



RESEARCH ARTICLE

EXPLORATION OF THE LEVELS OF HEAVY METALS AND SOME PHYSICO-CHEMICAL  
PARAMETERS IN FARM SOILS AND IRRIGATION WATER IN SELECTED WOREDAS OF GURAGE  
ZONE, ETHIOPIA

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ARTICLE INFO

Article History:

Received 18<sup>th</sup> February, 2018  
Received in revised form  
08<sup>th</sup> March, 2018  
Accepted 29<sup>th</sup> April, 2018  
Published online 23<sup>rd</sup> May, 2018

Key words:

Kjeldahl,  
Heavy Metals,  
Soil, Digestion,  
Flame atomic Absorption  
Spectrometer.

ABSTRACT

Human activities such as industrial production, mining, agriculture and transportation, release high amounts of heavy metals into surface and ground water, soils and ultimately to the biosphere. In the present study the levels of some selected heavy metals (Mn, Zn, Cr, Ni, Cu, Cd and Pb) in soil and irrigation water sampled from selected Woredas of Gurage Zone (i.e. Meskan, Mareko, Sodo, Muhir and Cheha Woredas), Southern Region, Ethiopia were analyzed. 1 kg from every sample was air-dried, mechanically ground using a stainless steel roller and sieved to obtain 2 mm fraction. A 20–30 g subsample was drawn from the bulk soil (2 mm fraction) and reground to obtain 200  $\mu$ m fraction using a mortar and pestle. The digestion method optimized for soil sample by FAO- Aqua-regia Digestion method has been used for extraction of heavy metals from the soil samples. Accordingly 0.5 g of dried and homogenized soil sample was taken in to a flask and treated as follows. To each 6 mL of aqua-regia (3:1 ratio of 37 % HCl to (69-72 %) HNO<sub>3</sub>, respectively) and followed by 1.5 mL of 30 % H<sub>2</sub>O<sub>2</sub> were added. The mixture was digested on a Kjeldahl digestion apparatus with optimized parameters such as temperature and time. The contents of the minerals in the digests were analyzed using flame atomic absorption spectrometer (FAAS). The following concentration ranges (mg/kg) were found in soil: Zn (110.97 - 177.55), Cu (14.6 - 28.4), Mn(740 - 1972), Cr (49.2 - 70.4), Ni (36.6 - 67.6), Pb (2 - 18) and Cd were ND( i.e. Below method detection limit) in all woreda samples. In this study, all heavy metals were not found (below method detection limit) in water samples. The concentration of heavy metals in the soil which was collected from sites in which vegetables grown was determined in this study. The range level of Zn, Cu, Mn, Cr, Pb and Ni found in soil samples were 110.97 - 177.55, 14.60 - 28.40, 740 - 1972, 49.2 - 70.4, 2.000 - 18.00 and 28.8 - 67.6 mg/kg respectively. The soils of the study were found to contain high concentration of Mn followed by Zn, Cr, Ni, Cu, Pb. However, Cd was not detected (below detection limit) in soil samples. Levels of heavy metals determined in soils were compared with standard values and found below the tolerance level.

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Citation: Ashenafi Emiru Teka, Eyasu Gebrie Ajebe and Teshale Assefa Biru, 2018. "Exploration of the levels of heavy metals and some physico-chemical parameters in farm soils and irrigation water in selected Woredas of Gurage Zone, Ethiopia", *International Journal of Current Research*, 10, (05), 68937-68946.

INTRODUCTION

Human activities such as industrial production, mining, agriculture and transportation, release high amounts of heavy metals into surface and ground water, soils and ultimately to the biosphere. Accumulation of heavy metals in crop plants is of great concern due to the probability of food contamination through the soil root interface. Though the heavy metal like, Cd, Pb and Ni are not essential for plant growth, they are readily taken up and accumulated by plants in toxic forms. Ingestion of vegetables irrigated with waste water and grown

in soils contaminated with heavy metals possesses a possible risk to human health and wildlife. Heavy metal concentration in the soil solution plays an important role in controlling metal bioavailability to plants. Most of the studies show that the use of waste water contaminated with heavy metals for irrigation over long period of time increases the heavy metal contents of soils above the permissible limit. Ultimately, increasing the heavy metal content in soil also increases the uptake of heavy metals by plants depending upon the soil type, plant growth stages and plant species (Afzal Shah et al., 2017).

**Heavy metals in the environment:** Heavy metals are currently of much environmental concern. These metals are dangerous because they tend to bioaccumulate in the food chain and they are harmful to humans and animals (Alloway,

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1994). Both natural and anthropogenic sources are responsible for increasing the levels of heavy metals in the environment (Singah, 2007). The threat that heavy metals pose to human and animal health is aggravated by their long-term persistence in the environment (Alloway, 1994).

**Heavy metals pollution in soil:** Heavy metal pollution in soils refers to cases where the quantities of the elements in soils are higher than maximum allowable concentrations and this is potentially harmful to biological life at such locations (Adeleken, 2011). Metals enter the soil as stable organ complexes, such as those used in fertilization to correct micronutrient deficiencies or those possibly present in discharge from a nuclear fuel separation facility (Cataldo, 1978). Heavy metals occur at typical background in all ecosystems, however, anthropogenic releases can result in higher concentrations of these metals relative to their normal background values hence the pollution (Adeleken, 2011). Heavy metals released from vehicular emission can accumulate in surface soils and their deposition over time can lead to abnormal enrichment, thus causing metal contamination of the surface soils (Fong *et al.*, 2008). High concentrations usually occur in soils below or near landfills and agricultural lands that have been irrigated with contaminated water (Mamtaz, 2006). Studies have shown that both long term and short term contamination of soils have effects on microbial activity and enzyme activities of the soil (Alloway, 1994). The toxicity and mobility of heavy metals in soils depend not only on the total concentration but also on their specific chemical form, bonding state, metal properties, environmental factors, soil properties and organic matter content (Osu, 2011). Exposure of children, generally accepted as the highest risk group who have a higher adsorption rate of heavy metals because of their active digestion system and sensitivity of haemoglobin, to heavy metals, can greatly increase ingestion of metal laden soil particles via hand-to-mouth activities. In addition, adults may be exposed to threat since inhalation is easier pathway for toxic metals to enter their body (Fong *et al.*, 2008).

**Heavy metals in water:** The contamination of fresh waters with a wide range of pollutants has become a matter of great concern over the last few decades (Al-Weher, 2008). The aquatic systems receive a large amount of heavy metals from natural occurring deposits and natural processes and anthropogenic activities (Wogu, 2011). Anthropogenic sources arising from human activities such as industrial, municipal effluents, as well as non-point source run off are the main sources of metals in rivers (Pint, 1976). Discharge of heavy metals into rivers or any other aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behaviour (Al-Weher, 2008). Heavy metals dissolved in water also endanger the lives of the public who use it for drinking and also irrigation. When used for irrigation heavy metals have the danger of being incorporated in food chain and therefore ingested by the public (Wogu, 2011). Heavy metals accumulate in the soils at toxic levels as a result of long term application of untreated waste water and therefore soils irrigated by wastewater accumulate heavy metals in their soil surface. When the capacity of the soil to retain heavy metals is reduced due to repeated application of waste water, the metals leach into ground water or soil solution available for uptake (Sonaye *et al.*, 2009).

**Atomic spectroscopy:** This technique is applicable to most gas phase elements over a wide range of concentrations and involves detecting, measuring and analyzing radiation that is either absorbed or emitted from the atoms or ions of the element of interest. It involves three techniques: absorption, emission and fluorescence. In all the above, the sample is decomposed by intense heat into hot gases consisting of free atoms and ions of the element of interest (McMahon, 2007).

## Objectives

**General Objective:** To investigate the level of heavy metals in irrigation water and soil irrigated in selected woredas of Gurage Zone, Ethiopia.

## Specific Objectives

- To analysis physico-chemical parameters of water
- To determine heavy metals concentrations from soil which used for irrigation purpose
- To determine the levels of heavy metals in irrigation water
- To correlate the levels of heavy metals in soil samples
- To compare the obtained results with other accepted values

## METHODOLOGY

**Description of the study area:** This study was conducted in selected woredas of Gurage Zone in the Southern region of Ethiopia which largely produce vegetables by irrigation. Geographically, the study area (Gurage Zone) is located between 7.8° - 8.5° North latitude and 37.5° - 38.7° East longitude of the equator. Wolkite, the capital of the zone, is 155 km away from Addis Ababa to southwest direction. Gurage zone has a total area of 5932 km<sup>2</sup>. It has 13 Woredas with a total population estimated about 1,343,246 according to the survey conducted. The zone comprises altitudes ranging from 1,001 to 3,500 meters above sea level (m.a.s.l). The mean annual temperature of the zone ranges between 13-30 °C and the mean annual rainfall ranges 600-1600 mm. Woredas in which the study conducted were Meskan, Sodo, Mareko, Cheha and Muhir Aklil. The choices of the study sites (woredas) were on the basis of availability of vegetables in the regions.

**Apparatuses and instrument:** Polyethylene bags, crucibles, stainless steel knife, muffle furnace, a drying oven, and electronic blending device in addition to this mortar and pestle were used for grinding soil sample. Stainless steel soil sampling auger was used to collect soil samples. Soil samples were ground using ceramic mortar and pestle. An electric motor grinder was also being used to ground vegetables. A digital analytical balance with +0.0001 g precision was used to weigh vegetable and soil samples. Volumetric flasks (25, 50 and 100 mL) were used during dilution of samples and preparation of heavy metal standard solutions. A water deionizer was used to produce demineralized water. Measuring cylinders, pipettes, micropipettes were used during measuring different volumes of sample solutions, acid reagents and metal standard solutions. Flame atomic absorption spectrophotometer was used to analyze the concentrations of Cu, Mn, Zn, Cr, Cd, Pb and Ni in samples. Visible spectrophotometer was also used in the determination of available phosphorous in soil samples.

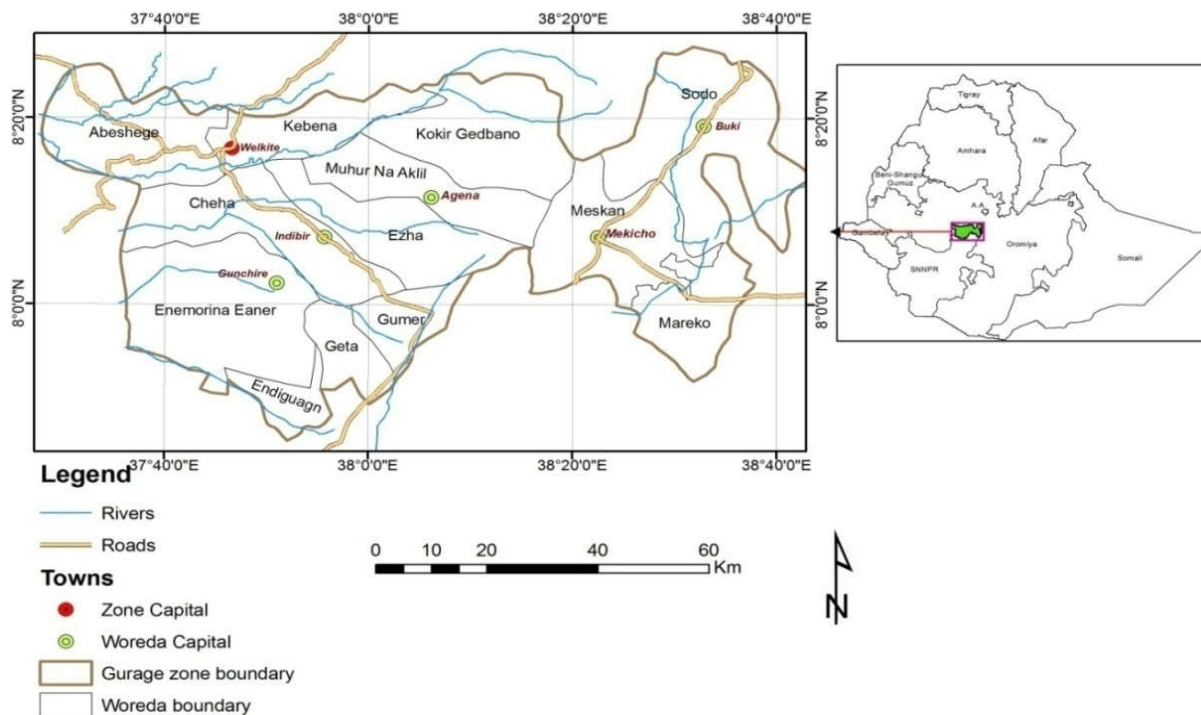


Figure 2.1: Map of the study areas (adapted from Abate *et al.* 2011)

The pH meter was used to determine the pH of soil and water samples after stirring by a magnetic stirrer. A conductometer was also used to measure the conductivity of water and soil samples.

**Reagents and chemicals:** All the chemical and reagents used were analytical grade. An acid mixture of conc. HCl (36 - 38%) and conc. HNO<sub>3</sub> (70%) were used for the digestion of the soil samples. Concentrated HNO<sub>3</sub> (70%) was also used in the solubilization of vegetable ashes and in preparation of stock standard solutions. (NH<sub>4</sub>)<sub>2</sub>Fe (SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, conc. orthophosphoric acid and 1, 10-phenanthroline ferrous sulfate solutions were used to determine soil organic matter. Standard stock solutions Zn, Cd and Cr were prepared from metal powders of each element after dissolving in a minimum volume of concentrated HCl (1:1 HCl: H<sub>2</sub>O) and diluted to 100 ml with 1% (v/v) HCl. Standard stock solution of Mn was prepared from metal powder of the element after dissolving in a minimum volume of concentrated HNO<sub>3</sub> (1:1 HNO<sub>3</sub>:H<sub>2</sub>O) and diluted to 100 ml with 1% (v/v) HCl and with deionized water respectively. Standard stock solutions of Cu and Pb were prepared from Cu metal powder and lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>, respectively, after dissolving in a minimum volume of (1:1) concentrated HNO<sub>3</sub> (1:1 HNO<sub>3</sub>:H<sub>2</sub>O) and diluted to 100 ml with 1% (v/v) HNO<sub>3</sub>. Standard working solutions were prepared freshly from the standard stock solutions (1000 mg/L) of each of the metals by appropriate dilution of the intermediate standard solution (100 mg/L).

**Sampling of soil:** Five separate soil samples were taken from each farm. Sludge and normal soil samples were collected during sampling. The soil sample was taken in different depths ranging from 0-20 cm using stainless steel sampler. Soil samples from the agricultural sites were randomly sampled and bulked together to form a composite sample. In all cases, soil samples were put in clean plastic bags and transported to the laboratory. Soil samples were then air-dried, crushed and passed through 2mm mesh sieve. The samples were then put in clean plastic bags and sealed.

Ground water samples were also collected from different water sources which were used for irrigation. Sampling procedure involves water samples from the surface and different depths to obtain representative samples. Onions from the agricultural sites were freshly harvested from farms and packaged into labeled polyethene bags, and transported to the laboratory awaiting analysis. Generally, a total of fifteen samples of onions and fifteen samples of water were collected from each site and homogenized to five representative samples of each woreda between December(2016)-March(2017). It is notice that the sampling points were statistically distributed all over the study area to ensure appropriate spatial coverage of the woreda. The considered sites were of commercial vegetable farms.

### Sample preparation

**Water sample preparation:** In this step of the research, water samples (five separate samples from the three points of sites) were carefully taken and filtered through Whatman number 42 μm filter paper. Filtered water samples were mixed and stored at less than 4°C until analysis.

**Soil sample preparation:** Different soil samples collected from different sites of each woreda were mixed to obtain homogenized sample. Analyzed soil sample was taken from the composted mixture. 1 kg from every sample was air-dried, mechanically ground using a stainless steel roller and sieved to obtain 2 mm fraction. A 20–30 g subsample was drawn from the bulk soil (2 mm fraction) and reground to obtain 200 μm fraction using a mortar and pestle. The digestion method optimized for soil sample by FAO- Aqua-regia Digestion method has been used for extraction of heavy metals from the soil samples. Accordingly 0.5 g of dried and homogenized soil sample was taken in to a flask and treated as follows. To each 6 mL of aqua-regia (3:1 ratio of 37 % HCl to (69-72 %) HNO<sub>3</sub> respectively) and followed by 1.5 mL of 30 % H<sub>2</sub>O<sub>2</sub> were added. The mixture was digested on a Kjeldahl digestion

apparatus with optimized parameters such as temperature and time.

**Instrument operating conditions and calibration:** Stock standard solutions were used for preparing intermediate standards and working standards by using deionized water. Working standards of metals solutions were prepared by diluting the intermediate standards solutions of the metal with deionized water. Five points of calibration curve were established by running the prepared working standard solutions in Flame Atomic Absorption Spectrometer. Immediately after calibration, the sample solutions were aspirated into the FAAS instrument and direct readings of the metal concentrations were recorded. Triplicate samples measurement was carried out on each sample. The same analytical procedure was employed in the determination of elements in each four digested blank. The operating conditions of FAAS employed for each analyte are given in Table 2.1.

**Method Validation:** To check accuracy of the extraction of soil samples and efficiency of the FAAS various methods like certified standard reference material analyzing, spiking sample and comparing the values conducting in a different method, laboratory or analyst may be used. In this work, spiked samples were prepared by adding a small known quantity of standard solutions to subsamples of certain samples; applying similar extraction procedure analyzing for the metals and calculating the recovery percent.

**Analysis of physico-chemical parameters:** Water samples obtained from different sampling areas were subjected for the analysis of their physical and chemical properties. The reason in determination of physico-chemical parameters is due the quality of water depends on their physical properties such as conductivity, acidity, colour and different chemical properties. The physical properties and chemical properties largely determine the suitability of a soil and water for their planned use and the management requirements to keep them most productive in agricultural purposes largely. The pH values were determined using Equiptronics pH meter as described by Jackson (Jackson, 1967). For this 20 g soil sample was mixed with 40 ml distilled water in 1: 2 ratio. The suspension was stirred with glass rod for 30 minutes and left for one hour. The combine electrode was inserted into supernatant and pH was recorded.

The power of hydrogen value as calculates of the hydrogen ion action of the soil and water and state the acidity and alkalinity of the soil and water. It is an important property of soil as it fixes the accessibility of nutrients and physical condition of soil. Electrical conductivity (EC) expresses ion contents of solution which determine the current carrying capacity thus giving a clear idea of the soluble salts present in the soil and water (Wagh *et al.*, 2013). Electrical conductivity of the soil was determined in the filtrate of the water extract using conductivity meter. The electrical conductivity of a soil samples was determined on a digital electrical conductometer for which 20 g soil was added in 40 ml distilled water. The suspension was stirred intermittently for half an hour and kept it for 30 minutes without any disturbances for complete dissolution of soluble salts. The soil was allowed to settle down and then conductivity cell was inserted in solution to take the reading to record the EC values. The quantity of organic carbon in the soil was estimated by using modified Walkley- black method (Walkley, 1934). 1 g finely ground dry

soil sample was passed through 0.5 mm sieve and was taken into 500 ml conical flask. To this 10 ml of 1N potassium dichromate and 20 ml con.  $H_2SO_4$  were added and the contents were shaken for a minute and allowed to set aside for exactly for 30 minutes and then 200 ml distilled water, 10 ml phosphoric acid and 1ml diphenylamine indicator were added. The solution was titrated against standard ferrous ammonium sulphate till colour changes from blue violet to green. The blank titration was also carried without soil. Available phosphorus was estimated by Olsen's method (Olsen *et al.*, 1954). The reagent for Olsen's P was 0.5 M  $NaHCO_3$  (pH 8.5) prepared by dissolving 42 g  $NaHCO_3$  in distilled water and made up to 1 L. The pH was adjusted at 8.5 with 20% NaOH solution. 2.5g of air dried soil was weighed into 250ml Erlenmeyer flask, 50ml of Olsen's reagent (0.5 M  $NaHCO_3$  Solution, pH 8.5) and one teaspoonful of activate charcoal were added. The flasks were shaken for 30 minutes and contents were filtered immediately through Whatman filter paper (No. 41). 5ml of the filtrate was taken out by pipette into 25ml of volumetric flask and was neutralized with 1:4  $H_2SO_4$  using p-nitrophenol as indicator and the volume was made up by adding distilled water. After addition of few crystals of stannous oxalate, blue color developed and intensity of blue color was read in visible spectrophotometer at a wavelength of 730nm. Available nitrogen was estimated by alkaline Permanganate method (Black, 1965). For water samples, different physicochemical parameters were also determined. pH and conductivity of water samples were determined using pH meter and conductometer respectively. Also total solid, total suspended solid and total dissolved solids were determined in water samples as follows:

**Total suspended solid:** Whatman filter paper rinsed in distilled water was dried in an oven at  $105^\circ C$  for one hour and cooled in a desiccator. Its weight ( $W_1$ ) was determined using a weighing digital balance. 100 ml of water sample was filtered through the paper and dried at  $105^\circ C$  for one hour. The weight ( $W_2$ ) of filter paper containing the residue was recorded and the total suspended solids were calculated.

**Total dissolved solid:** Amount of dissolved solids of the water sample was determined by subtracting the values of the suspended solids from the corresponding total solids of the samples.

**Total hardness:** The water sample was thoroughly shaken and 25 ml was taken and diluted to 50 ml with distilled water. 2 ml of phosphate buffer solution was added to bring the pH of the water sample to 10. Three drops of eriochrome black indicator was also added. This was titrated with 0.01 mol/L EDTA to a blue color end point.

**Heavy metals analysis:** After samples were digested; transparent solutions of water and cabbage samples were then filtered through Whatman number 42  $\mu m$  filter paper and diluted to 100 mL with distilled water. The clear filtrate was then subjected for determination of heavy metals levels using flame atomic absorption spectrophotometer.

**Data analysis:** The data derived from various determinations was subjected to statistical analysis including mean and ANOVA. The means for the levels in samples were determined. Using one way ANOVA, the means were compared to determine whether they were significantly different.

## RESULTS AND DISCUSSION

**Instrument calibration:** The instrument was calibrated using five series of working standards. The working standard solutions of each heavy metal were prepared fresh by diluting the intermediate standard solutions. The concentrations of working standard solutions and the correlation coefficient obtained for each heavy metal is given in Table 3.1.

In the current study, the organic carbon (% weight) present in analyzed soil samples was ranged from 0.59 to 0.97. The highest value of organic carbon was recorded in soil sample of Muhir Aklil while the lowest value was obtained from Sodo woreda. The organic soil matter includes all the dead plant materials and live or dead animals. Most living things in soils, including plants, insects, bacteria and fungi, are dependent on organic matter for nutrients and energy.

**Table 2.1. Instrumental operating conditions for the determination of heavy metals in different samples using FAAS**

No	Element	Parameters				
		Wavelength (nm)	Bandwidth (nm)	Lamp current (mA)	Instrumental Detection limit (mg/L)	
1	Zn	285.2?	0.4	5.0	0.0018	
2	Cu	324.7	0.4	3.0	0.0042	
3	Mn	279.5	0.2	2.0	0.005	
4	Cr	357.9	0.4	4.0	0.002	
5	Cd	228.8	0.4	2.0	0.0046	
6	Pb	283.3	0.4	2.0	0.01	
7	Ni	232.0	0.2	4.0	0.008	

**Table 3.1. Working standard solutions and correlation coefficients for heavy metals**

No	Element	Standard Concentration (ppm)	Correlation Coefficient
1	Zn	0.250, 0.500, 1.000, 1.500, 2.000	0.9975
2	Cu	0.500, 1.000, 2.000, 3.000, 4.000	0.9994
3	Mn	0.250, 0.500, 1.000, 1.500, 2.000	0.9997
4	Cr	0.250, 0.500, 1.000, 1.500, 2.000	0.9989
5	Cd	0.250, 0.500, 1.000, 1.500, 2.000	0.9965
6	Pb	0.250, 0.500, 1.000, 1.500, 2.000	0.9998
7	Ni	0.250, 0.500, 1.000, 2.000, 3.000	0.9997

**Table 3.2: Physicochemical properties of soil samples from different woredas of Gurage zone**

No	parameters	Woredas				
		Meskan	Mareko	Sodo	Muhir Aklil	Cheha
1	pH	7.9	8.2	7.4	6.8	7.7
2	Electrical Conductivity	0.85	1.23	0.94	0.17	0.58
3	%C	0.67	0.64	0.59	0.97	0.85
4	%N	0.071	0.065	0.056	0.024	0.051
5	%P	0.018	0.017	0.01	0.012	0.02
6	Moisture content					

### Physico-chemical parameters of water samples

Physicochemical properties of water samples were studied. The results obtained in the analysis of water samples are summarized in Table 3.2. As indicated in Table 3.2, the analyzed soil samples have pH values ranging from 6.8 to 8. These pH values show that alkaline nature of soil exceptional to soil sample obtained from Muhir Aklil. Soil electrical conductivity is an important characteristic that can be used for nutrient availability and the soluble salt present in the soil (Saramanda *et al.*, 2017). It is commonly used as a measure of salinity (Jackson, 1967). Excess salinity may cause moisture stress within the plant. However, too pure of can also be detrimental. Water with too few salts can lead to surface soil dispersion and soil crusting. Salinity is a measure of the total amount of soluble salts in soil. As soluble salt levels increase, it becomes more difficult for plants to extract water from soil (Saramanda *et al.*, 2017). Soil with EC below 0.4 mS/cm are considered marginally or non-saline, while soils above 0.8 mS/cm are considered severely saline (Wagh *et al.*, 2013). In the present study, electrical conductivity (EC) of soil samples was varied from 0.17 to 1.23 mhos (Table 3.2). The highest value recorded for EC was in Mareko while the lowest value was obtained from Muhir Aklil. As literature indicates, the soil samples under analysis were moderately saline and present under normal condition.

Soils have varying organic compounds in varying degrees of decomposition. Organic matter holds soils open, allowing the infiltration of air and water, and may hold as much as twice its weight in water (Wagh *et al.*, 2013). The potential of poor soil organic carbon (SOC) reduces microbial biomass, activity, and nutrient mineralization due to a shortage of energy sources (Saramanda *et al.*, 2017). The available nitrogen (%weight) present in the soil samples was varied from 0.024 to 0.071 (Table 4.2). The maximum nitrogen (0.71%) was present in Meskan soil sample and minimum nitrogen (0.024%) was obtained from the soil sample of Muhir Aklil woreda. Percentage of phosphorous was varied from 0.1 to 0.2 (Table 4.2). Highest concentration of phosphorous was registered at Cheha soil sample while lowest concentration was obtained at Muhir Aklil. In analyzed water samples, the pH values were ranged from 7.4 to 8.5 (Table 3.3). Maximum pH value was obtained at Mareko and minimum was recorded at Muhir Aklil woreda. The pH above 7.5 exhibits a basic nature. Therefore, the water samples analyzed in the current study were basic in nature exceptional to Muhir aklil. According to the Pakistan environmental quality standard and Food and agriculture organization (FAO), the permissible pH values for irrigation water for growing vegeTable s are 6 - 10 and 6.5 - 8.4 respectively. The pHs of the analyzed water were within NEQS (Pakistan Government, 1997) limits and pH was also within the Food and Agriculture Organization (FAO)

**Table 3.3. Some physicochemical parameters of water samples from different woredas of Gurage zone**

No	parameters	Woredas				
		Meskan	Mareko	Sodo	Muhir Aklil	Cheha
1	pH	7.8	8.5	8.1	7.2	7.7
2	Electrical Conductivity	0.64	0.76	0.71	0.41	0.63
3	Total suspended solid (mg/L)	350	353	362	280	313
4	Total dissolved solid (mg/L)	210	215	230	130	165
5	Total hardness (mg/L)	150	152.5	166	88	122.5

**Table 3.4. Concentration (mean  $\pm$  SD, n = 3, mg/kg) of heavy metals in Soil samples**

No	Element	Woredas				
		Meskan	Mareko	Sodo	Muhir Aklil	Cheha
1	Zn	118.37 $\pm$ 4.01	133.36 $\pm$ 6.39	110.97 $\pm$ 3.91	121.8 $\pm$ 5.01	177.55 $\pm$ 9.55
2	Cu	14.6 $\pm$ 0.81	20.6 $\pm$ 1.12	15.4 $\pm$ 0.50	16.4 $\pm$ 0.73	28.4 $\pm$ 1.80
3	Mn	1552 $\pm$ 10.41	1485.5 $\pm$ 19.26	1500 $\pm$ 13.77	740 $\pm$ 9.12	1972 $\pm$ 17.39
4	Cr	51.2 $\pm$ 3.32	69.8 $\pm$ 5.05	69.4 $\pm$ 3.29	49.2 $\pm$ 2.23	70.4 $\pm$ 3.63
5	Cd	ND	ND	ND	ND	ND
6	Pb	8 $\pm$ 0.68	8 $\pm$ 1.31	2 $\pm$ 0.52	14 $\pm$ 2.21	18 $\pm$ 1.67
7	Ni	36.6 $\pm$ 3.26	36.6 $\pm$ 1.41	67.6 $\pm$ 3.35	28.8 $\pm$ 1.97	61.8 $\pm$ 3.93

**Table 3.5. Concentration (mean  $\pm$  SD, n = 3, mg/kg) of heavy metals in water samples**

No	Parameters	Woredas				
		Meskan	Mareko	Sodo	Muhir	Cheha
1	Zn	ND	ND	ND	ND	ND
2	Cu	ND	ND	ND	ND	ND
3	Mn	ND	ND	ND	ND	ND
4	Cr	ND	ND	ND	ND	ND
5	Cd	ND	ND	ND	ND	ND
6	Pb	ND	ND	ND	ND	ND
7	Ni	ND	ND	ND	ND	ND

**Table 3.6. Recommended maximum limit of concentration of heavy metals in soil and irrigation water (Ewers, 1987)**

Parameter	soil (mg/kg, dry wt)			Water(mg/l)		
	Indian Standard	European st Standard	WHO standard	FAO Standard	National Environment Quality Standard	
Zinc	-	300	300	2	5	
Copper	135 - 270	140	100	0.2	1	
Manganese	-	-	2000	0.2	1.5	
Chromium	300 - 600	150	100	0.1	1	
Cadmium	3 - 6	3	3	0.01	0.1	
Lead	-	-	100	0.065 <sup>a</sup>	-	
Nickel	50 -75	75	50	0.2	1	

**Table 3.7. One way-ANOVA for comparison of heavy metals in soil samples at 95% CL**

Heavy metals	Mean (SD)					F-test		Remark
	Meskan	Mareko	Sodo	Muhir	Cheha	F-calculated	F-critical	
Zn	118.37(4.01)	133.36(6.39)	110.97(3.91)	121.8(5.01)	177.55(9.55)	55.83	3.478	Significant difference
Cu	14.6(0.81)	20.6(1.12)	15.4(0.50)	16.4(0.73)	28.4(1.80)	59.86	3.478	Significant difference
Mn	1552(10.41)	1485.5(19.26)	1500(13.77)	740(9.12)	1972(17.39)	2021.1	3.478	Significant difference
Cr	51.2(3.32)	69.8(5.05)	69.4(3.29)	49.2(2.23)	70.4(3.63)	25.92	3.478	Significant difference
Cd	ND	ND	ND	ND	ND	-	-	-
Pb	8(0.68)	8(1.31)	2(0.52)	14(2.21)	18(1.67)	54.64	3.478	Significant difference
Ni	36.6(3.26)	36.6(1.41)	67.6(3.35)	28.8(1.97)	61.8(3.93)	103.42	3.478	Significant difference

guidelines (Ayers, 1985) for the quality of irrigation water. The electrical conductivity for water samples was also analyzed and values were ranged from 0.41 to 0.76 mhos (Table 3.3) which are present in the normal range. The total hardness is the total soluble magnesium and calcium salts

present in the water expressed as CaCO<sub>3</sub>. In most natural water, the predominant ions are those of bicarbonates associated mainly with calcium to lesser degree with magnesium. Total hardness in determined water samples lie between 88 and 166 mg/l.

Table 3.8. Pearson correlation coefficient for heavy metals in soil samples

	Zn	Cu	Mn	Cr	Pb	Ni
Zn	1					
Cu	0.9806	1				
Mn	0.6075	0.6096	1			
Cr	0.4502	0.5912	0.6770	1		
Pb	0.7904	0.7058	0.06029	-0.1396	1	
Ni	0.3042	0.3605	0.66049	0.7263	0.568	1

Table 3.9. Comparison of determined mean concentrations of heavy metals in soils, (mg/kg, DW) with reported values

Heavy metal	Conc. of Current study mg/kg	Reported value	Country	Ref.
Zn	110.97 - 177.55	217.63	Serbia	(Senad, 2014)
		1.30-8.02	Pakistan	(Ajmal <i>et al.</i> , 2013)
		30.54±0.61	Nigeria	(Yusuf <i>et al.</i> , 2015)
		81.40-282.54	China	(Shi-Bo, 2011)
		68.43-290.71	Nigeria	(Warmate <i>et al.</i> , 2011)
Cu	15.4 - 28.4	34.95	South africa	(Callistus, 2012)
		79.7	Serbia	(Senad, 2014)
		1.06-5.42	Pakistan	(Ajmal <i>et al.</i> , 2013)
		0.277±0.02	Nigeria	(Yusuf <i>et al.</i> , 2015)
		21.6±3.1	Spain	(Micó <i>et al.</i> , 2016)
Mn	1552 - 1972	20.20-72.40	China	(Shi-Bo <i>et al.</i> , 2011)
		39.30-58.60	Nigeria	(Warmate <i>et al.</i> , 2011)
		5.91	South africa	(Callistus, 2012)
		8.7-30.07	pakistan	(Ajmal <i>et al.</i> , 2013)
		320±41	Spain	(Micó <i>et al.</i> , 2016)
Cr	49.2 - 70.4	440	South africa	(Callistus, 2012)
		37.47	Serbia	(Senad, 2014)
		35.08-92.78	India	(VaralakshmiA <i>et al.</i> , 2010)
		51.75±2.93	Nigeria	(Yusuf <i>et al.</i> , 2015)
		28.3±5.4	spain	(Micó <i>et al.</i> , 2016)
Cd	ND	40.10-77.42	China	(Shi-Bo <i>et al.</i> , 2011)
		ND	Serbia	(Senad, 2014)
		1.92 -2.90	India	(VaralakshmiA ?)
		0.05 – 0.92	pakistan	(Ajmal <i>et al.</i> , 2013)
		0.38±0.2	Spain	(Micó <i>et al.</i> , 2016)
Pb	2-18.	0.4	South africa	(Callistus, 2012)
		56.98	Serbia	(Senad, 2014)
		47.04-68.12	India	(VaralakshmiA <i>et al.</i> , 2010)
		2.11-30.86	Pakistan	(Ajmal <i>et al.</i> , 2013)
		117.3±7.13	Nigeria	(Yusuf <i>et al.</i> , 2015)
Ni	21.8 - 61.8	26.70-83.54	China	(Shi-Bo <i>et al.</i> , 2011)
		108.50-493.13	Nigeria	(Warmate <i>et al.</i> , 2011)
		9.72	South africa	(Callistus, 2012)
		36.15	Serbia	(Senad, 2014)
		48.2-57.3	India	(VaralakshmiA <i>et al.</i> , 2010)
		0.28-1.76	Pakistan	(Ajmal <i>et al.</i> , 2013)
		23.7±3.7	Spain	(Micó <i>et al.</i> , 2016)
		20.11-52.00	Nigeria	(Warmate <i>et al.</i> , 2011)

It was below the permissible limit of 170 mg/l. Total dissolved solids (TDS) and total suspended solids (TSS) values were well within the permissible limits of NEQS (55) and FAO (Ayers, 1985).

**Distribution pattern of heavy metals in soil samples:** Soil samples were analyzed to assess the level of heavy metals and the results are given in Table 3.4. Soil samples were analyzed and was found to contain detected heavy metals Zn, Cu, Mn, Ni, Cr and Pb. However, Cd was undetected in all soil samples obtained from five sampling areas. As given in Table 4.7, Zn was detected in appreciable amount in all soil samples. Concentrations of Zn were ranged from 110.97 to 177.55 mg/kg. Among the studied areas, highest Zn concentration was recorded at Cheha woreda while lowest concentration of Zn was obtained from Sodo woreda. The accumulation of copper in soil samples was found to be the range of 14.6 to 28.4 mg/kg.

A high amount of Cu was determined in the soil sample of Cheha woreda. The lowest Cu concentration level obtained from this study was determined at Mareko soil sample. In our findings, Manganese was recorded in highest amount as compared to other heavy metals in analyzed soil samples. Its concentration in different soil samples was varied from 740 to 1972 mg/kg. In this study, maximum concentration of Mn was recorded at Cheha soil sample while Muhir Aklil soil had the lowest concentration. As indicated in Table 3.4, results showed that the mean concentration of chromium lie between 49.2 to 70.4 mg/kg. Among the analyzed soil samples, Cr was detected in highest amount from Cheha woreda while minimum concentration of Cr was recorded at Muhir Aklil soil sample. Cadmium was undetected (below detection limit) in all soil samples. Even though lead was not registered in any of vegetable samples but it was found in considerable amount in soil samples. The average concentration of lead in soil samples was ranged from 2 to 18 mg/kg with the highest value of Pb

(18 mg/kg) at Cheha woreda and lowest value of Pb (2 mg/kg) at Sodo soil (Table 3.4). Amount of Nickel was varied from 36.6 to 67.6 mg/kg (Table 3.4). The highest Ni concentration obtained from this study was determined for Sodo (67.6 mg/kg) and the least for Mareko and Meskan (36.6 mg/kg). In general, the concentration pattern of heavy metals in soil was decreased as Mn >> Zn > Cr > Ni > Cu > Pb for all soil samples. The level of Cd in soil samples were found to be below the detection limit of the method used in this study. The quality guidelines for soil heavy metal concentrations developed in certain countries indicate wide variations. The levels of heavy metals found in different sources of the present study were compared with the prescribed safe limit provided by WHO/FAO (2007), European standard (European Union, 2006) and Indian standard (Gupta, 1986). The concentrations of Cr and Cu obtained in different soil samples were below the permissible limit reported by Indian (300 – 600 mg/kg for Cr and 135 – 270 mg/kg for Cu) and European (150 mg/kg for Cr and 140 mg/kg for Cu) standards. Zinc and manganese concentrations in soil from different sampling areas examined in the present study were below the permissible levels as recommended by WHO (2007) and European standard (European Union, 2006). Also Nickel and Lead values obtained in the present study were below the tolerance level of WHO (2007), European standard (European Union, 2006) and Indian standard (Gupta, 1986).

**Distribution pattern of heavy metals in water samples:** In all water samples, heavy metals were below method detection limit (ND).

**Statistical analysis:** It is also important to compare these toxic agents available in different samples statistically to know whether they differ significantly or not. In this study, we had compared samples for their heavy metal levels obtained from different sampling areas and mean concentrations of heavy metals among vegetables were also compared. Statistical values for one way ANOVA analysis are listed from Table 3.7. From the statistical analysis indicated in Table 3.7, the mean concentrations of heavy metals (except Cd) were indicating a significance difference in analyzed soil samples across the studied areas.

**Pearson correlation of heavy metals:** A correlation coefficient (r) is a number between -1 and +1 that measures the degree of association between two variables (call them concentration of metal X and Y). A positive value for the correlation implies a positive association (large values of X tend to be associated with large values of Y and small values of X tend to be associated with small values of Y). A negative value for the correlation implies a negative or inverse association (large values of X tend to be associated with small values of Y and vice versa) (Olsen *et al.*, 1954). In this work, Pearson correlative analysis was done for the heavy metal within soil sample and vegetables with the soil where they are grown.

**Pearson correlation of heavy metals within soil samples:** As shown in Table 3.8, Zn has high positive correlation with Cu, Pb and Mn. While it has moderate positive correlation with Cr and Ni. The concentration of Cu in soil is positively affected by the presence of other heavy metals. Mn has high positive correlation with all analyzed heavy metals except with Pb which has almost no correlation. Pb found in soil sample has positive correlation with Zn, Cu and Ni and moderate negative relation with Cr. However, its concentration is not affected by

presence Mn. As given in Table 3.4, mean concentration of zinc (110.97 - 177.55mg/kg) obtained in this study was lower as compared to the values reported in Nigeria (Yusuf *et al.*, 2015), Serbia (Senad, 2014) and Nigeria (Warmate *et al.*, 2011). However, it was found to be higher than those reported in Pakistan (Ajmal *et al.*, 2013) and South Africa (Callistus, 2012). The mean concentration of Cu in soil was varied from 15.4 - 28.4 mg/kg. This concentration was lower than the values indicated in Serbia (Senad, 2014), China (Shi-Bo *et al.*, 2011) and Nigeria (Warmate *et al.*, 2011). But it was found in higher levels than that given in Pakistan (25), Nigeria (Yusuf *et al.*, 2015) and South Africa (Callistus, 2012). The concentration of Cu obtained in Spain (Micó *et al.*, 2006) was comparable with the present work. The concentrations of manganese (1552-1972mg/kg) found in the present study were much higher than those values reported in Pakistan (Yusuf *et al.*, 2015), Spain (Micó *et al.*, 2006) and South Africa (Callistus, 2012). The concentration of chromium in this study was somewhat higher than values reported in Serbia (24) and Spain (Micó, 2006). However, the content of Cr in this study was comparable to those in Nigeria (Yusuf *et al.*, 2015), India (Varalakshmi *et al.*, 2010) and China (Shi-Bo *et al.*, 2011). As shown in Table 4.10, the cadmium was not detected in all soil samples which is similar with the value reported in Serbia (Senad, 2014). However, appreciable amount of Cd was reported in Pakistan (Ajmal *et al.*, 2013), Spain (Micó *et al.*, 2016), India (Varalakshmi *et al.*, 2010) and South Africa (Callistus, 2012). Present results showed that the lead level (2 - 18 mg/kg) in onion was found to be comparable with the value reported in Pakistan (Ajmal *et al.*, 2013) but it was found in lower levels than that given in Serbia (Senad, 2014), Nigeria (Yusuf *et al.*, 2015), India (Varalakshmi *et al.*, 2010), China (Shi-Bo *et al.*, 2011) and Nigeria (Warmate *et al.*, 2011). The concentrations of Ni reported in soil samples of the current study were higher than those reported in Pakistan (Ajmal *et al.*, 2013) and comparable with values indicated in Serbia (Senad, 2014), India (Varalakshmi *et al.*, 2010) and Nigeria (Warmate *et al.*, 2011).

## Conclusion and Recommendation

**Conclusion:** The level of heavy metals in soil and water of some selected woredas of Gurage Zone that used for irrigation purpose were determined by flame atomic absorption spectrometer. All samples were subjected to digestion with optimized procedures prior to their heavy metals determinations. Water and soil samples were also investigated for their some physico-chemical properties. From the results of the analysis, pH value for soil samples were ranged from 6.8 to 8.4 while the conductivity was ranged from 0.17 - 1.23 and 0.41 – 0.76. Organic carbon content (%C), available phosphorous (%P) and available nitrogen (%N) for soil were varied from 0.59 - 0.97, 0.01 - 0.02 and 0.024 - 0.071 respectively. Similarly the pH value for water samples lie in between 7.1 to 8.2 and conductivity varied from 0.41 – 0.76. Total suspended solid (mg/L), total dissolved solid (mg/L) and total hardness (mg/L) present in water samples were varied from 280 – 362, 165 – 230 and 88 – 166 respectively. From different standards, all soil and water physical and chemical parameters are within the normal range. Therefore, application of the ground water and soil for agricultural purposes in these areas were found favourable. In this study, all heavy metals were not found (below method detection limit) in water samples. The concentration of heavy metals in the soil which was collected from sites in which vegetables grown was



determined in this study. The range level of Zn, Cu, Mn, Cr, Pb and Ni found in soil samples were 110.97 - 177.55, 14.60 - 28.40, 740 - 1972, 49.2 - 70.4, 2.000 - 18.00 and 28.8 - 67.6 mg/kg respectively. The soils of the study were found to contain high concentration of Mn followed by Zn, Cr, Ni, Cu, Pb. However, Cd was not detected (below detection limit) in soil samples. Levels of heavy metals determined in soils were compared with standard values and found below the tolerance level.

**Recommendations:** Though the levels of heavy metals in vegetables lower than the accepted values in most international standards, high consumption of vegetables in the area results the following recommendations:

- Decision makers must formulate relevant agricultural policies encompassing education and training of farmers to make them understand the effects of these heavy metals on human health and the importance of nutrient management.
- Continuous monitoring of soil, plant and water quality together with prevention of metals entering vegetables is a prerequisite in order to prevent potential health hazards to human beings.

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