HEAVY METAL CONTAMINATION OF VEGETABLES IRRIGATED WITH WASTE WATER IN GUJRANWALA DISTRICT, PUNJAB, PAKISTAN

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A thesis submitted in fulfillment of the requirements for the award of the degree MS (Environmental Policy and Management)

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ABSTRACT

Heavy metals are the foremost contaminants of food crops especially vegetables, hence considered a peril to environment. Wastewater irrigation as a substitute to freshwater has further aggravated the situation by increasing metal load in agricultural soils and food commodities especially vegetables. Intake of heavy metals via consumption of contaminated vegetables is notorious for a wide variety of deleterious health impacts in human population.

In Gujranwala, along with other sources such as tube well and canal water irrigation, wastewater irrigation in urban and peri-urban areas for the cultivation of vegetables is a common practice which could be a potential source of metal contamination. The study area hosts several commercial and industrial centers as well as support a good amount of agriculture. The current study was therefore carried out is to evaluate concentration of toxic metals viz Lead, Cadmium, Chromium, Nickle, Mercury and Arsenic in vegetables (chilli, tomato, onion, spinach, okra, coriander, watermelon, cauliflower, capsicum and bitter gourd) irrigated with waste water, tubwell water and canal water in Gujranwala and estimate associated health risk in the inhabitants due to dietary exposure via consumption of afore mentioned vegetables.

The concentration levels of Pb, Cr, Cd, As and Hg assessed with the aid of atomic absorption spectrophotometer in vegetables were in range 0.09 - 6.46, 0.00 - 7.69, 0.01 - 4.32, 0.00 - 2.31 and 0.00 - 0.78 mg/kg respectively. Overall trend generated on the basis mean concentration in vegetables is Pb> Cr > Cd > As > Hg. Hazard Index (HI) values for cauliflower (2.95), spinach (1.68), onion (1.42), chilli (1.24), watermelon (1.05) and coriander (1.03) were exceeding 1 for adults, whereas for children HI values for cauliflower (4.42), spinach (2.59), onion (2.21), chilli (1.78), tomato (1.63), coriander (1.62), watermelon (1.60) and okra (1.34) were higher the standard indicating potential non-carcinogenic risk associated with their consumption on a longer run. Results revealed that children are at higher risk than adults.

Cancer risks associated with Pb, Cr, Cd and As ranged 1.74E-06 - 1.05E-05, 1.13E-04 - 6.40E-04, 1.27E-05 - 2.67E-04 and 0.00E+00 - 9.74E-04 respectively for adult consumers. In children risk of cancer was higher for Pb, Cr, Cd and As, ranging from 3.74E-06 - 2.24E-05, 1.62E-04 - 9.22E-04, 1.83E-05 - 3.85E-04 and 0.00E+00 - 1.40E-03 respectively. It can be concluded that consumers are at low cancer risk due to consumption of vegetables understudy. However, heavy metals even at low concentration are not desirable and continuous monitoring on regular basis is a dire need for safe and health consumption of vegetables as well as to avoid ecological hazards.

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LIST OF ABBREVIATION

AAS	-	Atomic Absorption Spectrophotometer
ATSDR	-	Agency for Toxic Substances and Disease Registry
As	-	Arsenic
Cd	-	Cadmium
Cr	-	Chromium
CSF	-	Cancer Slope Factor
DDW	-	Deionized Distilled Water
DIM	-	Daily Intake of Metal
FAO	-	Food and Agricultural Organization
GDP	-	Gross Domestic Product
GT Road	-	Grand Trunk Road
HI	-	Hazard Index
HQ	-	Hazard Quotient
ILTCR	-	Incremental Lifetime Cancer Risk
LRRI	-	Land Resource Research Institute
MHS	-	Mercury Hydride System
NARC	-	National Agricultural Research Center
Pb	-	Lead
WHO	-	World Health Organization

CHAPTER 1

INTRODUCTION

The ever-increasing industrialization, urbanization, and use of extensive agrochemicals has led to the excess level of heavy metals in the environment. Around the globe, metal pollution has become a stern global concern being foremost contaminants of the food chain, although the severity and levels of pollution differ from place to place (Kacholi and Sahu, 2018; Ali et al., 2013; Singh et al., 2012). Due to toxic, persistent and non-degradable nature, heavy metals have gained a lot of attention as environmental contaminants and are considered as a severe menace worldwide (Qadir et al., 2015; Yang et al., 2015; Ali et al., 2013; Kamkar et al., 2010) Heavy metal pollution has recently become a severe menace worldwide, and especially in South Asia, where high exposure of the human population stems from lack of awareness and from depressed socioeconomic conditions (Mohmand et al., 2015).

With respect to the environmental, ecological and economic implications, heavy metal pollution is a matter of serious concern. As a result of different natural and anthropogenic activities, these hazardous and unseen toxic elements are emitted in the environment via a wide range of pathways and processes including air, surface waters, ground water, soil and sediments. The escalating developmental processes can also be attributed for the release of hazardous and unseen toxic metals in the environment. Worldwide, more than 10 million soil sites considered as soil polluted sites covering an area of more than 20 million ha, of which more than 50% are contaminated due to release of heavy metals and/or metalliods (Kumar et al., 2019). There has been increasing pollution of cropland by heavy metals around the world, especially in China (Yang et al., 2016). Fang et al. (2016) attributed to the rapid economic development for the heavy metal pollution in Hangzhou Bay, China.

Agricultural soils are at greater risk to metal contamination due to application of sludge and waste water from industrial and municipal sectors for irrigation purpose; activities like mining, smelting, combustion of fossil fuels, vehicular emission, atmospheric deposition; emissions of different waste materials from industries; administration of fertilizers and metal based pesticides; harvesting process and storage (Guvenç et al., 2003; Ali et al., 2015[a]; Ali et al., 2015[b]; Qadir et al., 2015). Due to complex anthropogenic activities agricultural soils of Pakistan are alsosubjected to elevated levels of heavy metals in the urban and peri urban areas of Sialkot, Gujranwala, Lahore, Kasur, Peshawar, Karachi (Midrar-ul-haq et al., 2003; Tariq et al. 2005; Tariq et al. 2006; Malik et al. 2010; Mushtaq et al. 2010; Ali et al., 2015[b]). Heavy metals are known to affect crop quality/production, threatening human and livestock health through plant produce consumption.

Environmental and human health is at risk due to accumulation of heavy metals in soils and waters. If these elements are present in sediments then these reach the food chain through plants and aquatic animals (Singh et al., 2012). Heavy metals such as Pb, Cd, As, Ni, Cu, are the prime contaminants of food supply especially vegetables as they have tendency to absorb heavy metals from contaminated soil, water and air. Moreover, these elements tend to accumulate in the body tissues of living organism due to bioaccumulation and biomagnification and their concentrations increase as they pass through successive trophic levels (Ali et al., 2013). Although toxicity and the resulting threat to human health of any contaminant are, of course, a function of concentration (Llobet et al., 2003). Exposure to heavy metals occur via several pathways, with relative importance of each path depending upon the heavy metal contamination in different exposure media. Although some individuals are primarily exposed to these contaminants in the workplace, for most people the main route of exposure to these toxic elements is through the diet, so it’s very important to monitor the dietary intake to assess human health risks (Llobet et al., 2003).

1.1 Essential and Non-Essential Heavy Metals

The term "heavy metals" refers to any metallic element that has atomic number greater than 20 and specific gravity (density) of more than about 5 g/cm^3 and is toxic or poisonous even at low concentration (Ali and Khan, 2018; Onakpa et al., 2018). On the basis of their role in biological systems, heavy metals are categorized as essential and non-essential metals. Essential heavy metals are those which are required by living organisms in very small amount for proper functioning of different biochemical and physiological processes. Elements such as Mn, Fe, Co, Cu, and Zn are very critical in biological systems due to narrow window between their essentiality and toxicity, as they may be very toxic even at low concentrations (Ali et al., 2013; Dasbasi et al., 2016; Ali et al., 2017; Ali and Khan, 2018). On the other hand, non-essential heavy metals are those which are not required by living organisms and have no known biological functions. Moreover, these metals have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Llobet et al., 2003). The four environmentally most hazardous heavy metals and metalloids, that is, Cd, Pb, Hg, and As are generally regarded as non-essential elements. In cooperation with the U.S. Environmental Protection Agency, the Agency for Toxic Substances and Disease Registry (ATSDR) has compiled a priority list in 2001 called the "Top 20 Hazardous Substances". The heavy metals Arsenic, Lead, Mercury, and Cadmium ranked 1st, 2nd, 3rd, and 4th in the list, respectively (Saracoglu et al., 2007; Cruz et al., 2009; Kazi et al., 2010; Ali et al, 2013; Mehrnia and Bashti, 2014; Ali and Khan, 2018).

1.2 Sources of Heavy Metals

Heavy metals find their way in to the agricultural soils through multiple sources either point sources or non-point sources. Point metal sources include discrete and localized contamination source such as industrial and/or municipal activities, mining and smelting, whereas nonpoint metal sources embody diffuse processes covering large areas such as fossil fuel burning, adverse agricultural practices and atmospheric deposition. Both natural and anthropogenic activities are responsible for the release of heavy metals in the environment. Natural or geogenic sources include weathering of metal bearing parent rocks, erosion and volcanic eruption. On the other hand, anthropogenic sources comprised of mining operations, domestic and industrial wastewater, sludge dumping, surface runoff, combustion of fossil fuels, electroplating, pigment, and plastic industries; phosphate fertilizers; leaded gasoline; widespread of metal containing pesticides; paints; metal smelting; tannery industry effluents; marble industry effluents; stone crushing; poultry and animal industry (Duruibe et al., 2007; Dissanayake and Chandrajith 2009; Sabiha-Javied et al. 2009; Ali et al. 2013; Zahra et al., 2014; Mohmand et al., 2015; Mulk et al. 2015; Eqani et al., 2016[a]; Hashem et al. 2017; Ali and Khan, 2018).

1.3 Wastewater Irrigation

Agriculture sector plays an inevitable role in the economic growth of Pakistan with the contribution of 24% in GDP, 35% of export share whereas export of vegetables contributes about 0.22% (Government of Paksitan 2008-09; Qadir et al., 2015). Moreover, agriculture is a water intensive sector consuming 96% of the fresh available water (Pakistan Economic Survey 2009-2010). High demand of water in municipal and industrial sectors has declined the availability of irrigation water in many arid and semi-arid regions of the world especially Africa, South Asia and Middle East (Ali et al., 2015[a]; Qadir et al., 2015; Sharma and Nagpal, 2020). Decline in availability of freshwater has diverted the farmer communities to use wastewater for the irrigation purpose due to its availability, low cost, high concentration of organic components and some nutritional values. Even though wastewater is a good alternative of fresh water and its application has many advantages in agriculture but it is a potential source of heavy metal contamination. Toxic, persistent and nondegrabale heavy metals has tendency to accumulate in plants and enter the food chain, thus posing serious threat to the public health (Ali et al., 2015; Sabeen et al., 2020; Sharma and Nagpal, 2020).

In most of the developing and under-developed countries use of untreated wastewater is common practice (WHO, 2006). In Central Punjab Province of Pakistan, increase build-up of toxic metals such as cadmium (Cd), cobalt (Co), Nickle (Ni), chromium (Cr) in the soil samples of agricultural land due to irrigation with wastewater

(Sharma and Nagpal 2020). In Gujranwala, along with other sources such as tube well and canal water irrigation, wastewater irrigation in urban and peri-urban areas for the cultivation of vegetables is a common practice which could be a potential source of metal contamination. Lack of proper monitoring, rules and least awareness of farmers have further aggravated the problem of food contamination.

1.4 Vegetables- A Source of Nutrition or Poison

Vegetables are consumed in both cooked and raw forms as a significant part of diet worldwide. Vegetables not only add colour to the plate, also provide nutrients, trace elements such as iron (Fe), calcium (Ca), vitamin and proteins. In addition, vegetables also act as buffering agent during the process of food digestion for acidic substances (Onwukeme et al., 2014; Kacholi and Sahu, 2018; Atamaleki et al., 2019; Kumar et al., 2019; Sharma and Nagpal, 2020). According to WHO/FAO, an individual must consume 400g/ day vegetables to combat cancer, obesity and cardiac problems. As per literature, average consumption of vegetables per capita per day is merely 100g in Pakistan, India and Mali. Low consumption is attributed to high prices of food commodities due to less production or availability (Sharma and Nagpal, 2020).

Unfortunately, despite being a source of nutrients and essential minerals vegetables have tendency to uptake toxic metals from contaminated soils beyond the permissible limits. In order to meet food requirements of growing population and to ensure food security demand for food supply has been increased. Moreover, due to decrease in the per capita availability of arable land cultivation of vegetables is forced in closed vicinity of industrial estates, urban and peri-urban areas of metropolitans and contaminated lands which increase the chances of metal contamination in food crops. The situation is further worsen due to use of untreated wastewater for irrigation, extensive use of agrochemicals and improper agricultural practices. . Hazardous metals like lead, cadmium and arsenic released in the environment eventually find their ways to the food chains and biota. Furthermore, their tendencies of bioaccumulation and biomagnification within living tissues and organs pose serious threats to the well-being of humans.

A closer view of the literature shows high metal content in the soils and vegetables grown in different areas of Pakistan. Mehmood-ul-Hassan et al. (2012) reported high metal content in soil and vegetables irrigated with untreated wastewater in four cities of Pakistan (Gujranwala, Sialkot, Hyderabad, Mirpurkhas). Khan et al. (2010) reported the high concentrations of Cu, Ni, Pb and Zn were observed in the edible parts of Malva neglecta, Brassica oleracea, Minthasylvestris and Brassicacampestris, respectively in Gilgit. Mushtaq et al. (2010) investigated heavy metal contents in the Rawalpindi soils irrigated with municipal and industrial wastewaters. They reported total metal levels of Cd, Ni, and Fe which exceeded threshold concentrations in investigated arid soils. Ahmed et al. (2012) investigated metal levels in the vegetables from wastewater irrigated farms and local market from district Rawalpindi. Higher metal levels (Cd,Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were reported in bitter melon, cucumber, bellpepper, eggplant, and tomato grown in soils irrigated with wastewater.

1.5 Health Impacts of Heavy Metals

Toxic metals such as lead, chromium, cadmium, mercury and arsenic are well known for their injurious effects on human health. Human exposure to the these toxic, persistent and non-biodegradable metals may occur through three different routes i-e., ingestion of contaminated food and water; inhalation of metal contaminated dust; and dermal contact Toxic elements may be very detrimental even at low concentrations when ingested above the permissible limit over a long time. Ingestion of contaminated vegetables is one of the major route for metal toxicity in humans which may lead to various long term lingering diseases. Cadmium is classed as carcinogenic which lead to the breast and lungs cancer. Continuous exposure of Cd can cause pulmonary effects like emphysema, bronchiolitis, and alveolitis, while short-term exposure of Cd can cause renal didorder. Lead toxicity causes dysfunction of kidney, reproductive and cardiovascular systems, joints problems, lessening in haemoglobin formation, and enduring impairment to the central and peripheral nervous systems. Pb combined with Hg, Cu, and Cd can damage the kidney, while Cr which leads to health issues such as hemolysis, hemorrhage, gastrointestinal and respiratory.

1.6 Problem Statement

Pakistan is a developing country highly dependent on its agriculture. Rural population of Pakistan depends on the agriculture sector for their livelihood. Unfortunately, despite of being a major contributor in GDP this sector is highly neglected and is facing many problems. In order to meet the growing demand of food supply, measures to enhance the food quantity are more focused whereas aspect of food quality is overlooked. Extensive use of agrochemicals like metal based fertilizer, pesticides, insecticides, fungicides; ill-managed agricultural practices; combustion of fossil fuels; poor management strategies and inadequate remediation measures to treat soil problems have added metal contamination at alarming level. Furthermore, decline in availability of fresh water and poor irrigation techniques have compelled the farmers to use industrial effluent/ wastewater for irrigating agricultural fields. High metal content in agricultural fields and vegetable food crops is hampering the food security in Pakistan.

Gujranwala district situated in Punjab province, Pakistan is important from industrial as well as agricultural point of view. The area hosts several commercial and industrial centers for the manufacturing of ceramics, metal tools, leather, utensils, fans, textiles, pipe fittings, agricultural tools etc. Moreover, cultivation of vegetables such as potatoes, cauliflower, turnip, onion, peas, carrot, tomato, okra, garlic and bitter gourd in urban and peri-urban areas with the administration of untreated industrial effluent for irrigation is a common practice. Along with environmental stability public health due to consumption of metal contaminated vegetables is also a matter of serious concern.

1.7 Significance of the Study

Food security does not comprise of mere availability of food. It is important to ensure the quality of food as well which is safe for human consumption. Ingestion of contaminated vegetables having metal content beyond the permissible limits pose serious threat to the well-being of humans. Assessment of human health risk due to dietary exposure of hazardous metals due to consumption of contaminated vegetables is important to be considered. However, the metal accumulation in food crops and associated risk has thus far not been comprehensively explored in areas proximal to industrial sites in Pakistan.

The current study was therefore carried out to assess the metal accumulation in the selected vegetables cultivated in the peri-urban areas of Gujranwala district irrigated with untreated industrial effluent, tube well and canal water. The purpose of study was to investigate the selected hazardous metals in the vegetable samples, their comparison with the permissible limits set by WHO/FAO and to assess associated health risk for the exposed population.

1.8 Aim and Objectives

"Overall objective of the study is to evaluate concentration of toxic metals viz Lead, Cadmium, Chromium, Nickle, Mercury and Arsenic in vegetables irrigated with waste water, tubwell water and canal water in Gujranwala and estimate health risk in the inhabitants due to dietary exposure". Specific objectives of the current study are:

1) To assess concentration of heavy metals in selected vegetable irrigated with three different sources viz waste water, tube well and canal water in Gujranwala.
2) To evaluate of daily intake of metal (DIM) for selected metals present in vegetable samples for the exposed population.
3) To evaluate Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk for exposed population in Gujranwala District.

CHAPTER 2

METHODOLOGY

This section sketches all the methods and procedures that were employed to conduct research project on the evaluation of toxic metals in the vegetables grown in the agricultural fields of Gujranwala District irrigated with industrial effluents, canal water and tube well water, and determination of dietary exposure of inhabitants to Pb, Cr, Cd, Hg and As. All methods were used to meet aim and objectives of the study.

2.1 Study Area Description

The current study was undertaken in Gujranwala district lies between 31◦32'–32◦33'latitudes N and 73◦11'–74◦28' longitudes E in the northeastern region of Punjab, covering an area of 3,622 square kilometers, inhibited by 3 million population. The climate of the district is hot and dry during summer and moderately cold in winter with average annual rainfall of 888 millimeters. The district consists of four tehsils: Gujranwala, Kamoke, Nowshera Virkan and Wazirabad. District is situated on the Grand Trunk Road (GT Road), built in 16^{th} Century by the Emperor Sher Shah Suri. Gujranwala city is connected with Lahore and Peshawar via rail and GT Road. Gujranwala city is very important from the point of view of industrial activities, and is designated as 5th largest city of the Punjab and 7th amongst the big populous cities of Pakistan. Gujranwala contribute for 9 percent in national production and 8 percent in the revenue (Dawn, 2006). The study area hosts several commercial and industrial centers for the manufacturing of ceramics, metal tools, leather, utensils, fans, textiles, pipe fittings, agricultural tools etc.

The soil is alluvial and fertile supporting a good amount of agriculture. Rice, Wheat and Sugarcane are the main crops grown in the district. The source of irrigation is perennial and non perennial canals supplemented by tub wells. Rice and Wheat are major food crops while Rice dominates with earnings of about Rs.15 million as foreign exchange. Besides, Jawar, Bajra, Mash, Moong, Masoor, Gram, Maize, Tobacco, Oil Seed such as Rape/Mustard and sunflower are also grown in minor quantities in the district. Guavas and Citrus are main fruits grown in the district. Besides, Peaches, Jaman and Banana are also grown in minor quantities in the district. The major vegetables grown in the district are potatoes, cauliflower, turnip, onion, peas, carrot, tomato, okra and garlic. Besides, Bitter Gourd and Chilies are also grown in the district in minor quantities.

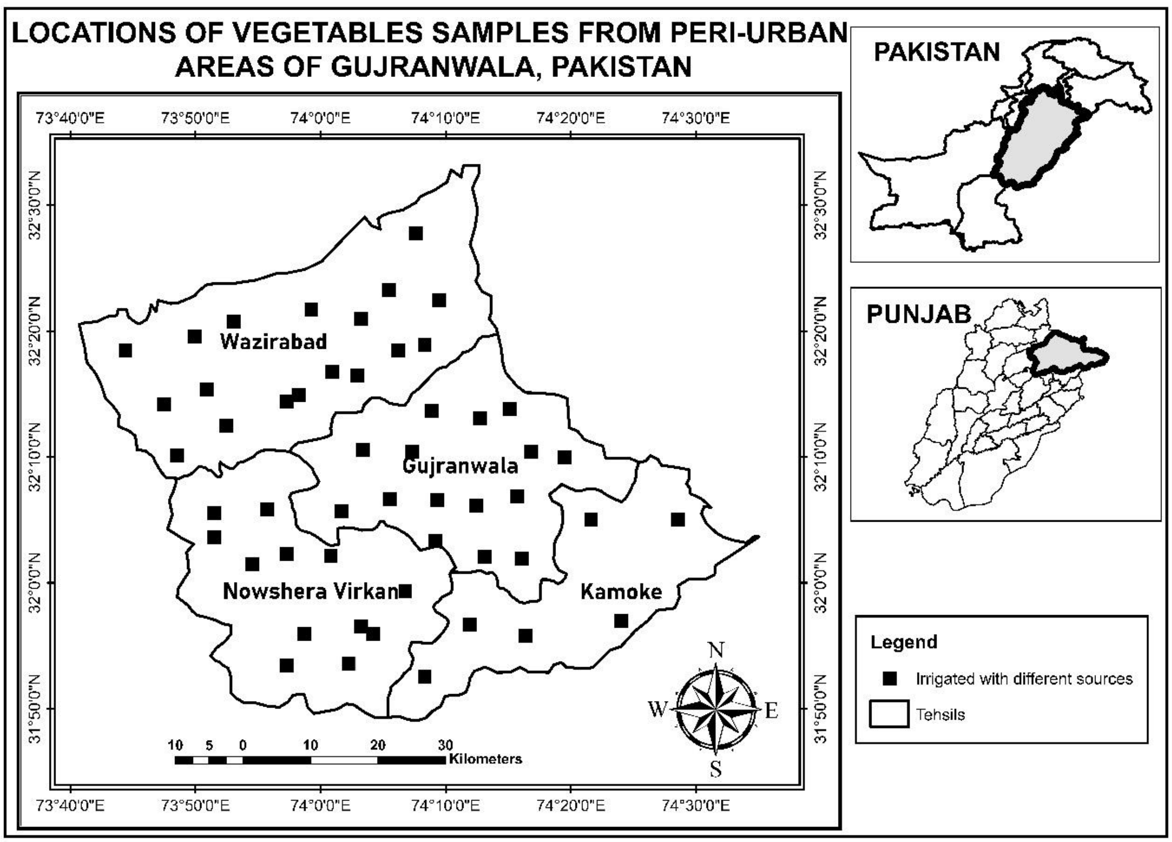

Figure 2.1 Map of study area showing points of sample collection.

2.2 Sample Collection

The study was carried out between April and November 2020, in Gujranwala District, Pakistan. Vegetable samples were collected from the peri urban areas of the Gujranwala. A total of 53 vegetable samples were collected from the selected fields from 22 different locations chosen randomly irrigated with different sources viz; waste water, canal water and tube well water in Gujranwala district. 3-5 samples for each selected vegetable was collected randomly from each field and were mixed together to make a composite sample. Rabi vegetables selected for present research work depending on their availability includes chili, tomato, onion, okra, coriander, spinach, watermelon, cauliflower, capsicum, bitter melon (Table 2.1). Specific sampling details includes 15 chili, 5 tomato, 7 onion, 4 spinach, 4 okra, 8 coriander, 3 cauliflower, 3 watermelon, 2 capsicum and 2 bitter gourd samples. Vegetables were hand plucked using vinyl gloves. In order to remove the soil vegetable samples were shaken and cleaned using a dry pre-cleaned vinyl brush and carefully packed into polyethylene bags and brought to Soil Chemistry Laboratory of Land Resource Research Institute (LRRI, NARC), Islamabad for analysis.

Table 2.1 English, local and botanical names of the selected vegetables and the parts used for analysis.

Sr. No.	English Name	Vernacular Name	Botanical Name	Part Used
1	Chilli	Mirch	*Capsicum frutescens*	Fruit
2	Tomato	Tamatar	*Solanum lycopersicm*	Fruit
3	Onion	Piyaaz	*Allium cepa*	Bulb
4	Okra	Bhindi	*Abelmoschus esculentus*	Fruit
5	Coriander	Dhania	*Coriandrum sativum*	Leafy parts
6	Spinach	Palak	*Spinecia oleracea*	Leafy parts
7	Watermelon	Tarbooz	*Citrullus lanatus*	Fruit
8	Cauliflower	Ghobi	*Brassica oleracea*	Inflorescence
9	Capsicum	Shimla mirch	*Capsicum annuum*	Fruit
10	Bitter melon	Karela	*Momordica charantia*	Fruit

2.3 Sample Preparation

Vegetable samples were first rinsed with the top water in order to remove any adhered dust particles, mud, fertilizers, pesticides and any air-born pollutants that may be present, and followed by three washings with deionized distilled water (DDW). For analysis only edible portion of the vegetable samples were used whereas nonedible parts were discarded. Vegetable samples were cut into small pieces using a knife, thereafter air and oven dried at 70˚C for 48 hours to constant the weight. Further, dried samples were ground into powdered form using a sample mill (Cyclotec 1093) and sieved with a sieve (2 mm), and stored in properly labelled clean dry air-tight polyethylene bags at room temperature.

2.4 Vegetable Digestion

Further, carefully weighed one gram of powdered vegetable sample was taken in a digestion flask, 15ml mixture of HNO_3, $HCLO_4$, H_2SO_4 (5:1:1) was added. Afterwards, it was heated on a hot plate at 100˚C until the plant sample was digested completely and solution became transparent. All this process was carried out in a fume hood to ensure maximum safety. After confirmation of digestion, the liquid digested samples were allowed to cool down and filtered using Whatman No. 42 filter paper and funnel and the volume was adjusted up to 50ml using DDW (USEPA Method: 3005A). The blank solution was also prepared as per above mentioned digestion protocol without plant material. The ready samples were carefully kept in previously cleaned and dry plastic bottles and stored at 4˚C until further analysis of heavy metals Cr, Pb, Hg, Cd and As using Atomic Absorption Spectrophotometer (AAS).

2.5 Determination of Heavy Metals

Content of heavy metals understudy in the vegetable samples were determined using Atomic Absorption Spectrophotometer (Perkin Elmer, AAnalyst 700) coupled with Graphite Furnace and Mercury Hydride System (MHS), in Soil and Environment

Laboratory of LRRI, NARC Islamabad. As per instructions provided in the Instrument operational manual, the analysis of Pb, Cr, Cd was carried out on Graphite Furnace AAS and Hg and As on atomic absorption using MHS.

2.5.1 Preparation of Standards

In order to calibrate the instrument and to check its performance standards were run for each metal prepared from their stock solutions. Standard stock solutions (1000 mgL^{-1}) of Pb, Cr and Cd were diluted with DDW to make sub stock and working solutions. Working solutions of 5, 10, 20, 40, 60, 80 and 100 μgL^{-1} were used to calibrate the curve. Standard stock solutions (1000 mg L^{-1}) of Hg and As were used to make sub stock and working solutions by diluting it with 1.5 % hydrochloric acid (HCl). In case of Hg one drop of potassium pomegranate was also added. Working solutions of 20, 40, 60, 80 and 100 µg L^{-1} was prepared.

2.5.2 Analysis Conditions

Vegetable samples were analyzed for concentration of Pb, Cr, Cd, Hg and As at standard operating conditions ($r > 0.999$) with detection limits 15, 3, 0.8, 0.1 and 0.1 µg L^{-1} respectively (Table 2.2). The freshly prepared analytical working solutions and samples were transferred to Graphite Furnace AAS in order to determine the concentration of Pb, Cr and Cd.

1.5 % hydrochloric acid as a carrier solution and 3 % sodium borohydride in 1 % sodium hydroxide as a reductant was used in MHS – AAS to quantify the content of Hg and As. For the purpose, 5 mL of freshly prepared standards were transferred to plastic tubes using a pipette and mixed with 5 mL 1.5 % HCl, to calibrate the instrument. Afterwards, 10 mL 1.5 % HCl was run as a blank. 1 mL acid digested samples were taken with the help of a micropipette and mixed with 9 mL of 1.5 % HCl in plastic tubes and were transferred to the MHS – AAS. In case of Hg one drop $KMnO_4$ was also added during sample preparation.

Table 2.2 Instrumental analysis conditions for analysis of heavy metals.

Metal	**Wavelength (nm)**	**Slit width (nm)**	**Detection limit (µg/L)**
Pb	283.3	0.7	15
Cr	357.9	0.7	3
Cd	228.8	0.7	0.8
Hg	253.7	0.7	0.1
As	193.7	0.7	0.1

2.5.3 Data Conversion

Metal concentrations in µg L^{-1} in sample solutions obtained from AAS analysis were converted in mg kg^{-1} by using Temminghoff and Houba's formula.

$$C = \frac{(a-b)\ \times v}{w\ \times 1000}$$

Where C is the metal concentration in mg kg^{-1}, a is metal concentration in µg L^{-1} in samples, b is the concentration of heavy metal in blank, v is the total volume of the digest and w is the weight of the vegetable sample taken during digestion. Concentration of metals determined in vegetable samples using AAS were compared with permissible limits set by FAO/WHO.

2.6 Reagents and Quality Assurance

All reagents and chemicals used in the current study were purchased from Merck (Germany). For the calibration of instrument, standards were prepared on daily basis prior to use and it was ensured they present a straight line curve. Samples were analyzed in duplicate to minimize the chances of error. Blank was run after every 7 samples. All glassware were soaked in 10 % HNO_3 followed by washing with DDW.

2.7 Human Exposure and Health Risk Assessment

Humans are exposed to toxic metals through different pathways, most important of them is the dietary exposure. Consumption of vegetables having high level of contamination as a part of daily human diet in many countries is the most eminent route of exposure to these contaminants. Risk assessment is the procedure of assessing the possibility of likelihood of an incident and presumptive extent of adverse effects on human health due to the vulnerability of environmental hazards (Abbas et al., 2017). Health risks were evaluated separately for adults and children using standard assumption from an integrated United States Environmental Protection Agency (US EPA) risk analysis methodology, since with each exposure media (in this case food) contact pathway changes with age. In the current study, dietary exposure due to consumption of contaminated vegetables was estimated by assessing Daily Intake of Metal (DIM), Hazard Quotient (HQ), Hazard Index (HI) and cancer risk for the exposed population using health risk assessment model provided by USEPA (2011).

2.7.1 Daily Intake of Metal (DIM)

DIM is defined as daily intake of metal, it is an approximate estimation of the intake of HM through daily diet. DIM is computed on thru basis of extent of contamination in the respective food material and the intake rate of the food in the target population. For the purpose, in the current study DIM in mg/kg bw/day was calculated using following formula (USEPA 2011; Sarwar et al., 2019):

$$DIM = \frac{C \times IR \times C_f \times EF \times ED}{BW \times AT}$$

Where C stands for metal concentration in vegetable samples in mg/kg, IR stands for intake rate of vegetable in kg/day, C_f stands for conversion factor (fresh vegetable weight into dry vegetable weight), EF stands for exposure frequency in days/year, ED stands for exposure duration in years, BW stands for body weight in kg and AT stands for average time in days. Assumed values of these parameters are described in Table 2.3.

Table 2.3 Values of exposure parameters to evaluate daily intake of metal.

Factor	Description	Unit	Value		References
			Adult	Children	
C	Concebtration of HM in vegetables	mg/kg	-	-	Present study
IR	Intake rate of vegetables	kg/day	0.345	0.232	Iqbal et al., 2016; Khan et al., 2010
C_f	Conversion factor		0.085	0.085	Mahmood and Malik, 2014
ED	Exposure duration	years	30	6	USEPA, 2011 ; 2013
EF	Exposure frequency	days/year	350	350	USEPA, 2011 ; Abbas et al., 2017
AT	Average time for non-carcinogenic risk	days	350 x ED	350 x ED	USEPA, 2011 ; Abbas et al., 2017
BW	Body weight	kg	70	32.7	USEPA, 2011 ; 2013 ; Abbas et al., 2017

2.7.2 Non-carcinogenic Risk

HI and HQ are used to express non-carcinogenic health risk pose to the exposed inhabitants. HI is defined as the combine risk of various HM and computed as a sum of all the HQ assessed individually for each metal. In the present work, both HQ and HI were calculated to non-carcinogenic risk associated with the consumption of contaminated vegetables. HI was calculated as follow:

$$HI = HQ_{Pb} + HQ_{Cr} + HQ_{Cd} + HQ_{Hg} + HQ_{As}$$

HQ is defined ratio of DIM to oral reference dose (RfD). HQ for each metal under study was evaluated on the basis of previously calculated daily intake of metal and prescribed oral RfD for each metal. Oral RfD is an estimate of a daily oral exposure for an acute duration (24 hours or less) to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (US EPA IRIS, 2011). Following relation was used to predict HQ for Pb, Cr, Cd, Hg and As.

$$HQ = \frac{DIM}{RfD}$$

According to USEPA Integrated Risk Information System recommended oral RfD (mg/kg) values for Pb, Cr, Cd, Hg and As are enlisted in the Table 2.4. When HI < 1 value, the exposed population is considered as safe and there is no possible risk, if HI ≥ 1 then there is possibility non-carcinogenic risk and if HI ≥ 10 then the non-carcinogenic risk is considerable.

Table 2.4 Values of oral reference dose for heavy metals assessed in present study.

Metal	**Oral RFD (mg/kg bw/day)**	**Reference**
Pb	0.004	USEPA IRIS, 2006; Yang et al., 2018
Cr	1.5	USEPA IRIS, 2006; Khanum et al., 2017
Cd	0.001	USEPA IRIS, 2006; Manhood and Malik, 2014
Hg	0.0003	USEPA, 2000; Ghasemidehkordi et al., 2018
As	0.0003	USEPA, 2010; Islam et al., 2018

2.7.3 Cancer Risk

The incremental lifetime cancer risk (ILTCR) is expressed as probability of development of cancer in an individual due to prolong exposure to potential carcinogen. ILTCR was determined using following formula:

$$ILTCR = DIM \times CSF$$

Where CSF stands for cancer slope factor in mg/kg. Values of CSF for Pb, Cr, Cd, Hg and As used to predict cancer risk associated with the exposure of heavy metal via dietary pathway are enlisted in Table 2.5. According to US EPA, values between 10^{-6} and 10^{-4} are consider acceptable, values smaller than 10^{-6} are safe whereas values greater than 10^{-4} indicate considerable cancer risk.

Table 2.5 Values of cancer slope factor for heavy metals assessed in present study.

Metal	**Cancer Slope Factor (mg/kg bw/day)**	**Reference**
Pb	8.50E-03	UEPA, 2010; Abbas et al., 2017
Cr	0.42	Hossain et al., 2018
Cd	0.38	Yang et al., 2018
Hg	-	-
As	1.5	USEPA, 2010; Islam et al., 2018

2.8 Statistical Analysis

The results of this study were analyzed using Microsoft excel (2013) to obtain mean, range (minimum and maximum), number of samples above permissible limit. The office and excel software 2013 was used to plot graph and tables. Arc GIS 10 software was used to make map of study area indicating sampling points.

CHAPTER 3

RESULTS AND DISCUSSION

The purpose of the study was to analyze vegetable samples collected from Gujranwala District irrigated with different sources, for the content of heavy metals and to assess the associated risk pose to consumers. This section highlights the results obtained after analyzing the samples using AAS and their comparison with permissible limits set by FAO/WHO for heavy metal content in vegetables. Furthermore, risk assessment was also done to get a picture of health risk associated with the consumption of these vegetables. Health risk was calculated separately for adults and children.

3.1 Fate of Heavy Metals in Vegetables

Heavy metals are of utmost importance in ecotoxicology and ecochemistry owing to their toxic nature and ability to accumulate in human organs (Abbas et al., 2010). Plants have intuitive tedancy to uptake a wide variety of potentially toxic HM from soil and incorporate in their body segments depending upon the bioavailability of the HM and the conditions under which plant is grown (Abbas et al., 2017).

In the current study, content of Pb, Cr, Cd Hg and As was determined with the aid of AAS. As per recorded values, concentration of Pb was highest among the rest followed by Cr, Cd, As and Hg. Significant variation was recorded in the concentration of HM among the 10 selected vegetables. Descriptive statistics for the concentration of HM in the vegetable samples are given in Table 3.1. On the basis of mean values of the selected HM in the vegetables understudy following trend was generated.

Pb > Cr > Cd > As > Hg

Table 3.1 Mean values of the heavy metals in mg/kg understudy in the vegetable samples.

Parameters	Pb	Cr	Cd	As	Hg
Mean	2.02	1.98	0.87	0.43	0.07
Range	0.09 - 6.46	0.00 - 7.69	0.01 - 4.32	0.00 - 2.31	0.00 - 0.78
Above MPL* %	83%	35.8%	58.5%	50%	13%

*Maximum Permissible Limit

3.1.1 Lead (Pb)

Concentration of Pb was recorded highest with mean value of 2.02 mg/kg as compared to the other elements understudy. Concentration of lead ranged from 0.09 mg/kg in onion collected from Froze wala to 6.46 mg/kg in chili from Naroki, whereas 83% of the samples showed value of the lead more than permissible limit prescribed by FAO/WHO (0.3 mg/kg). Highest mean value was recorded for tomato (2.94±1.49 mg/kg) followed by onion (2.32±1.90 mg/kg) > spinach (2.30±0.99 mg/kg) > cauliflower (2.30±0.07 mg/kg) > okra (2.21±1.38 mg/kg) > chilli (2.04±1.68 mg/kg) > coriander (1.87±1.38 mg/kg) > watermelon (1.32±1.59 mg/kg) > bitter gourd (1.00±0.62 mg/kg) > capsicum (0.49±0.29 mg/kg).

Average concentration of the Pb in ten studied vegetables was more than permissible limit. Among the other vegetables tomato shows maximum mean value of Pb, followed by onion, spinach, cauliflower whereas watermelon, bitter gourd and capsicum showed lower level Pb content (Figure 3.1 and Table 3.2). This variation is highly dependent on the source of irrigation in the vegetable fields. Wastewater irrigation in urban and peri urban areas is one of the major culprit for the metal contamination in food crops. Higher level of Pb comparing to rest of the metals is attributed to the anthropogenic sources because it is least mobile in earth crust. Moreover, anthropogenic emissions such as wastewater irrigation, atmospheric deposition and traffic activities are bioavailable as well as water soluble increasing the chances of uptake by vegetables (Abbasi et al., 2013; Kacholi and Sahu, 2018). Mahmood-ul-Hassan et al. (2012) reported higher level of Pb in agricultural soils as well as in vegetables irrigated with wastewater in Gujranwala as compared to present study. Results reported by Iqbal et al (2016) for Pb contamination in vegetables collected from Bhawalpur ranged from 0.04-0.08 mg/kg. Results of current study are in accordance with the research conducted by Ghasemidehkordi et al. (2018) in Markazi province of Iran. They reported high Pb content in vegetables and herbs ranging between 1733.62 ± 226.4 to 990.14 ± 85.27 µg/kg and spinach showing elevated level as compared to the rest of the plant samples due to its higher ability to absorb and accumulate toxic metals in its tissues.

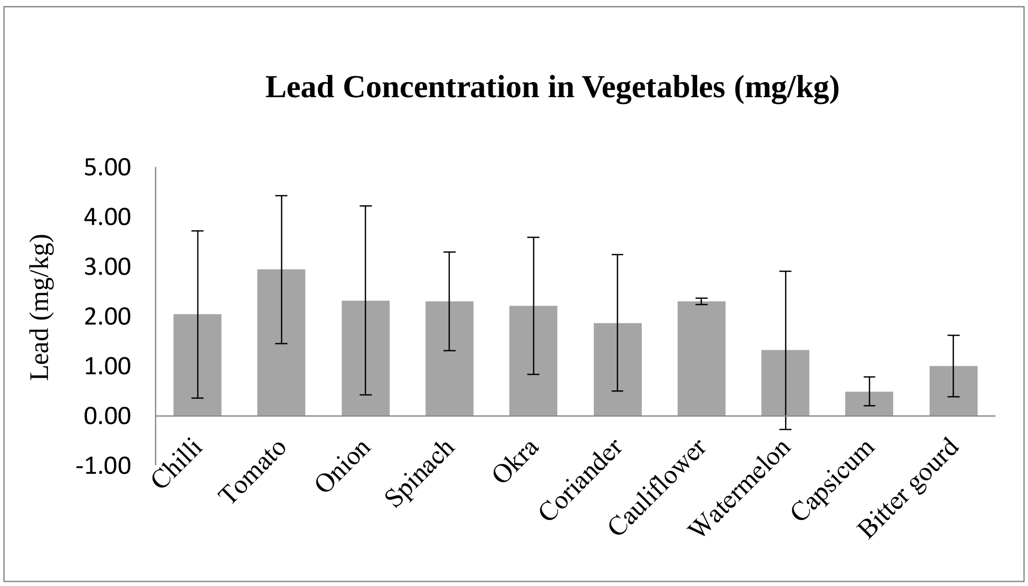

Figure 3.1 Lead concentration (mg/kg) in vegetable samples collected from peri-urban areas of Gujranwala District.

3.1.2 Chromium (Cr)

Out of 53 collected samples 35.8% of the samples showed values more than permissible limit (2.3 mg/kg) recommended by FAO/WHO. Level of chromium determined in the selected vegetable samples ranged from 0.00 mg/kg in chilli collected from Alipur Chowk to 7.69 mg /kg in onion collected from Faranscic chowk whereas average value is 1.98 mg/kg. Out of 10 vegetables average concentration of Cd in onion, spinach, coriander, watermelon was exceeding prescribed standard value. On the basis of mean concentration, overall trend generated in descending order was watermelon (3.64±0.68 mg/kg) > spinach (3.36±1.55 mg/kg) > coriander (3.35±1.32 mg/kg) > onion (2.59±2.33 mg/kg) > bitter gourd (1.8±0.88 mg/kg) > capsicum (1.49±0.81 mg/kg) > tomato (1.38±0.90 mg/kg) > cauliflower (1.38±0.14 mg/kg) > okra (1.12±0.79 mg/kg) > chilli (0.64±0.75 mg/kg).

Results revealed significant variation for Cr concentration among the vegetables randomly collected from peri-urban areas of Gujranwala District irrigated with different sources. Figure 3.2 indicates maximum level of Cr was recorded for watermelon which might be due to irrigation with industrial effluent as well as differences in absorption capacities of vegetables and their translocation in plant tissues (Kacholi and sahu, 2018). High content of Cr in spinach and coriander might be due to ability of leafy vegetables to accumulate more toxic metals in their body tissues. In leafy vegetables rate of transpiration is fast resulting in transpiration pull causing metal absorption from soil to shoots which might be responsible for metal buildup in plant parts (Abbas et al., 2017; Khanum et al., 2017). Sabeen et al. (2020) conducted a study in Hattar Industrial and reported Cr content in food crops in a range (1.28-355 mg/kg) which is higher than the results of current study. In 2012, Mahmood-ul-Hassan et al. conducted a study in Hyderabad, Gujranwala, Sialkot and Mirpur Khas on the vegetables irrigated with industrial effluents and reported high Cr level. Results of the present study are higher than Cr concentration reported by Islam et al. (2018) in vegetables collected from Patuakhali province in Bangladesh.

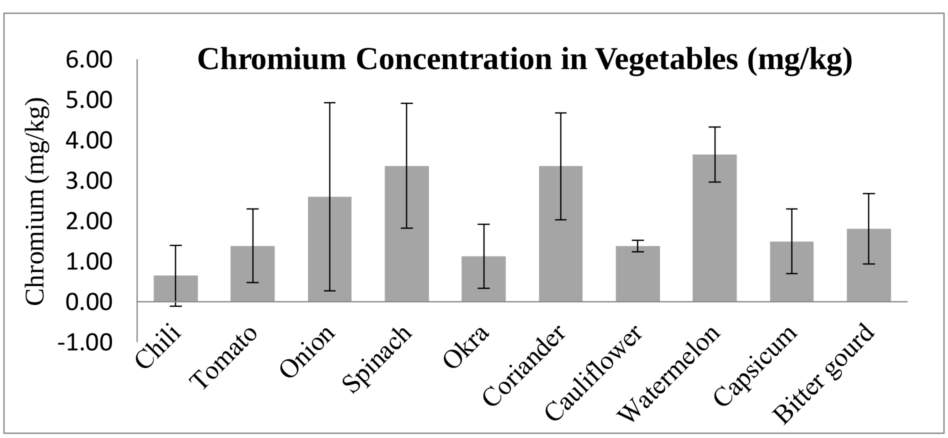

Figure 3.2 Chromium concentration (mg/kg) in vegetable samples collected from peri-urban areas of Gujranwala District.

3.1.3 Cadmium (Cd)

Concentration of Cd determined in the vegetable samples collected from peri-urban areas of Gujranwala District ranged between 0.01 to 4.32 mg/kg in onion collected from Shahkot and coriander from Hassan Para respectively. Results revealed significant variation in Cd level among different selected vegetables with the mean value of 0.87 mg/kg. Out of 53 samples analyzed 58.5% showed concentration more than standard value set by FAO/WHO (0.2 mg/kg). Average concentration of Cd was exceeding in all vegetable samples except coriander, bitter gourd and capsicum whereas trend observed in descending order is spinach (1.68±1.50 mg/kg) > cauliflower (1.19±0.56 mg/kg) > chilli (0.86±1.14 mg/kg) > onion (0.81±1.12 mg/kg) > tomato (0.48±0.48 mg/kg) > watermelon (0.42±0.44 mg/kg) > okra (0.41±0.35 mg/kg) > coriander (0.17±1.72 mg/kg) > bitter gourd (0.14±0.10 mg/kg) > capsicum (0.01±0.35 mg/kg).

As per results, highest accumulation of Cd was found in spinach (1.68±1.50 mg/kg) followed by cauliflower (1.19±0.56 mg/kg) whereas all others vegetable samples exhibit value less than 1 (Figure 3.3 and Table 3.2). Higher levels of Cd content in spinach might be due to greater tendency of leafy vegetables to accumulate metals from polluted soils. In 2012, Mahmood-ul-Hassan et al. reported Cd concentrations in soil of Gujranwala District 5.9 ± 1.8 mg/kg and 5.1 ± 2.1mg/kg at the depths of 0-15 cm and 15-30 cm respectively. On the other hand, disparities in metal accumulation by different vegetables can be attributed to the location of the field, source of irrigation water as well as differences in absorption capacities of vegetables and their translocation in plant tissues (Kacholi and sahu, 2018). Mahmood and malik, (2013) reported Cd content in vegetables collected from different irrigation sources in range of 0.08 -3.08 mg/kg, which is in agreement with the current obtain result. In Gujranwala, Mahmood-ul-Hassan et al. (2012) also reported similar results for Cd accumulation in vegetables irrigated with industrial effluents.

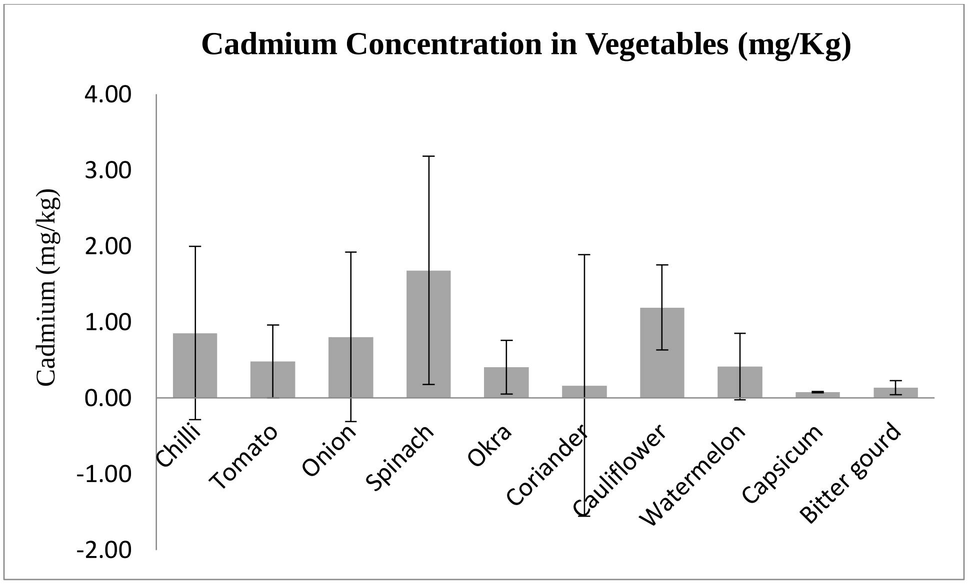

Figure 3.3 Cadmium concentration (mg/kg) in vegetable samples collected from peri-urban areas of Gujranwala District.

3.1.4 Arsenic (As)

Total of 53 samples with replicates were analyzed to determine As accumulation in vegetable samples collected from peri-urban areas of Gujranwala District. Out of 53 samples 50% were found to be exceeding permissible limit (0.1 mg/kg) recommended by FAO/WHO. Minimum As concentration recorded was 0 mg/kg in capsicum and bitter gourd whereas maximum concentration recorded was 2.31 mg/kg in coriander collected from Faranscic chowk. Capsicum Samples were collected from Naroki and Sialkot Road whereas bitter gourd samples were collected from Sialkot road and Kot Ghulam Rasul. On the basis of mean value recorded in each vegetable type, trend generated in descending order is cauliflower (1.55±0.12) > onion (0.59±0.74 mg/kg) > coriander (0.54±0.72 mg/kg) > chilli (0.39±0.53 mg/kg) > watermelon (0.37±0.32 mg/kg) > spinach (0.33±0.24 mg/kg) > tomato (0.32±0.35 mg/kg) > okra (0.16±0.16 mg/kg).

Average concentration for As in all vegetables was more than permissible limit except for capsicum and bitter gourd (Table 3.2). Figure 3.4 reveals cauliflower with maximum concentration followed by onion and coriander comparing to the rest of the vegetables which might be due to metal uptake from wastewater irrigated soil (Khanum et al., 2017). Application of industrial effluents as a source of irrigation on a longer run increases the metal load in the soils and eventually led to the metal accumulation in plant tissues grown in such soils. Abbas et al. (2010) conducted a study in Sindh province, Pakistan to evaluate metal content in vegetables grouped in four categories viz., leafy, cucurbits, roots and tuberous, fruity. They reported As content less than permissible limit. In Bangladesh, Islam et al., (2018) reported As content in vegetables more than prescribed permissible limit and declare consumption of such vegetables unsafe for public.

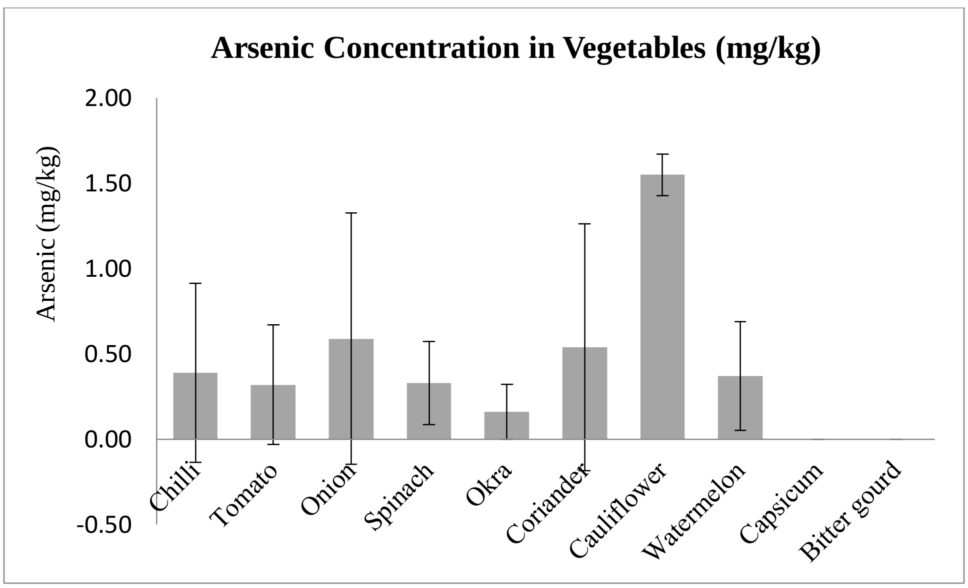

Figure 3.4 Arsenic concentration (mg/kg) in vegetable samples collected from peri-urban areas of Gujranwala District.

3.1.5 Mercury (Hg)

The level of Hg in vegetable samples collected from peri-urban areas of Gujranwala District ranged between 0 mg/kg in cauliflower collected from Sherakot and 0.78 mg/kg in spinach collected from sangowali. Only 13% of samples were found to be exceeding standard (0.1 mg/kg) recommended by FAO/WHO whereas mean concentration of Hg was found to be 0.08 mg/kg. Comparison of vegetables revealed highest mean value for spinach (0.2±0.34 mg/kg) followed by capsicum (0.16±0.16

mg/kg), bitter gourd (0.16±0.16 mg/kg) and watermelon (0.16±0.22 mg/kg) > okra (0.14±0.24 mg/kg) > chilli (0.09±0.19 mg/kg) > tomato (0.02±0.03) > onion (0.008±0.02) > coriander (0.005±0.01mg/kg) > cauliflower (0.00±0.00 mg/kg).

Of all vegetables mean concentration for Hg in spinach, okra, capsicum, watermelon and bitter gourd was high comparing to the standard value (Figure 3.5 and Table 3.2). Level of Hg was recorded highest in the samples of spinach which might be attributed to high accumulation of toxic metals in the body tissues of leafy vegetables. Abbas et al., (2010) stated maximum concentration of Hg in leafy vegetables. In Iran, results reported by Ghasemidehkordia et al. (2018) for Hg content in vegetable samples were in agreement with result of current study.

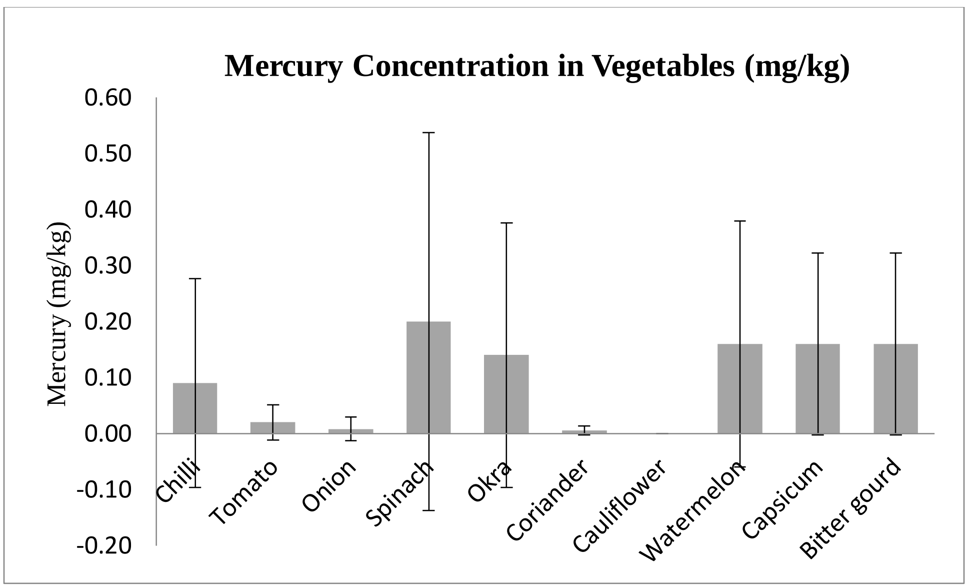

Figure 3.5 Mercury concentration (mg/kg) in vegetable samples collected from peri-urban areas of Gujranwala District.

Table 3.2 Descriptive statistics of selected heavy metals in vegetable samples collected from peri-urban areas of Gujranwala District.

Sr. No.	Vegetables		Pb	Cr	Cd	As	Hg
1	Chilli	Range	0.33 - 4.06	0.0 - 2.86	0.07 - 4.32	0.00 - 1.92	0.0 - 0.65
		Mean ± SD	2.04±1.68	0.64±0.75	0.86±1.14	0.39±0.53	0.09±0.19
2	Tomato	Range	0.58 – 5.52	0.33 - 2.66	0.11 - 1.36	0.00 - 0.96	0.0 - 0.09
		Mean ± SD	2.94±1.49	1.38±0.90	0.48±0.48	0.32±0.35	0.02±0.03
3	Onion	Range	0.07 – 4.81	0.53 - 7.81	0.01 - 3.02	0.00 - 2.27	0.05-0.07
		Mean ± SD	2.32±1.90	2.59±2.33	0.81±1.12	0.59±0.74	0.008±0.02
4	Spinach	Range	0.14 -3.38	1.09- 5.37	0.04 - 3.58	0.03 - 0.66	0.004 - 0.78
		Mean ± SD	2.30±0.99	3.36±1.55	1.68±1.50	0.33±0.24	0.2±0.34
5	Okra	Range	0.15 – 3.69	0.34 - 2.41	0.19 - 1.02	0.00 - 0.38	0.00 - 0.55
		Mean ± SD	2.21±1.38	1.12±0.79	0.41±0.35	0.16±0.16	0.14±0.24
6	Coriander	Range	0.12 – 4.67	2.0 – 6.09	0.02 - 4.23	0.00 - 2.31	0.00 - 0.008
		Mean ± SD	1.87±1.38	3.35±1.32	0.17±1.72	0.54±0.72	0.005±0.01
7	Cauliflower	Range	2.1 - 2.41	1.14 - 1.9	0.71 - 1.98	1.20 - 1.80	–
		Mean ± SD	2.30±0.07	1.38±0.14	1.19±0.56	1.55±0.12	0.00±0.00
8	Watermelon	Range	0.18 - 3.82	3.04 - 4.68	0.03 - 1.03	0.00 - 0.77	0 - 0.48
		Mean ± SD	1.32±1.59	3.64±0.68	0.42±0.44	0.37±0.32	0.16±0.22
9	Capsicum	Range	0.2 - 0.84	0.68 - 2.43	0.08 - 0.1	–	0.00 - 0.35
		Mean ± SD	0.49±0.29	1.49±0.81	0.01±0.35	0.00±0.00	0.16±0.16
10	Bitter gourd	Range	0.31 – 1.79	0.94–2.8	0.04 - 0.23	–	0.00 - 0.35
		Mean ± SD	1.00±0.62	1.8±0.88	0.14±0.10	0.00±0.00	0.16±0.16
Permissible Limit (FAO/WHO)			0.3	2.3	0.1	0.1	0.2
Above MPL %			83%	35.80%	58.50%	50%	13%

3.2 HUMAN EXPOSURE AND HEALTH RISK ASSESSMENT

Consumption of vegetables grown in contaminated soils irrigated with industrial effluents for a long duration, has enhanced the health risk for human beings. It is inevitable to assess potential level of exposure and associated health hazards by tracking pathway of these toxic metals exposure in target population. To get a picture of health risks associated with the consumption of contaminated vegetables DIM, HQ, HI and CR was estimated.

3.2.1 Daily Intake of Metal

Daily intake of each metal was determined using mean concentration level of metals in vegetables understudy to estimate dietary exposure of toxic heavy metals due to consumption of polluted vegetables. Trend for daily Pb intake was observed in order of tomato > onion > spinach and cauliflower > okra > chilli > coriander > watermelon > bitter gourd > capsicum with estimated values of 1.23E-03; 9.72E-04; 9.64E-04; 9.64E-04; 9.26E-04; 8.55E-04; 7.83E-04; 5.53E-04; 4.19E-04 and 2.05E-04 mg/kgbw/day in adults respectively whereas 2.64E-03; 2.08E-03; 2.06E-03; 2.06E-03; 1.98E-03; 1.23E-03; 1.68E-03; 1.18E-03; 8.97E-04; 4.39E-04 mg/kgbw/day in children respectively.

The DIM values of Cr in watermelon > spinach > coriander > onion > bitter gourd > capsicum > tomato and cauliflower > okra > chilli were 1.52E-03; 1.41E-03; 1.40E-03; 1.09E-03; 7.54E-04; 6.24E-04; 5.78E-04; 5.78E-04; 4.69E-04 and 2.68E-04 for adults whereas for children values were 2.20E-03; 2.03E-03; 2.02E-03; 1.56E-03; 1.09E-03; 8.99E-04; 8.32E-04; 8.32E-04; 6.75E-04; 3.86E-04 mg/kgbw/day respectively.

Daily intake of Cd was recorded highest in spinach 7.04E-04 and 1.01E-03 followed by Cauliflower 5.49E-04 and 7.90E-04 > Chilli 3.59E-04 and 5.17E-04 > Onion 3.38E-04 and 4.86E-04 > Tomato 2.02E-04 and 2.91E-04 > Watermelon 1.75E-04 and 2.51E-04 > Okra 1.71E-04 and 2.46E-04 > Coriander 6.91E-05 and 9.95E-05 > Bitter gourd 5.66E-05 and 8.14E-05 > Capsicum 3.35E-05 and 4.82E-05 for both adults and children respectively.

As per results achieved using mean concentration of As in selected vegetables, DIM values for capsicum and bittergourd was 0.00E+00 in both adults and children. While the daily consumption of As through ingesting rest of vegetables was in order of Cauliflower 6.49E-04 and 9.35E-04 > Onion 2.47E-04 and 3.56E-04 > Coriander 2.26E-04 and 3.26E-04 > Chilli 1.63E-04 and 2.35E-04 > Watermelon 1.55E-04 and 2.23E-04 > Spinach 1.38E-04 and 1.99E-04 > Tomato 1.34E-04 and 1.93E-04 > Okra 6.70E-05 and 9.65E-05 mg/kgbw/day for adults and children respectively.

Daily intake of mercury via consumption of vegetables understudy was observed in order of Spinach 8.22E-05 and 1.18E-04 > Capsicum 6.81E-05 and 9.80E-05; Bitter gourd 6.81E-05 and 9.80E-05 > Watermelon 6.49E-05 and 9.35E-05 > Okra 5.87E-05 and 8.44E-05 > Chilli 3.66E-05 and 5.27E-05 > Tomato 7.16E-06 and 1.03E-05 > Onion 3.59E-06 and 5.17E-06 > Coriander 2.17E-06 and 3.13E-06 > Cauliflower 0.00E+00 and 0.00E+00 mg/kgbw/day in adults and children respectively.

In order to assess daily human exposure to selected toxic metals, daily intake of each metal in chilli, tomato, onion, spinach, okra, coriander, cauliflower, watermelon, capsicum and bitter gourd was calculated using mean concentration of metal in respective vegetables. Intake levels of all the metals in each vegetable were higher in children comparing to adults when exposed to same level of contamination through ingestion. In adults DIM values for Cr and Pb were much higher than the rest of the metals whereas total daily intake of Cr, Pb, Cd, As, Hg were 8.69E-03, 7.87E-03, 2.66E-03, 1.78E-03 and 3.91E-04 mg/kgbw/day respectively. Figure 3.6 reveals that daily intake of Cr was highest due to consumption of watermelon, spinach and coriander whereas DIM value of Pb for tomato was maximum.

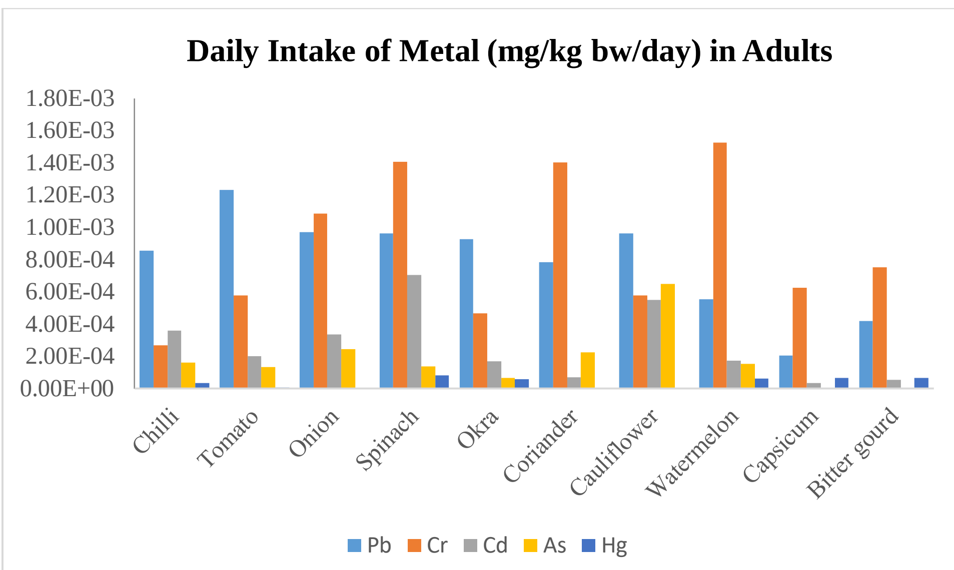

Figure 3.6 Comparison of predicted daily intake of Pb, Cr, Cd, As and Hg in adults due to consumption of vegetables collected from peri-urban areas of Gujranwala District.

On the other hand, in children total daily intake of Pb was highest 1.63E-02 followed by Cr (1.25E-02) > Cd (3.82E-03) > As (2.56E-03) > Hg (5.63E-04). Figure 3.7

depicts high daily intake of Pb for tomato, onion, spinach, cauliflower and okra and in case Cr elevated levels of daily intake was shown by watermelon, spinach and coriander in children which might pose health issues. Kacholi and Sahu (2018) observed high daily intake of Pb via consumption of vegetables in Temeke district, Tanzania. In 2018, Islam et al. conducted a study in Bangladesh and reported total daily intake in mg/kg of Cr (1.751), Ni (2.157), Cu (0.198), As (0.096), Cd (0.466) and Pb (1.751) in Brinjal, Green amaranth, Red amaranth, Bottle gourd, Tomato, Pumpkin, Chili, Carrot, Bean, Onion, Potato and Lentil. The DIM values reported for Cr, Cd, As and Pb in this srudy are much higher than the results of current srudy.

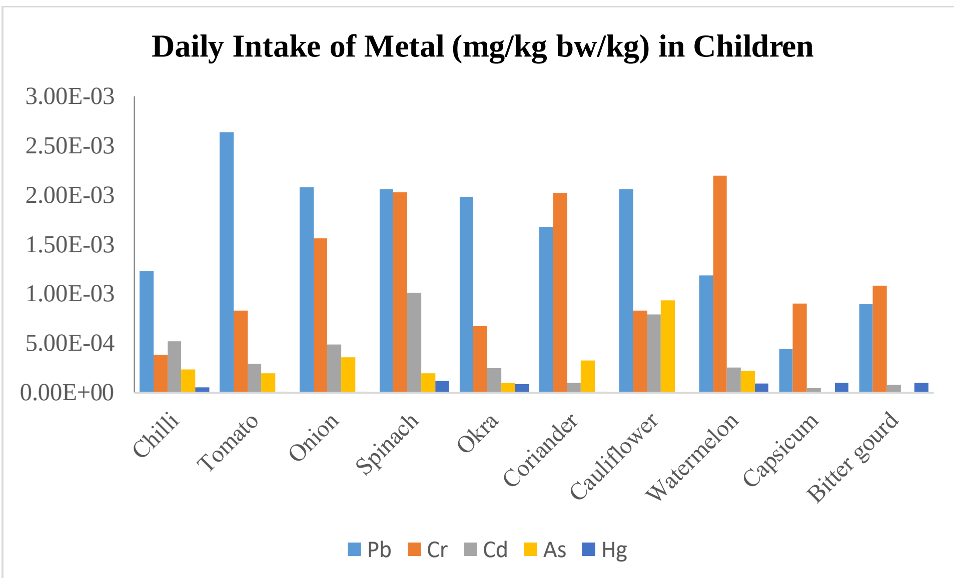

Figure 3.7 Comparison of predicted daily intake of Pb, Cr, Cd, As and Hg in children due to consumption of vegetables collected from peri-urban areas of Gujranwala District.

3.2.2 Non-carcinogenic Risk

Non-carcinogenic risks linked with consumption of vegetables grown in peri-urban areas of Gujranwala District were assessed in terms of HQ and HI. Table 3.3 clearly demonstrates HQ values predicted for all the metals in vegetables understudy for adults were less than unity declaring their consumption safe except for cauliflower. Estimated HQ for As associated with consumption of cauliflower (2.16) was exceeding 1 indicating potential non-carcinogenic risks posed to consumers. Table 3.4 enlists HQ values for all metals in each vegetable predicted for children via ingestion of vegetables grown in peri-urban areas. For all metals HQ values in each vegetable were < 1, hence considered safe for consumption except for As in cauliflower (3.12), onion (1.19) and coriander (1.09) and Cd in spinach (1.01) which might pose adverse health effects in children.

Table 3.3 Estimated values of HQ and HI for heavy metals associated with the consumption of vegetables in adults.

Sr. No.	Vegetable	Pb	Cr	Cd	As	Hg	HI
1	Chilli	2.14E-01	1.79E-04	3.59E-01	5.45E-01	1.22E-01	1.24E+00
2	Tomato	3.08E-01	3.85E-04	2.02E-01	4.47E-01	2.39E-02	9.81E-01
3	Onion	2.43E-01	7.23E-04	3.38E-01	8.24E-01	1.20E-02	1.42E+00
4	Spinach	2.41E-01	9.38E-04	7.04E-01	4.61E-01	2.74E-01	1.68E+00
5	Okra	2.31E-01	3.13E-04	1.71E-01	2.23E-01	1.96E-01	8.21E-01
6	Coriander	1.96E-01	9.36E-04	6.91E-02	7.54E-01	7.24E-03	1.03E+00
7	Cauliflower	2.41E-01	3.85E-04	5.49E-01	2.16E+00	0.00E+00	2.95E+00
8	Watermelon	1.38E-01	1.02E-03	1.75E-01	5.17E-01	2.16E-01	1.05E+00
9	Capsicum	5.13E-02	4.16E-04	3.35E-02	0.00E+00	2.27E-01	3.12E-01
10	Bitter gourd	1.05E-01	5.03E-04	5.66E-02	0.00E+00	2.27E-01	3.89E-01

Table 3.4 Estimated values of HQ and HI for heavy metals associated with the consumption of vegetables in children.

Sr. No.	Vegetable	Pb	Cr	Cd	As	Hg	HI
1	Chilli	3.08E-01	2.57E-04	5.17E-01	7.84E-01	1.76E-01	1.78E+00
2	Tomato	6.59E-01	5.55E-04	2.91E-01	6.43E-01	3.44E-02	1.63E+00
3	Onion	5.20E-01	1.04E-03	4.86E-01	1.19E+00	1.72E-02	2.21E+00
4	Spinach	5.16E-01	1.35E-03	1.01E+00	6.63E-01	3.94E-01	2.59E+00
5	Okra	4.95E-01	4.50E-04	2.46E-01	3.22E-01	2.81E-01	1.34E+00
6	Coriander	4.19E-01	1.35E-03	9.95E-02	1.09E+00	1.04E-02	1.62E+00
7	Cauliflower	5.16E-01	5.55E-04	7.90E-01	3.12E+00	0.00E+00	4.42E+00
8	Watermelon	2.96E-01	1.46E-03	2.51E-01	7.44E-01	3.12E-01	1.60E+00
9	Capsicum	1.10E-01	5.99E-04	4.82E-02	0.00E+00	3.27E-01	4.85E-01
10	Bitter gourd	2.24E-01	7.24E-04	8.14E-02	0.00E+00	3.27E-01	6.33E-01

The potential health risk can be elevated many folds when considering intake of all metals altogether (Kacholi and sahu, 2018). For the purpose, HI as the sum of HQ for all metals in each vegetable was assessed for both adults and children. For adult population, HI values ranged from 3.12E-01 to 2.95E+00 with the mean value of 1.19E+00 and for children values ranged from 4.85E-01 to 4.42E+00 with the mean value of 1.83E+00.

Figure 3.8 portrays HI values for adult consumers in order of cauliflower (2.95E+00) > spinach (1.68E+00) > onion (1.42E+00) > chilli (1.24E+00) > watermelon (1.05E+00) > coriander (1.03E+00) > tomato (9.81E-01) > okra (8.21E-01) > bitter gourd (3.89E-01) > capsicum (3.12E-01). Results reveal that consumption of cauliflower, spinach, onion, chilli, watermelon and coriander might pose adverse health effects in adults as their HI values are exceeding the standard (1). On the contrary, consumption of tomato, okra, bitter gourd and capsicum is nearly free of risks for adult population. In China, HI values for adults associated with the consumption of vegetables grown in mine-affected areas for As, Cd and Pb were higher compared to the current study (Yang et al., 2018). Khan et al., (2015) reported Hazard Risk Index (HRI) values for Pb and Cd exceeding 1 in market food crops in Gujranwala and Sialkot Districts.

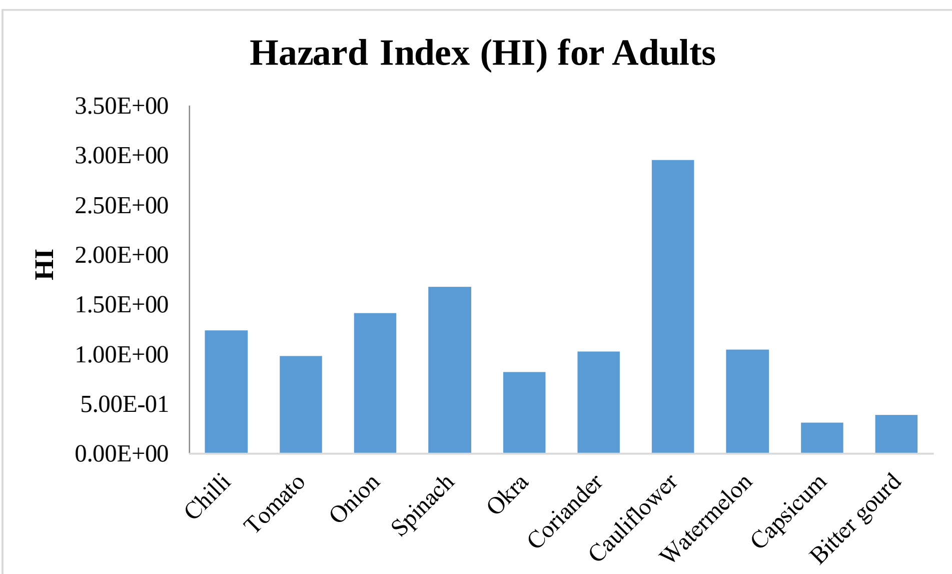

Figure 3.8 Estimated HI associated with the vegetables in adults.

In children, HI values for capsicum and bitter gourd were below safe level whereas rest of the vegetables showed values > 1 making their consumption full of health risk (Figure 3.9). In the present study, HI value exhibited by cauliflower (4.42E+00) was maximum followed by spinach (2.59E+00) > onion (2.21E+00) > chilli (1.78E+00) > tomato (1.63E+00) > coriander (1.62E+00) > watermelon (1.60E+00) > okra (1.34E+00) > bitter gourd (6.33E-01) > capsicum (4.85E-01). In a longer run, ingestion of all vegetables except bitter gourd and capsicum can have significant deleterious health effects in children. Non-carcinogenic risks assessed in the current study due to dietary exposure of heavy metals were higher in children than adults. Higher HI values for children depict elevated health risks than adults which might be due to lower body weight (Atamaleki et al., 2019). Iqbal et al., (2016), reported high health risk to children than adults due to consumption of vegetables irrigated with sewage water in Bahawalpur.

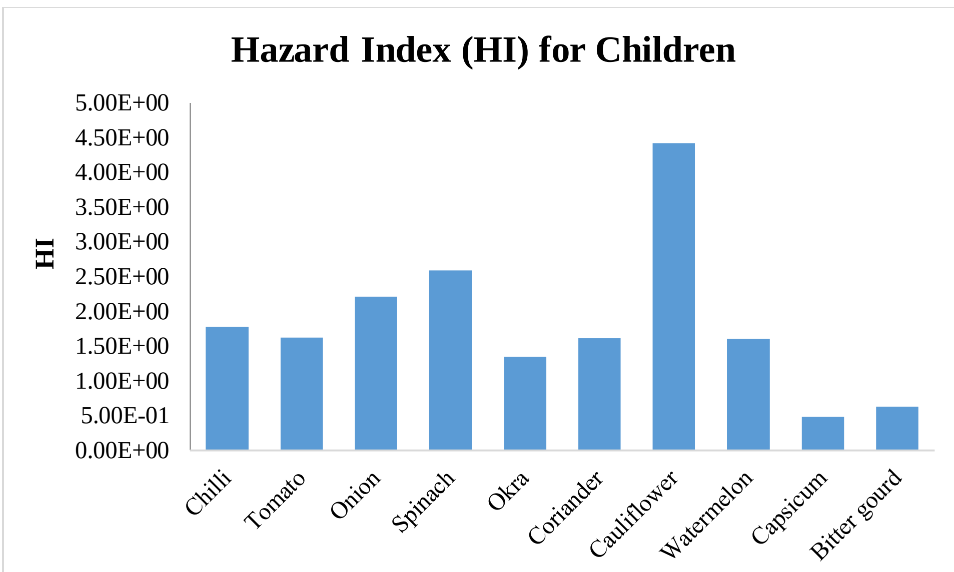

Figure 3.9 Estimated HI associated with the vegetables in children.

3.2.3 Cancer Risk

The incremental lifetime cancer risk (ILTCR) was assessed for Pb, Cr, Cd and As via consumption of vegetables understudy for both adults and children. Due to lack of oral slope factor for Hg prediction of associated cancer risk was limited to afore mentioned metals. Cancer risks associated with Pb, Cr, Cd and As ranged 1.74E-06 - 1.05E-05, 1.13E-04 - 6.40E-04, 1.27E-05 - 2.67E-04 and 0.00E+00 - 9.74E-04 respectively for adult consumers. In children risk of cancer was higher for Pb, Cr, Cd and As, ranging from 3.74E-06 - 2.24E-05, 1.62E-04 - 9.22E-04, 1.83E-05 - 3.85E-04 and 0.00E+00 - 1.40E-03 respectively.

Table 3.5 reveals that ILTCR values for Cr, Cd and As for consumption of each vegetable lies in the acceptable cancer risk range (10^{-4} to 10^{-6}) except for As in cauliflower (1.40E-03) which is greater than 10^{-4}, indicating considerable cancer risk. In case of Pb, lower level of cancer risk was observed comparing to others. In adults values for Pb were considered safe (< 10^{-6}) indicating no significant cancer risk in all vegetables except for tomato which follows in the acceptable cancer risk range (Table 3.5). In contrast for children, values for Pb lie in acceptable range for all vegetables except for capsicum and bitter gourd. Yang et al. (2018) predicted higher cancer risk for children than adults for China which is in consistent with present results. In 2016, Rehman et al. reported minimal potential cancer risk associated with inorganic As through ingestion of vegetables in southern districts of Pakistan.

Table 3.5 Cancer risk value for heavy metals through ingestion of vegetables.

Sr. No.	Vegetable	Pb		Cr		Cd		As	
		Adult	Child	Adult	Child	Adult	Child	Adult	Child
1	Chilli	7.26E-06	1.05E-05	1.13E-04	1.62E-04	1.36E-04	1.96E-04	2.45E-04	3.53E-04
2	Tomato	1.05E-05	2.24E-05	2.43E-04	3.50E-04	7.67E-05	1.10E-04	2.01E-04	2.89E-04
3	Onion	8.26E-06	1.77E-05	4.56E-04	6.56E-04	1.28E-04	1.85E-04	3.71E-04	5.34E-04
4	Spinach	8.19E-06	1.75E-05	5.91E-04	8.51E-04	2.67E-04	3.85E-04	2.07E-04	2.99E-04
5	Okra	7.87E-06	1.68E-05	1.97E-04	2.84E-04	6.49E-05	9.34E-05	1.01E-04	1.45E-04
6	Coriander	6.66E-06	1.43E-05	5.89E-04	8.49E-04	2.63E-05	3.78E-05	3.39E-04	4.88E-04
7	Cauliflower	8.19E-06	1.75E-05	2.43E-04	3.50E-04	2.09E-04	3.00E-04	9.74E-04	1.40E-03
8	Watermelon	4.70E-06	1.01E-05	6.40E-04	9.22E-04	6.63E-05	9.55E-05	2.33E-04	3.35E-04
9	Capsicum	1.74E-06	3.74E-06	2.62E-04	3.77E-04	1.27E-05	1.83E-05	0.00E+00	0.00E+00
10	Bitter gourd	3.56E-06	7.62E-06	3.17E-04	4.56E-04	2.15E-05	3.09E-05	0.00E+00	0.00E+00

CONCLUSIONS

This study clearly indicates that metal contamination in food crop is a matter of serious concern as it may lead to deleterious health impacts in consumer population. In addition to use of agrochemicals, application of untreated industrial effluent in metropolitans has worsen the situation by increasing the metal load in agricultural soils and water. These metals eventually find their ways in vegetable food crops putting human health at stake.

The current study firstly evaluated content of heavy metals in chilli, tomato, onion, spinach, okra, coriander, cauliflower, watermelon, capsicum and bitter gourd and found them in order of Pb > Cr > Cd > As > Hg. The heavy metal concentrations in vegetables are largely dependent on the source of irrigation and the ability to accumulate heavy metals. Vegetables irrigated with untreated industrial effluents showed remarkably high metal content than those irrigated with canal water and tube wells. Metal content even at low level is not desirable as it is associated with disastrous health impacts in exposed population.

For the purpose, non-carcinogenic and cancer risk was assessed for the intake of heavy metals through ingestion of vegetables for adults and children. . For adult population, HI values ranged from 3.12E-01 to 2.95E+00 with the mean value of 1.19E+00 and for children values ranged from 4.85E-01 to 4.42E+00 with the mean value of 1.83E+00. Hazard Index (HI) values for cauliflower (2.95), spinach (1.68), onion (1.42), chilli (1.24), watermelon (1.05) and coriander (1.03) were exceeding 1 for adults, whereas for children HI values for cauliflower (4.42), spinach (2.59), onion (2.21), chilli (1.78), tomato (1.63), coriander (1.62), watermelon (1.60) and okra (1.34) were higher the standard, consequently increasing the chance of non-carcinogenic risks in the inhabitants of Gujranwala District. Moreover, children are at higher risk than adults.

Cancer risks associated with Pb, Cr, Cd and As ranged 1.74E-06 - 1.05E-05, 1.13E-04 - 6.40E-04, 1.27E-05 - 2.67E-04 and 0.00E+00 - 9.74E-04 respectively for adult consumers. In children risk of cancer was higher for Pb, Cr, Cd and As, ranging from 3.74E-06 - 2.24E-05, 1.62E-04 - 9.22E-04, 1.83E-05 - 3.85E-04 and 0.00E+00 - 1.40E-03 respectively. As per estimated values, population is at low cancer risk due to consumption of vegetables understudy. However, this fact cannot be forsaken and continuous monitoring on regular basis is a dire need for safe and health consumption of vegetables as well as to avoid ecological hazards.

RECOMMENDATIONS

Based on the findings and conclusion of the study, the following recommendations are proposed:

1. Preventive approaches to limit the application of untreated wastewater for irrigation purpose should be considered.
2. Application of wastewater after treatment in green belts and lawns in urban areas instead of food crops should be encouraged.
3. Prior to disposal in canals and drains industrial effluents should be treated as it might increase metal load in water sources used for irrigation purpose.
4. Regular monitoring of the heavy metals present in soil, irrigating water, and foodstuff is suggested to avoid extreme accumulation in the food chain and thus elude human health risks.
5. Sustainable agricultural practices should be encouraged to ensure soil security and provision of safe and contamination free food.
6. It is also advisable that farmlands be located away from traffic emissions.
7. Public awareness should be created to avoid consumption of vegetables cultivated on contaminated land and irrigated with untreated industrial effluent.

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