Addis Ababa University

College of Natural Sciences

Center for Food Science and Nutrition

Assessment of Heavy Metal Accumulation and associated potential health Risk in Green Leafy Vegetables Grown on Urban Wastewater Irrigated soil in Southern Addis Ababa, Ethiopia (case of Chromium, Lead and cadmium)

By

Yonas Beyene

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN FOOD SCIENCE AND NUTRITION

June, 2015

ASSESSEMENT OF HEAVY METAL ACCUMULATION AND ASSOCIATED POTENTIAL HEALTH RISK IN GREEN LEAFY VEGETABLES GROWN ON URBAN WASTEWATER IRRIGATED SOIL IN SOUTHERN ADDIS ABABA, ETHIOPIA (CASE OF CHROMIUM, LEAD AND CADMIUM)

Yonas Beyene

A THESIS SUBMITTED TO THE CENTER FOR FOOD SCIENCE AND NUTRITION

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Under the Supervision of

Tetemke Mehari (PhD)

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Center for Food Science and Nutrition

This is to certify that the thesis presented by Yonas Beyene, entitled ‘Assessment of Heavy Metal Accumulation and associated potential health Risk in Green Leafy Vegetables Grown on Urban Wastewater Irrigated soil in Southern Addis Ababa, Ethiopia (Case of Chromium, Lead and cadmium).’ submitted in partial fulfillment of the requirements for the degree of Master of Science (Food Science and Nutrition) complies with the regulations of the university and meets the accepted standards with respect to the originality and quality.

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DECLARATION

I the undersigned, declare that this thesis is my original work and has not been presented for the award of a degree at any university and all the sources of materials used for this thesis have been duly acknowledged.

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Tetemke Mehari (PhD)	_________________________________	_______________
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DATE AND PLACE OF SUBMISSION:

Center for Food Science and Nutrition, Addis Ababa University

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ABSTRACT

Assessment of Heavy Metal Accumulation and associated potential health Risk in Green Leafy Vegetables Grown on Urban Wastewater Irrigated soil in Southern Addis Ababa, Ethiopia (case of Chromium, Lead and Cadmium).

Yonas Beyene

A total of 16 Samples of wastewater, vegetable washing water, soil, root, stem, and leaf parts of the vegetables (Ethiopian Kale, Lettuce and Chard) were collected directly from the farm. All the samples were analyzed for the concentration of the three heavy metals lead (Pb), chromium (Cr), and cadmium (Cd).

The concentrations of Pb, Cr and Cd in the leaves, stems and roots of Ethiopian Kale, Lettuce and Chard were found to be in mg kg-1 Cadmium (Ethiopian Kale :0.011±0.0000, 0.007±0.0002 and 0.011±0.0003; **Lettuce:** 0.014±0.0002, 0.016±0.0003 and 0.125±0.0003; **Swiss chard:** 0.014±0.0000, 0.007±0.0000and 0.005±0.0002, **Chromium (Ethiopian Kale:** 0.124±0.0117, 0.044±0.0137 and 0.075±0.0021; **Lettuce:** 0.193±0.0105, 0.033±0.0018 and 0.112±0.0074; **Swiss chard:** 0.103±0.0088, 0.067±0.0072 and 0.162±0.0000) and **Lead (Ethiopian Kale:** 0.620±0.0132, 0.221±0.0156 and 0.373±0.0021; **Lettuce:** 0.019±0.0187, 0.009±0.0089 and 0.002±0.0022; **Swiss chard:** 0.689±+0.0093, 1.336±0.0043 and 0.133±0.0168) on dry matter basis, respectively.

Results showed that, all the samples contain the three heavy metals below safe value limit recommended by FAO/WHO. Accumulation factor has the maximum value in the stem and root parts of Swiss chard (i.e. 0.035 and 0.018 for Pb), respectively. Accumulation factor also has the maximum value in lettuce root and chard leaf parts of the vegetable (i.e. 0.048 and 0.041 for Cr) and 0.250, 0.032 in the lettuce stem and leaf parts for Cd, respectively. The BCF value of Pb is approximately 2- fold in stem than the root. However, all the 3 vegetables samples can be considered excluders of the 3 heavy metals (i.e.BF< 1). PCA (Principal Component Analyses) shows impact of wastewater irrigation and Pb contamination is serious in wastewater-irrigated agricultural soils of the study area.

The potential health risk calculated by THQs of all three heavy metals in the three leafy vegetables were less than 1.0 for adults , indicating that the adult residents in the Addis Ababa are not exposed to significant health risks associated with consumption of green leafy vegetables grown around the study area.

Keywords ; Wastewater Irrigated soil; Green leafy vegetables; Heavy metals; Bio concentration factor; Target hazard quotient

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LIST OF ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Disease Registry
CAC	Codex Alimentarius Commission
CSEM	Case Studies in Environmental Medicine
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization
FDA	Food and Drug Administration
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
GMP	Good Manufacturing Practice
IPCS	International Program on Chemical Safety
JECFA	Joint Expert Committee for Food Additives
NAS	National Academy of Science
NCC	National Codex Committee
NRC	National Research Council
UNDP	United Nations Development Program
WHO	World Health Organization

1. INTRODUCTION

As it is indicated by researches conducted, between 1993 and 2005, urban crop production increased its share of world food production from 15% to 33% and the number of urban farmers producing for the market from 200 million to 400 million (Mougeot, 2000).Urban crop production has been viewed as one strategy where recent research suggests that food insecurity could be tackled (Mkwambisi, 2008). Besides, urban crop production has been shown to be an important source of food in developing countries and a critical food ‘insurance policy’ for poor urban households (Reardon, Berdegué, & Escobar, 2001).Moreover, urban crop production also affects household nutrition as it provides a source of fresh, locally grown crops that meets the micronutrient requirements in poor households’ diets (Hendriks, 2003).

Other benefits of urban agriculture, includes increase in household incomes due to the sale of urban agricultural produce (Bryld, 2003). Therefore, because of the urban population growth world-wide, the phenomenon of urban agriculture as a food, income and employment generator is likely to increase(Afolabi, 2007).

However, the scarcity of fresh water has promoted a growing interest in the use of untreated wastewater for irrigation activities in urban and peri-urban areas(Qadir et al., 2010). This wastewater comprises domestic effluent such as kitchen and bathroom, water from commercial establishments and institutions including hospitals, industrial effluent including chemicals and dyes, storm water and other urban runoff(Seneviratne, 2007). However, untreated wastewater use has been associated with contamination of the soil and cultivated crops by heavy metals because of heavy metal concentration above the recommended limit by Food and Agriculture Organization of United Nations (FAO) for irrigation water and in soil(Eshtawi & Kanyoka, 2012). Wastewater may contain heavy metals such as Zinc (Zn), Chromium (Cr), Manganese (Mn), Lead (Pb), Cadmium (Cd), Mercury (Hg) Nickel (Ni) and Iron (Fe) (He, Yang, & Stoffella, 2005). However, studies show that the adsorption of heavy metals into the biomass depends upon the metal speciation and concentration, reactivity of the biomass and the composition of other wastewater component(Krishnani, Meng, Christodoulatos, & Boddu, 2008). Also precipitation of heavy metals depends on available pH.

According to researches on the concentration of trace metals in vegetables that were grown with wastewater, high concentrations of Cadmium, Chromium, Copper, Mercury, Nickel and Zinc give evidence of industrial pollution traced back in agricultural crops(Uher, Mirande-Bret, & Gourlay-Francé, 2011). Dietary exposure to heavy metals like, cadmium, lead, and Chromium has been identified as a risk to [human health through the vegetables consumption ((Peralta-Videa, Lopez, Narayan, Saupe, & Gardea-Torresdey, 2009).

Urban farming is not new to Addis Ababa; it has been a major part of the urban scene from the very beginning of the city's development as the capital of Ethiopia. In Ethiopia 30% vegetable supply is urban or peri-urban produced which is 303 hectares, 129,880 quintiles veg. per annum which directly supports over 51,000 families of which farming represents 65% of total income. There is urban agriculture core process in Addis Ababa with aim to increase urban agriculture production and productivity(Teshome, 2006).

Two major rivers flow through the city, namely *Tinishu Akaki* (Little Akaki) and *Tiliku Akaki* (Great Akaki) Rivers. These rivers, which are tributaries of *Awash* River, originate from *Entoto Mountains* that are located north to Addis Ababa and flow to *Aba Samuel* Lake (43 km to the South)(Mekonnen et al., 2012).

One of the most extensively used river valleys for irrigating urban farms in Addis Ababa is the Little Akaki. Little Akaki remains to be the primary recipient of most of the industrial effluents discharged within the city(Aschale, Sileshi, Kelly-Quinn, & Hailu, 2015). High concentration and variation of pollutants along the river course was found mostly inside and outside (downstream) the city of Addis Ababa(Tegegn, 2012).

This variation likely arises due to the rapid urbanization and industrialization of the city. (Belachew).

The rivers serve as drains for excessive storm water and the disposal of domestic and industrial wastewater (Wakida & Lerner, 2005). Water from the rivers is being used for various purposes; Irrigation, sand mining, industrial consumption, washing of materials, and bathing, cattle consumption and waste disposal. Irrigation is a visible water use practice in the city. According to the local Urban Agriculture Office, an estimated 1,574 farmers (28% women) are working on a total farm area of 400ha throughout Addis. All of them are irrigating with Akaki River. Irrigated vegetable production accounts for about 60% of the total market supply for the city (Van Rooijen, Biggs, Smout, & Drechsel, 2010).

Old Saris Alcohol Factory (Kebele 58) area of Southern Addis Ababa is the oldest vegetable production base in Addis Ababa using Little Akaki wastewater and produces large quantity of vegetables per year. The vegetables are mainly consumed by Addis Ababa residents. Because of increasing Urbanization and Industrialization, the Little Akaki River is experiencing substantial industrial, domestic, commercial and agricultural pollutions in recent decades. Associated Geogenic and air pollution can enhance pollutant accumulation in vegetables, especially those of hazardous heavy metals further increasing potential human health risks.

To this end, the present study assessed the extent of heavy metal accumulation in green leafy vegetables parts commonly grown around old Saris Alcohol Factory (Kebele 58) wastewater irrigated farm and associated potential health risks, considering the significance of heavy metals contamination from industrial and other sources through the consumption of vegetables by Addis Ababa residents.

2. OBJECTIVES

2.1. General objective

To determine Cd, Pb and Cr concentration in green leafy vegetables grown by urban wastewater irrigated farm around old Saris Alcohol Factory (Kebele 58) area of southern Addis Ababa and associated Potential health risks.

2.2. Specific objectives

- To determine Cd, Cr and Pb concentrations in the soil of the vegetable growing farm, water used for irrigation, vegetable crops parts (root, stem and leaf) and in the washings of the vegetable crops.
- To investigate Bioaccumulation of heavy metals from soil to vegetables
- To Identify heavy metal sources
- To determine Potential health risk associated with consumption of green leafy vegetables

3. LITRATURE REVIEW

3.1. Heavy metals in the environment

Metals can be found in the solid phase and in solution, as free ions, or adsorbed to soil colloidal particles. Heavy metals are found in topsoil as a result of soil-forming as well processes, as agricultural and human activities (Gratão, Polle, Lea, & Azevedo, 2006).

This days heavy metals are of much environmental and health concern. Heavy metals are dangerous because they tend to bioaccumulation in the food chain and they are harmful to humans and animals. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. The risk that heavy metals pose to human and animal health is become worse by their long-term persistence in the environment (Davies & Mundalamo, 2010).

Assessment of the relocation ability of any pollutant in the natural environment is considered to be a necessary stage for guessing the ecological situation. The heavy metals accumulation processes in agricultural crops are interesting because they contribute toxic elements into the human food chain(Peralta-Videa et al., 2009).

Plants are important components of ecosystems as they transfer elements from abiotic into biotic environments. Chief sources of elements from the environment to plants are: air, water and the soil (Kabata-Pendias, 2004).Plants can uptake toxic elements through their roots from contaminated soils, and even leaves can absorb toxic elements deposited on the leaf surface (H. Liu, Probst, & Liao, 2005).

Concentration of heavy metal in different parts of plants is heavily dependent on plant species. The capability of different plant species to accumulate heavy metals has been attributed to their genetic differences (Keller et al., 2003). Besides plant species, the availability of metals to plants will depend on their chemical speciation and is determined by the physical and chemical properties of the soil (Zhang, Zhao, Sun, Davison, & Mcgrath, 2001). Understanding of metal-plant interactions is important for the safety of the environment and for reducing the risks associated with the introduction of trace metals into the food chain.

Therefore, the metal can inactivate many important enzymes resulting in inhibition of photosynthesis, respiratory rate and other metabolic processes in plants (Hou, Chen, Song, Wang, & Chang, 2007).

Even though there is a difference in mobility of metal ions in plants, the metal content is generally greater in roots than in the aboveground tissues (Meagher, 2000). Heavy metals and other contaminants in bulk soil might be transferred into soil solution, making them available to roots (Chary, Kamala, & Raj, 2008). Reductions in yield and plant growth retardation have been generally induced by high concentrations of metals in soils (Schützendübel & Polle, 2002). Maize plantation at Awassa have been seriously affected both in yield and quality due to metals from industrial waste on farm lands(Itanna, 1998). Prospective danger from metal accumulation by plants grown on such soil is becoming an increasing problem in many countries. The above problems mentioned with respect to the heavy metals are created a demand for an intensive research effort aimed at predicting the availability of heavy metals in the soil environment; as study conducted by Fisseha Itana, 1998 and some others mentioned special attention should be paid to the dangerous health elements and to most consumed agricultural crops.

3.2. Cadmium

3.2.1. Sources, Uses, and Transport of Cd

Cadmium is a naturally occurring element, it is rarely found as a pure metal in nature. It is generally associated with oxygen, chlorides, sulfates, and sulfides. It is often a byproduct of the extraction of Pb, Zn, and Cu from their respective ores (LeCoultre, 2001). Other sources of cadmium include carbonaceous shale, coal, and other fossil fuels .the largest natural source of cadmium is volcanism (Winder, 2004). Commercially available fertilizers and the disposal of sewage sludge as soil amendments are the anthropogenic sources of Cd in the soil and groundwater (Wuana & Okieimen, 2011).

There are high concentrations of cadmium accumulated in the soils. John et al., (1972) report a Cd concentration of 95 ppm in a sample collected near a battery smelter near Vancouver, BC, Canada. Cadmium is recalcitrant in the soil profile, particularly in the surface horizons (LeCoultre, 2001).

Most soil profiles have an A horizon, which is primarily topsoil composed of decaying organic matter such as leaves and grass, and a B horizon, which is composed of smaller clay-sized particles. In wide-ranging, heavy metal concentrations are higher in the B horizons than in the A horizons (Hamon et al., 2004).

Accumulations of heavy metals tend to be in the clay fraction of most soil profiles (Palumbo et al., 2000). The concentration of heavy metals in soil is dependent on clay content because clay-sized particles have a large number of ionic binding sites due to the higher amount of surface area (Dhillon & Dhillon, 2003). This is to mean that if heavy metals are immobilized that means there is only very little leaching through the soil profile in clay soil (Wuana & Okieimen, 2011).

Immobilization can increase the Cd concentration of the soil and ultimately lead to the increased toxicity of the contaminated soil. The higher soil Cd concentrations can result in higher levels of uptake by plants (Kabata-Pendias, 2010).

Nevertheless, the specific soil properties can have a significant effect on the amount of heavy metal assimilated by the plant (Rascio & Navari-Izzo, 2011).

Concentrations of Cd in the soil that produced a 50% inhibition in growth were higher at the seedling stage than at the edible stage. John et al., (1972) also showed that plant size and yield were reduced when 50 mg Cd (dosed as $CdCl_2$) was added to 500g of soil(LeCoultre, 2001).

3.2.2. Toxicity of Cd

Even though we ingest Cd from varies sources, intake of Cd can double if one smokes cigarettes because each cigarette contains about 2 μg Cd(Thompson & Bannigan, 2008).

Doses ranging from 10 to 30 mg/kg-day of cadmium can cause acute severe gastrointestinal irritation, vomiting, diarrhea, and excessive salivation, and doses of 25 mg CdI_2/kg body weight can be lethal(LeCoultre, 2001). Low-level chronic exposure to Cd can cause adverse health effects including gastrointestinal, hematological, musculoskeletal, renal, neurological, and reproductive effects. Most important target organ for Cd following chronic oral exposure is the kidney (J. Liu, Liu, Goyer, Achanzar, & Waalkes, 2000). Since cadmium tends to accumulate in the kidneys, the EPA has based the RfD for cadmium on the concentration of the metal in the human renal cortex (Hays, Nordberg, Yager, & Aylward, 2008).

Maximum Cd level in the renal cortex that does not causes significant proteinuria is set as 200μg Cd/g (Satarug & Moore, 2004).

According to ATSDR there is insufficient evidence to determine whether oral exposure to Cd increases the risk for cancer. However, the United States Department of Health and Human Services (DHHS) has stated that cadmium compounds may be carcinogenic (Afridi et al., 2006). The International Agency for the Research on Cancer (IARC) has classified Cd and Cd salts as possible human carcinogens. This classification is based on human lung cancer data from occupational inhalation (Huff, Lunn, Waalkes, Tomatis, & Infante, 2007).

3.3. Lead

3.3.1. Sources, Uses, and Transport of Pb

Lead is a naturally occurring heavy metal. It is seldom found in its elemental form; however, it is part of several ores including its own (galena, PbS)(Sipter, 2008). Pb is also a product of the radioactive decay of uranium 206, thorium 208, and actinium 207 (Bollhöfer, Honeybun, Rosman, & Martin, 2006). Pb has many industrial and commercial uses. It is used in the production of ammunition, as solder, in ceramic glass, and the production of batteries (Ziegfeld, 1964). Other sources of Pb in the environment include automobile exhaust, industrial wastewater, wastewater sludge, and pesticides (Karvelas, Katsoyiannis, & Samara, 2003). Because of its high toxicity, the use of lead in some products has been discontinued. Lead is no longer used in house paint because of the concern about the toxic effects of the accidental ingestion of paint chips or the inhalation of aerosolized lead from decaying paint. In 1991, the amount of Pb was greatly reduced in gasoline (Cherniak & Watson, 2001). Most of the environmental lead contamination comes either from landfill leachate or from airborne lead particles deposited onto the soil (Belluck, Benjamin, Baveye, Sampson, & Johnson, 2003).

Pb behavior in soil is similar to Cd behavior in soil. However, Khan and Frankland, (1983) showed that Pb was less mobile in soil than Cd. Very little of either Pb or Cd was leached through the soil profile(Vig, Megharaj, Sethunathan, & Naidu, 2003). In fact, more Pb and Cd were removed from the soil by plants than was leached through the profile (Roy & McDonald, 2013).

Several factors may influence the content and distribution of heavy metals in soil. Some of these factors are parent material, organic matter, particle size distribution, drainage, pH, type of vegetation, amount of vegetation, and aerosol deposition (Sieghardt et al., 2005). Heavy metals, including Pb, tend to accumulate in the clay fraction of the soil profile (Kabata-Pendias, 2010).

Strong ionic bonds are formed between the cation and the clay particle. Acidic conditions will cause desorption of these cations into solution making them available for uptake by plants. Desorption to the soil solution also increase cation mobility through the profile (De Matos, Fontes, Da Costa, & Martinez, 2001). Decreased growth and yield have been observed in plants grown in Pb contaminated soils(Pulford & Watson, 2003). Significant decrease in plant biomass yield with increasing Pb treatments that varied with soil type(Schnitzer et al., 2011). The highest adverse effects were on those plants grown in soils with high clay content(Pugnaire & Luque, 2001). (Yang, Zhang, Li, & Jiang, 2009) also showed decreased plant growth and yield in soils with Pb contamination.

3.3.2, Toxicity of Pb

Ninety-nine percent (99%) of the lead that enters the adult human body and 33% that enters a child's body is excreted in about 2 weeks (LeCoultre, 2001). Because of this, lead poisoning is a greater concern in children. Most of the accumulated lead is sequestered in the bones and teeth. This causes brittle bones and weakness in the wrists and fingers. Lead that is stored in bones can reenter the blood stream during periods of increased bone mineral recycling (i.e., pregnancy, lactation, menopause, advancing age, etc.). Mobilized lead can be redeposit in the soft tissues of the body and can cause musculoskeletal, renal, ocular, immunological, neurological, reproductive, and developmental effects (JO & Nwabue, 2012).

Replacement of calcium in the bone and muscle tissue by lead can impair normal bone growth, and bone density and calcium content can decrease. High exposures (i.e., > 30 mg Pb/kg/day) to lead cause muscle weakness, cramps, and joint pain. Impaired kidney function and a weakened immune system can also result from over-exposure to Pb. Various reproductive effects including decreased pregnancy rate, ovarian damage, testicular damage, testicular atrophy, cellular degeneration, and irregular estrous cycles have been shown in animal studies (Uzumcu & Zachow, 2007). Renal toxicity is now used as a biochemical and physiologic marker of chronic subclinical lead toxicity (Jurczuk, Moniuszko-Jakoniuk, & Brzóska, 2006).

Although over-exposure to lead causes serious health effects in adults, especially pregnant women, the toxicity of lead is greatly increased in children(Tong, Schirnding, & Prapamontol, 2000). The Centers for Disease Control (CDC) report that nearly 1 million children in the United States have blood-lead levels that exceed the 10 μg Pb/dL level of concern (Targeting, 2000).

Dirt, dust, and lead based paint chips from old houses can be sources of increased exposure to children(Rasmussen, Subramanian, & Jessiman, 2001).

Because lead can cross the placenta, prenatal exposure can be significant. A pregnant woman and her fetus will have virtually the same blood-lead level (Levin & Goldberg, 2000). In utero exposure can lead to low birth weight, premature birth, or miscarriage(Henderson, Gray, & Brocklehurst, 2007).

Lead can also be transmitted through breast milk. Anemia, colic, impaired vitamin D metabolism, and growth retardation result from lead exposure during infancy or early childhood. Lead exposure is also associated with several neurological effects, such as delayed neurological development, cognitive impairment, IQ deficits, and effects on general brain function(Fenichel, 2009).

Some of these effects are irreversible and continue into adulthood(Richardson et al., 2009). The United States Environmental Protection Agency has classified inorganic lead as a possible human carcinogen. Although human data are insufficient, there are significant increases in renal tumors with high (i.e., >500 ppm) exposure of lead based on animal studies (Ahmed, 2001).

3.4. Chromium

3.4.1. Sources, Uses, and Transport of Cr

Chromium is a naturally occurring element found in rocks, soil, plants, animals, and in volcanic dust and gases(Selinus, 2004). It is present in the soil as (Cr III) or chromate (Cr VI) ions (Shanker, Cervantes, Loza-Tavera, & Avudainayagam, 2005). Chromium (III) is an essential nutrient in the diet, but it is required in a very small amount (Förstner & Wittmann, 2012).

Chromium is used for making steel and other alloys, bricks in furnaces, and dyes and pigments, and for chrome plating, leather tanning, and wood preserving(Jacobs & Testa, 2005). Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts color glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make moulds for the firing of bricks. Chromium (IV) oxide (CrO_2) is used to manufacture magnetic (Vilar et al., 2011).

Most of the chromium in soil does not dissolve easily in water and can attach strongly to the soil. A very small amount of the chromium in soil, however, will dissolve in water and can move deeper in the soil to underground water(Das, Dhundasi, & Das, 2011).

The movement of chromium in soil depends on the type and condition of the soil and other environmental factors (Bronick & Lal, 2005). A smaller percentage of total chromium in soil exists as soluble chromium (VI) and chromium (III), which are more mobile in soil(Kotaś & Stasicka, 2000). The mobility of soluble chromium in soil will depend on the sorption characteristics of the soil. The relative retention of metals by soil is in the order of lead > antimony > copper > chromium > zinc > nickel > cobalt > cadmium (Mallick).

The sorption of chromium to soil depends primarily on the clay content of the soil and, to a lesser extent, on Fe_2O_3 and the organic content of soil(Sauve, Hendershot, & Allen, 2000). Organic matter in soil is expected to convert soluble chromate, chromium (VI), to insoluble chromium (III) oxide, Cr_2O_3 (Stanin, 2005). Chromium has a low mobility for translocation from roots to aboveground parts of plants(Pulford & Watson, 2003). However, depending on the geographical areas where the plants are grown, the concentration of chromium in aerial parts of certain plants may differ by a factor of 2–3 (Kabata-Pendias, 2010). Transport of Chromium in root is very slow (Zayed & Terry, 2003) accounting for the low levels of Cr in the tops of plants. Evidently, the element enters the vascular tissue with difficulty but once it enters, it is rapidly transported. Reduced chlorophyll content has been found due to reduced rate of photosynthesis by Chromium in Lemma minor (Vajpayee, Tripathi, Rai, Ali, & Singh, 2000).

3.4.2. Toxicity of Cr

Medical warning was issued that inhalation of dust containing Cr in high oxidation states (IV) and (VI) was associated with malignant growth in the respiratory tract and painless perforation in nasal spectrum among trivalent and hexavalent states, being the most stable and common in terrestrial environments(Mohammed, Kapri, & Goel, 2011). Hexavalent Chromium is the form considered to be the greatest threat because of its high solubility, its ability to penetrate cell membranes and its strong oxidizing ability. Hence, Cr (VI) is more toxic than Cr (III) because of its high rate of absorption on living surface (Rai et al., 2002).

3.5. Geogenic contaminants

The geology of an area has a direct impact on the regional input of elements into the soil, air and water(Driscoll et al., 2001). In turn, these inputs, depending on composition, may result in adverse health effects in humans, animals and/or plants. Health issues related to a region's geology are visible in both humans and animals on almost every continent, and can range from

As contaminated groundwater in Bangladesh to molybdenosis in Canadian cattle (Schwarz, Echols, Wolcott, & Nelson, 2004). (Alemayehu, Ayenew, & Kebede, 2006) suggested that the rock and soil out crops of Addis Ababa are anomalously rich in heavy metals derived from hydrothermally affected volcanic rocks of the geogenic processes. In the soil analysis result of (Alemayehu, 2006) it was clearly seen that the metal concentrations were in toxic level in the northern part of the city.

Today, the diverse geographical and geochemical source of human foods in developed nations creates a “homogenized diet” reflecting materials grown on a range of soil types, each with different chemical characteristics and potentially imported from a number of countries. As a result of this complex sourcing mechanism, element deficiencies or toxicities are generally rare in regards to dietary intake. Additionally, element imbalances in the soil are often amended before the growth of crops, thus eliminating any subsequent problems (Bowman, Bobrowsky, & Selinus, 2003). Recently the relation between adverse health effects and heavy metals in the environment has gained considerable attention in various professional journals as well as in the broader public media. Heavy metals or potential pollutants have been termed ‘geogenic contaminants’ and include such elements as As, Pb, Cd and Hg. Elevated levels of these and other potential pollutants have been recorded in many areas of the world including Canada, USA, India, China and Bangladesh. The recognition that an intimate relationship exists between geology, as measured by geochemistry, and human/animal health, has led to the development of a new field of science called Medical Geology (Gomes, Silva, & Gomes, 2011). Ensuring human, animal and plant health requires accessibility to both essential (e.g. Cr, Cu, Fe, Ca, Se) and non-essential (e.g. toxic Pb, As, Hg) elements. Such elements occur in varying concentrations and forms throughout the atmosphere, lithosphere and hydrosphere. As a result, plants, animals and humans are regularly exposed to these and other elements.

With respect to each essential element, all organisms depend on a specific range of tolerance or adequate range of exposure that is safe (Kabata-Pendias & Mukherjee, 2007). Deficient or excess levels of concentration for the essential elements can lead to adverse health effects, and in certain cases, death. The concentration values of the elements are represented in a ‘dose response curve’, which is a graphical representation indicating the ideal amount of an element needed for maintaining good health, as well as amounts contributing to deficiency or toxicity levels

(Tallarida & Jacob, 2012). The dose response curve for any given element may differ from organism to organism, but the underlying principle of deficiency, ideal concentration and toxicity remains constant(Peijnenburg & Jager, 2003). For example, V is essential for photosynthesis by blue green algae, and yet this element is highly toxic to humans.

Similarly, Co is required for fixing N_2 in blue green algae and other microorganisms, however, it is unknown if it is needed in higher plants (Kabata-Pendias, 2004).

3.6. Bioavailability of heavy metals in crops

3.6.1. Bioavailability

Bioavailability is the proportions of total metals that are available for incorporation into biota (bioaccumulation). Total metal concentrations do not necessarily correspond with metal bioavailability. For example, sulfide minerals may be encapsulated in quartz or other chemically inert minerals, and despite high total concentrations of metals in sediment and soil containing these minerals, metals are not readily available for incorporation in the biota; associated environmental effects may be low(Baldocchi et al., 2001).

Metals of major interest in bioavailability studies, as listed by the U.S. Environmental Protection Agency (EPA), are Al, As, Be Cd, Cr, Cu, Hg, Ni, Pb, Se, and Sb. Other metals that are presently of lesser interest to the EPA are Ag, Ba, Co, Mn, Mo, Na, Ti, V, and Zn. These metals were selected because of their potential for human exposure and increased health risk (Birungi, Masola, Zaranyika, Naigaga, & Marshall, 2007).

3.6.2. Factors affecting heavy metals mobility and bioavailability in plants.

Plant uptake of trace elements is generally the first step of their entry into the agricultural food chain. Plant uptake is dependent on movement of elements from the soil to the plant root, elements crossing the membrane of epidermal cells of the root, transport of elements from the epidermal cells to the xylem, in which a solution of elements is transported from roots to shoots, and possible mobilization, from leaves to storage tissues used as food (seeds, tubers, and fruit), in the phloem transport system. After plant uptake, metals are available to herbivores and humans both directly and through the food chain. The limiting step for elemental entry to the food chain is usually from the soil to the root (Chaney, 1989).

Plant species and relative abundance and availability of necessary elements also control metal uptake rates. Abundant bioavailable amounts of essential nutrients, including phosphorous and calcium, can decrease plant uptake of non-essential but chemically similar elements, including arsenic and cadmium, respectively.

Bioavailability may also be related to the availability of other elements. For example, copper toxicity is related to low abundances of zinc, iron, molybdenum and (or) sulfate (John & Leventhal, 1995).

The bioavailability of elements to plants is also controlled by many factors associated with soil and climatic conditions, plant genotype and agronomic management, including: total concentration and speciation (physical-chemical forms) of metals, mineralogy, pH, redox potential, temperature, total organic content, and suspended particulate content, the type of plant root system and the response of plants to elements in relation to seasonal cycles (Kabata-Pendias, 2010). Many of these factors vary seasonally and temporally, and most factors are interrelated. Consequently, changing one factor may affect several others. In addition, other poorly understood biological factors seem to strongly influence bioaccumulation of metals and severely inhibit prediction of metal bioavailability (Papa, Bartoli, & Fioretto, 2012).

3.7. Vegetable as a source of heavy metals, consumption and health risk

In developing countries, the consumption of vegetables is generally lower than the FAO recommendation of 75 kg/year/inhabitant (205 g/day/capita)(Tixier, de Bon, & Holmer, 2006).The importance of vegetable consumption depends on the population group. Over the period1994–1998, consumption in Vietnam was higher in urban areas (182 g/capita/day) than in rural areas (122 g/capita/day)(Tixier & de Bon, 2006). Therefore, heavy metal contamination of vegetables cannot be underestimated as these foodstuffs are important components of human diet(Sharma, Agrawal, & Marshall, 2009).

4. MATERIAL AND METHOD

4.1. Study location

The research area is located in Southern part of Addis Ababa, old Saris Alcohol Factory (Kebele 58) at latitude 473429N, 989182E and elevation of 2213 masl in Akaki Sub city (Fig.1).

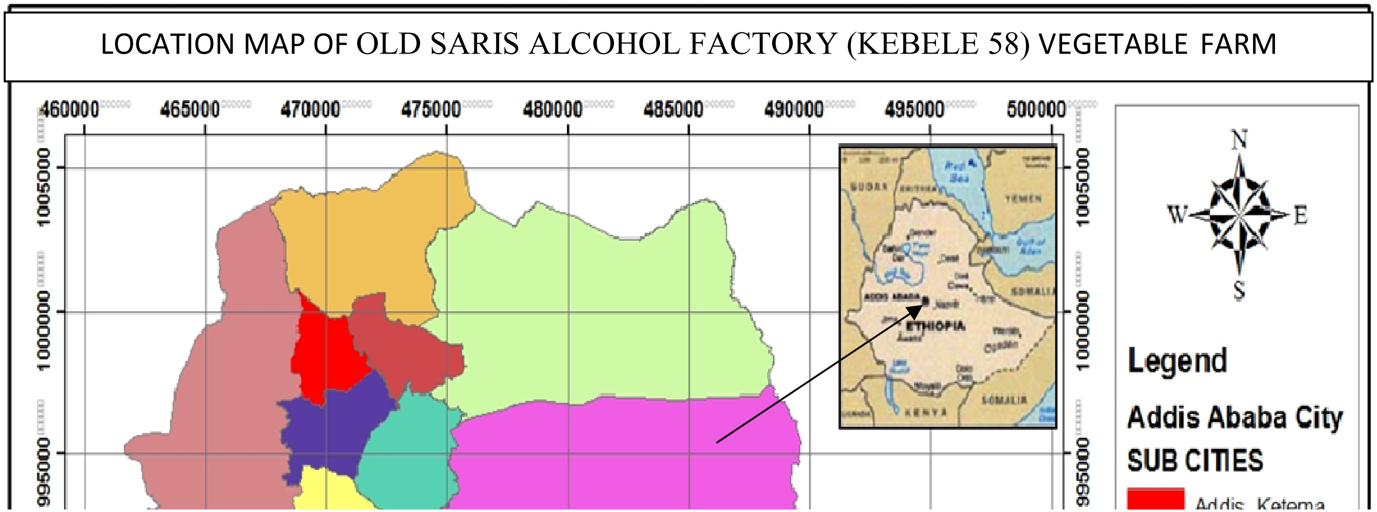
LOCATION MAP OF OLD SARIS ALCOHOL FACTORY (KEBELE 58) VEGETABLE FARM

Figure 1: Location maps of the study vegetable farm – old Saris Alcohol Factory (Kebele 58) area in Southern Addis Ababa, Ethiopia

4.2 Sample collection

4.2.1 Soil, River water, Vegetable samples and vegetable washings

Samples of Soil, River water and Vegetable samples were collected from the farm land irrigated with little Akaki river around old Saris Alcohol Factory (Kebele 58) area during December 2014 (Fig. 2). The samples were collected randomly from all the vegetable farms at 2 meter distance from each other. All the samples were collected in screw cap poly ethylene bottles and poly ethylene bags.

Figure 2. Leafy Vegetable farm around old Saris Alcohol Factory (Kebele 58) and little Akaki wastewater storm.

4.2.2 Samples and sample preparation

4.2.2.1 Green leafy vegetables

The samples of vegetables (Lettuce, Swiss chard, and Ethiopian Kale) were randomly collected at a 2 meter distance from each other from the vegetable farms. Leafy vegetables were preferred for sampling because previous researches indicate that they accumulate heavy metals at a greater capacity than other vegetables.

Pretreatment

The collected vegetable samples were washed with distilled water to remove dust particles. The samples were then cut to separate the roots, stems and leaves using a knife. Different parts (roots, stems and leaves) of vegetables were air-dried and dried in an oven at 100 ^{o}C over 3 days.

Dried samples of different parts of vegetables were ground into a fine powder (80mesh) using a commercial blender and stored in polyethylene bags, until used digestion

4.2.2.2 Soil sample

After considering average field conditions i.e. extreme high and low value, for example, slope, appearance of crop and a grid line were established at regular intervals (15-30 cm) and each intersection 1 m diameter area were sampled by taking 8-10 course. The depth of sampling was chosen according to land use. For shallow rooted crops 0-6 cm and for long rooted crops 6-12 cm was suitable. Contamination was prevented at all stages. As crushing is easier at right moisture level, the soil was passed through 2- 3 mm nylon sieve and air dried and then oven dried at 100c over 3 days. The sample was stored in poly ethylene bag.

4.2.2.3 Waste Water sample

Water sample was collected in 1 liter capacity plastic bottles. Before sampling, all plastic and glassware were cleaned by soaking in diluted HNO3 (10% v/v) and rinsed with distilled water prior to use. The source for the water samples was water from the river used for the irrigation where it enters the channel of the farm land, the sample bottles were rinsed several times with this water and 1 liter was taken as sample. The water samples were brought to the laboratory and filtered with 0.45 µm filters and preserved with 1 ml of 70% HNO3. The filtered samples were stored in a refrigerator without freezing to minimize volatilization and biodegradation until analysis (Weldegebriel, Chandravanshi, & Wondimu, 2012).

4.2.2.4 Samples of washings of the vegetables

Washings of the vegetable were collected in a screw cups plastic bottles after all the roots, stem and leafs of the vegetables were separated using knife and washed thoroughly using distilled water. The collected washings of the vegetable were filtered with 0.45 µm filters and preserved with 1 ml of 70% HNO3. The filtered samples were stored in a refrigerator without freezing to minimize volatilization and biodegradation until analysis (Weldegebriel et al., 2012)

4.2.2.5. Study design

In a laboratory based work, the concentration of heavy metals Cr, Cd and Pb were analysed using FAAS in Green Leaf Vegetables. Green leafy vegetables grown at old Saris alcohol factory (Kebele 58) area irrigated with waste water from the little Akaki river was analysed for its heavy metal concentration level. The green leafy vegetables collected from the area were Lettuce, Swiss chard and Ethiopian Kale. The bioaccumulation of these heavy metals was determined in different parts (roots, stems and leaves) of these vegetables. The concentration of Cr, Cd and Pb is also determined in the river water sample, soil sample from the farm land and the washings of the vegetable. Besides the source for these heavy metals in the vegetables parts were identified and their potential health risks were calculated.

Sample preparation for instrumental analysis was done at research laboratory of the Center for Food Science and Nutrition, and Department of Chemistry of Addis Ababa University. The determination of metal level was done at Department of Chemistry of Addis Ababa University.

4.2.2.6. Laboratory Analysis

All plastic and glassware were cleaned by soaking in diluted HNO3 (10% v/v) and rinsed with distilled water prior to use. All reagents were of analytical reagent grade 99% purity Aldrich Germany. Double distilled deionized water was used for all dilutions. The element standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg/L of each element.

4.2.2.7. Digestion of the samples Microwave

1 gram of vegetable, soil and 1mL of water sample were digested with 4 mL of HNO3 (65%) and 2 mL of H2O2 (30%) in microwave digestion system. After digestion, the solution was diluted with 10 ml de ionized water. A blank digest was carried out in the same way. The samples were digested in 1200 W Power for 30 min (Tüzen, 2002).

4.2.2.8. Preparation of standards and analysis of samples:

Working standard solutions of lead (Pb), chromium (Cr), and cadmium (Cd) were prepared from the stock standard solutions containing 1000 ppm of element in 2N nitric acid using serial dilution method. Calibration and measurement of elements were done on FAAS. The calibration curves were prepared for each element individually applying linear correlation by least square method. Blank readings were also taken and necessary correction was made during the calculation of concentration of various elements.

4.2.2.9. Instrumental Conditions

Maximum absorbance was obtained by adjusting the cathode lamps at specific slit and wavelengths:

Parameter	Wavelength (nm)	Slit width (nm)	Optimum working range (µg/L)
Cr	357.9	0.2	0.05-0.25
Pd	283.3	1.2	0.3-1.5
Cd	228.8	1.2	0.012-0.06

Table 1. Instrumental condition

4.2.2.10. Determination of heavy metals and its quality control method

Heavy Metal analysis was carried out using Graphite furnace Atomic Absorption Spectrophotometer (GFAAS) at Addis Ababa University Chemistry department. For all metal determinations, analytical blanks were prepared in a similar manner. The instrument was set to zero by running the prospective reagent blanks. Reagent blank was run at intervals of every five samples analysis to eliminate equipment drift. The accuracy of the analytical procedure was checked by introducing known metal standards into already analysed samples and re-analysed. All digestion glassware's were soaked in a solution of 10 % nitric acid for 48 h followed by thorough rinsing with deionized water. Average values of three replicates were taken for each determination for reproducibility accurate checks and precision and were subject to statistical analysis.

4.2.2.11. Estimation of the bioconcentration factors (BCF) of heavy metals

BCF calculation

BCF was calculated as follows:

$$BCF = C_{\text{vegetable}} / C_{\text{soil}} \qquad (1)$$

Where $C_{\text{vegetable}}$ is the total concentration of a particular heavy metal in the vegetable (mg kg $^{-1}$dw), and C_{soil} is the corresponding heavy metal concentration in the soil habitat of the vegetable (mg kg $^{-1}$).

4.2.2.12. Vegetable Consumption-Associated Health risk Assessment

Potential health risks of heavy metal exposure to Addis Ababa residents through local leafy vegetable consumption were assessed using THQ that was first proposed by the United States Environmental Protection Agency (USEPA) for assessing the potential health risks of pollutant exposure to human health (X. Liu et al., 2013).

THQ is defined as the ratio of the body intake dose of a pollutant to the reference dose (Eqs.1 and 2). If THQ>1, there will be a potential risk associated with this pollutant. If THQ<1, there will be no obvious potential risk associated with this pollutant.

Single pollutant: $THQ = ((C \times IR_{\text{vegetable } x}\ EF \times ED)/ (BW \times AT \times RfD)) \times 10^3$ (2)

Total pollutants: $THQ\ total = \sum THQ_{\text{(single pollutant)}}$ (3)

Where C is the mean concentration of a particular metal in a vegetable, IR is the daily vegetable intake by the Addis Ababa residents (including local and extraneous vegetables), EF is the exposure frequency (exposure days per year), ED is the exposure duration, BW is the average weight of local residents, AT is the average exposure time for non-carcinogens (exposure days within whole lifetime), and RfD is the reference dose.

It must be noted that the present study concerns metal health risks due to the consumption of local leafy vegetables. Thus, parameters of fv (local vegetables/total vegetables consumption), fa (leafy vegetable/local vegetable), and fb (fruit vegetable/local vegetable) were introduced in the estimates of daily local leaf vegetable intake.

4.2.2.13. Statistical analysis

All samples of water, soil and leaves, stems and roots of each vegetable were assayed and analysed individually in triplicate. Data was reported as mean ± SD. One way analysis of variance (ANOVA was used to determine significant difference between groups, considering a level of significance of less than 5% ($p<0.05$) by using SPSS Version 20. Charts and graphs were produced using Microsoft Excel 2007. The map of soil and vegetable sampling locations (Fig.1) was constructed in Arc Gis 10.1.

5. RESULT AND DISCUSSION

The calibration curves were prepared separately for all the metals by running different concentration of standard solutions. The calibration curves for Cd, Cr, and Pb were checked to ensure the accuracy and reliability of the instrument before running the GFAAS, which are moderately linear as shown in appendix.

5.1. Concentration of heavy metals in irrigation Wastewater

The concentrations of Cr, Cd and Pb for the irrigation wastewater obtained from Little Akaki River around old Saris Alcohol Factory (Kebele 58) farm were detected mg kg^{-1} 0.009±0.278, 0.001±0.046, 0.031±0.110 respectively. (Table 2).

Sample Type	Pb (mg/l)	Cr (mg/l)	Cd (mg/l)
Wastewater	0.031±0.0025	0.009± 0.0028	0.001± 0.0000

Guide line for irrigation b*	0.065a*	0.55a*	0.01b*

a* Source: USEPA, 2001

b* Source: Ayres and Westcott, FAO (1994).

Table 2**:** Heavy metal concentration (mg/kg) in irrigation wastewater of the vegetable farm. (Mean± S.D)

A relatively high concentration of these heavy metals obtained compared to tap water or upstream part of the river (Abraham GebreKiden, 2000) (Itana 1998). The wastewater which is used to irrigate the vegetable farm had mean concentration lower than the recommended maximum level for irrigation (Table 2).

Any differences in heavy metal concentration current study from previous studies might be taken as due to the difference in sampling point and their proximity to the industrial sites. In addition it might be related to difference in sampling period.

5.2. Heavy metals Concentration in vegetables farm soil

Sample Type	Pb (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
Soil	38±0.0011	4±0.0029	0.5 ±0.0000
Guide line for irrigation c*	100	100	3

c* Source: Ewers 1991

Table 3.Heavy metals concentration (mg/kg) in soils around old Saris Alcohol Factory (Kebele 58) Vegetable farm areas of Southern Addis Ababa, Ethiopia. (Mean± S.D)

5.2.1. Cadmium

It is observed that the concentration of Cd in soil is 0.5 ± 0.0000 mg/kg dry weight (Table.3). Fisseha Itana (1998) reported that the Cd content of the Kera area was (0.05mg/kg), which is by 10 fold less than the concentration around old Saris Alcohol Factory (Kebele 58) area. The Cd concentration of the farms in the present study (0.5 ± 0.0000 mg/kg) is lower than the previously reported results in other part of Addis Ababa i.e., 0.7mg/kg for peacock farm and 0.95 mg/kg for Akaki vegetable farms ,but greater than 0.4 mg/kg for Kera farm, 0.4mg/kg for Kolfe (Itanna, 2004).

5.2.2. Chromium

The concentration of Cr in the study farm soil (4±0.0029) is lower than the previous concentration in soils of other vegetable farms of Addis Ababa.

This previous study conducted by Fisseha Itanna and Olsson (2004) shows 81.0 mg/kg, 115 mg/kg, 283 mg/kg and 86 mg/kg for the peacock farm, Kera, Kolfe and Akaki vegetable farms (Itanna, 2004).

5.2.3. Lead

The level of lead in soil of the study farms (38±0.560) showed lower concentration values than the previously reported concentration. Fisseha Itanna and Olsson (2004) indicated the concentration of Pb in soils at the different vegetable farms of Addis Ababa, 46.7 mg/kg, 110 mg/kg, and 48.74 mg/kg for peacock, Kera, and Akaki vegetable farms respectively, which have higher concentration value from this study except for Kolfe which is 32.7 mg/kg and lower in concentration. Other study conducted by (Alemayehu et al., 2006) reported that the mean concentration of lead in soils of Burayu area was 12.5 mg/kg which is lower than result of the current study.

5.3. Heavy metal concentration in vegetables

	Pb (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
Ethiopian Kale Root	0.620±0.0132	0.124±0.0117	0.011±0.0003
Ethiopian Kale stem	0.221±0.0156	0.044±0.0137	0.007±0.0002
Ethiopian Kale leaf	0.373±0.0021	0.075±0.0021	0.011±0.0000
Lettuce Root	0.019±0.0187	0.193±0.0105	0.014±0.0002
Lettuce Stem	0.009±0.0089	0.033±0.0018	0.016±0.0003
Lettuce Leaf	0.002±0.0022	0.112±0.0074	0.125±0.0002
Chard Root	0.689± 0.0093	0.103±0.0088	0.014±0.0000
Chard Stem	1.336±0.0043	0.067±0.0072	0.007±0 .0000
Chard Leaf	0.133±0.0168	0.162 ± 0.0000	0.005±0.0002
Rec. Max. limit for Vegetables(FAO/WHO)	0.3	0.2	2.3

Table 4. Heavy metals concentration (mg/kg) in different parts (root, stem and shoot) of Lettuce, Swiss chard and Ethiopian Kale around old Saris Alcohol Factory (Kebele 58) area farm (Mean± S.D).

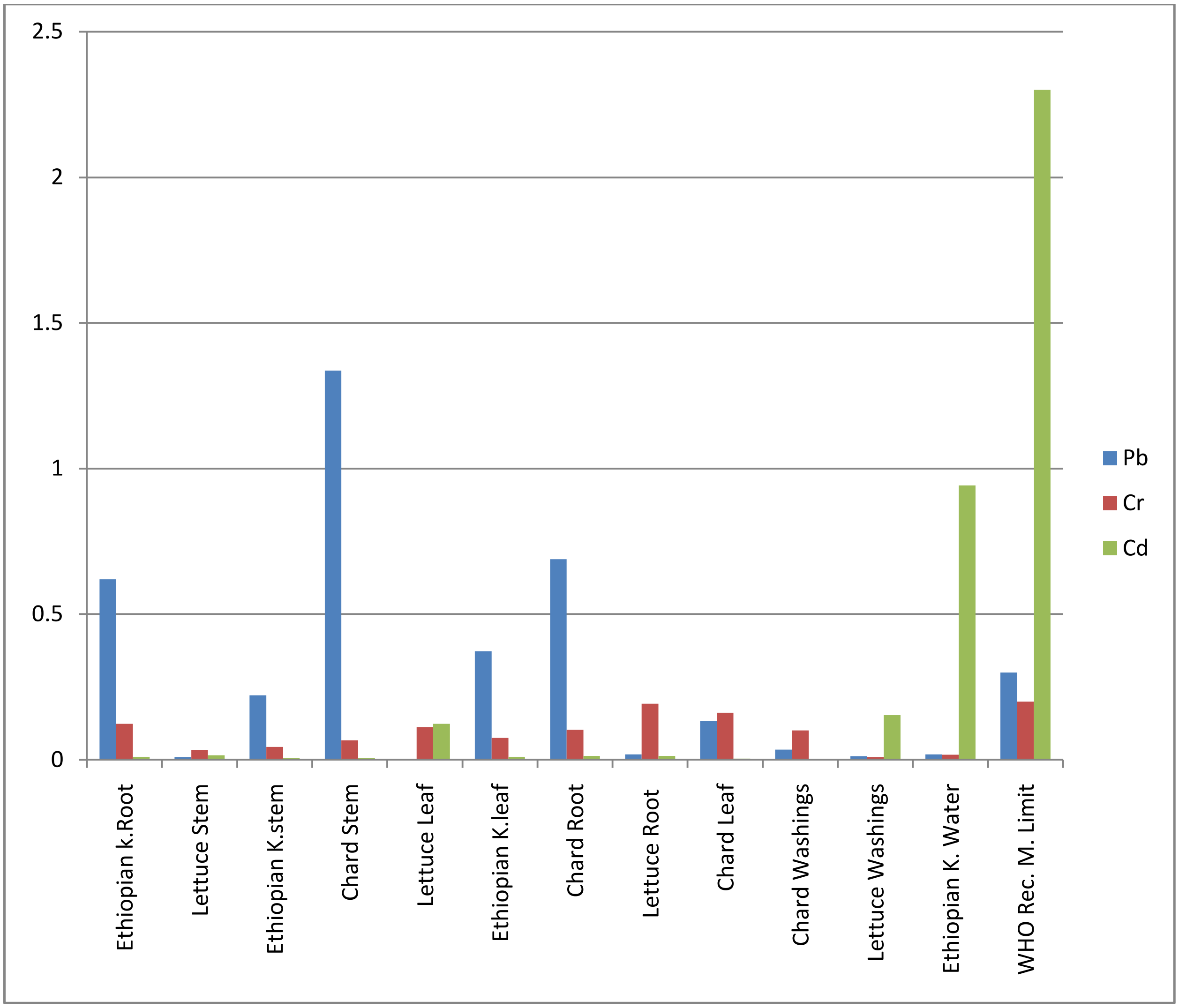

Figure 4. Heavy metals concentration (mg/kg) at different parts (root, stem and shoot) of Lettuce, Swiss chard and Ethiopian Kale around old Saris Alcohol Factory (Kebele 58) area farm (Mean± S.D).

5.3.1. Cadmium

Ethiopian Kale: The mean concentrations of Cd in different vegetable parts root, stem and leaf are in mg/kg 0.011±0.0003, 0.007+0.0002 and 0.011±0.0000 respectively. This shows that the Ethiopian Kale accumulates more Cd in root part than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

Lettuce: The mean concentrations of Cd in different vegetables parts root; stem and leaf are in mg/kg 0.014±0.0002, 0.016±0.0003 and 0.125±0.0002 respectively. This shows that the leaf of Luttice accumulates more Cd than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

Swiss chard: The mean concentrations of Cd in different vegetables parts root; stem and leaf are in mg/kg 0.014±0.0000, 0.007±0.0000 and 0.005±0.0002 respectively. This shows that the root of Chard accumulates more Cd than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

5.3.2. Chromium

Ethiopian Kale: The mean concentrations of Cr in different vegetable parts root, stem and leaf are in mg/kg 0.124±0.0117, 0.044±0.0137 and 0.075±0.0021 respectively. This shows that the Ethiopian Kale accumulates more Cr in root part than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

Lettuce: The mean concentrations of Cr in different vegetables parts root; stem and leaf are in mg/kg 0.193±0.0105, 0.033±0.0018 and 0.112±0.0074 respectively. This shows that the root of Lettuce accumulates more Cr in root part than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

Swiss chard: The mean concentrations of Cr in different vegetables parts root; stem and leaf are in mg/kg 0.103±0.0088, 0.067±0.0072 and 0.162±0.0000 respectively. This shows that the leaf of Chard accumulates more Cr in than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

5.3.3. Lead

Ethiopian Kale: The mean concentrations of Pb in different vegetable parts root, stem and leaf are in mg/kg 0.620±0.0132, 0.221±0.0156 and 0.373±0.0021respectively. This shows that the root of Ethiopian Kale accumulates more Pb than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

Lettuce: The mean concentrations of Pb in different vegetables parts root stem and leaf are in mg/kg 0.019±0.0187, 0.009±0.0089 and 0.002±0.0022 respectively. This shows that the root of

Luttice accumulates more Pb than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

Swiss chard: The mean concentrations of Pb in different vegetables parts root stem and leaf are in mg/kg 0.689±0.0093, 1.336±0.0043 and 0.133±0.0168 respectively. This shows that the stem of Chard accumulates more Pb than other parts around old Saris Alcohol Factory (Kebele 58) area vegetable farm of Southern Addis Ababa.

The results show that Pb is the major heavy metal pollutant accumulated in leaf vegetables grown in agricultural soils around old Saris Alcohol Factory (Kebele 58) area which exceeds maximum limit in leaf and root of Ethiopia kale and root and stem part of Swiss chard. But, the concentrations of Pb, Cr and Cd in other parts of the three vegetables are below the recommended maximum acceptable levels proposed by the Joint FAO/WHO Expert Committee on Food Additives as shown in Table 3. The maximum accumulation of Pb (1.336±0.142 mg/kg) is observed in stem part of Swiss chard; Cr (0.193±0.165 mg/kg) is observed in root part of Lettuce; and Cd (0.125± 0.261 mg/kg) is observed in leaf part of Lettuce.

5.4. Heavy metal concentration in washing water

The concentrations of Pb, Cr and Cd in washing water of the green vegetables grown around old Saris Alcohol Factory (Kebele 58) area are shown in table 4. This shows that if the vegetable is not properly washed additional heavy metal can be consumed from the surface above the permissible limit because of the sum of the accumulation in the part and on the surface of the vegetable part (example Cd in Swiss chard leaf and washing water). The surface contamination can be caused by air, irrigation water or dust during collection and transportation.

Sample Type	Pb	Cr	Cd

	(mg/l)	(mg/l)	(mg/l)
Chard Washings	0.035±0.0007	0.101±0.0084	0.001±0.0000
Lettuce Washings	0.012±0.0011	0.009±0.0004	0.154±0.0000
Ethiopian K. Washings	0.019±0.0006	0.017±0.0221	0.943±0.0000

Table 5. Heavy metals concentration (mg/kg) at in washed water of Lettuce, Swiss chard and Ethiopian Kale around old Saris Alcohol Factory (Kebele 58) area farm (Mean± S.D).

5.5. Bioaccumulation of heavy metals from soil to vegetables

	Ethiopian k. Root	Lettuce Stem	Ethiopian K. stem	Chard Stem	Lettuce Leaf	Ethiopian K. leaf	Chard Root	Lettuce Root	Chard Leaf
Pb	0.016	0.000	0.006	0.035	0.000	0.010	0.018	0.001	0.004
Cr	0.031	0.008	0.011	0.017	0.028	0.019	0.026	0.048	0.041
Cd	0.022	0.032	0.014	0.014	0.250	0.022	0.028	0.028	0.010

Table 6. The bioaccumulation factor value of three heavy metals (Pb, Cr and Cd) in three kinds of leaf vegetables parts (root, stem and leaf) collected from agricultural soils around old Saris Alcohol Factory (Kebele 58) area Southern Addis Ababa.

5.5.1. Cadmium

Ethiopian Kale: The BCF values of Cd in Ethiopian Kale in different vegetable parts root, stem and leaf are 0.022, 0.014 and 0.022 respectively.

Lettuce: The BCF values of Cd in Luttice in different vegetable parts root, stem and leaf are 0.028, 0.032 and 0.250 respectively.

Swiss chard: The BCF values of Cd in Swiss chard in different vegetable parts root, stem and leaf are 0.028, 0.014 and 0.010 respectively.

5.5.2. Chromium

Ethiopian Kale: The BCF values of Cr in Ethiopian Kale in different vegetable parts root, stem and leaf are 0.031, 0.011 and 0.019 respectively.

Lettuce: The BCF values of Cr in Luttice in different vegetable parts root, stem and leaf are 0.028, 0.083 and 0.025 respectively.

Swiss chard: The BCF values of Cr in Swiss chard in different vegetable parts root stem and leaf are0.026, 0.017 and 0.041 respectively.

5.5.3. Lead

Ethiopian Kale: The BCF values of Pb in Ethiopian Kale in different vegetable parts root, stem and leaf are 0.016, 0.006 and 0.010 respectively.

Lettuce: The BCF values of Pb in Luttice in different vegetable parts root, stem and leaf are 0.001, 0.000 and 0.000 respectively.

Swiss chard: The BCF values of Pb in Swiss chard in different vegetable parts root, stem and leaf are 0.018, 0.035 and 0.004 respectively.

The BCF values of Pb in vegetables parts especially in stem and root part of Swiss chard is significantly higher (0.035 and 0.018) respectively. The BCF value of Pb is approximately 2-fold in stem than the root. The BCF value of Pb, Cr and Cd in leaf of the Swiss chard is approximately 18-fold, 1.5- fold and 0.04- fold compared to lettuce leaf respectively. Since a greater BCF value indicates a higher accumulation potential of metals in vegetables (Chumbley and Unwin 1982;Cuiet al.2004), the above results indicate that Cd has higher capacity for transferring from soil to the edible parts of vegetables as shown in lettuce leaf than the other two heavy metals in agricultural soil around old Saris Alcohol Factory (Kebele 58) area farm.

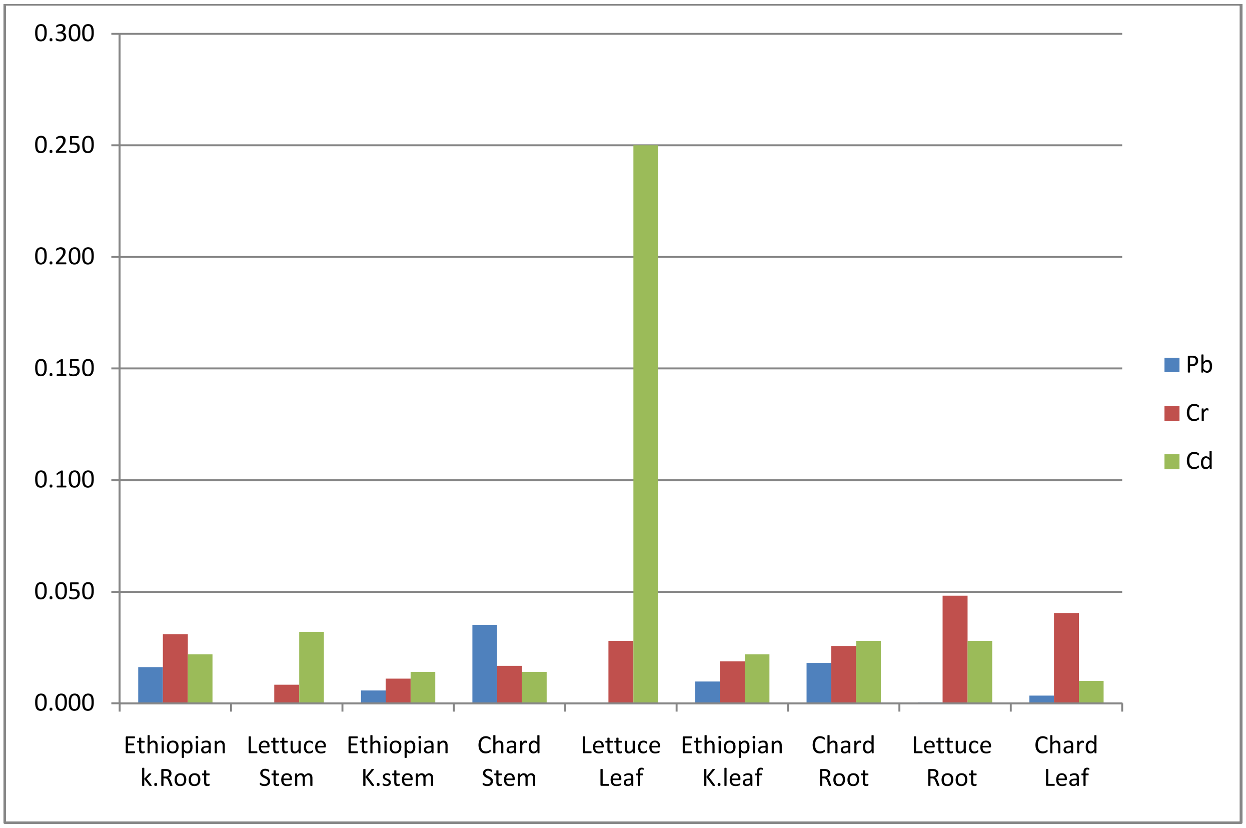

Fig. 5 Bioconcentration factor (BCF) values of three heavy metals (Pb, Cr and Cd) in three kinds of leaf vegetables parts (root, stem and leaf) collected from agricultural soils in the around old Saris Alcohol Factory (Kebele 58) area Southern Addis Ababa.

5.6. Identification of heavy metal sources

	PC1	PC2	PC3
Pb	0.817	0.062	0.574
Cr	-0.536	0.801	0.266
Cd	-0.705	-0.538	0.462
Eigen value	1.452	0.935	0.614
Variability (%)	48.394	31.153	20.453
Cumulative %	48.394	79.547	100.000

Table 7. Matrix of principal component analysis of the bioconcentration factor values of of three heavy metals (Pb, Cr and Cd) in three kinds of leaf vegetables parts (root, stem and leaf) collected from agricultural soils around old Saris Alcohol Factory (Kebele 58) area Southern Addis Ababa.

PCA (Principal Component Analyses) has commonly been used for investigating metal sources, anthropogenic activities, or soil parent materials (Facchinelli et al. 2001; Loska and Wiechu ła 2003; Bor ůvka et al. 2005; Cai et al.2012). In the present study, three principal components (PC) were extracted from the BCF values of heavy metals in leafy vegetables (Table 6). The first principal component (PC1) explains 48.39 % of the total variance and loaded heavily on Pb (0.817) which shows that Pb contamination is serious in wastewater-irrigated agricultural soils around old Saris Alcohol Factory (Kebele 58) area. Based on the above finding, it is speculated that PC1 reflects the impacts of sewage irrigation which exhibits characteristics disposal of battery wastes from the garages around the area and of gas emission from the heavy traffic in around old Saris Alcohol Factory (Kebele 58) area.

The second principal component (PC2) accounts for 31.15 % of the total variance and is dominated by Cr (0.801). The second principal component (PC2) shows that Cr contamination is serious in wastewater-irrigated agricultural soils around old Saris Alcohol Factory (Kebele 58) area. The second principal component (PC2) is speculated to reflect the impacts of sewage irrigation which exhibits characteristics of tannery industry effluence.

The third principal component (PC3) represents 20.45 % of the total variance and is dominated by Pb (0.574), Cd (0.462) and Cr (0.266). The concentration of the three heavy metals in PC3 can be mainly attributed to soil parent sources. The Cd accumulated in vegetables is also anticipated to come from Cd rich high phosphate and sewage sludge fertilizers and nickel-cadmium batteries.

5.7. Potential health risk associated with consumption of leafy vegetables

The method for the determination of THQ was provided in the United States EPA Region III Risk based concentration table (Wang, Sato, Xing, & Tao, 2005). The dose calculations were carried out using standard assumptions from an integrated United States (US EPA, 2007) risk analysis and (McKinlay, Plant, Bell, & Voulvoulis, 2008).

Assumptions for the health risk calculations are;

1. Ingested dose is equal to the absorbed pollutant dose(Zheng, Wang, & Zheng, 2007).
2. Cooking has no effect on the pollutants (Han et al., 1998; Zheng et al., 2007).
3. The average body weight of an Ethiopian is assumed to be 70 kg for adult and 19.25 kg for children of 0-6 years old (Guerra, Trevizam, Muraoka, Marcante, & Canniatti-Brazaca, 2012).
4. Average lifetime of an Ethiopian is 65.35 years (You, 2013)
5. Average exposure frequency (365 days/year)
6. C = (μg/kg, on dry weight basis):
   Mean Cadmium (Leaf + Stem) of Lettuce, Ethiopian Kale, and Swiss chard
   Mean Chromium (Leaf + Stem) of Lettuce, Ethiopian Kale, and Swiss chard
   Mean Lead (Leaf + Stem) of Lettuce, Ethiopian Kale, and Swiss chard
7. Average Daily green vegetable intake (mg/kg/day) = 49.3 (Zalucki et al., 2012)for adult and 1/3 times for children
8. Reference Dose (mg/kg/day) Oral

   -Cadmium= (1×10^{-3}) (Z. Liu et al., 2009).
   -Chromium= (1.5) (WHO)
   -Lead= (0.0035) (WHO)

		HQa	HQc	THQa	THQc
Ethiopian. K	Pb	0.209173	0.760629	0.211012	0.255772
	Cr	2.79E-05	0.000102		
	Cd	0.001811	0.006586		
S.chard	Pb	0.517298	1.881083	0.518559	0.628556
	Cr	5.38E-05	0.000195		
	Cd	0.001207	0.00439		
Lettuce	Pb	0.007747	0.028171	0.036188	0.043864
	Cr	6.81E-05	0.000248		
	Cd	0.028373	0.103173		

Table 8. The target hazard quotient (THQa-adult, c-children) (a) and total THQ of three heavy metals to children and adults via vegetable (Leaf and stem part) consumption in the Southern Addis Ababa, around old Saris Alcohol Factory (Kebele 58) area, Ethiopia.

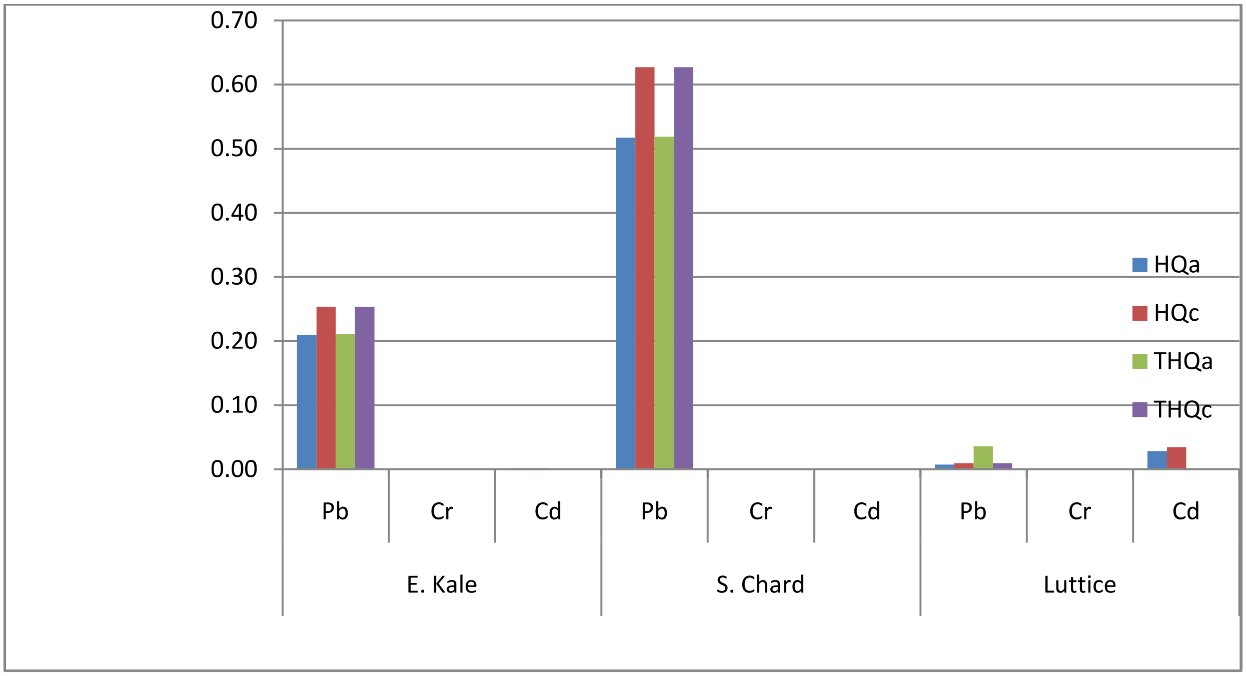

Figure 6.Target hazard quotient (THQ) of residents from consumption of heavy metals in green leafy vegetable (Leaf and stem part) grown around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa irrigated by wastewater.

The potential health risks were assessed using THQ, which were calculated according to Eqs 1 and 2. The parameters used in the equations were taken from WHO , FAO, US EPA and World Bank. The potential health risk to Addis Ababa residents associated with vegetable consumption was assessed with the THQ index (Tables 7). Of the three heavy metals, Pb posed the greatest health risk to both adult and children consumers of vegetables grown in study areas especially Swiss chard, followed by Ethiopian Kale. (Fig. 6).

For both adults and children the THQs of all three heavy metals in the three leaf vegetables were less than 1.0 (Table 7), indicating that the residents in the Addis Ababa are not exposed to significant health risks associated with consumption of green leafy vegetables grown around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa.

The interpretation of the THQ value is binary: THQ is either > 1 or < 1, where THQ > 1 indicates a reason for health concern (Iwegbue, Nwozo, Overah, Bassey, & Nwajei, 2013).

It must be noted that THQ is not a measure of risk (Petroczi & Naughton, 2009) but indicates a level of concern and while the THQ values are additive, they are not multiplicative; e.g. the level of concern at THQ of 20 is larger but not tenfold of those at THQ = 2 (Abraham et al., 2008)

It should be noted that the present study only estimated the health risk of heavy metals to the Addis Ababa residents via consumption leafy vegetables wastewater irrigated and grown around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa. That means, this work only takes into account part but not the total risks to Addis Ababa residents associated with consumption of green leafy vegetables. In addition, the total risks of heavy metals are related to the main polluted metals, and their long-term interactions which can impose distinct ecological or health risks via antagonistic, additive, and/or synergistic effects (Bitanihirwe & Woo, 2011) were not considered. Thus, the potential health risks of heavy metal exposure to local residents through consumption of green leafy vegetables might be underestimated.

6. CONCLUSION AND RECOMMENDATION

In the assessment of the three heavy metal concentrations in different vegetables parts around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa Pb in Swiss chard has high concentrations than other green leafy vegetables. The three heavy metal concentrations in edible part of the three vegetables grown around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa were below the permitted limit (WHO) except Swiss chard on its stem parts.

The BCF results indicate that Cd has higher capacity for transferring from soil to the edible parts of vegetables than the other two heavy metals in agricultural soil of the around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa. Among the three leafy vegetables, Lettuce has the lowest average BCF values of heavy metals (except for Cd in its leaf).Thus, there is a relatively low potential for metal accumulation in Lettuce grown around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa. Therefore old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa can be planted with Lettuce.

PCA (Principal Component Analyses) has commonly been used in the present study to investigate metal sources as anthropogenic activities, or soil parent materials. Three principal components (PC) were extracted from the BCF values of heavy metals in leafy vegetables. The first principal component (PC1) shows that Pb contamination is serious in wastewater-irrigated agricultural soils around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa.

Based on the above finding, it is speculated that PC1 reflects the impacts of sewage irrigation which exhibits characteristics disposal of battery wastes from the garages around the area and of gas emission from the heavy traffic around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa.

The second principal component (PC2) shows that Cr contamination is serious in wastewater-irrigated agricultural soils around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa. The second principal component (PC2) is speculated to reflect the impacts of sewage irrigation which exhibits characteristics of tannery industry effluence. In the third principal component, the concentration of the three heavy metals in PC3 can be mainly attributed to soil parent sources. The Cd accumulated in vegetables is also anticipated to come from Cd rich high phosphate and sewage sludge fertilizers and nickel-cadmium batteries.

The potential health risks were assessed using THQ in this study for both adults and children. The THQs of all three heavy metals in the three leafy vegetables were less than 1.0 (Table 7), indicating that the residents in the Addis Ababa are not exposed to significant health risks associated with consumption of green leafy vegetables grown around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa.

Finally, the study recommends the following points in order to minimize the potential health risk on the consumers of green leafy vegetables grown with wastewater irrigation around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa.

- For its low bioaccumulation Lettuce can be planted as edible crop around old Saris Alcohol Factory (Kebele 58) area, southern Addis Ababa.
- Vegetables, should be washed properly before consumption.
- More attentions should be paid to children due to their higher sensitivity to heavy metal exposure than that of adults.
- Monitoring the food for heavy metal concentration is necessary by developing and implementing prospective plans and policies for environmental protection, food safety and public health
- It is important to enforce and monitor treatment the discharge of untreated effluent, solid wastes and wastewater from industries, households and institutions before discharging to the stream
- Putting in place industrial pollution control mechanisms such as environmental auditing, discharge permit and enforce limits to the disposal of effluents into the environment.
- Commercial activities such as car washing and fuel stations that discharge waste oil and be controlled for environmental pollution.
- Enhance public sensitization programs on hygiene, sanitation and environmental issues.
- Chemical inputs like fertilizers and pesticides in agriculture should be reduced and biological weed controls should be introduced, as used in some western countries.
- Other alternative irrigation techniques other than furrow irrigation shall be advised
- Further more detailed researches on the assessment of bioaccumulation, source and potential health risk.

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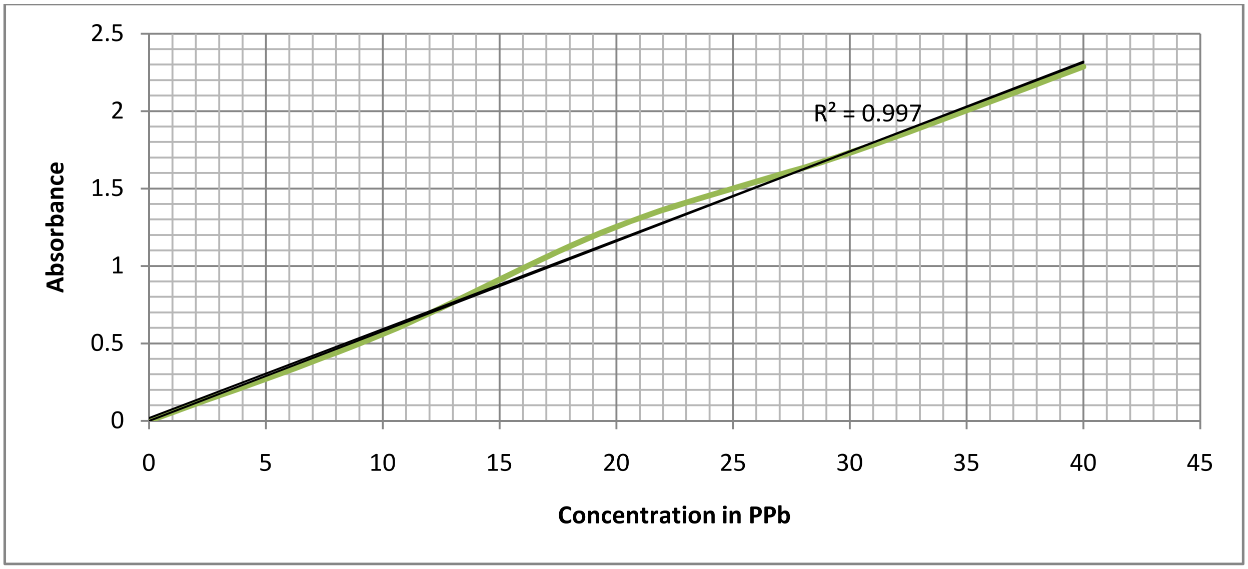
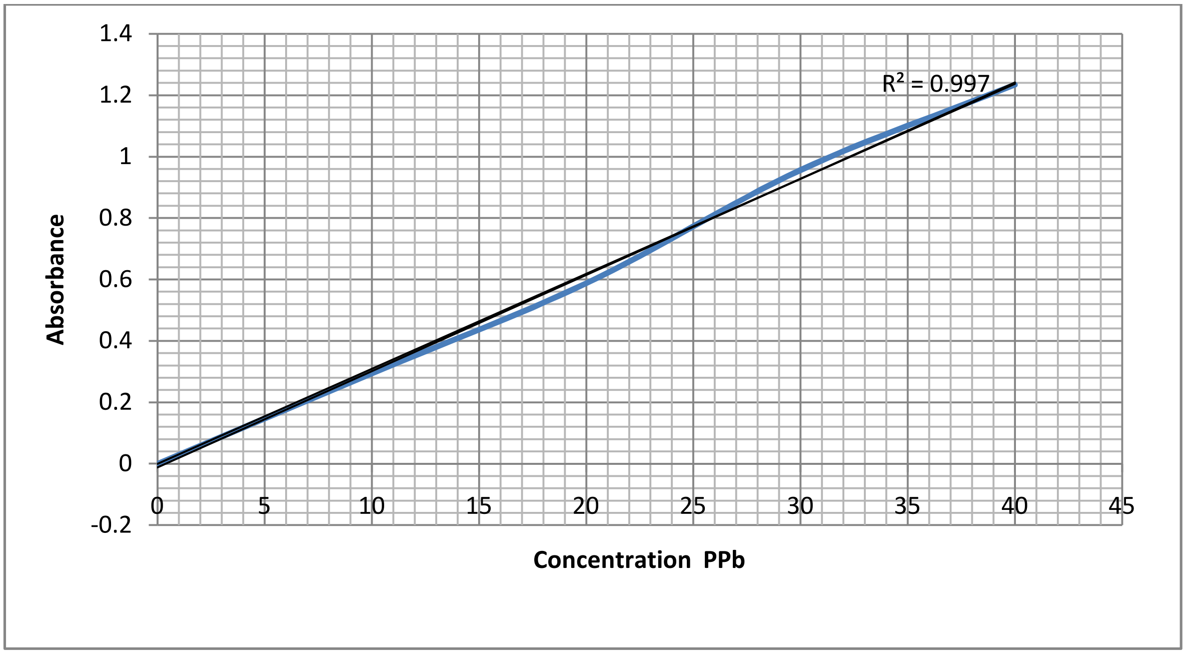
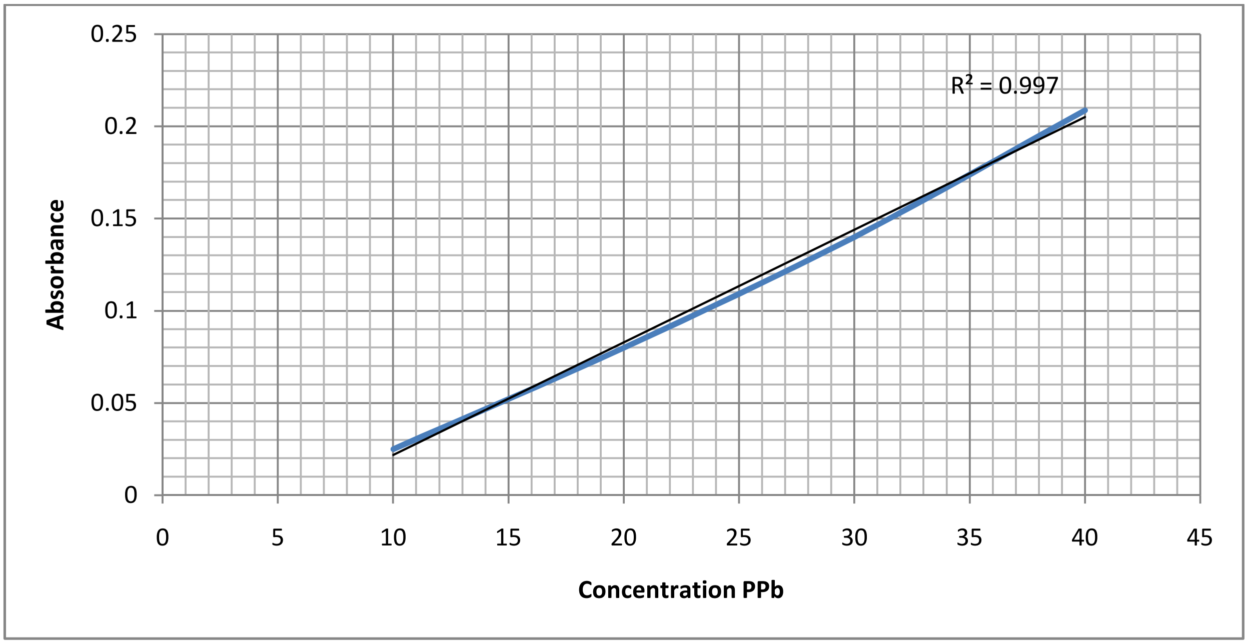
8. ANNEX.



(a) Calibration curves: Cd



(b) Calibration curves: Cr



(C) Calibration curves: Pb