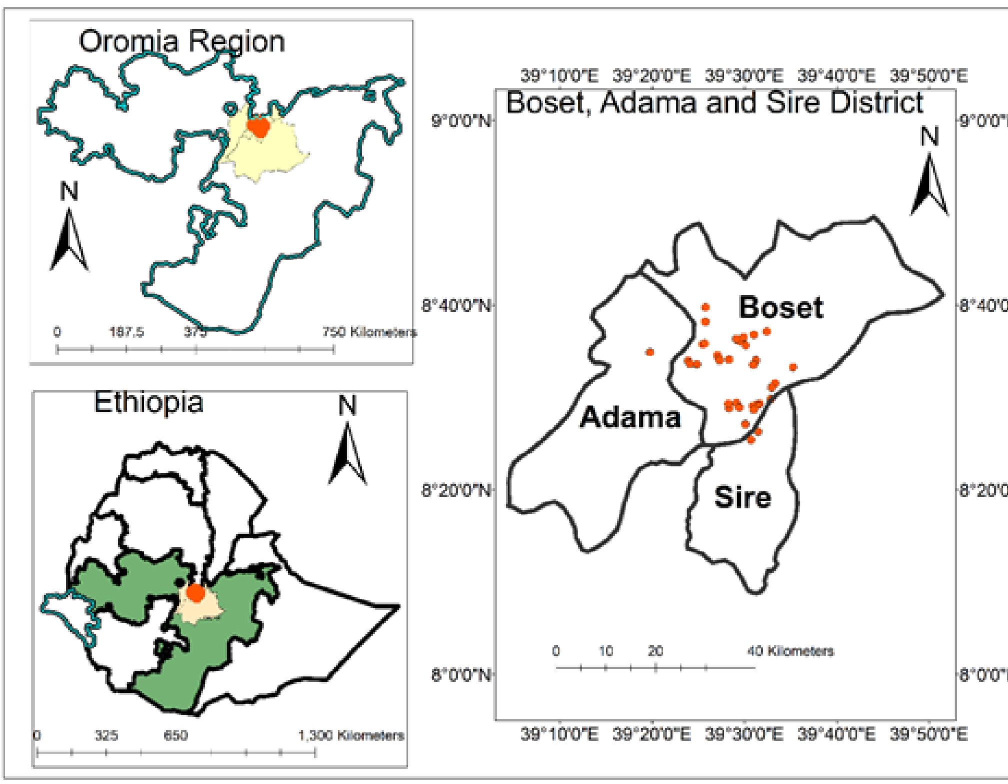


Figure 1: The location of the study area in central rift valley, Ethiopia

Sample Preparation and Analysis

Soil: The collected soil samples were air dried in a dry and dust free place at room temperature (25˚C) for 5 days, followed by an oven dry until constant weights were attained. The samples were then ground with a mortar and pestle to pass through a 2 mm sieve and homogenized. The dried, sieved, and homogenized soil samples were finally stored in polyethylene bags and kept in desiccators until digestion and analysis. Afterwards, thorough digestion of the representative samples was done. For each sample, 1g was digested in 10mL of 1 :1 HNO3 and heated to 95^{o}C to dry and thereafter refluxed for 10 minutes without boiling. After cooling, 5mL of concentrated HNO3 was once again added and refluxed for 30 minutes till brown fumes were produced. The process of adding 5mL of concentrated HNO3 was repeated over and over till white fumes appeared.The solutionwas vaporized to about 5 onmantle set at 95°C with a watch glass over it. After cooling the resulting sample, 2mL of H2O and 3mL of 30% H2O2 were added and the solution was placed on the micro wave dageter to start the oxidation of peroxide until effervescence subsided.The vessel was cooled and the acid-peroxide digestate heated to about 5mL at 95°C. Later, addition of 10mL concentrated HCl to the sample digestwas done and the solution was placedon the heating source and refluxed for 15minutes at 95°C. Finally, the digestate was filtered and the filtrate collected for analysis of heavy metals in the microwave plasma atomic emission spectroscopy (MP-AES)[26].

Vegetables

Vegetable samples were washed with distilled water to eliminate suspended particles. The leafy stalk was removed from all samples and these were sliced and dried on a sheet of paper to eliminate the excess moisture, and then carefully dried in an oven at 70°C for 24 h. 100g of the plant material was weighed and ground in a pestle and mortar for further extraction through microwave extraction followed by the standard procedures[27, 28].

Water

The collected water samples were acidicfied by adding adding 2mLof concentrated HNO3 and 5mL of concentrated HCl to a 100mL aliquot of collected water sample. The solution was covered with a watch glass and heated at 95°C till volume reduced to 15mL before being allowed to cool. Thereafter, the final volume was adjusted to 100mL with distilled water and replicates were processed on a routine basis to determine precision.The concentrations of heavey metals in the filtrate of water were determined using the microwave plasma atomic emission spectroscopy (MP-AES).

Heavy Metal Analysis By Mp-Aes

The heavy metal analyses of the soil, vegetable, and water samples with three repetitions were carried out by using microwave plasma atomic emission spectroscopy (MP-AES). The heavy metals (Cd, Co, Cu, Cr, Pb, Fe, Ni, and Zn) analysis adjustment of the operating condition was a very essential target. The instrument's setting and operational conditions (wavelength, slit width, the limit of detection, etc) were adjusted following the manufacturer's specifications for the analysis of (Cd, Co, Cu, Cr, Pb, Fe, Ni, and Zn). The instrument was calibrated with analytical grade metal standard stock solutions within triplication. The serious of standard solutions of heavy metals were prepared for the calibration curve.

Quality Assurance Analysis

Assessment of contamination and reliability of data was done as part of quality control measure. Blank samples were analyzed after every ten reading of samples for the purpose of ensuring that obtained results are within the range.The levels of heavy metals were calculated based on a dry weight and all the samples were triplicated. The standard reference materials (SRM) for each heavey metal obtained from the Sigma-Aldrich standareds were used to check for accuracy and precision of analysis of each metal and caliberation curve development.

Soil-Plant Transfer Coefficient (%)

The soil-transfer coefficient was calculated as ratio of a heavy metal in a plant (dry weight) to a total heavy metal concentration in the soil as shown in the following equation:

$$\text{TC} = \frac{C\,plant}{C\,soil} \times 100$$

where TC is transfer coefficient (%), *C*plant is heavy metal concentration in vegetable tissue (ppm), and *C* soil is metal concentration in soil (ppm dry soil).

Average daily intake (adi).

The ADI of a heavy metal was calculated as a product of average vegetable daily consumption per person, percentage of dry weight of vegetables, and average heavy metal concentration per dry weight vegetable as shown in the following equation:

ADI = Av consumption ×%DWvegetable × *C* heavy metal,

where ADI is average daily intake of heavy metal per person per day (mg/person/day), Av consumption is average daily consumption of vegetable per person per day (g/day), %DWvegetable is percentage of dry weight of vegetable (%DW = [(100 − %moisture)/100]), and *C* heavy metal is average heavy metal concentration of dry weight vegetable (ppm).

Hazard Quotient (HQ)

The hazard quotient (HQ) is calculated as a fraction of determined dose to the reference dose as shown in the following equation:

$$\text{HQ} = \frac{\text{ADI}}{RfD}$$

Where ADI is the average vegetables intake per day (mg/kg/day) and *RfD* is the oral reference dose of the metal (mg/kg/day). *RfD* is an approximation of daily tolerable exposure to which a person is expected to have without any significant risk of harmful effects during a lifespan.

Hazard Index (HI)

The hazared index(HI) is calculated as an arithmetic sum of the hazard quotients for each pollutant as shown in the following equation:

$$\text{HI} = \sum_{i=1}^{9} \text{HQ} = [\frac{ADI\ Cd \times C\ hm\ Cd}{RfD\ Cd} + \frac{ADI\ Co \times C\ hm\ Co}{RfD\ Co} + \frac{ADI\ Cr \times C\ hm\ Cr}{RfD\ Cr} + \frac{ADI\ Cu \times C\ hm\ Cu}{RfD\ Cu} + \frac{ADI\ Fe \times C\ hm\ Fe}{RfD\ Fe} + \frac{ADI\ Mn \times C\ hm\ Mn}{RfD\ Mn} + \frac{ADI\ Ni \times C\ hm\ Ni}{RfD\ Ni} + \frac{ADI\ Pb \times C\ hm\ Pb}{RfD\ Pb} + \frac{ADI\ Zn \times C\ hm\ Zn}{RfD\ Zn}]$$

Where HQ is hazard quotient of a heavymetal, ADI is average daily intake of a heavymetal, *C* hm is concentration of a heavy metal, and *RfD* is a reference dose of a heavy metal.

Data Analysis

The obtained data were subjected tocomputed using MP-AES to calaculate the concentration of heavy metals through external heavy metal stanadard cocentrations. The data obtained were subjected to the ANOVA to investigate the effect of sample origin on the concentration of heavy metals. In all statistical analyses, the confidence level was held at 95% and $P<0.05$ was considered as significant. We performed the statistical analysis by using the raw data. Relationships between metals and other controlling factors were determined by bivariate correlation using the Pearson coefficient in a two-tailed test ($r < 0.01$ and 0.05) [29, 30].

Results and Discussion

The Concentration of Heavy Metals in Soil, Water, and Vegetables

The concentration of each heavy metals in all samples of the four sites were calculated using the calibration curve and analyzed. Table 2 shows mean concentrations of heavy metals investigated in the soil, water, and edible vegetable commonly consumed in the central rift valley, Ethiopia. The values are given as mean ± SD and the results are means of three replicates. In all locations (Bole (Bishola Awash), Kela -59, Edibetso, and Dufundufiye) samples collected from the study areas, the mean values showed the presence of Cr, Cu, Fe, Mn, Ni, Pb, and Zn. These heavy metal elements except Cd and Co were found to be above their detection limits within (soil, water, and vegetables) samples. The mean comparison of the level of heavy metals in soil, water, and vegetables among the four study sites is given in Table 2.

Table 2: Mean* (±SD) values of heavy metals concentration in soil, vegetable and water for different areas of the study(n=64)

Location	Sample types	Heavy metals concentrations in ppm								
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Bole (Bishola Awash)	Soil	- 0.025±0.000	-0.363±0.004	1.961±0.052	0.463±0.003	428.210±18.94	43.510±4.045	-0.374±0.007	0.353±0.051	1.799± 1.005
	Water	- 0.017±0.001	-0.093±0.001	0.160±0.000	0.057±0.000	1.743±0.017	1.353±0.000	0.040±0.001	0.143±0.001	0.237± 0000
		- 0.005±0.000	-0.075±0.004	0.175±0.000	0.065±0.003	2.160±0.012	2.300±0.020	0.050±0.005	0.027±0.000	0.185± 0.000
	tomato	- 0.015±0.000	-0.160±0.000	0.920±0.000	0.248±0.000	148.490±4.348	16.438±0.007	-0.120±0.002	0.225±0.032	31.693± 3.215

	onion	- 0.023±0.000	-0.173±0.000	0.947±0.060	0.247±0.005	216.397±0.607	14.803±0.190	-0.010±0.000	0.247±0.001	1.100± 0.560
	Lettuce	-0.01±0.000	1.34±0.0.005	0.31±0.006	534.67±1.850	47.83±0.240	-0.45±0.006	0.25±0.006	2.63±0.057	1.34± 0.057
Dufundufiye	Soil	- 0.460±0.000	-0.310±0.000	2.194±0.145	0.334±0.060	389.978±0.230	55.391±4.086	-0.552±0.000	0.416±0.000	1.694± 0.310
	Water	-0.07±0.000	-0.30±0.006	1.72±0.006	0.25±0.000	600.31± 2.850	52.57±1.450	-0.69±000	0.43±0.040	2.4567± 0.010
	lettuce	0.009±0.000	0.070±0.000	0.223±0.030	5.480±0.564	5.917±1.740	1.030±0.032	0.160±0.005	0.317±0.000	0.543± 0.043
	tomato	0.005±0.003	-0.075±0.000	0.135±0.000	0.120±0.321	2.250±0.512	0.205±0.003	0.025±0.000	0.11±0.000	0.39± 0.000
	cabbage	- 0.008±0.007	-0.090±0.000	0.190±0.003	0.075±0.000	4.415±1.976	4.255±2.345	0.035±0.053	0.048±0.009	0.220± 0.000

Edibesto	soil	- 0.034±0.001	- 0.235±0.000	1.107±0.128	0.244±0.009	250.49±45.900	29.150±12.90	-0.378±0.000	0.353±0.070	1.179± 0.023
	water	- 0.025±0.000	- 0.325±0.001	1.000±0.043	0.355±0.008	256.765±32.00	28.875±3.453	-0.290±0.004	0.340±0.765	1.480± 0.213
	tomato	- 0.011±0.000	- 0.223±0.000	0.614±0.004	0.208±0.032	112.389±17.90	14.836±5.900	-0.176±0.097	0.285±0.008	0.740± 0.064
Kela-59	soil	- 0.113±0,000	- 0.288±0.000	1.383±0.070	0.353±0.000	294.058±24.76	31.805±8.907	-0.198±0.000	0.308±0.004	1.500± 0.907
	onion	0.003±0.080	- 0.267±0.000	0.533±0.040	0.190±0.000	148.220±13.98	954.847±76.9	-0.143±0.000	0.070±0.056	0.877± 0.000
	tomato	- 0.015±0.004	- 0.360±0.000	- 0.360±0.000	0.295±0.000	324.460±32.90	51.020±13.98	-0.615±0.000	0.450±0.090	1.355± 0.000
	Cabbag e	-0.02±0.000	-0.15±000	0.16± 0.006	0.13±000	0.65±0.005	0.65±0.005	0.07±0.000	0.25±0.006	0.21± 0.006

* Values are mean of the three determinations at 95 % confidence level

$$\mu = X \pm \frac{ts}{\sqrt{n}}$$

Where: μ - the expected value of the determination X - mean of the replication
t- Statistical factor whose value is determined by number of samples and the desired confidence level s- The standard deviation of the measured value
n- The number of replicate measurement

The concentration of toxic heavy metals varied within the type of samples and sampling areas. In the Bole site, in all the analyzed metals iron content the higher and while cobalt was showed the lower as compared to other metals. Its mean concentration value of iron and cobalt was 428.210 and -0.363 ppm in soil respectively. The order of its concentration soil > onion > tomato > cabbage > water. In the Dufindufiye site, in all the analyzed metals iron content was high as compared to other metals. Its mean concentration ranges from 2.250 to 600.310 ppm. The water samples provided a maximum of the mean concentration of 600.31 ppm in Fe. While its concentration was found minimum in Cd -0.460 ppm and the order of its concentration is water> soil > lettuce > cabbage >tomato. The second most accumulated trace metal next to iron found in soil was manganese. The total accumulation of manganese was in the order of concentration is soil > lettuce > water > cabbage >tomato. Of the toxic metals, in all soil samples in Dufindufiye site the concentration of iron was relatively highest amount than any other trace metal analyzed and also its concentration is above WHO/FAO in all sample types of study. The concentration of iron in all study sites highest in soil samples compared with other trace metals analyzed. In the Kela-59 site, the concentration of iron toxic metal was found the highest in the tomato rather than vegetables. While, the manganese toxic metal was found the highest in the onion rather than other vegetables, soil, and water samples. In the Kela-59 site, the highest and the least concentrations were obtained 954.847 ppm and -0.360 ppm in Mn and Co respectively. The concentration pattern of Manganese follows in order of onion > tomato > soil > cabbage. The other toxic metal accumulated in the Edibesto sampling site was iron content high and cobalt content low concentrations in the value of 256.765 ppm and -0.325 ppm respectively.

Comparing metal concentrations in soil, water, and vegetables presented in Table 2 indicate that apart from Fe and other metals showed the highest value than other metals. The concentration of Fe between soils, waters, and vegetables were shown a highly significant difference. The concentration metals of Cr, Co, Cu, Fe, Ni, and Pb except Zn and Mn were showed a highly significant difference between each soil, water, and vegetables. This is indicative of the significance of the organic matter in the sorption of micropollutants in soil. The total metal concentrations in the present study were compared to other studies, particularly in Ethiopia. As noted earlier, the very few studies were on assessments the level of heavy concentration and apart from Cr, Co, Cu, Fe, Ni, Pb, and Zn which were found within the range reported mean concentrations of Fe and the other metals were above levels recorded in the literature [31-34].

The average concentrations with the standard deviations of lead (Pb), cobalt (Co), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), chromium (Cr), manganese (Mn) and iron (Fe) were described below in Table 3. The trend of the metals considering average concentrations (ppm) was Ni<Co<Cd<Pb<Cu< Cr<Zn<Mn< Fe.

Table 3: Statistical analysis of the element concentrations (ppm) determined by MP-AES

Elements	Average	Minimum	Maximum	Range	Std. dev.
Cd	-1.179	-18.5	0.083	18.42	2.605
Co	-7.553	-33.833	0.167	33.67	9.831
Cr	35.909	0.583	227.833	227.25	56.881
Cu	8.924	-1	40	39.00	11.527
Fe	10260.737	2.167	41535.5	41533.33	13420.574
Mn	1191.924	0	23376.98	23376.98	3110.327
Ni	-8.479	-63.167	4	59.17	15.787
Pb	7.909	-2.5	43.667	41.17	10.650
Zn	142.523	0.333	6146.333	6146.00	764.532

Some variations of heavy metal concentrations in this study area were attributed to industrial facilities, agro farm, city wastes and others to agronomic practices through downstream of Awash River. Higher standard deviations revealed higher variations in heavy metal distribution from the source of discharge to the adjacent areas. Low concentrations of heavy metals in the soil might be ascribed to their continuous removal by vegetables grown in the designated areas. Among the elements examined in the soil, vegetable and water the concentrations of Zn, Mn, and Fe were much greater as were the variations in their concentrations.

Table 4: Mean concentration of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in vegetable product and the environment from a different area of study

Concentration in ppm		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Products	cabbage	-0.009	-0.096	0.178	0.082	2.760	2.724	0.048	0.080	0.204
	lettuce	0.004	0.388	0.245	137.778	16.395	0.660	0.183	0.895	0.743
	onion	-0.010	-0.220	0.740	0.218	182.308	484.825	-0.077	0.158	0.988
	tomato	-0.011	-0.206	0.817	0.218	134.156	17.931	-0.192	0.269	8.511
Enviro nment s	Soil	-0.127	-0.302	1.634	0.345	341.521	39.592	-0.396	0.372	1.542
	Water	-0.028	-0.205	0.700	0.188	186.512	19.063	-0.192	0.257	1.022

The metals average concentration in the four sampling sites and analyzed vegetable products and environmental samples for selected toxic heavy metals are described in the above Table 4. Vegetables are an important part of every human diet. Consumptions of toxic heavy metals in unsafe concentrations through vegetables may lead to accumulation of Pb and cadmium in the kidney and liver and could cause problem such as Lead – brain damage, seizure, central nervous system disorders, kidney disease both acute and chronic, gastrointestinal disturbances, slight liver impairment and damage a child's central nervous system, kidneys, and reproductive system [35]. Cadmium - accumulates in kidneys, where it damages filtering mechanisms. It also causes diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly even infertility, damage to the central nervous system, damage to the immune system, psychological disorders and possibly DNA damage.

The comparison of the average heavy metals concentration among the four study sites of all vegetable (tomato, onion, cabbage and lettuce), soil and water samples showed the presence of Fe, Mn, Zn, Cu, Pb, Ni and Cr. The element Cd and Co were showed below the detection limit except for lettuce sample. Comparison of the level of metal in tomato, onion, cabbage and lettuce, soil and water samples among the four sites are given in Figure 1.

Tomato Sample

In all the analyzed metals Iron content was highest as compared to other metals (Figure 1a). Its concentration ranges from 2.25 to 324. 46 mg/kg and the order of its concentration is Kela-59 > Bole > Edibesto > Dufendufiy site. The second most accumulated trace metal next to iron found in tomato were zinc and manganese.

Cabbage Samples

Figure 1 b, shows the level of heavy metals in cabbage and their average concentration among the study areas. The concentrations of the elements in the analyzed samples were quite varied. Iron was observed at a higher concentration than other metals with a concentration range from 0.65 mg/kg in Kela-59 to 4.415 mg/kg in Dufendufiy followed by Mn with a mean concentration range of 0.510 mg/kg to 4.255 mg/kg.

Lettuce Samples

The mean value of lettuce in different sampling sites showed in Figure 1C. The values of heavy metals varied from each metal and the Cu metal was the highest concentration ranges from 5.480mg/kg in Dufendufiy to 34.670 mg/kg in Bole.

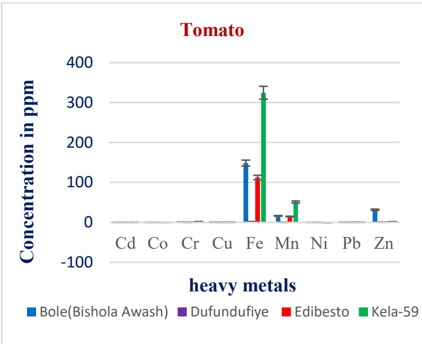
Onion Samples

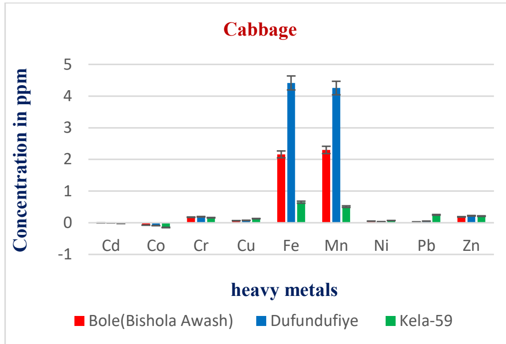
Figure 1d, shows the level of metals and their average concentration among the study areas. The concentrations of the elements in the analyzed samples were quite varied. In the onion sample the same to that of tomato, Mn and Fe were observed at a higher concentration than other metals with a concentration range from 14.803 mg/kg in Bole to 954.847 mg/kg in Kela-59 and from 148.220 mg/kg in Kela-59 to 216.397 mg/kg in Bole respectively.

Soil And Water Samples

Figures 1 e and f, were showed the accumulation of heavy metals in different study sites. The major accumulation of heavy metals was showed in soil compared with the water samples. In both samples, the concentration of Fe and Mn has observed the highest concentration than other heavy metals. The accumulation of heavy metals in all elements in the soil samples was higher than the water sample. This indicated that the accumulations of soil were higher than water.

The result showed the level of Fe, Mn and Zn were showed the highest concentration of their average concentration among the study areas. The concentrations of the iron toxic element in the analyzed samples were the highest value in all study sites and the other toxic elements were quite varied. In general, as can be seen from Figures 1 the levels of all the heavy metals in all the vegetables, soil and water collected from the farmer sites and the production site of the central rift valley, Ethiopia. In central rift valley use natural waters for irrigation from Awash River with the help of a water pump, industrial wastes and other city wastes which leads to a high concentration of metals. However, high concentration was observed which may be from the soil and environmental pollution. The concentrations of all metals obtained from all sites in some vegetable samples are within permissible levels given by the FAO and WHO and are safe for human consumption. But, the concentrations of iron metals obtained from all sites in soil samples and some vegetable types are above the permissible levels given by the FAO and WHO and are not safe for human consumption.





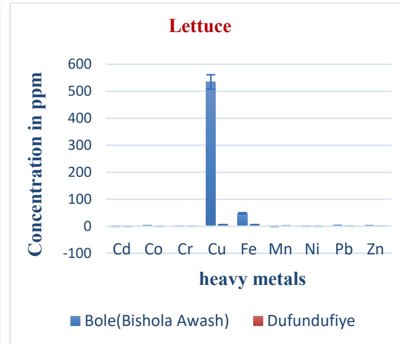
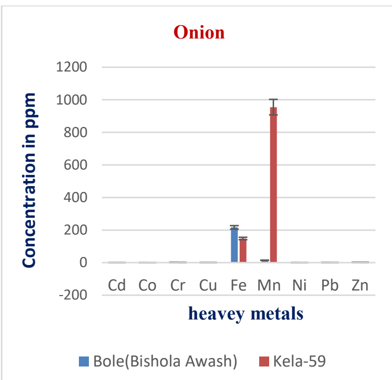
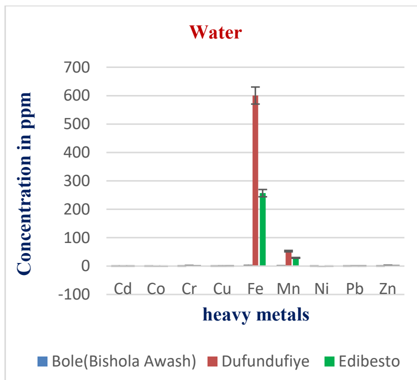


Figure 1a Figure 1b Figure 1c





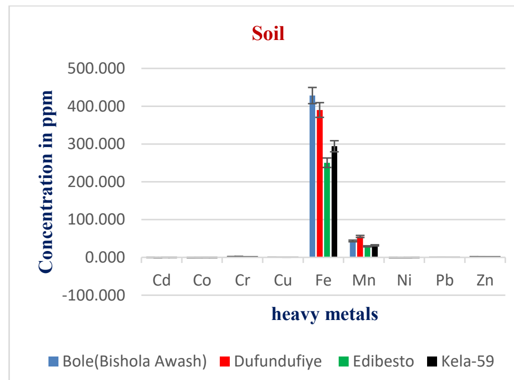


Figure 1d Figure 1e Figure1f

Figure 1: Mean concentration of heavy metals in tomato, cabbage, lettuce, onion, water and soil from different areas of the study.

Soil-Plant Transfer Coefficient (%)

The soil-plant transfer coefficient, also known as enrichment factor, enumerates comparative variations in heavy metals' bioavailability to plants. The coefficient depends on both soil and plant properties. The accrual of metals from soil to plant depends on factors like plant species absorption capacity, soil type, and a metal chemical form. Soil-plant transfer coefficient is an imperative component of human exposure toheavy metals through food chain as it describes movement of contaminants from soil to plants [38, 40]. The result of soil-plant transfer coefficient on cabbage, lettuce, onion and tomato presented in Table 5.

Table 5: Soil-Vegetable Transfer Coefficients (%) Of Heavy Metals(N=64)

Vegetables	Cd	Co	Co	Cu	Fe	Mn	Ni	Pb	Zn	Mean
Cabbage	7.09	31.79	10.89	23.77	0.81	6.88	-12.12*	21.51	13.23	11.54
Lettuce	-3.15*	-128.48*	14.99	39935.65*	4.80	1.67	-46.21*	240.59*	48.18	4452.01
Onion	7.87	72.85	45.29	63.19	53.38	1224.55*	19.44	42.47	64.07	177.01
Tomato	8.66	68.21	50.00	63.19	39.28	45.29	48.48	72.31	551.95*	105.26
Average	5.12	11.09	30.29	10021.45	24.57	319.60	2.40	94.22	169.36	

*The negative sign indicated the concentration soil is below the detection level and the perecentage of the heavey metal elements more than 100 showed the average concentration of vegetables higher than the mean values of concentration of soil.

The findings in Table 5 indicated that all the four vegetables had high Cu, Cr, Fe, Mn, Pb and Zn transfer coefficients. Among the vegetables, onion and tomato had highest transfer coefficients for all selected hevey metal analyzed. Cu, Mn, Zn, and Pb had higher the average transfer coefficient. Zn. The average soil-plant transfer coefficients for the vegetable while the efficacy in absorbing heavy metals is in order of lettuce > onion > tomato > cabbage. From the findings, the soil-plant transfer coefficients are directly related to the observed levels of heavy metals. The highest coefficient value for Cu and Mn might be due to higher mobility of these heavy metals with a natural occurrence in soil and the lower retention of them in the soil than other cations. The higher concentrations of these heavy metals could be due to increased contamination through waste water irrigation, solid waste disposal and sludge applications, solid waste combustion, agrochemicals and vehicular exhausted[36].

Average Daily Intake (ADI)

Average daily intake (ADI) can define as that is sufficient to meet the nutrient requirements of half of the healthy individuals in a particular life stage and gender group. Fruits and vegetable consumption are muscularly linked with several health benefits due to their high nutritional value and medicinal properties [37] as a result, they have a value of average daily intake in a daily foodstuff. According to [37]reports low fruit and vegetable consumption places, among its twenty risk factors in global mortality, just behind the most known killers such as tobacco and high cholesterol levels. Consumption of fruit and vegetable will irrefutably contribute against the development of coronary heart disease, hypertension, and chronic obstructive pulmonary disease due to the presence of carotenoids, polyphenols and Vitamins. Unlike anti-oxidants and vitamins, vegetables are source of minerals. As a result, highly consumptions of fruit and vegetable is recommended by WHO. In recent years, consumption of fruits and vegetables has increased considerably because of their benefits for good health. Despite irrefutable evidence of the benefits of frequent consumption of fruits, their consumption is very low in low and middle-income countries. The average daily consumption of vegetables suggested by WHO guidelines in human diet is 300 to 350 g per person. The mean of 325 g/person/day was used in calculating the ADI values in this paper. An average weight of person was considered to be 60 kg [38].

Table 6: Average Daily Intake (± Standard Deviation) Of Heavy Metals (Ppm)(N=64).

Vegetables	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cabbage	-0.29	-3.08	5.72	2.63	88.62	87.47	1.54	2.57	6.55
Lettuce	0.07	7.16	4.52	2543.38	302.65	12.18	3.38	16.52	13.72
Onion	-0.45	-9.80	32.97	9.71	8123.19	21602.59	-3.43	7.04	44.02
Tomato	-0.21	-3.85	15.27	4.07	2507.04	335.09	-3.59	5.03	159.05
Mean	-0.22	-2.39	14.62	639.95	2755.38	5509.33	-0.52	7.79	55.83
PMTDI									

*The negative sign indicated the concentration of heavy metal is below the detection level.

Hazard Quotient (HQ)

Many biochemical and epidemiological studies indicated consumptions of fruit and vegetables contribute to the reduction of several diseases, including cardiovascular, neurological and carcinogenic illnesses (42). On the other hand, the consumption of vegetables that have grown in such contaminated environmental areas will have a higher risk than its advantages. As a result, fruit and vegetable growing areas should be free from heavy metal contaminants because it is obvious that heavy metals cause serious problems to our health.

Hazard quotient is a proportion of the probable exposure to an element/chemical and level at which no negative impacts are expected. When the quotient is <1, this means no potential health effects are expected from exposure, but when it is >1, it signifies that there are potential health risks due to exposure[39]. *RfD* for Pb, Zn, Cu, Fe, Cr, Cd, Ni, Co and Mn is 0.004mg/kg/day, 0.3mg/kg/day, 0.04mg/kg/day, 0.7mg/kg/day, 0.0037mg/kg/day, 0.0057mg/kg/day, 0.1277mg/kg/day, 0.03 mg/kg/day and 0.014 mg/kg/day respectively[40].

Table 7: Hazard Quotient For Each Studied Sample (Ppm)(N=64).

Vegetables	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cabbage	-57.80	- 102.75	1905.19	65.83	12660.51	6247.69	77.06	642.20	21.83
Lettuce	14.77	238.7 5	1507.57	63584.55	43235.96	870.26	168.91	4130.43	45.72
Onion	-89.12	326.76	10990.85	242.84	1160455.53	1543042.14	171.55	1760.02	146.74
Tomato	-41.11	128.32	5089.23	101.85	358148.61	23934.68	179.40	1256.73	530.16

*The negative sign indicated the concentration of heavy metal is below the detection level.

Hazard Index (HI)

Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons[41]. The heavy metals or other nutrient minerals that come along with vegetables could expose to toxicity. Hazard Index means the sum of more than one hazard quotient for multiple substances, multiple exposure pathways, or both. An exposure to more than one pollutant results in additive effects. Thus, hazard index (HI) is a vital index that assesses overall likely impacts that can be posed by exposure to more than one contaminant. When the HI is >1, this suggests that there are significant health effects from consuming pollutants contained in a foodstuff.

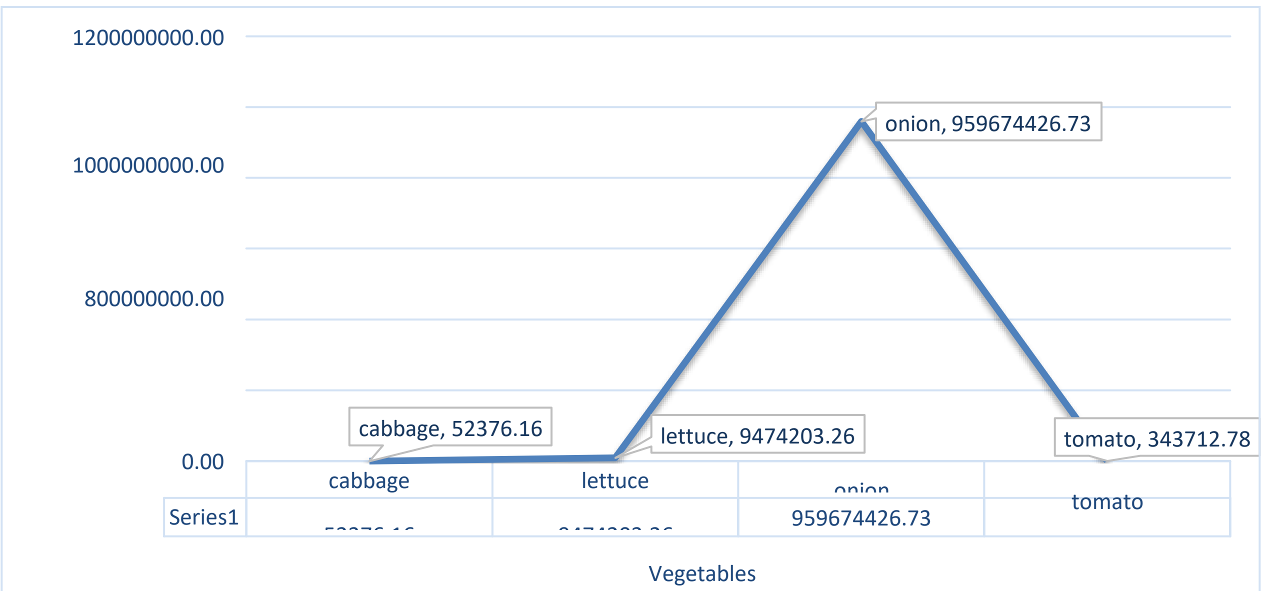


Figure 3: Hazard index (HI) for each studied vegetable

Pearson Cross-Correlation Results

The element concentrations (ppm) obtained from MP-AES analysis were used to calculate the Pearson cross-correlations which were given in Table 8.

Table 8: Pearson cross-correlation matrices among the element concentrations in soils, water and horticultural crops samples.

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ni									
Co	0.213549								
Cr	-0.56251	-0.55115							
Cu	-0.54005	-0.65489	0.581881						
Fe	-0.47958	-0.68009	-0.68009	0.694056					
Mn	-0.01694	-0.30925	0.141663	0.165497	0.165497				
Ni	0.146848	0.878988	-0.54577	-0.50888	-0.56985	-0.33888			

The element concentrations with the correlations ≥ 0.5 were boldfaced

The cross-correlations between Fe, Cu, Cd, Mn, Cr, Co, Ni, Pb, and Zn were significant at $p<0.05$. The correlations between the element pairs of Co-Ni (0.879), Cr-Cu (0.582), Fe-Cr (0.597), Fe-Cu (0.581), Fe-Pb (0.587), and Fe-Cu (0.694) were found to be high and positive. Metals with high positive correlations indicate the same behavior in the environment, increasing or decreasing together in the environment. The correlations obtained between Cr-Mn, Cr-Zn, Cu-Mn, Cu-Zn, Mn-PB, and Ni-Zn were the moderately highest among the others. The moderately high correlations between these metals indicated that the pollutants possibly shared the same source whereas the others may have arisen from individual sources in the region.

Conclusion and Recommendation

The results of the present study have revealed that heavy metal contamination of soil, water, and vegetables in varying magnitude among soil, water and vegetables in the study area. The average concentration gradient of metals in the soil, water, and vegetables (ppm) was Ni<Co< Cd<Pb<Cu<Cr<Zn<Mn<Fe. In soil exhibits higher Fe and Mn concentrations than other elements, whereas elevated Mn and Fe were also exhibited by onion. However, water was found to be the least accumulator of heavy metals than soil. According to the statistics, Pearson cross-correlation analysis results for the element pairs of Co-Ni (0.879), Cr-Cu (0.582), Fe-Cr (0.597), Fe-Cu (0.581), Fe-Pb (0.587) and Fe-Cu (0.694) were showed the highest and positive.

Hence, it poses an important public health risk. So, monitoring heavy metals in plant tissues, water and soil are essential to prevent excessive build-up of these metals in the human food chain. Consequent to our findings, it is recommended that government should provide appropriate places that will serve as an automobile village where auto repairs are being carried out.

Acknowledgments

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Data Availability Statement

The authors' can prove all necessary row data presented in these results sections for any person/s need for this publication process.

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