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Accessing Potential Bioaccumulation of Heavy Metals in Selective Vegetables from Gujranwala District, Pakistan

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Abstract
Heavy metals, such as cadmium, copper, lead, chromium and mercury, are important environmental pollutants, particularly in areas with high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in traces can cause serious problems to all organisms, and heavy metal bioaccumulation in the food chain especially can be highly dangerous to human health. Heavy metals enter the human body mainly through two routes namely: inhalation and ingestion, ingestion being the main route of exposure to these elements in human population. Heavy metals intake by human populations through food chain has been reported in many countries. Soil threshold for heavy metal toxicity is an important factor affecting soil environmental capacity of heavy metal and determines heavy metal cumulative loading limits. For soil-plant system, heavy metal toxicity threshold is the highest permissible content in the soil (total or bioavailable concentration) that does not pose any phytotoxic effects or heavy metals in the edible parts of the crops does not exceed food hygiene standards. Factors affecting the thresholds of dietary toxicity of heavy metal in soil-crop system include: soil type which includes soil pH, organic matter content, clay mineral and other soil chemical and biochemical properties; and crop species or cultivars regulated by genetic basis for heavy metal transport and accumulation in plants. In addition, the interactions of soil-plant root-microbes play important roles in regulating heavy metal movement from soil to the edible parts of crops. Agronomic practices such as fertilizer and water managements as well as crop rotation system can affect bioavailability and crop accumulation of heavy metals, thus influencing the thresholds for assessing dietary toxicity of heavy metals in the food chain. This paper reviews the phytotoxic effects and bioaccumulation of heavy metals in vegetables and food crops and assesses soil heavy metal thresholds for potential dietary toxicity.

1. INTRODUCTION

Pakistan is an agriculture country and plays vital role in economic growth. In Pakistan agriculture got second priority after defense and contributes 24% in GDP. Agriculture can improve living standard of almost 70% of rural population by giving 51% of employment hence contribute to 35% of export share. Agriculture can cause both favorable and unfavorable impacts on environment (Ghandi, 2000; Abbas *et al*., 2010). The export of vegetables contributes about 0.22 % (Government of Pakistan 2008-09; Abbas *et al*., 2010). Freshwater is a unique natural resource which is scarce and declining as demand for water has increase thrice since 1950s (Gleick, 2003; Rehman *et al*., 2013) particularly in arid and semi arid regions of world such as Africa, South Asia and Middle East. Worldwide, agriculture is one of the leading sectors by consuming 85% global fresh water (Jury & Vaux, 2007; Rehman *et al*., 2013). According to Intergovernmental Panel on Climate Change, millions of people will face serious water shortage due to global warming in the near future (Singh *et al*., 2001; Hanif *et al*., 2006; Rehman *et al*., 2013).

Heavy metals pollution considered to be a worldwide threat now-a-days and responsible for environmental contamination (Jozic *et al*., 2009; Khan *et al*., 2011) due to their high toxicity and persistency in the environment (Khan *et al*., 2011). Most of the heavy metals have no biological function and toxic even at low concentration. But some heavy metals are essential for the human body however they may be toxic if present in a higher concentration. They have the ability to bioaccumulate and disrupt functions of vital organs and glands in the human body such as brain, kidney and liver (Dzomba *et al*., 2012). Heavy metal consumption at lower levels caused neurotoxin and carcinogenic impacts (Sathawara *et al*., 2004; Abbas *et al*., 2010).

There are also many factors which contribute to heavy metal contamination such as contaminated irrigation water, fertilizers and pesticides applications, emissions of different waste materials from industries, lack of good transportation facilities, harvesting process and storage. The natural contribution of heavy metals (parent material weathering) is very small but major contributing factor is anthropogenic activities which are potentially increasing its concentration in soil, plant and water. These include zinc mining, iron foundries, use of sewage sludge, vehicle exhaust and agronomic practices such as use of city effluent as irrigation in agriculture (Lombi *et al*., 2002), fossil fuel combustion, pesticides (Yang *et al.,* 2002), application of phosphate fertilizers and several other industrial processes (Bernard, 2008).

Rapid urbanization lead to higher demand of food crops hence in peri-urban areas of mega cities vegetables are grown in shorter periods with greater profit. Leafy vegetables are teeming for accumulation of heavy metals in food chain. The heavy metals accumulation causes two impacts. First they enter in our diet and Second crop production decline due to inhibition of metabolic processes (Sanders *et al*., 1987; Singh and Aggarwal, 2006; Singh *et al*., 2012). Pakistan is producing thousand tons of vegetables like potato, okra, bitter melon, eggplant, tomato, cucumber, bell pepper, spinach, cauliflower, pumpkin, carrots etc. But these vegetables are contaminated with heavy metal due to use of untreated waste water for irrigation. Vegetables are the most important components of human diet and are rich in vitamins, minerals and fibers. But due to contamination of heavy metal, the intake of these vegetables has shown risk to the human health (Ahmad *et al*., 2012).

Vegetables cultivated in wastewater-irrigated soils accumulate heavy metals in their edible and non-edible parts (Perveen *et al*., 2012) in large enough quantities to cause potential health risks to the consumers (Khan et al., 2011). Plants have a natural propensity to take up metals. Some of them like Cu^{2+}, Co^{2+}, Fe^{2+}, Mo^{2+}, Mn^{2+}, and Zn^{2+} are essential plant micronutrients (Baker *et al*., 1991; Achakzai *et al*., 2011) while few others like Hg^{2+}, Cd^{2+}, Ni^{2+} and Pb^{2+} are toxic to plants. However, such toxic effects are even varying from genotype to genotype of the same crop (Liu *et al*., 2001; Achakzai *et al*., 2011). Toxic heavy metals are associated with cardiovascular, kidney, nervous and bone diseases. Vomiting, diarrhea, stomach irritation, decreases in reaction time, kidney problems, anemia and blood disorders in humans are some of the diseases associated with heavy metals. They may also cause respiratory tract cancer and mucodermal ulceration (Ahmed *et al*., 2012).

Owing to canal water shortage for irrigation, waste water use seems to continue to grow in the days to come which have to contaminate soils and plants with toxic metals. Current scenario demands to assess heavy metal contamination in soil, their bioaccumulation in vegetables and finally entering into the food chain that affects human health. Therefore it is very important to clean up soil and groundwater to prevent the toxic effects of heavy metals (Ullah *et al*., 2012).

Keeping in view this investigation was design

To assess the bioaccumulation of heavy metals in vegetable in metals contaminated soil

To quantify the heavy metals in different vegetable irrigated in Gujranwala area.

2. Materials and method

2.1 Study area

Gujranwala is the 6th largest city (World Gazetteer, Retrieved 22 August 2012) of Pakistan. It is an industrial city with a population of approximately 2,661,360 as of 24 June 2011. Extensive road and rail links help the city to flourish in agriculture and manufacturing markets. It is in between Lahore, Gujrat and Wazirabad. It is situated on GT road so an easily connection to Islamabad, Lahore and Peshawar.

In vicinity of Gujranwala small towns like Alipur Chatha, Kamonke and some small villages exist. These villages produce agricultural products like wheat, barley, rice and millet. Gujranwala is the fastest growing cities of Pakistan. The major export products of Gujranwala include sugarcane, melons, grains and world's finest quality of rice. Major manufacturing products include fans, ceramics, engineering tools, electrical switch gears, cutlery, crockery, iron safes, woolen sweaters, sanitary fittings and tannery production. These products exhibits in hand made exhibition of Gujranwala. This city contributes to 9% in national production and 8% in revenue generation.

Local language is Punjabi but Urdu and English are used in schools and offices. And the traditional foods of Gujranwala include Chanp, Chirray, kabab and tikka. The favorite food is rice and lentils commonly known as Dal Chawal. It is also known as City of wrestlers or Phelwana da shehar in Punjabi.

(Retrieval date: June 1, 2013)

2.1.1 Site Description

Gujranwala is located at 32.16° north, 74.18° east and is 226 metres (744 ft) above sea level. It shares borders with Ghakhar Mandi, Alipur Chatha, kamonke and some small towns and villages. It is an industrial city in the north-east of the Punjab province of Pakistan.

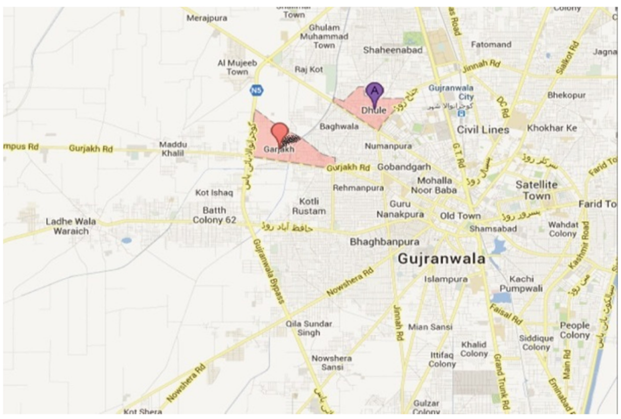


Figure 2.1: Map of study area showing sampling sites.

The climate of Gujranwala changes quite drastically through the year. The summer periods last from June through to September where the temperature reaches 36-42 degrees Celsius. The coldest months are usually November to February. The temperature can drop to seven degrees Celsius on average. The highest precipitation months are usually July and

August when the monsoon season hits the Punjab province. During the other months the average rainfall is roughly 25 mm. The driest months are usually November through to April, when little rainfall is seen.
(Wiki/ Gujranwala; retrieved June 1, 2013)

2.1.2 Selection of sampling sites:

Two sampling sites were selected from industrial estate of Gujranwala because effluent water is used in these areas for irrigation. Two sites which we selected for our research are Garjakh and Dhule.

1. Garjakh: It is located near Gujranwala bypass. We referred this site as a more polluted site.
2. Dhulley: It is located near G.T. road of Gujranwala. We referred this site as a less polluted site.

2.2 Field sampling

Fresh samples of seven vegetables and soil were taken from two agricultural areas exposed to different degrees of environmental pollution (Naser *et al*. 2009). Area 1: More polluted. Area 2: Less polluted. The collected samples included cabbage *(Brassica oleracea),* spinach (*Spinacia oleracea),* potato (*Solanum tuberosum*), turnip (*Brassica rapa rapa*), radish (*Raphanus sativus*), carrot (*Daucus carota*) and round gourd (*Praecitrullus fistulosus*). Vegetable samples were handpicked using vinyl gloves and carefully packed into polyethylene bags (Alam *et al*. 2003; Osma *et al*. 2012). Soil samples from rizosphere of respective vegetables (0-15cm) were collected with a stainless steel auger. Three subsamples of each sample were randomly collected and combined into a composite sample (Naser *et al*. 2009). Total 1.5 kg composite sample were taken for each sample back to laboratory for sample preparation and analysis (Sainger *et al*. 2011). Only the edible parts of each vegetable were used for analysis (Osma *et al*. 2012).

a. Preparation and preservation of samples

2.3.1 Vegetable samples

All samples were taken to Environmental Biology Laboratory in College of Earth and Environmental Sciences, University of the Punjab, Lahore. All vegetable samples were washed in fresh running water to eliminate dust, dirt, possible parasites or their eggs and then were again washed with deionized water. The samples were then cut to separate the edible parts of vegetables using a knife. Edible parts were then cut into small pieces then were air dried and then placed in an electric oven at 65°C for 48-72 h depending on the sample size. The dry vegetable samples were homogenized by grinding using a kitchen grinder (Naser *et al*. 2009) and stored in polyethylene bags, until used for acid digestion (Farooq *et al.* 2009).

2.3.2 Soil samples

All soil samples were spread on plastic trays and allowed to dry at ambient temperature for 8 days. The soil samples after drying were ground with a grinder and sieved through a 2mm sieve. The final samples were kept in labeled polyethylene bags at ambient temperature before analysis (Naser *et al*. 2009).

2.3.3 Reagents and Glassware

All reagents used were of analytical grade. All the plastic and glassware were cleaned by soaking them in a 10 % nitric acid solution and rinsing them with distilled water prior to use (Bagdatlioglu *et al.* 2010).

2.4 Plant analysis (Digestion of vegetables)

One gram of dry matter was weighted into 50-ml beakers, followed by the addition of 10-ml mixture of analytical grade acids HNO_3:$HClO_4$ in the ratio 5:1.The digestion was performed at a temperature of about 190^{o}C for 1.5 h. After cooling, the solution was made up to a final volume of 30 ml distilled water. The metal concentrations were determined by atomic absorption spectrometry using a Thermo S-Series AA Spectrometer. Analysis of each sample was carried out three times to obtain representative results and the data reported in mg/Kg on dry weight basis.

2.5 Soil analysis

Brief description of procedures followed for the determination of physical and chemical characteristics of soil is given in this section. Analyses for soluble ions were, in general, done following methods described by the U.S. Salinity Laboratory Staff (1954) or Page *et al*. (1982) except otherwise mentioned (Motsara and Roy, 2008).

2.5.1.AB-DTPA extractable metals

The AB-DTPA extracting solution was prepared by dissolving 79.06 g NH4HCO3 and 1.97 g DTPA in a liter volume of solution. Soil (10 g) was placed in a 250 mL Erlenmeyer flask, added 20 mL of freshly prepared extracting solution, shook on reciprocating shaker at the rate of 180 cycles per minute for 15 minutes by keeping flasks open (Soltanpour, 1985), filtered and analyzed the extract for metals with the help of Atomic Absorption Spectrophotometer (Model Thermo S-Series).

2.5.2.Total metals

One gram of dry matter was weighted into 50-ml beakers, followed by the addition of 10-ml mixture of analytical grade acids HNO_3:$HClO_4$ in the ratio 5:1.The digestion was performed at a temperature of about 190^{o}c for 1.5 h. After cooling, the solution was made up to a final volume (30 ml) distilled water. The metal concentrations were determined by atomic absorption spectrometry using a Thermo S-Series Atomic absorption spectrophotometer (AAS). Analysis of each sample was carried out three times to obtain representative results and the data reported in mg/Kg.

2.5.3. Bioaccumulation factor (BAF)

Bioaccumulation factor (BAF) is defined as the ratio of total metal concentration in plant species to that in soil, which is a measure of the ability of a plant uptake and transport metals to the shoots (Caille *et al.*, 2005; Sainger *et al.*, 2011). The Bioaccumulation factor calculated in this study was based on the total metal content of the plant without taking into consideration the various parts of the plant.

$$BAF = \frac{\text{concentration of metal in edible part}}{\text{Concentration of metal in soil}}$$

2.6 Statistical analysis

The basic statistics of metals in soil and vegetables such as mean, standard deviation, graphs and correlation were calculated using Microsoft excel, SPSS, R and Statistics 8.1 software.

3. RESULTS

Soil samples from two sites were analyzed for physicochemical parameters are given in table 3.1

3.1 Physiochemical parameters of Soil

Physiochemical parameters of soil samples viz; Texture, Saturation percentage, CEC, OM ,pH ,SAR, EC, TSS, CO_3^{2-},HCO_3^-, Cl^-, SO_4^{2-} , Ca^{++} plus Mg^{++}, Na^+ and K^+ were analyzed and collected from two different areas of Gujranwala. These parameters are shown in table 3.1.

Table 3.1 Physiochemical parameters of more polluted and less polluted soils.

Characteristic	Unit	More Polluted	Less Polluted
Texture	%	Clay Loam	Clay Loam
Sand	"	41.12 ± 0.72	41.25 ± 0.37
Silt	"	28.2 ± 0.39	29.625 ± 0.27
Clay	"	30.675 ± 0.44	29.125 ± 0.36
Saturation %	"	38±1.49	37±0.81
CEC	$cmol_c\ kg^{-1}$	6.33±0.04	6.64±0.08
OM	%	0.98±0.06	1.14±0.08
pH	-	7.625±0.03	7.65±0.03
SAR	$(mmol_c\ L^{-1})^{1/2}$	3.96±0.08	3.83±0.02
EC_e	$dS\ m^{-1}$	2.025±0.02	1.4425±0.06
TSS	$mg\ L^{-1}$	20.25±0.21	14.425±0.6
Soluble Ions			
CO_3^{2-}	$mmol_c\ L^{-1}$	2.275±0.20	0
HCO_{3-}	"	5.175±0.13	2.675±0.128
Cl^-	"	8.5±0.19	9.225±0.16
SO_4^{2-}	"	4.3±0.36	2.525±0.44
$Ca^{2+} + Mg^{2+}$	"	17.975±0.25	19.45±0.335
Na^+	"	11.875±0.19	11.95±0.05
K^+	"	1.82±0.05	1.80±0.05

3.2 Heavy metals in soil

Total metals and AB-DTPA extractable metals (Cd, Cr, Cu, Mn, Ni and Pb) were analyzed in soil. Total metals were determined by the digestion of the soil while AB-DTPA extractable metals are only available metals which extract through AB-DTPA solution. In total metals analysis of soil, the maximum concentration of Mn was recorded in more polluted soil followed by Cr, Ni, Pb and Cu but in case of less polluted soil, maximum concentration of Mn was found, after this Ni, Cr , Pb and Cu. The concentration of Cd was found minimum in both type soil (less or more polluted).total metals are given in table 3.2.

Table 3.2 concentration (mean ± SD) of total metals in soil

Total Metals	Unit (mgKg-1)	MP	LP
Cd	"	0.62±0.05	0.13±0.02
Cr	"	124.5±3.45	24.78±1.99
Cu	"	21.02±0.97	5.15±0.30
Mn	"	353.29±6.69	47.33±2.82
Ni	"	62.37±3.08	33.63±2.40
Pb	"	54.45±3.42	7.145±0.49

3.2.2 AB-DTPA extractable metals in soil

Concentration of metals was recorded by AB-DTPA method and maximum concentration Mn was found in more and less polluted soil while Cd had less concentration in both type of soil. One of them treated with more polluted water and other treated with less polluted soil. The more concentration of Cr, Ni, Pb and Cu was found in less and more polluted soil after the Mn. AB-DTPA metals are given in table 3.3.

Table 3.3 AB-DTPA extractable metals (mean±SD) in soil

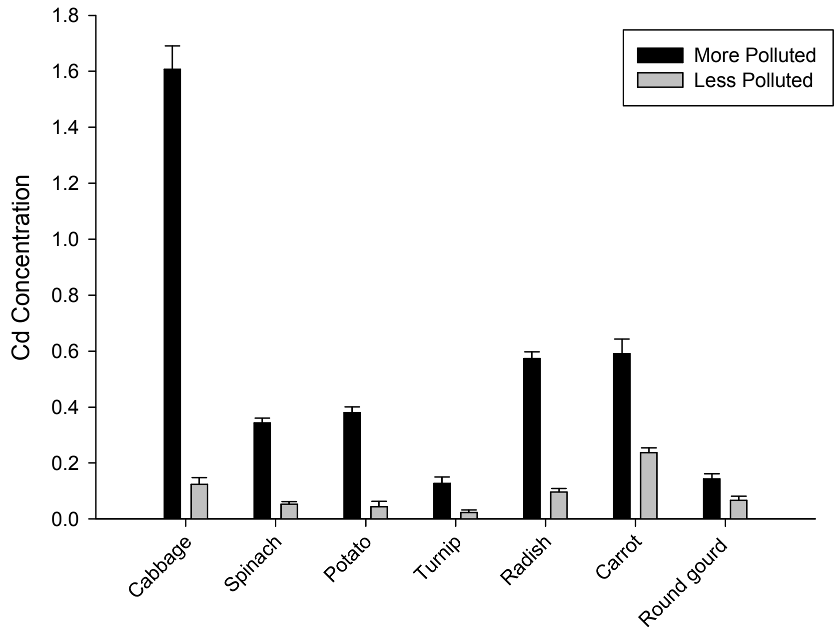
AB-DTPA	Unit (mgKg-1)	MP	LP
Cd	"	0.098±0.012	0.013±0.0025
Cr	"	19.9±0.408	1.9±1.36
Cu	"	2.575±0.268	0.865±0.069
Mn	"	35.825±2.12	11.223±0.67
Ni	"	4.25±0.173	1.32±0.2
Pb	"	3.8±0.48	1.8±0.16

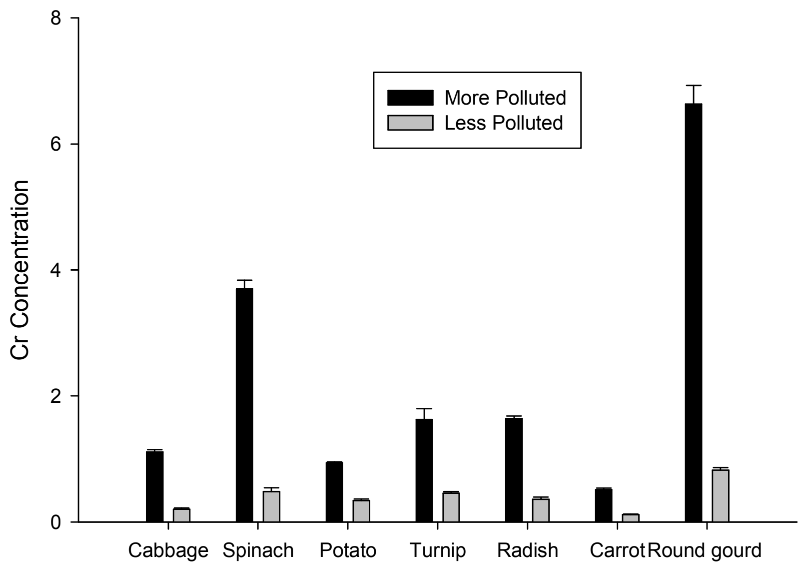
3.4 Metals in vegetables

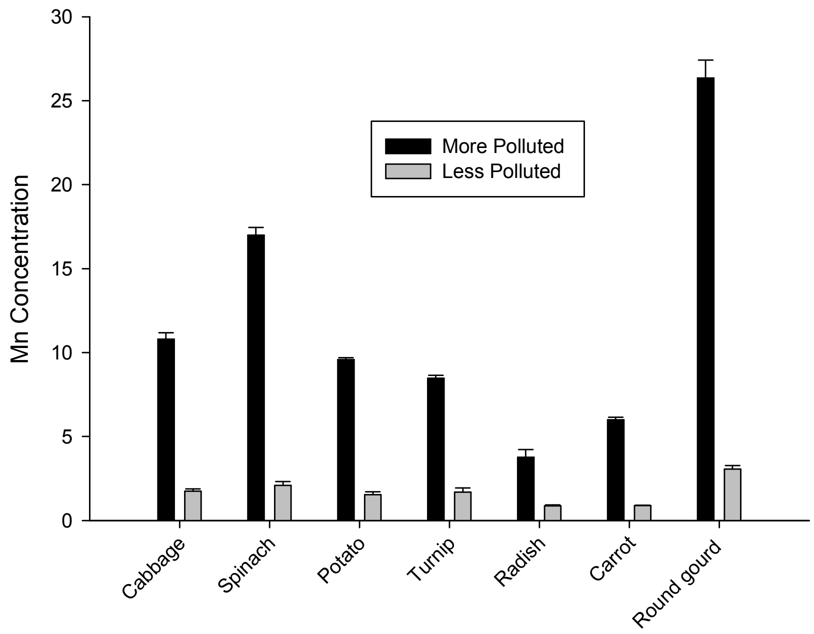
Total 14 vegetables samples were taken from two different areas of Gujranwala, 7 same samples from each site. Heavy metal concentration was determined by acid digestion method. Mean concentration of heavy metals is given in table 3.4.

Table 3.4 Heavy metal concentration (Mean±SD) in vegetables

Type	Vegetables	Cd	Cr	Cu	Mn	Ni	Pb
More polluted	Cabbage	1.61±0.15	1.11±0.06	9.47±0.37	10.80±0.66	1.72±0.16	2.68±0.21
	Spinach	0.34±0.03	3.70±0.25	29.1±2.36	17.00±0.79	3.58±0.28	3.43±0.32
	Potato	0.38±0.04	0.94±0.03	7.62±0.57	9.59±0.20	2.27±0.13	5.45±0.32
	Turnip	0.13±0.04	1.62±0.30	6.11±0.29	8.47±0.31	1.50±0.21	0.06±0.04
	Radish	0.57±0.04	1.64±0.06	5.83±0.42	3.78±0.77	0.94±0.33	0.18±0.07
	Carrot	0.59±0.09	0.51±0.05	2.40±0.26	6.00±0.26	3.17±0.25	0.65±0.04
	Round gourd	0.14±0.03	6.63±0.51	6.33±0.81	26.36±1.85	2.27±0.15	0.87±0.04
Less polluted	Cabbage	0.12±0.04	0.20±0.03	2.52±0.41	1.75±0.25	0.29±0.05	0.08±0.01
	Spinach	0.05±0.02	0.48±0.10	4.99±0.66	2.10±0.38	0.25±0.06	0.07±0.03
	Potato	0.04±0.04	0.34±0.05	1.51±0.26	1.55±0.28	0.13±0.04	0.33±0.05
	Turnip	0.02±0.02	0.46±0.04	1.03±0.11	1.69±0.45	0.24±0.04	0.05±0.02
	Radish	0.10±0.02	0.36±0.07	0.58±0.04	0.88±0.08	0.31±0.12	0.06±0.02
	Carrot	0.24±0.03	0.11±0.03	0.42±0.05	0.88±0.04	0.52±0.06	0.14±0.03
	Round gourd	0.07±0.03	0.82±0.07	1.18±0.1	3.07±0.35	0.25±0.03	0.21±0.05


Cd Concentration
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
More Polluted
Less Polluted
Cabbage
Spinach
Potato
Turnip
Radish
Carrot
Round gourd


Cr Concentration
8
6
4
2
0
More Polluted
Less Polluted
Cabbage
Spinach
Potato
Turnip
Radish
Carrot
Round gourd



3.6 Bio-accumulation factor in vegetables

Table 3.12 Bioaccumulation factor of more polluted vegetables

Bioaccumulation Factor of vegetables from more polluted site						
Vegetables	Cd	Cr	Cu	Mn	Ni	Pb
Cabbage	17.85	0.06	4.51	0.31	0.38	0.99
Spinach	3.12	0.21	15.56	0.47	1.05	1.11
Potato	2.92	0.05	2.63	0.29	0.37	1.30
Turnip	0.97	0.08	2.26	0.26	0.28	0.02
Radish	8.19	0.08	2.77	0.11	0.23	0.05
Carrot	3.28	0.03	1.00	0.14	0.81	0.16
Round gourd	1.02	0.33	1.98	0.83	0.50	0.20

Different vegetables accumulated different concentration of metals from more polluted soil. In case of Cd, maximum accumulation factor was observed in cabbage followed by radish, carrot, spinach, potato round gourd while less BAF in turnip from more polluted soil. Regards to Cr and Cu concentration, maximum BAF was observed in spinach and less in carrot. BAF of Mn concentration was maximum in round gourd and minimum in radish. Higher concentration of Ni was accumulate in spinach while Pb in potato and lower concentration of Ni was observed in radish while Pb in turnip from more polluted soil (table 3.12)

Table 3.13 Bioaccumulation factor in less polluted vegetables

Bioaccumulation Factor of vegetables from less polluted site						
Vegetables	Cd	Cr	Cu	Mn	Ni	Pb
Cabbage	4.11	0.11	3.15	0.19	0.14	0.04
Spinach	2.81	0.20	5.73	0.17	0.17	0.06
Potato	2.55	0.29	1.56	0.15	0.10	0.22
Turnip	0.58	0.19	1.33	0.23	0.14	0.03
Radish	5.09	0.12	0.61	0.09	0.19	0.05
Carrot	7.40	0.05	0.58	0.08	0.34	0.08
Round gourd	4.44	0.41	1.21	0.25	0.19	0.13

In less polluted site trend of BAF for Cd in vegetables was Carrot>Radish>Round gourd>Cabbage>potato>Turnip. Trend of BAF for Cr was Round gourd>Potato>Spinach>Turnip>Radish>cabbage>Carrot. For Cu trend of BAF Spinach>Cabbage>Potato>Turnip>Round gourd>Carrot>Radish was found. BAF trend for Mn Round gourd> Turnip> Cabbage> Spinach> Potato> Radish> Carrot was observed. For Ni the trend was Carrot>Radish>Round gourd>Spinach>Turnip>Cabbage>Potato. And trend for Pb was Potato>Round gourd>Carrot>Spinach>Radish>

Cabbage>turnip. Minimum BAF of Cd was observed in turnip, Cr, Mn and Cu in carrot, Ni in potato and Pb in turnip (Table 3.13).

4. Discussion

The study was conducted to investigate concentration of heavy metals in soil and vegetables due to industrial effluent to estimate their possible concentrations. So for the very purpose soil and vegetables samples from two sites of Gujranwala were analyzed and studied for different physicochemical parameters. Metal concentrations were also determined in samples for Cd, Cr, Cu, Ni, Mn and Pb. Environmental degradation and soil and plant contamination become a hot issue as its adverse effects observed on human health, plants ,animals (Irshad *et al.* 1997 ; Abbas *et al*.2010).

Even so the metal contamination depends on type and origin. Significant variation was observed while analysis of plant and soil. More polluted areas showed the highest result followed by less polluted areas irrespective of the studied metals. Several studies have indicated that vegetables grown in heavy metals contaminated soils have higher concentrations than those grown in uncontaminated soils (Guttormsen *et al*. 1995; Dowdy and Larson, 1995; Naser *et al.,* 2009). During present study, concentrations of heavy metals in vegetables were significant as these results are conformed by Literature.

Cd content was found lesser than our values, 0.3mg/Kg in top soil and 0.2 mg/Kg in sub soil reported by Haung *et al*. (2007) while our value was 0.62mg/Kg (MP) and 0.132mg/Kg (LP). The Cd metal means concentration reported by Wei and Yang. (2010) was 0.43mg/Kg which lies between our MP and LP. Cr metal reported by Haung *et al*. (2007) was in lesser amount 77.2mg/Kg in top soil and 82.7 mg/Kg in sub soil than our values 124.5mg/Kg (MP) and 24.775mg/kg (LP).The Cr mean concentration determined by Wei and Yang. (2010) was 58.87 mg/kg which lies between our MP and LP. Cu content of our study was 21.02mg/kg (MP) and 5.15mg/kg (LP), lower than top soil 33.9mg/Kg and 31.4 mg/Kg in sub soils. (Haung *et al*.2007). The Cu means concentration determined by Wei and Yang. (2010) was 31.71 mg/Kg which was significantly higher than our both sites value. Ni content was higher for our values than 62.375 mg/kg (MP) and 33.625 mg/kg (LP) as compared to Haung *et al*. (2007) i.e. 38.5 in top soil and 35.2 in sub soil. Mean concentration of Ni determined by Wei and Yang. (2010) was 27.53 mg/kg which was significantly lower than our both sites value. Our Pb values was 45.45mg/kg (MP) and 7.145 mg/kg (LP) higher than 35.7mg/kg in top soil and 25.7mg/kg in sub soil reported by Haung et al.2010. 2599.8mg/kg. Pb Mean concentration determined by Wei and Yang. (2010) was 37.55 mg/kg which was significantly higher than our both sites value. Iqbal and Shah (2011) conducted an experiment and reported Mn concentration in soil during two season summer (393.5 mg/kg) and winter (453.6 mg/kg) which are higher than our values.

Ullah *et al*. (2012) showed concentrations of some heavy metals extracted by AB-DTPA solution from the soil irrigated with sewage contaminated water. Mean values obtained from his work were Cd (1.26mg/kg), Cr (1.19mg/kg), Cu (11.11 mg/kg), Ni (3.96 mg/kg), Pb (8.71mg/kg).Our values of Cd, Cr, Cu, Pb was significantly lower than values reported by Ullah *et al*.(2012) and Ni content in our MP soil was greater and in LP soil less than the reported values. According to Saif *et al.* (2005) the range of Mn in soil 8.98-17.07 mg/kg was observed.

Cd level measured in vegetables in our study were significantly higher than the reported values of Abbas *et al*. (2010) and Al Chaarani *et al.* (2009). Abbas *et al*. (2010) reported Cd concentration in different vegetables i.e., 0.087µg/g (spinach), 0.045µg/g (Potato), 0.057µg/g (Radish), 0.050µg/g turnip and 0.049µg/g (cabbage) which are lower than our study on more polluted and less polluted areas. Al Chaarani *et al.* (2009) showed Cd concentration in carrot 0.59 µg/g, which is also lower than our study on both areas. The FAO/WHO permissible limit for Cd is 0.1µgg^{-1} (Abbas *et al* 2010). The higher values were observed in Spinach, potato, Radish, turnip, cabbage, Carrot and round gourd than permissible limits.

Cadmium has the tendency to binds with OM and thus taken up by plant and enter to the food supply. Cd will enter in our body through lungs hence causing severely damage and causes lungs cancer. Kidney diseases may also result due to the breathing air with lower levels of Cd over long period of time. Food or drinking water that has high Cd level irritates the stomach, vomiting and diarrhea. Exposure of Cd for a long time causes bones to become fragile (ATSDR). Cr levels found in our study were higher than reported values of Singh *et al.* (2010) and Al Chaarani *et al*. (2009). Singh *et al*. (2010) reported Cr concentration for cabbage (0.175), Spinach (0.149) and Radish (0.230) while in our research the content of Cr metals was high in these vegetables. Al Chaarani *et al*. (2009) reported Cr content for Potato (161.8) and carrot (0.0763) while in potato Cr content was higher and in carrot its amount was lower in our research. According to Parveen *et al*. (2012) Turnip has 1.64 which is greater than our value for turnip.

The Cr health effect on respiratory track, these include irritation of the lining of the nose, runny nose, and breathing problems (asthma, cough, shortness of breath, wheezing).skin rashes and breathing difficulties is a major problem. Cr (VI) causes anemia, ulcer and irritation in stomach. It also destroys male reproductive system and sperm producing ability. Lung and intestinal track cancer, stomach tumors proved to cause by Cr (VI) exposure. (ATSDR). Cu concentration was significantly higher than reported values of Luo et al. (2011), Jan *et al.* (2010)0 and Arora *et al*. (2008). Luo *et al*. (2011) showed Cu concentration for Cabbage (1.42), which was less than our study. Jan et al. (2008) stated Cu value for potato 2.052 mg/kg was less than our study. Arora *et al.* (2008) showed Cu concentration in radish (5.96 mg/kg), Spinach (16.5 mg/kg), turnip (16.1 mg/kg) and carrot (16.8mg/kg). Radish, spinach and carrot values reported by Arora *et al. (*2008) were higher than our values. For turnip our value higher than reported value. Copper is necessary for good human health but long term exposure can be harmful. Long term exposure of copper dust can cause irritation to your nose, eyes and mouth and cause dizziness, nausea, diarrhea and headaches. Water that contains higher level of copper may cause nausea, vomiting and stomach cramps. High intake of copper can cause kidney and liver damage and sometimes death. Copper can also cause cancer in humans (ATSDR).

Lower Mn values were observed in Spinach in our study than value given by Murtaza *et al.* (2010) i.e., 102.2 mg/kg. Mn concentration in Turnip, Carrot and Potato was higher than Arora *et al.* (2008) i.e., Turnip (18.2 mg/kg), Carrot (17.4 mg/kg). Radish has lesser value than Arora *et al.* (2008) reported value i.e., 12.8.Potato (0.808mg/kg) value reported by Jan *et al.* (2010). As low level of manganese intake are essential for human health but exposure to high level of manganese are toxic. Inhaled manganese is directly transported to brain before metabolized to liver. Permanent neurological disorder known as magnetism is a result of manganese toxicity and symptoms of that is tremors, difficulty walking and facial muscle spasms. High level of manganese inhalation can cause series of serious and disabling neurological effects in humans (ATSDR). According to Jan *et al.* (2010) Ni content in spinach (1.267mg/kg), carrot (0.984 mg/kg), Potato has (1.229 mg/kg) was lesser than our study and turnip (1.167 mg/kg) has greater than our value. Khan *et al.* (2008) reported that Ni in radish (0.27 mg/kg) and cabbage (0.40 mg/kg), lesser than our study. Ni concentration in radish has a lesser value in our study than Parveen *et al.* (2012) reported value 42.4mg/kg.

Nickel exposure can occur in general population via nickel inhalation, oral and dermal routes of exposure. Contact dermatitis is most commonly adverse health effect due to nickel exposure. Contact dermatitis is due to allergic reaction to nickel exposed via dermal contact with airborne nickel or contact with jewelry that is made of nickel. General population which is sensitized to nickel is 10-20%. Cancerous and noncancerous both respiratory effects have been found in animals and humans due to the exposure of airborne nickel compounds. Emphysema, chronic bronchitis, impaired lung function and pulmonary fibrosis have been observed in nickel foundry workers and welders (ATSDR).

Pb permissible limit is $0.2\mu gg^{-1}$. Lower values were observed in our study than Parveen *et al*. (2012) for cabbage (48.8), radish (21.5) and turnip (22).Al Chaarani *et al*. (2009) showed Pb content in potato (0.0764) and carrot (0.1531) which was less than our study. A significantly lower value was observed in spinach in our research than Saif *et al*. i.e. greater than 30. The Lead poisoning mainly affects Nervous system. It can causes weakness in fingers, wrists or ankles. Small increases in blood pressure especially in middle aged and can cause anemia. High levels of lead cause brain and kidney damage leading to death. In case of pregnant woman higher lead levels cause miscarriage and in men they destroy sperm producing organ. The harmful effects of Pb to unborn children include smaller babies, premature births and decreased memory of infants and growth problems (ASTDR).

5.1 Conclusion

This study was conducted to evaluate some selected metals (Cr, Cd, Cu, Ni, Pb and Mn) in soil and vegetables from different areas of Gujranwala with respect of Industrialization. Physiochemical parameters pH, OM, SP, EC, CEC, TSS, Co_3^{2-} , HCO_3^{2-} etc were analyzed. Change in pH value affect carbonates and bicarbonates concentrations. Concentration of heavy metals in soil and vegetables depends on nutrient load in waste water and industry type. Among heavy metals, Mn was with highest concentration (357.75mg/kg) and (47.325mg/kg) in MP and LP soil respectively. In vegetables Cu has highest value 29.10mg/kg in spinach and Mn has 26.36 mg/kg in round gourd.

Cd concentration was found maximum (1.61mg/kg) in cabbage, minimum (0.24mg/kg) in carrot. In soil the maximum concentration was (0.62 mg/kg).Cr concentration was maximum (3.70 mg/kg) in spinach, minimum (0.24mg/kg) while in soil maximum concentration was (124.5 mg/kg). Cu concentration was maximum (29.1 mg/kg) in spinach, minimum (4.99 mg/kg) in spinach and soil has maximum value (21.02 mg/kg). Mn has maximum (26.09 mg/kg) in round gourd and minimum (0.88 mg/kg) in carrot and radish while its soil has maximum value (353.33 mg/kg). Ni has maximum (3.58 mg/kg) in spinach, minimum (0.13 mg/kg) in potato and its soil has maximum value (62.37 mg/kg) and Pb maximum concentration (54.45 mg/kg) in soil and in vegetables maximum (5.45 mg/kg), minimum (0.05 mg/kg) in turnip. In vegetables general trend found was Cu >Mn>Cr >Ni> Pb> Cd and in soil the trend was Mn>Cr>Ni>Pb>Cu >Cd.

Significant positive Correlation was found between all total metal and AB-DTPA extractable metal. Correlation was also determined in less polluted and more polluted vegetables which also showed positive relation.

The trend of Bioaccumulation factor for Cabbage was Cd> Cu> Pb>Ni>Mn>Cr. In Spinach trend was Cu>Cd>Pb>Ni>Mn>Cr. Potato trend was Cd> Cu>Pb>Ni>Mn>Cr. Turnip showed trend Cu>Cd>Ni>Mn>Cr>Pb. Radish has trend Cd>Cu>Ni> Mn>Cr>Pb. Carrot trend was Cd>Cu>Ni>Pb>Mn>Cr and in round gourd trend was Cu>Cd>Mn>Ni>Cr>Pb. Industrial effluents and urban pollution associated with sewage sludge, municipal waste water might have increased the levels of Pb, Ni, Cr, Cd, Mn, Cu intake of vegetables and soil. All these metals have toxic potential, but the detrimental impact become apparent as our values are significant. Monitoring of heavy metals in plant tissues is essential in order to prevent excessive build-up in human body and food chain.

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