Determination of the Level of Metallic Contamination in Irrigation Vegetables, the Soil, and the Water in Gondar City, Ethiopia

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Background: The sources of edible vegetables in Gondar, Ethiopia, are mainly from irrigation farms grown on the banks of polluted rivers. The aim of the current study was to determine the metallic contamination level of vegetables (Ethiopian kale, cabbage, Swiss chard, lettuce, onion, tomato, and potato), the soil they are grown in, and the water used for irrigation.

Methods: The concentrations of copper (Cu), manganese (Mn), zinc (Zn), chromium (Cr), cadmium (Cd), nickel (Ni), and lead (Pb) were determined using flame atomic absorption spectrometry. A composite purposive sampling method was used to collect samples from the Keha river irrigation site of Gondar city, Ethiopia. Acid digestion was performed before the samples were analyzed. Microsoft Excel was used for descriptive statistical analysis, and ANOVA was employed to compare the mean difference.

Results: In the vegetables samples, the mean concentrations of Cd, Ni, and Pb (0.23–6.25, 7.41–51.85, and 0–9.52 mg/kg, respectively) were found to be above the limits set by the joint WHO/FAO. Swiss chard and potato were found to contain the highest levels of Pb, while Ethiopian kale was highly contaminated with Cd and Cr. For the soil samples, the Pb (138.09–259.24), Ni (85.18–259.26), and Cd (4.63–20.37) mean concentrations (mg/kg) exceeded the recommended maximum limits set by the FAO. The mean concentrations (in mg/L) of Cr (0.5), Cd (0.046), and Cu (1.80) in the irrigated water samples were above the limit set by US EPA (2004).

Conclusion: The vegetables were contaminated with heavy metals that could be unsafe for chronic human consumption. In particular, leafy vegetables showed higher heavy metals levels compared to non-leafy vegetables.

Keywords: heavy metal, safe limits, soil, vegetables, wastewater irrigation

Introduction

Environmental pollution is posing significant public health risks worldwide, becoming a major concern in developing countries because of rapid economic activities and poor waste management. It is challenging to establish an association between environmental pollution and health effects because of the nature of pathways to exposure, limited data availability and the absence of a monitoring system. Furthermore, associations between environmental pollution and health are difficult due to the occurrence of multiple exposures, and the latency period of effect.^{1–4} Smith et al⁵ estimated that about 25–30% of the total burden of disease in the world is related to environmental factors, including chemical toxicants. For example, Goyer⁶ reported that lead is believed to be

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responsible for 3% of cerebrovascular disease burden worldwide. It has been reported that the prevalence level of lead in the blood of children worldwide is estimated at 40%, where the risk is more concerning in developing countries.⁷ In 2011, arsenic-contaminated water was responsible for 9,100 deaths and 125,000 disabilities in Asia.^{6,8} Epidemiological studies have established an association between exposure to heavy metals and the incidence of cancer.^{9–12} Toxic heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), and chromium (Cr) have the potential to bioaccumulate and interfere with biologically essential micronutrients such as zinc (Zn), cobalt (Co), and manganese (Mn).¹³ For example, dietary exposure to Pb and Cd can seriously deplete the level of iron (Fe), vitamin C, and other essential nutrients in biological systems, leading to a reduced immunological defense, retardation of intra-uterine growth, and neurobehavioral disorders.^{9,13} Essential heavy metals are required biologically in trace amounts. Otherwise, if they exceed the level, they become toxic. Heavy metals, specifically lead, mercury, cadmium, arsenic, and chromium, are well known for causing birth defects. They can easily cross the placenta and deposit in a growing fetus.^{9,11}

Even if the concentrations in the irrigation water or soil could be low, consumption of vegetables may lead to an uptake of a trace amount of heavy metals, contributing to the buildup of these toxicants in the body, bone, and other tissues, and ultimately may result in a detrimental health effect. In many developing countries including Ethiopia, it is common practice to grow vegetables using rivers passing through urban centers. Rivers crossing urban areas have been reported to be contaminated with heavy metals because of urbanization and increasing anthropogenic activities.^{14–16} A study in Ethiopia has shown that effluent discharge from industries, households, and institutions, solid wastes, and oily wastes from garages and fuel stations are the major sources of river pollution.¹⁵ Therefore, irrigation of urban lands with this contaminated water led to the accumulation of heavy metals in the soil and vegetables and thus uptake by plants, a problem that risks human health.^{14,–17–21} In Gondar city, vegetables and fruits are being grown by using water from the river Keha, where it passes within the city. The river is contaminated by untreated wastewater generated by the city. Vegetables from such irrigation fields are entering into the market and thus being consumed by people. The aim of the study was to determine concentrations of heavy metals (Pb, Cd, Cr, Cu, Zn, Ni, and Mn) in the soil, Keha river water used for irrigation, and the vegetables cultivated.

Methods and Materials

Study Area and Period

The study area was a vegetable farming site at “Mariyam sefer”, kebele 18, Gondar city, Ethiopia. Gondar city has a total population of around 224,000 (Ethiopian census 2014/15). The study period was from January–June in 2018.

Sample Digestions

Vegetables sample digestion and analysis were performed according to previous methods.^{22,23} Water and soil sample digestion and analysis were based on the method of Radulescu et al²⁴ and Tüzen,²⁵ respectively. Digestion of the vegetable and water samples were performed using concentrated hydrochloric acid (HCl), nitric acid (HNO₃), and perchloric acid (HClO₄) acid mixtures, while hydrofluoric acid (HF) was additionally required for soil sample digestion. To start, 1.0 g of the vegetable or 0.5 g of soil sample was weighed out into a flask and mixed with 5 mL of concentrated HNO₃, then left to stand overnight for predigestion. On the next day, for vegetable and soil samples in the flask were heated at 100°C for 15 minutes, next at 150°C for 30 minutes, followed by exposing at 200°C for the next 30 minutes until boiling stops or 2–3 mL solution remains. After cooling, for both sample types, 5 mL Conc. HCl was added for further digestion with the same temperature and time, again after cooling 3 mL HClO₄ was added and the digestion continued for 30 minutes. For soil samples, 2 mL HF was added to decompose silicates by heating.

A 50 mL aliquot of well-mixed water samples was digested by adding 5 mL of conc. HNO₃ and heated at 95°C until the volume reduced to 5 mL, then cooled followed by 5 mL of concentrated HCl addition. Because of precipitation formation, 1 mL of HClO₄ was added and heated for further decomposition. Finally, all the digested samples were filtered using Whatman no. 42 filter paper and the filtrate was stored until analysis.

The level of heavy metals in the filtrate was determined using a 210VGP model Flame Atomic Absorption Spectrophotometer (FAAS). After digestion, samples were analyzed with triplicate injections.

Quality Assurance and Control Methods

The procedure used for digesting the vegetable, soil, and water samples was checked by spiking the vegetable, soil, and water samples with standard solutions of each metal having a known concentration.

Calibration curves were prepared to determine the concentration of the heavy metals in the sample solutions. An intermediate standard solution (5 mg/L) of the respective metals was prepared from standard solutions comprising 1,000 mg/L of each heavy metal. Working standards were prepared by serial dilution using distilled water. Analytical wavelengths, energy, and slit width were adjusted using the manual. Working standards were aspirated into the FAAS and their absorbance were recorded. Calibration curves were plotted for each of the metals using absorbance Vs concentrations (mg/L). After establishing a calibration using the standard solutions, the sample solutions were aspirated into the FAAS instrument and readings were recorded. Blank measurements were conducted.

Statistical Analysis

Microsoft Excel was used for descriptive statistical analysis, while ANOVA was used to examine the significance level of all parameters measured.

Results

Concentration of Metals in Vegetables

The mean concentrations of the metals (Cr, Cu, Zn, Ni, Cd, and Pb) in the investigated vegetables are given in Table 1. The observed ranges in the concentrations of metals (mg/kg) were found to be Pb (0–9.52), Cd (0.23–6.25), Cr (5.83–13.33), Cu (1.61–11.29), Zn (19.16–88.31), Ni (7.41–51.85), and Mn (0.91–76.67).

Concentration of Metals in the Soil

The pH, conductivity and T^0 of the soil were 5.9, 91.2 $\mu\text{S}/\text{cm}$, and 22.7°C, respectively. The data presented in Table 2 shows the range of mean concentration of metals in the soil. For the soil samples, Pb, Ni, and Cd mean concentrations exceed the Recommended Maximum Level (RML) set.²⁶

Metals Concentration in Irrigated Water

The physical characteristics of Keha river water were pH=7.65, EC=0.813, and T^0 =23.4. Concentrations of metals in the irrigation water samples collected from the farming site are given in Table 3.

Discussion

This study was undertaken to determine the level of heavy metals' loads in the vegetables grown in irrigated lands in Gondar City. The levels of Pb, Cd, Cr, Cu, Zn, Ni, and Mn

were determined at the soils the vegetables were grown, in the water used for irrigation, and the vegetables, and the results were compared against the WHO/FAO joint standard values.

The mean concentrations of Cr, Pb (except in onion), and Cd detected in vegetables were higher than the limit set by the WHO/FAO, while the levels of Cu, Mn, Zn, and Ni concentrations were within the standard.²² Elevated concentrations of heavy metals, especially Cr and Cd, will result in cancer risk when the daily intake exceeds the recommended value.^{27–29} From the vegetable samples, swiss chard and potato (both 9.52 mg/kg) were highly contaminated by Pb, followed by Ethiopian kale (7.14 mg/kg) and Tomato (5.95 mg/kg). In 2013, FAO set the maximum limit for cadmium to be 0.05, 0.1, and 0.2 in mg/kg for fruity, tuber, and leafy vegetables, respectively while for lead it was 0.1 mg/kg for fruity and tuber vegetables, and 0.3 mg/kg for leafy vegetables.³⁰ Leafy vegetables are found to be more likely to absorb Pb than fruity vegetables. This is in line with a study conducted by Gezahegn et al.¹³ High concentrations of Pb above the permissible level in leafy vegetables were reported in a study conducted in Akaki, Addis Ababa.³¹ Prisacaru et al.³² have reported that Pb and Cd are preferentially absorbed by leafy vegetables. The accumulation of elevated levels of Pb in leafy vegetables in the current study might be associated with the influence of wastewater irrigation that receive effluents from garages, hospitals, and painting materials in the city.

Bioaccumulation Factors (BAF), which is the ratio of the concentration of metal in the vegetable to concentration of metal in soil, is used to show the absorption of heavy metals in the soil and vegetables. A BAF of above 1.0 shows a higher uptake of heavy metals in vegetables compared to the soil. In all vegetables, except Zn for Ethiopian kale, the BAF was found to be below 1.0 (data not shown) which indicated a low uptake of heavy metals by them. The high BAF of Zn signifies its higher mobility from soil to vegetables or bioavailability. In contrast, in the current study lead has shown the lowest transfer factor. Gupta et al.³³ found out that the lead transfer factor was very low compared to Fe, Cd, Mn, and Cr. Generally, the transfer of metals from soil to vegetables may depend on the soil nature, composition of the metal parent material, vegetable species, and solubility of the metals.^{23,34,35} When BAF is >0.05 , it shows that the contamination is probably because of an anthropogenic source.²¹ Significant

differences between mean concentrations of heavy metals in the soil and vegetable was observed (data not shown).

Consumption of these vegetable contaminated with Pb has public health implications, since lead and other heavy metals have a tendency to bio-accumulate in human body tissues leading to toxicological effects. Lead is a known human toxic metal that can cause kidney dysfunction and neurological damage at a low concentration in the blood level.^{36–39}

A higher concentration (above the limit) of Cd was detected in Ethiopian kale (6.25 mg/kg >0.2 mg/kg limit) followed by potato (6.02 mg/kg 0.1 mg/kg limit), onion (3.93 mg/kg >0.05 mg/kg limit) and tomato (1.97 mg/kg >0.05 mg/kg limit). The Cd level found in this study was far greater than the level (<0.2 mg/kg) reported in a study conducted by Misganaw and Nardos.⁴⁰ Chromium load in Ethiopian kale (13.33 mg/kg) was highest, followed by Swiss chard (11.67 mg/kg), and Cabbage (10 mg/kg). The higher concentrations for these metals were observed in leafy vegetables, which is supported by previous studies.^{41–43} This implies that consumption of leafy vegetables compared to root vegetables might contribute to a higher human exposure.

In the water samples, only Cr, Cd, and Cu were found above the limit set by the US EPA, 2004.⁴⁴ The reason that

the concentration of metals in the vegetables was greater than the irrigated water could be the bioaccumulation capacity of plants. In addition, the physiology of the various plants may determine the level of accumulation of heavy metals starting from up taking in soil to a preferential storage in the plant parts such as roots and leaves.^{41,45,46} A pH level of soil can determine the mobility and uptake of heavy metals by plants.⁴⁰ The current study showed that toxicological important heavy metals (Pb, Cr, and Cd) were in higher quantity in leafy vegetables compared to the rest of studied heavy metals, which are less toxic.

The mean concentrations of Cr, Cd, and Cu in irrigated water were above the limit set by the US EPA (2004). This shows that the continuous use of sewage and wastewater for agricultural land can increase the burden of heavy metals on the soil.⁴⁷ For most of the metals, as shown in Table 3, the concentration of metals was decreasing from the river water to the water reached in the farm where vegetables were grown. This could be because of the natural deposition of metals when the water flows slowly along the irrigation channel.

The highest and lowest Pb were observed in cabbage soil (295.24 mg/kg) and Ethiopian kale soil (138.09 mg/kg),

Table 1 Mean Concentration of Metals (in mg/kg) in Vegetables

Vegetables	Metals (Mean±SD)						
	Pb	Cd	Cr	Cu	Zn	Ni	Mn
Cabbage	3.80±3.66	1.62±1.29	10±3.16	2.82±0.67	27.87±4.41	7.41±4.54	7.27±3.54
Swiss chard	9.52±4.12	1.38±1.20	11.66±5.77	1.88±1.23	48.65±8.33	51.85±25.6	76.66±5.25
Ethiopian kale	7.14 ±0	6.25 ±1.20	13.33±2.88	2.41±0.80	88.3±6.145	11.11±5.55	30.61±2.62
Tomato	5.95 ±2.91	2.43 ±0.85	5.8 ±3.76	2.01±1.11	24.61±0.79	13.88±7.65	2.42±1.37
Potato	9.52±4.12	6.01±0.80	6.66±2.88	11.29±0	56.70±8.34	20.37±3.2	0.91±0.91
Onion	0 ±0	3.93±1.06	6.66±2.88	2.15±1.67	19.15±9.12	9.25±6.41	3.94±2.28
Lettuce	2.38 ±4.12	0.23±0.40	6.66±2.88	1.61±1.39	64.55±6.46	48.14±3.21	41.52±1.89

Table 2 Metals Mean Concentration in Soil (mg/kg)

Soil	Metals (Mean±SD)						
	Pb	Cd	Cr	Cu	Zn	Ni	Mn
Cabbage	295.2±75.9	9.027±1.70	48.33±9.83	119.89±19.55	250.19±38	203.7±50	851.8±88.06
Swiss chard	242.85± 0	4.62 ±2.12	40±10	104.83±5.81	191.95±12	188.9±50.9	730.30±3.78
Ethiopian kale	138.1±8.24	20.37±2.12	46.66±5.77	138.7±8.98	55.93±17.8	259.25±17	932.72±183
Tomato	154.76±16	12±1.89	36.66±8.16	66.9±1.16	197.3±14.6	140.74±24	734.54±29.5
Potato	180.95±21.8	8.79±1.60	33.33±5.77	28.06±39.95	194.63±30	122.2±50.9	676.36±57.7
Onion	176.2±29.73	14.35±2.12	33.33±5.77	87.09±19.35	246.36±53	140.74±16	869.69±23
Lettuce	171.4±28.5	8.79±1.60	30± 0	82.79±17.69	270.5±24.9	85.18±32	815.2±117

Table 3 Mean Concentrations of Metals in Irrigation Water (mg/L)

Water	Metals (Mean±SD)						
	Pb	Cr	Cd	Cu	Ni	Mn	Zn
Keha (outside the field)	0.26±0.21	0.5±0.54	0.046±0.01	1.80±0.14	0.17±0.15	0.478±0.16	0.86±0.01
Within the field	0.09±0.15	1.33±1.03	0.043±0.01	0.01±0.01	0.11±0.14	0.46±0.049	0.86±0.006
Before entering the field	0.214±0.2	1±0.63	0.035±0.02	0.019±0.02	0.076 ±0.09	0.43±0.048	0.868±0.01
EPA MRL (2004)	5	0.1	0.01	0.2	0.2	0.2	2

respectively. Cd was highest in the soil of Ethiopian kale (20.37 mg/kg) and lowest in Swiss chards soil (4.63 mg/kg). The highest concentration of Cr was observed from the cabbage soil (48.33 mg/kg) while the lettuce soil was found to contain the lowest (30 mg/kg). The highest concentration of Cu was observed in Ethiopian kale soil (138.71 mg/kg) followed by potato soil (28.06 mg/kg). Lettuce soil was found to hold the highest Zn content (270.5 mg/kg), whilst Ethiopian kale soil possessed the lowest (55.94 mg/kg) Zn concentration. The Ethiopian kale soil (259.26 mg/kg) and Lettuce soil (85.18 mg/kg) were found containing the highest and lowest Ni concentrations, respectively. The current results showed that soils in which vegetables were grown are contaminated by metals. Therefore, the exceeded value found in the vegetable parts is likely the result of the contaminated soil.

In summary, from all the studied heavy metals, the concentrations of the most toxic metals, namely Cr, Cd, and Pb, found in all of the vegetables studied were above the safe limits, whilst Zn, Ni, Cu, and Mn were within the limit set.²⁶ Leafy vegetables were found to contain higher heavy metals levels than roots, which implies that leafy vegetables may pose a greater risk for chronic human consumption. The reported high level of heavy metals in the vegetables and soils indicated that the irrigation water has been possibly contaminated by anthropogenic sources. The bio-accumulative nature of these heavy metals in the human body could bring a long-term health impact.

Limitation of the Study

The study was only conducted in the dry season.

Data Sharing Statement

Data will be available upon request.

Ethical Consideration and Consent to Participate

A Letter of Ethical approval was received from the Institute of Public Health ethical clearance committee. An official

letter of co-operation was also obtained from Gondar city urban Agricultural office. Individual informed consent was taken from the owners and farmers of the vegetation after a brief explanation about the purpose of the study.

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Author Contributions

All authors contributed to data analysis, drafting, or revising the article, have agreed on the journal to which the article will be submitted, gave final approval of the version to be published, and agree to be accountable for all aspects of the work.

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Disclosure

The authors declare that they do not have competing interests.

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