



Determination of Levels of As, Cd, Cr, Hg and Pb in Soils and Some Vegetables Taken from River Mojo Water Irrigated Farmland at Koka Village, Oromia State, East Ethiopia

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Abstract

This study was aimed to determine the concentrations of As, Cd, Cr, Hg and Pb in soils and garlic, kale, onion, pepper and potato samples from farmlands irrigated with River Mojo water, at Koka village, Oromia state, east Ethiopia. Flame and Hydride Generation Atomic absorption Spectrometry methods were employed. The test results showed that in all soil samples, all the five trace heavy metals exist. The order of the metals mean concentrations (mg/kg) in soil is: As (32.72 ± 22.50), Pb (22.99 ± 11.09) > Cd (5.23 ± 5.94) > Cr (3.60 ± 2.81) > Hg (2.41 ± 1.24). The mean concentrations of Hg and Cr analyzed were above the FAO/WHO and below Austria and Poland set standards. The level of analyzed Cd is above the standards of European Union, India, United States, Poland, Germany and Austria. The arsenic concentration lies below all the standards except for that of United States. Pb result is within the set standards of Austria, Germany, Poland, US, EU, FAO but exceeds that of EC and India.

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The plant results show that all the trace metals under analysis were observed to exist in all vegetables. Cd absorption by potato ranked first and Cr was the second absorbed by Garlic. Hg is the least biotransferred metal. All the vegetables are positively correlated with each other. Garlic and onion are strongly significantly ($r = 0.972$, $p < 0.01$) positively correlated and garlic - pepper ($r = 0.917$), onion - Kale ($r = 0.940$) and pepper - onion ($r = 0.905$) are strongly significantly ($p < 0.05$) correlated. Except for As - garlic ($r = 0.184$) and As - potato ($r = 0.261$) (8%), all the metals - vegetables are negatively correlated (92%). All mean concentration of the metals in all analyzed plant samples fall above the maximum permissible limit standard values in vegetables set by FAO/WHO. Therefore, the consumption of these vegetables is at health risk and integrated pollution management is highly required and prevention measures and regular monitoring should be enforced on those industries contributing to River Mojo pollution.

Keywords: Bioavailability; Biomagnifications; Transfer Factor; Concentration; Correlation, Contaminants; Pollution.

1. Introduction

Soil is the dynamic body of natures and complex system in which all the times: chemical, biological, physical, geological, biogeophysicochemical reactions are taking place with characteristics that vary over time and space.

This study is intended at assessing the concentration of As, Cd, Cr, Hg and Pb and the pollution status of the irrigated soils of the farmlands and some vegetables grown with River Mojo water irrigation. The plant types were selected on the basis of its availability during sampling and consumption rates by the larger communities. The location of the research site is in the central Rift Valley of Ethiopia, which most of the time the annual rainfall is short and hence River Mojo plays so crucial role to the communities dwelling on its both sides. From the source to its mouth, the local communities highly depend on this river, especially in its lower course; the communities use the river water throughout the year for different agricultural economic activities. The volume of the water fluctuates recording very minimal during dry season and with the largest volume filling beyond its course at rainy time, *Ganna*. The irrigation activities takes place most of the time during dry season, *Bona*. The river is so important for the local peoples/farmers in building of their livelihoods in addition to irrigation: washing, swimming, watering of animals, construction activities, etc.

Irrigation activities on the River Mojo yield different vegetables, cereals and fruits (Kale, carrot, cabbages, peppers, tomatoes, potatoes, onions, garlic, maize, wheat, watermelon, wine, papaya, oranges, etc.) that are worth to the local farmers for consumptions and markets. However, in recent times, industrial activities are mushrooming along both sides of the river course: tanneries, textile industries, meat processing plants, cement factories, edible oil processing plants, car battery refilling processes and car washing activities, etc. The effluents and solid wastes from these industries/plants without any treatment or sorting out, find their ways to the river.

The research conducted by Tamene Fite D. and Seyoum Leta [1] on River Mojo showed that the concentrations of As, Cd, Cr, Hg and Pb were spatially and temporally increase along the river from upstream to

downstream and this river water is not in a position for using animal watering and irrigation purposes.

At present time, human beings are changing feeding styles from animal based foodstuffs to plant sources like vegetables and fruits because of their nutritional values [2, 3]. Though, the toxic effects of heavy metals might depend upon the levels and oxidation states, types of sources and form of depositions [4 5], they can affect the quality of agricultural soils, including phytotoxicity. Of course, soil is considered as the central medium for the trace heavy metals transportations to human beings through crop or vegetable uptake [5].

Dean Hesterberg [6] notified that the most direct transportation routes of trace heavy metals into crops are by root uptake of dissolved elements in soil pore water or by leaf uptake of dissolved elements in irrigation water. Uptake and release of trace heavy metals from soil particles depends not only on total element concentrations but more importantly on the amounts and types of soil minerals and organic matter [7] and on soil chemical properties such as pH and oxidation--reduction potential.

Trace heavy metals like As, Cd, Cr and Pb are omnipresent in industrialized sites and they do have potential of contaminating soils which can be transported to plants, animals and humans causing their health effects: carcinogenicity, mutagenicity, disruption of DNA, etc, [8, 9]. The different research works executed by Lasat, M.M and Song, W.Y [10, 11], explained that heavy metals have persistent power in soil much longer than in other parts of the biosphere (air or water). Additionally, the repeated use of water for irrigation may lead to the accumulation of heavy metals in agricultural soils and plants [12].

The flow of trace heavy metals between the soil, plants, water and the atmosphere is the part of a complex and complicatedly connect biogeochemical cycling processes in nature. In addition to the natural weathering, anthropogenic activities are considered to be significantly responsible for elevated trace metals concentrations in soils [13 - 16]. Furthermore, environment and human health impact of toxic trace metals contaminations are a function of mobility and phytoavailability. As a result, factors controlling the total and bioavailable concentrations of trace heavy metals in the soil are of great importance in terms of soil – plant – human transfer and biomagnifications of trace metals contamination which are topical issues in environmental studies [17 - 19]. Many researchers [9, 10, 20 - 22] confirmed that trace heavy metal pollution of surface soils due to intensive and extensive industrialization and urbanization has become a serious concern in many developing countries because soil pollution is the starting point of transportation of the pollutant to plants and animals and even to the atmosphere.

The work of Okonkwo [23] on the risk and health implications of polluted soils for crop production detailed that the source of heavy metal in plant is the environment in which they grow and their growth medium, the soil, from which heavy metals are taken up by roots or foliage of plants. The independent study carried out by Akinola [24], on the determination of Pb, Cd and Cr in the tissue of an economically important plant grown around a textile industry revealed that plants grown in polluted environment can accumulate heavy metals at high concentration causing serious risk to human health when consumed.

2. Materials and Methods

2.1 Description of the Study Area

The study area is situated in eastern Oromia State, about 70 – 105km away from the capital city, Addis Ababa, to the east. At Koka village, the location has a northing 37P, 0503188 and easting UTM, 0931513 with an elevation 1601 - 1608 meters above sea level respectively. The study was focused at the irrigable farmland being used for irrigation purposes for a long period of ages from River Mojo water.

2.1.1 Sampling Site

Probability sampling approach was followed for sample location selection. Two sampling sites were designed, one from the irrigable farmland, estimated to be 12,000m² (200m x 60m) and the other from non – irrigable non – ploughable land (S₀) about 1km away from the irrigable sampling location. The sampling site is assumed quadrilateral as illustrated in figure 1. A grid sampling layout composed of five zigzag lines on a near level surface form was set to encompass the sampling area.

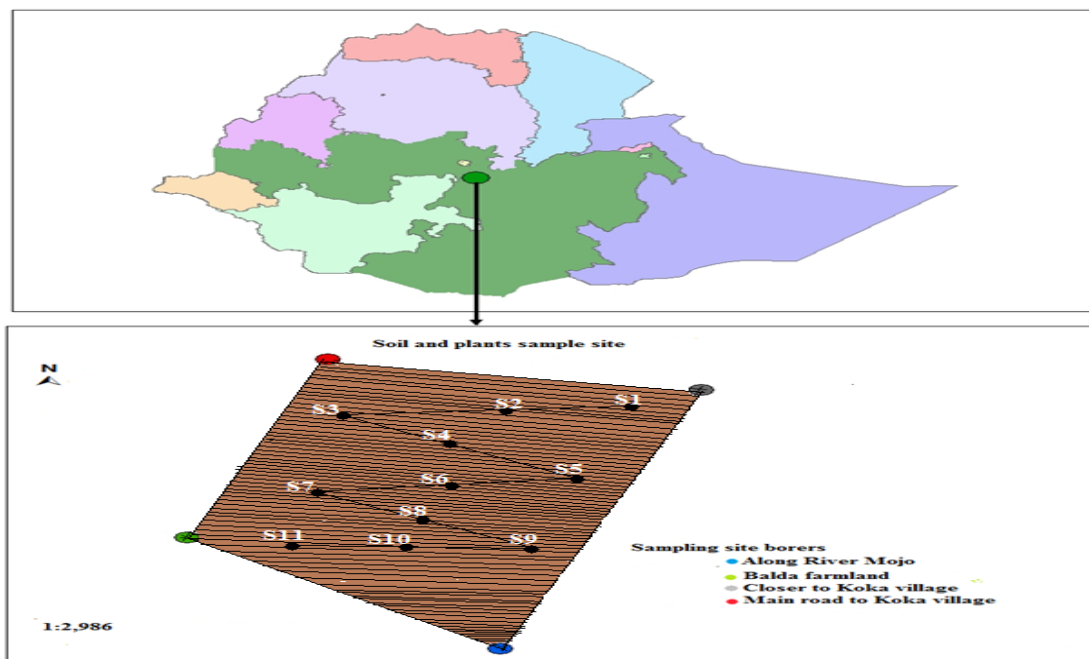


Figure 1: geographical location of the study area

2.2 Soil Sampling and Preparation

Composite soil sampling method was applied; the number of composite subsample for each point was eight which each subsample location was about 5 to 6 meters away from one another. Proper scientific sampling materials were used. Sampling was carried out at 9:00am. The soil sampling was done according to the method

of James and Wells [25]. The farmland is conventionally tilled fields and hence all soil samples were taken from the depth of 2 – 20cm. Sabbe and Marx [26] sampling method was employed for every sample. Samples obtained from 8 sample cores in a scientifically determined pattern, viz a zigzag sampling pattern (Figure 1) were thoroughly mixed, to deal with variability in the field and to get a reasonably representative soil samples. At each point, the surface soil was removed and about 3 to 5 cm hole was dug. Nearly about 125gm was sampled from each 8 subsampling point for a single subsample and then mixed together to form one kg of composite sample. For each 12 (11 from irrigable land and 1 from reference point, n = 12). The sampling was conducted during irrigation activities peak period, 03 March, 2014. The collected samples were kept in polypropylene bags and transported to Addis Ababa Environmental Protection Authority (AAEPA) laboratory on the same sampling dates respectively.

Soil sample preparation was carried out starting with removal of sands, small stones and any other non soil ingredients; air dried at room temperature, oven drying (Gemmy 888) at 105°C. Then air dried sample was crushed to pass a 200 mesh sieve. Acid digestion was conducted according to USEPA Method 3050B. The chemicals: HNO₃, (68%, Sigma Aldrich), HCl (analytical grade d = 1.18, 36%, Fisher Scientific); H₂SO₄, (97 - 98.2%, Sigma Aldrich), HClO₄ (70%, Sigma Aldrich) and H₂O₂ (BDH Lab. Supplies, 6% w/v) were used.

2.3 Plants Sampling and Preparation

Sampling was carefully done not to collect tissue that is covered with soil or dust or from plants that are damaged by insects, mechanically injured, or diseased. Dead plants tissues were removed and suitable weather circumstances were selected avoiding moisture or temperature stress. Five plants samples (n = 5), viz, Garlic (*Allium sativum*), Kale (*Brassica oleracea*), onions (*Allium cepa*), pepper (*Piper nigrum*), potato (*Solanum tuberosum*), were sampled from the irrigation farmlands where soil samples were collected during their harvest times. Kale samples were collected according to the sampling procedures of Jones and Case and Jones, et al [27, 28]. The youngest fully matured 20 – 30 leaves from different Kale plants on main branches and stems were sampled just prior to flowering time. Randomly each one kg of onion, garlic, pepper and tomato samples were respectively sampled from irrigation farmland. All the mixed plant samples of each on the base of their types were stored in polypropylene bags and transported to AAEPA laboratory for preservation and experimental analyses. The sample digestion procedures were conducted based on USEPA method 3050B. Cleaning/decontamination processes were done washing with 0.1 – 0.3% detergent solution followed by rinsing with distilled water to remove dust and other contaminants. After cleaning, drying was facilitated as rapidly as possible to minimize chemical and biological changes. Moisture removal was carried out in oven (Gemmy 888) at optimum temperature of 60 - 70°C for 24hours to minimize appreciable thermal decomposition.

HNO₃, (68%, Sigma Aldrich), HCl (analytical grade d = 1.18, 36%, Fisher Scientific); H₂SO₄, (97 - 98.2%, Sigma Aldrich), HClO₄ (70%, Sigma Aldrich) and H₂O₂ (BDH Lab. Supplies, 6% w/v) were used. Plant tissues samples previously dried, ground, and weighed are prepared for elemental analysis through decomposition of organic matter by wet ashing (acid digestion) [29]. After ashing, the vessel was removed, cooled and the ash was dissolved in nitric acid (HNO₃) and hydrochloric acid (HCl), then the vessel was filled to volume and

diluted as needed to meet range requirements of the analytical instrument.

2.4 Experimental

2.3.1 Analysis of Soil and Plant Samples

Trace heavy metals like Cd, Cr, and Pb in soil and plant samples were analyzed by Flame Atomic absorption Spectrometry (FAAS, novAA 400, analikjena), direct air- acetylene method. Hg and As were analyzed by Hydride Generation Atomic absorption Spectrometry (HG – AAS, novAA 400, analikjena) methods at laboratory of Addis Ababa Environmental Protection Authority (AAEPA) based on USAEPA 3050B methods. The results of the analyses are summarized in Table 1 and 3. All the results were statistically significant at $P < 0.05$.

Table 1: Statistical description of the experimental results of soil samples

Soil sample	Parameters and their analyzed concentrations (mg/kg) and pH Values					
site (N = 12)	As	Cd	Cr	Hg	Pb	pH
S ₀	0.23	ND	ND	0.03	ND	7.32
S ₁	25.64	8.20	1.69	2.03	21.23	6.74
S ₂	22.77	7.68	3.82	3.14	23.05	6.67
S ₃	1.33	21.12	3.20	1.15	35.79	7.61
S ₄	56.89	3.05	3.12	2.20	32.70	7.43
S ₅	23.54	4.58	11.40	5.06	22.30	6.55
S ₆	47.50	2.30	2.50	3.08	23.92	7.12
S ₇	21.13	9.80	4.20	1.85	41.20	6.85
S ₈	56.36	0.65	3.80	2.12	29.60	7.45
S ₉	16.62	2.14	1.61	3.02	12.78	6.78
S ₁₀	57.50	2.70	2.70	2.06	15.58	7.23
S ₁₁	63.15	0.56	5.20	3.17	17.80	7.44
Min.	0.23	0.00	0.00	0.03	0.00	6.55
Max.	63.15	21.12	11.40	5.06	41.20	7.61
X _m	32.72	5.23	3.60	2.41	22.99	7.10
STD	22.50	5.94	2.81	1.24	11.09	0.36
X _m +SD	32.72 ± 22.50	5.23 ± 5.94	3.60 ± 2.81	2.41 ± 1.24	22.99 ± 11.09	7.10 ± 0.36
One sample test, Sig.(2-tailed)	t= 5.35 p = 0.001	t = 3.05 p = 0.01	t = 4.44 p = 0.001	t =6.73 p = 0.001	t = 7.18 p = 0.001	

X_m – mean value, SD – standard deviation

Table 2: Guideline for the maximum permissible limit (MPL) values of the trace heavy metals in agricultural soil by different standards

Standards/Guidelines	Trace heavy metals					References
	As	Cd	Cr	Hg	Pb	
FAO/WHO, mg/kg	-	-	0.1	1.0	90-400	1985, 1992/1993
EC, mg/kg	20.0	0.003	0.15	-	0.30	EC: 2002, EU
Indian, mg/kg	-	0.003 - 0.006	-	-	0.50	Awashthi 2000
EC, mg/kg	-	1 - 3	50	1-1.5	50 -300	[26, 27], EC 1986
United States, mg/kg	14	1.6	1500	0.5	50-300	[26, 27], 1993
Poland, mg/kg,	30	1-3	50-80	5	70-150	[26, 27], 1993
Germany, mg/kg,	20	1.5-3.0	100	2	100	[26, 27], 1984 -1992
UK, mg/kg	10	3-15	-	-	-	[26, 27]
Austria, mg/kg	50	5	100	5	100	[26, 27]
Experimental mean results	32.72	5.23	3.60	2.41	22.99	Table T1

EC: European council for European communities; Sources: FAO: 1985, 1992, WHO: 1993, EC: 2002, [26, 27]

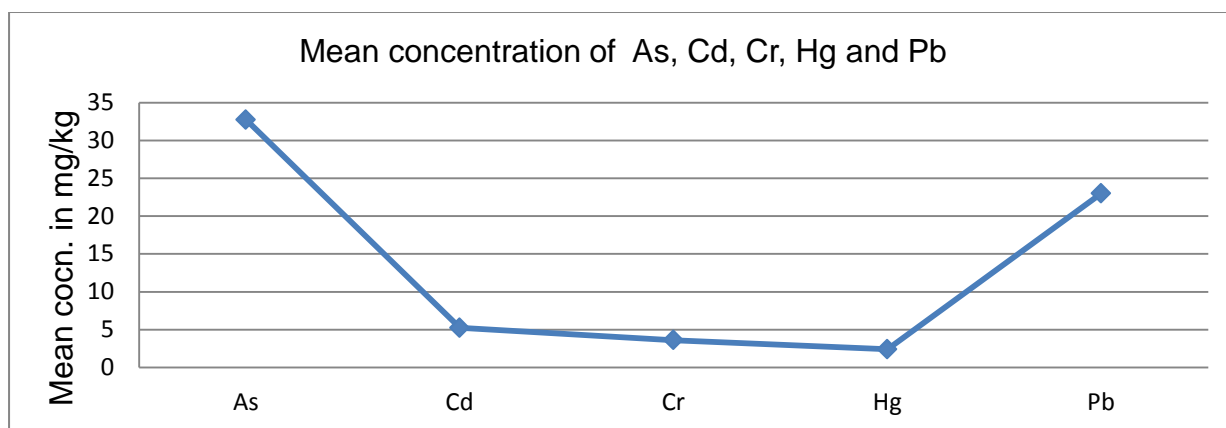


Figure 2: The graph showing mean concentration of the trace metals in all soil samples

2.3.2 Analysis of Plant Samples

The procedurally prepared plant samples were experimented according to the parameters to be tested, viz, the test for Hg and As were done by Hydride Generation Atomic absorption Spectrometry (HG – AAS, novAA 400,

analikjena) method while the analysis for Cd, Cr and Pb was performed by Flame Atomic absorption Spectrometry (FAAS, novAA 400, analikjena), direct air- acetylene method at laboratory of AAEP. The results of the analyses are summarized in Table 3. All the results were statistically significant at $P < 0.05$.

3. Results and Discussions

The results of heavy metal concentrations in the irrigated farmland soil and plant samples are presented in table 1 and 3 respectively. In all soil samples, the test results showed the presence of all the five trace heavy metals but Cd, Cr and Pb were not detected at site S_0 . The range of the concentration (mg/kg) of As, Cd, Cr, Hg and Pb is respectively: 0.23 – 63.15, 0.00 – 21.12, 0.00 – 11.40, 0.03 – 5.06 and 0.00 – 41.20. In the reference sample (S_0), except for As and Hg, the concentration of the other metals has fallen below the detection limit of the instrument. Tamene Fite D and Seyoum L. [2] showed that the concentration of mercury was significantly high in the River Mojo water. At the sampling site, irrigation farming with River Mojo water occurs intensively and extensively throughout the dry months of the year. In addition to that during extremely wet season the river water fills its course and come out and covers the farmland for one to two months, which also be the cause of the increase of the concentration of the metals under study. The order of the metals mean concentrations in soils (mean \pm STD) is: As (32.72 ± 22.50), Pb (22.99 ± 11.09) > Cd (5.23 ± 5.94) > Cr (3.60 ± 2.81) > Hg (2.41 ± 1.24). The arsenic concentration interruptedly increases from control site S_0 to site S1 perhaps because of the use of arsenic containing chemical inputs such as pesticides and herbicides [30, 31], the parent materials for soil formations [32] and industrial effluents [33]. The high values of, As, Pb, Cd and Cr might be due to the uses of pigments/paints, fertilizers, tanneries, fossil fuels, car battery wash wastewaters and plastic materials production processing at upper course of the river [34]. Arsenic and mercury were observed in the reference sample (S_0) while there was no registered values of Cd, Cr and Pb. This reflects a contamination of soils of non - irrigated farmland by other different sources rather than contamination from water. The concentration of Hg (1.15mg/kg) obtained from the sampling point S_3 is the lowest of all metals and all sampling points except for the control point. As well, the mean concentration of Hg is also the lowest of all recorded results (Table 1).

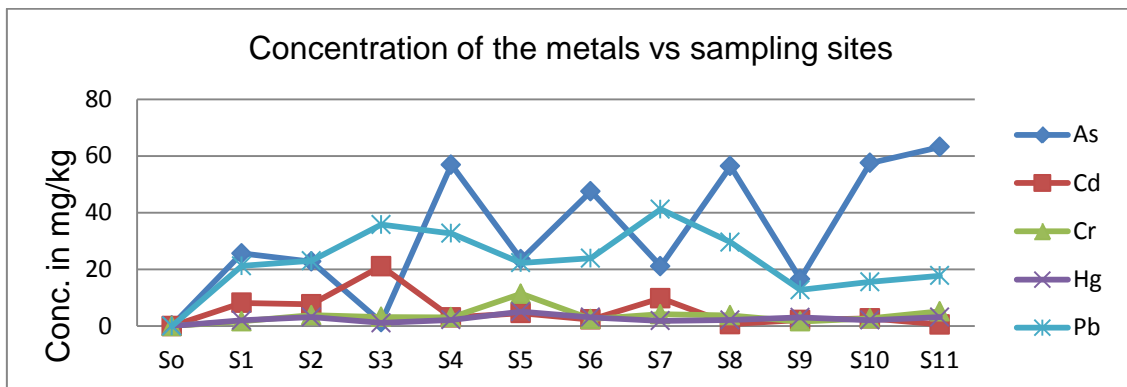


Figure 3: Graphs of As, Cd, Cr, Hg and Pb concentrations in all soil sampling sites

The mean concentrations of mercury and chromium analyzed were by far above the FAO/WHO and below Austria and Poland set standards (Table 2). The level of analyzed cadmium is above the standards of European council/union, India, United States, Poland, Germany and Austria. The arsenic concentration lies below all the standards except for that of United States. Lead analyzed concentration is within the set standards of Austria, Germany, Poland, US, EU, FAO and exceeds that of EC and India. Even though the study conducted by Tamane Fite D and Seyoum L [2] specified less concentration of the trace metals in River Mojo water, because of repeated and long age uses of the water for irrigation purposes, the levels of these metals is comparatively high, showing their accumulation potentials in the soil environments. The mean concentration of Pb is highest second to arsenic, this could be attributed to the fact that the sampling site is very near to the main asphalt road from Mojo town to Batu – Shashemene – Hawasa towns which entertains many vehicle traffics throughout 24 hours all the seasons and assists the more deposition of lead from car exhausts in to the nearby farmlands. Additionally, since Pb^{2+} is not biodegradable, once soil has become contaminated with it, it remains a long-term source of Pb^{2+} exposure.

As any other metal, mercury could occur in the soil in various forms. It dissolves as free ion or soluble complex and is nonspecifically adsorbed by binding mainly due to the electrostatic forces, chelating potential, and precipitated as sulphide, carbonate, hydroxide, and phosphate. According to Lindsay W.L [35], the expected contents (mg/kg) of As, Cd, Cr, Hg and Pb in soils are respectively: 1.00 – 50.00, 0.01 – 0.70, 1.00 – 1000.00, 0.01 – 0.30 and 2.00 – 200.00. From the results of this study, Cd and Hg are about 26 and 12 times higher than these ranges of values while As, Cr, and Pb are within the ranges.

The experimental results show that all the trace metals under analysis were observed to be absorbed by all vegetables (Table 3). Cd and Cr are the first (2.54 ± 1.81 , uptaken by Potato) and second (1.51 ± 0.37 , uptaken by Garlic) absorbed metals by all vegetables while Hg is the least (0.27 ± 0.05 , uptaken by Kale) biotransferred metal surpassed only by Pb. At S_1 , the recorded levels of As, Hg and Pb in all vegetables happened to be low and Cd registered maximum value (4.45mg/kg) in potato samples. At S_2 , the results seem to be at average for all metals in all vegetables. S_3 vegetables samples showed higher concentration of the metals. In the soil samples, the mean concentration (mg/kg) of As, Cd, Cr, Hg and Pb are respectively: 32.72 ± 22.50 , 5.23 ± 5.94 , 3.60 ± 2.81 , 2.41 ± 1.24 and 22.99 ± 11.09 . In the vegetables samples (garlic, kale, onion, pepper and potato), the mean ranges of concentrations levels for each is: $0.50 \pm 0.19 - 0.64 \pm 0.22$, $1.05 \pm 0.25 - 2.54 \pm 1.8$, $0.56 \pm 0.44 - 1.51 \pm 0.37$, $0.27 \pm 0.05 - 0.64 \pm 0.35$ and $0.30 \pm 0.12 - 0.69 \pm 0.16$ (for As, Cd, Cr, Hg and Pb respectively). These results depict despite low concentration of Cd and Cr in soil samples, they exhibited relatively high quantities in the plant samples. The accumulation of Cd in plant confirms the research results of Brian [36] that Cd is one of the elements that are intensively accumulated in plant bodies with $TF = 1.00 - 10.00$. Brian J. Alloway [36] classified some metals as less, medium and high potential to be accumulated in plants: $As > Pb > Hg$ are the metals showing medium accumulation with $TF = 0.01 - 1.00$, Cd is one of the elements that are intensively accumulated with $TF = 1.00 - 10.00$, elements showing slight accumulation with $TF = 0.001 - 0.01$ are $Be > Cr > I > F > Li > Mn$.

Table 3: Concentration and statistical description of trace heavy metals in vegetable samples.

mg/kg	Samples site	Garlic	Kale	Onion	Pepper	potato
As	S ₁	0.28	0.36	0.34	0.62	0.44
	S ₂	0.64	0.83	0.55	0.43	0.62
	S ₃	0.59	0.67	0.82	0.81	0.87
	Min	0.28	0.36	0.34	0.43	0.44
	Max	0.64	0.83	0.82	0.81	0.87
	X _m +SD	0.50 ± 0.19	0.62 ± 0.24	0.57 ± 0.24	0.62 ± 0.19	0.64 ± 0.22
	Cd	S ₁	1.21	0.94	2.61	1.12
S ₂		2.33	1.33	0.87	1.45	2.33
S ₃		1.13	0.87	0.65	0.87	0.85
Min		1.13	0.87	0.65	0.87	0.85
Max		2.33	1.33	2.61	1.45	4.45
X _m +SD		1.56 ± 0.67	1.05 ± 0.25	1.38 ± 1.07	1.15 ± 0.29	2.54 ± 1.81
Cr		S ₁	1.11	0.26	2.06	0.55
	S ₂	1.58	0.72	1.54	1.67	0.06
	S ₃	1.83	1.58	0.32	2.25	0.75
	Min	1.11	0.26	0.32	0.55	0.06
	Max	1.83	1.58	2.06	2.25	0.87
	X _m +SD	1.51 ± 0.37	0.85 ± 0.67	1.31 ± 0.89	1.49 ± 0.86	0.56 ± 0.44
	Hg	S ₁	0.23	0.26	0.24	0.32
S ₂		0.81	0.22	0.51	0.29	0.46
S ₃		0.87	0.32	0.67	0.77	0.73
Min		0.23	0.22	0.24	0.29	0.29
Max		0.87	0.32	0.67	0.77	0.73
X _m +SD		0.64 ± 0.35	0.27 ± 0.05	0.47 ± 0.22	0.46 ± 0.27	0.49 ± 0.22
Pb		S ₁	0.37	0.31	0.32	0.69
	S ₂	0.68	0.17	0.26	0.53	0.52
	S ₃	0.81	0.41	0.53	0.84	0.67
	Min	0.37	0.17	0.26	0.53	0.52
	Max	0.81	0.41	0.53	0.84	0.67
	X _m +SD	0.62 ± 0.23	0.30 ± 0.12	0.37 ± 0.14	0.69 ± 0.16	0.60 ± 0.08
	Statistics	One sample test, Sig.. (2 tailed)	t= 4.134 p = 0.014	t= 4.063 p = 0.015	t= 3.780 p = 0.019	t= 4.632 p = 0.010
FWM (µg/g)	As = 0.1, Cd	Cd = 0.1	Cr = 0.1 – 0.2	Hg = .03	Pb = 0.2	

X_m – mean, SD – Standard deviation, FWM – FAO/WHO Maximum Permissible Level (1999).

This is because once these metals are uptaken by the plants; then, they accumulate in different tissues of the plants. This continuous uptake and translocation can increase the concentrations of metals in plant tissues despite low metal concentrations in the soils. Contrary to this, As and Pb which showed large concentration in soil samples, had registered very low quantities in plants. This may be reasoned out that at higher pH, the availability of As and Pb in solution form is less which hinders the soil – plant transfer. Furthermore, vegetables’ and fruits’ Pb content is generally very low due to its low bioavailability.

The work of Maisto [37] marked the uptake of metals by plants varies from species to species, viz, some have high metal contents in their tissues compared to a very low soil metal concentration while other species have a low uptake of the metal at high soil concentrations. Lake DL [38] described some of the factors that affect the phytoavailability of heavy metals such as: atmospheric deposition, climate conditions, level of heavy metals in the soil, the nature of the soil and the maturity of the plants at the time of harvesting. In addition to these facts, adsorption – desorption, cation exchange capacity, precipitation - dissolution, preferential transport of metals, etc. can affect metal movements.

All mean concentration of the metals in all analyzed vegetables samples fall above the maximum permissible limit standard values (Table 5). And the analyzed results of Cd, Cr and Pb of this study are greater than the results of the similar research done by Saglam C. [39] on heavy metal concentration on edible oil parts of some cultivated plants and medical samples in southern Turkey. The results of this study showed that the mean concentrations of Cd ($1.05 \pm 0.25 - 2.54 \pm 1.81$) uptaken by the vegetables are higher than the concentrations of each trace metal under investigation. Arsenic is uptaken by all the vegetables almost equally. Cr is the 2nd metal uptaken by the five vegetables ($0.56 \pm 0.24 - 1.51 \pm 0.37$) (Figure 1).

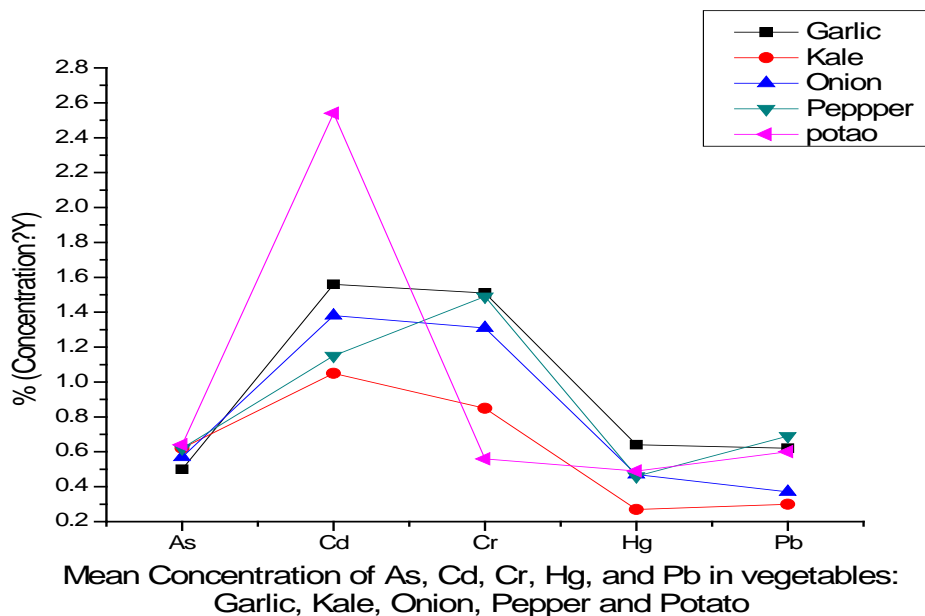


Figure 4: mean concentration of As, Cd, Cr, Hg and Pb in the vegetable samples

3.1 Soil – plant Transfer Factor (TF)

TF describes the amount of an element expected to enter a plant from its substrate, under equilibrium conditions that assumes a linear relationship between the concentrations of a certain element in the plant with that in the soil. It is the ratio of the concentration of metal in the plant to that of the soil. The metal concentrations in the extracts of the soils and plants are calculated on the basis of dry weight using the following simplified equation:

$$TF = \frac{C_p}{C_s} ,$$

Where, C_p and C_s are respectively the concentration of heavy metals analyzed in plant and soil samples (Table 4). As to the calculated results, If the ratios >1 , the plants have accumulated elements, the ratios around 1 indicate that the plants are not influenced by the elements, and ratios < 1 show that plants avoid the elements from the uptake. The trace heavy metals, Cd, Cr and Hg have greater soil – plant transfer rate to garlic, kale, onion pepper and potato than As and Pb (Table 4). The vegetables accumulate Cd in the following order: Potato $>$ Garlic $>$ Onion $>$ Pepper $>$ Kale. All the vegetables can accumulate Cr. As and Pb are the least to be accumulated by all the vegetables.

Table 4: Soil – Plant Transfer Factor (TF) of trace heavy metals

Vegetables	Soil – plant Transfer Factors values				
	As	Cd	Cr	Hg	Pb
Garlic	0.015	0.298	0.420	0.266	0.027
Kale	0.019	0.201	0.236	0.112	0.013
Onion	0.017	0.264	0.364	0.195	0.016
Pepper	0.019	0.220	0.414	0.191	0.030
Potato	0.02	0.4860	0.156	0.203	0.026

Perhaps the most threatening contamination problem is with inputs of added Cd in phosphate fertilizers to increase agricultural production yields. In addition to this, there could be a problem of the phosphate rocks used for making these fertilizers to contain relatively high concentration of Cd [36]. With the contexts of soil – plant interactions, the main soil processes controlling availability of both naturally occurring and contaminant trace and major elements to plants and their leaching down through the soil profile to the ground water are those which influence the adsorption and desorption of these elements within the soil. The sorption mechanisms include: cation or anion exchange processes, specific adsorption in which certain metal cations and most anions are held by ligand exchange in the form of covalent bond, co – precipitation in which ions are precipitated on surfaces simultaneously with other organic compounds, insoluble precipitates of elements on surface (e.g. formation of insoluble carbonates, phosphates, sulfides, hydroxides, etc.), and organic complexation with solid state organic matter ligands. The factors controlling of adsorption and desorption of ions in soils may include:

properties, speciation and concentration of the metallic elements, composition of soil – clay types (e.g. oxides of Fe, Al, Mn, free CaCO₃, and organic matter), soil physicochemical conditions such as pH, redox status, concentration of cations and anions and plant factors especially genotype differences.

Table 5: Maximum permissible limit standard values in vegetables

Trace heavy metals (mg/kg)	As	Cd	Cr	Hg	Pb
Max. permissible limit in leafy vegetables, FAO/WHO, 1999	0.10	0.10	0.05	0.030	0.20
Recommended Max. limit for vegetables, FAO/WHO, 2001	0.43	0.20	2.30	0.03	0.30
Metals permissible limit in vegetables, Codex Stan 1993, 1995	0.10	0.20	2.30	0.03	0.30
Experimental mean results	0.50-0.64	1.05-2.54	0.56-1.51	0.27-0.64	0.30-0.69

Adsorption of the metals to soil matters is usually very high in soils with pH higher than 6.5 and only traces of the element could remain in the solution. In addition, desorption process can be very slow and therefore only negligible release of the TF to the soil solution is often observed. As different studies [40 - 42] pointed, the absorbable availabilities of metals are not the only influencing factors for the biotransfer of these metals but also the plant species tendency to uptake a certain element from the soil. The soils at the site of sampling irrigation farmland were observed to be sandy in nature and this may contribute to the less availability of trace metals as soluble form in soil parts. The transfer factor of all elements for plants grown in the site soil are low may be due to soil alkalinity that reduces the mobility of ions [43]. Generally most of the heavy metals are less available to plants under alkaline conditions than under acid conditions. The high level of Cd and Cr in the plant at these sites might be due to direct deposition and foliar absorption more than the translocation from roots to the upper part of the plant.

Adriano [44] detailed that Cd, Hg and Pb, and to large extent arsenic have no known biological functions for the plants whatsoever and Sas - Nowosielska A [45] disclosed that mercury is known to affect photosynthesis and oxidative metabolism by interfering with electron transport in chloroplasts and mitochondria. Mercury also inhibits the activity of aquaporins and reduces plant water uptake. Of course, Cd, Hg, Pb and As are on the EPA's list of priority pollutants because of their widespread and intense occurrence at waste sites and their known detrimental effects on ecological and human receptors [46].

The pH is either directly or indirectly affects the migration, transformation [47] and many reaction pathways of metal retention by soils. It is one of the most major factors influencing mobility and adsorption of heavy metals in soils. The pH of the soil solution maintained at neutral to slightly alkaline condition shows low mobility of most heavy metals. For instance, the solubility of Pb in soil solution is pH dependent, i.e., as the pH is adjusted from 6 to 3, the mobility increases. At near neutral pH, the activity of Pb²⁺ shows no clear relationship to pH [47].

Table 6: Permissible limits of heavy metals given by WHO/FAO

Environmental mediums	Heavy Metals concentrations in mg/L					
	Cu	Mn	Fe	Zn	Ni	Pb
Water	0.05 – 1.5	0.01 – 0.5	0.03 – 1.0	5.0 - 10.0	0.2	0.1
Soil	0.27	-	-	0.6	0.075	0.006
Crops	0.001	0.003	0.003	0.001	0.001	0.001

Table 7: Industrial and agricultural source for metals in the environment [FAO, 1996]

Economic uses of materials	Possible Metals that might be observed
Batteries and other electrical materials	Cd, Hg, Pb, Zn, Mn, Ni,
Pigments and paints	Ti, Cd, Hg, Pb, Zn, Mn, Sn, Cr, Al, As, Cu, Fe
Alloys and solders	Cd, As, Pb, Zn, Mn, Sn, Ni, Cu
Biocides (pesticides, herbicides, preservations)	As, Hg, Pb, Cu, Sn, Zn, Mn
Catalysts	Ni, Hg, Pb, Cu, Sn
Glass	As, Sn, Mn
Fertilizers	Cd, Hg, Pb, Al, As, Cr, Cu, Mn, Ni, Zn
Plastics	Cd, Sn, Pb
Dental and cosmetics	Sn, Hg
Textile	Cr, Fe, Al
Refineries	Ni, V, Pb, Fe, Mn, Zn
Fuel	Ni, Hg, Cu, Fe, Mn, Pb, Cd

In acidic soil, Cd is associated with the exchangeable form. This increases its mobility and sorption with increasing pH. That is, the lower the pH value, the more metal can be found in solution and thus more metal mobilizes. When pH falls to below 5, the metal movement is enhanced as a result of the increased H⁺ concentration. At pH values > 7, some heavy metals tend to form hydroxy – complexes which will increase the solubility of the metal under consideration. For most metals, adsorption is greater at pH 6.5 than at pH 4.5. The adsorption of chromium compounds (chromates) does not change as significantly as other metals with pH changes. This is due to its oxyanion character in oxidizing condition and the adsorption mechanisms are very different compared to that of positively charged metals. These results confirm that adsorption for most metal cations increases as pH increases [48]. In this study, the average pH value is greater than 7 and as a result the concentration of Cr and Hg is declined.

The measured mean pH value of River Mojo water was 7.49 and high concentration of sulfates, phosphates and total dissolved solids were observed in the results of previous study of Tamene Fite D and Seyoum Leta [2]. For

the present study, at the maximum pH value, at site S₃, the concentrations of all metals are relatively small perhaps because of complex formation with the metals with sulfates and phosphates that obstructs the free metal ions availabilities. High concentrations of the metals were registered at pH < 7 specifically at pH = 6.55 and 6.85. The distribution of all metals at all sampling points is not uniform, viz, increasing at one sampling location and decreasing at another sampling site (Figure 3). This shows that the contaminants are not evenly distributed throughout the irrigation farmlands.

3.2 Soil Results correlation Analysis

Correlation analysis was carried out for inter-metallic and pH parameters association to understand the significance (p = 0.01, p = 0.05, p < 0.05) of association among the metals and the pH. The Pearson correlation coefficient matrix for trace heavy metals (As, Cd, Cr, Hg and Pb) and pH of the soil samples are presented in Table 8. The analysis of interrelationship between the heavy metals and pH offers remarkable information on the free ions availability. The computed statistical results shows that As has significant positive correlation with Hg (r = 0.806) while Cr, Hg and pH have weak negative correlation with Cd. Cr has weak insignificant positive correlation with Hg, Pb and pH (r = 0.321, 0.336, 0.463, respectively). Except for Cr all metals have weak negative correlations with pH (r = - 0.113, - 0.357, - 0.374, - 0.041, respectively for As, Cd, Hg and Pb) (Table 8). Lead is moderately significant with Cd (r = 0.583).

Table 8: Correlation coefficient matrix for the trace metals in soil samples

Pearson Correlation , Sig. (2-tailed), N = 12

Parameters	As	Cd	Cr	Hg	Pb	pH
As	1					
Cd	-0.354	1				
Cr	0.510	- 0.060	1			
Hg	0.806**	- 0.197	0.321	1		
Pb	0.158	0.583*	0.336	0.108	1	
pH	- 0.113	- 0.357	0.463	- 0.374	- 0.041	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

3.2.1 Plants' Correlation Analysis

Table 9 presents correlation statistics. All the vegetables are positively correlated. Garlic and onion are strongly significantly (r = 0.972, p < 0.01) positively correlated and garlic - pepper (r =0.917), onion – Kale (r = 0.940) and pepper – onion (r = 0.905) are strongly significantly (p < 0.05) correlated. This means that changes in one variable are strongly correlated with changes in the second variable. This means the changes in one variable are strongly correlated with changes in the second variable. Positive correlation tells us that as garlic variable

increases in value, the onion variable also increase in value. Similarly, as garlic variable decreases in value, the onion variable also decreases in value. Except for As – garlic ($r = 0.184$) and As – potato ($r = 0.261$) (8%), all the metals -vegetables are negatively correlated (92%). This is the results to be expected, because the plants absorb the soluble metal ions and decreases their concentration in soils. Garlic – Pb ($r = - 0.960$) and onion - Pb ($r = - 0.959$) are strongly significantly ($p < 0.01$) negatively correlated while Kale – Pb ($r = - 0.9240$ and pepper – Pb ($r = - 0.908$) are strongly significantly ($p < 0.05$) negatively correlated. The negative correlation values indicate that as one variable increases in value, the second variable decreases in value. The concentrations of As and Hg in table 3 shows that at the site As concentration was higher than that of the Hg. 60% of the metals are positively correlated (except for As - Cr, As - Hg and As – Pb and Cd – Cr). Hg and Pb are moderately correlated. The positive linear relationship of As – Cd, Cd – Pb, Cd – Hg, Cr – Hg and Cr - Pb is weak. Hg is moderately positively correlated with Pb. Only Hg and Pb are moderately positively correlated to each other, this is because both may have common sources or may be influenced by similar factors. The common sources of such contamination could either be the farming sites irrigated with polluted water or atmospheric deposition these metals due to the vehicle pollution or the sources of soil formations.

Table 9: Pearson Correlations of trace heavy metals with vegetables

	G	K	O	Pe	Po	As	Cd	Cr	Hg	Pb
G	1	0.852	0.972**	0.917*	0.623	0.184	- 0.487	- 0.188	- 0.733	- 0.960**
K		1	0.940*	0.801	0.723	- 0.236	- 0.532	- 0.039	- 0.497	- 0.924*
O			1	0.905*	0.640	- 0.032	- 0.581	- 0.041	- 0.626	- 0.959**
Pe				1	0.354	- 0.029	- 0.258	- 0.150	- 0.436	- 0.908*
Po					1	0.261	- 0.425	- 0.404	- 0.803	- 0.713
As						1	0.186	- 0.671	- 0.692	- 0.091
Cd							1	- 0.593	0.399	0.363
Cr								1	0.478	0.308
Hg									1	0.678
Pb										1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

[Note: G – Garlic, K – Kale, O – Onion, Pe – Pepper and Po – Potato]

4. Conclusion

The results of this study revealed that mean concentrations of Hg and Cr in the analyzed soil samples exceed the FAO/WHO and below Austria and Poland set standards (Table 2). The level of analyzed Cd in the soil samples is above the standards of European Union, India, United States, Poland, Germany and Austria. The major pollution source of the soil is might be the irrigation water from the River Mojo.

All mean concentration of the metals in all analyzed plant samples fall above the maximum permissible limit standard values in vegetables set by FAO/WHO. This shows that the metals accumulation is a severe phenomenon occurring in vegetables consumed in and Mojo area. The concentrations of As, Cd, Cr, Hg and Pb in garlic, Kale, onion, pepper and potato were above permissible limits and these agricultural products were exhibiting high accumulation of most of these metals. Thus, toxic metal accumulation in vegetables detected was severe and has potential to cause health risk to the communities consuming these vegetables frequently since these metals tend to bioaccumulate in consumers' bodies.

Therefore, their contaminations are detrimental to the members of the society, especially the children and the lactating mothers. One cannot under estimate the concentration level of these trace metals in the vegetables, because when frequently consumed they can bioaccumulate in the consumer's bodies and increase their concentration from non – toxic to toxic level through longer times or biomagnifies (Hg) in the ladder of energy levels. Thus, the vegetables are in a position not to be used for consumptions. It is suggested that the integrated pollution management is highly required and prevention measures and regular monitoring should be enforced on the River Mojo pollution from industrial pollutions.

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