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A comparative study of human health risks via consumption of food crops grown on wastewater irrigated soil (Peshawar) and relatively clean water irrigated soil (lower Dir)

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ABSTRACT

Food crops irrigated with wastewater are mostly contaminated with heavy metals and considered as a main pathway for human exposure. In this study, soil and food crops samples were collected from wastewater irrigated soils, background and relatively less polluted areas. Results of the sequential extraction and total metals concentrations in soils indicated that wastewater irrigation has significantly increased ($p \geq 0.001$) the bioavailable and total metal contents in wastewater irrigated soil as compared to background and control soils. Heavy metal concentrations in the food crops grown on wastewater irrigated soil were higher than those grown on background and control soils but were found within WHO/FAO permissible limits except for Zn. Health risk index values were less than 1 for both control and wastewater irrigated soils (except Mn). However, the food crops such as *Brassica rapa*, *Spinacia oleracae* L., *Lycopersicum esculantum*, *Mentha viridis*, *Coriandum sativum* and *Lactuca sativa* grown on wastewater irrigated soil can pose health risks because of the high concentration of Mn.

1. Introduction

Vegetables contain proteins, vitamins and essential metals and form an important part of the diet as well as act as buffering agents for acidic products formed during the digestion process. However, the plants contain a range of concentrations of both essential and toxic elements [1,2]. Wastewater is mostly used for the irrigation of crops in the urban environment due to freshwater shortage. Generally, wastewater irrigation is responsible for soil contamination with heavy metals which further lead to contaminate the food crops. It is a fact that heavy metals have adverse impact on soil ecosystem and lead to numerous human health risks because of the absence of proper excretion from the body and their toxicity [2]. The heavy metals uptake in high concentrations by plants can cause serious health problems for consumers. Human health exposure to metals occurs as a result of the consumption of contaminated vegetables and inhalation of contaminated dust particles [3].

Typically, the heavy metals excessively concentrate in the leafy vegetables as compared to other food crops [4]. A number of factors such as climate, atmospheric deposition, the concentrations of heavy metals in soil, the nature of soil on which vegetables are grown and the degree of maturity of plant affect bioconcentration of heavy metals in vegetables [5,6]. Numerous health problems such as intrauterine growth retardation, decreased immunological defenses, impaired psycho-social behavior disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer develop through the ingestion of heavy metal contaminated food [7,8].

Wastewater irrigation is practiced in some periurban areas of Peshawar City which is the capital of North West Frontier Province (NWFP), Pakistan. The aim of the present study was to investigate the effect of industrial effluents on the heavy metal contamination of the surrounding soil because the industrial effluents contain high concentrations of heavy metals [9] and subsequent uptake by food crops grown on these soils. The effects of wastewater irrigation on the soil heavy metal concentrations, uptake by food crops and health risk through the consumption of contaminated food were studied.

2. Materials and methods

2.1. Sampling areas

2.1.1. Peshawar

Peshawar is the provincial capital of NWFP and occupies an area of 77 km^2 with a population of more than one million [10].

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Kankola is a major food crops producing area situated in the northeast of Peshawar (Fig. 1). Food crops from Kankola are transported to Peshawar. Though the main irrigation source is a canal originated from Shalam River but on the other side a wastewater stream (originated from industrial zone located in Hayatabad) is also used for irrigation purposes [10].

2.1.2. Dir

Dir is divided into two districts namely Upper Dir and Lower Dir (Fig. 1) with a total population of 767,409. Topographically, Dir has been dominated by mountains and hills which are parts of ranges/branches of Hindukush and Hindu Raj. The mountain ranges run from north to south and from northeast to southwest along the northern borders with Chitral District. The important river is Panjkora which enters the district from northeast and flows southwest along the boundary of the Bajour Agency up to its co-fluence with Swat River. Panjkora River is made by several streams in the Lower Dir and a mainstream form Upper Dir called Dir River. Though individual streams in the catchments areas are used as a source of irrigation. River Panjkora is the main irrigation source in the downstream plain areas of Lower Dir [11].

2.2. Sampling and pre-treatment

Food crops and soil samples (0–20 cm) were collected from agricultural fields present in the study area (Fig. 1). The fresh vegetable samples were placed in clean plastic bags and transported to the laboratory for analyses. These samples were cleaned with de-ionized water and separated into leaf, stalk, fruit and root. All air-dried sub-samples of vegetables were grounded to fine powder and stored in polythene bags. Air-dried soil samples were crushed, and passed through a mesh sieve (0.18 mm) and stored for further analyses.

2.3. Reagents

Analytical grade chemicals were purchased and used for sample preparation and analyses. Solutions were prepared in double deionized water. For each metal calibration standards were prepared from the stock solution.

2.4. Fractionation of soil

Soil samples were sequentially extracted following a modified Tessier scheme [12–14] methods. For total metal determinations, soil samples were digested with aqua regia (HCl:HNO_3, 3:1). For recovery studies, the sum of metals extracted in each sequential extraction was compared with the total metal extraction procedure.

2.5. Digestion of vegetable samples

Food crop samples (0.5 g) were taken in crucibles (triplicates) and perchloric acid and nitric acid solution (1:4) were used for acid digestion. After cooling, the digested samples were filtered and made up to the final volume of 25 mL using de-ionized water. The heavy metals in the soil and vegetable extracts were analyzed using Atomic Absorption Spectrophotometer (Perkin Elmer AAS-700) at the Centralized Resource Laboratory, University of Peshawar. Precession and accuracy of analysis were also ensured through repeated analysis of the samples against certified reference materials (CRMs) of all metals. Due to the non-availability of CRMs of vegetables in our laboratory for quality assurance, recovery studies were conducted using standard spiking method.

2.6. Data analysis

2.6.1. Metal transfer factor

Soil to plant metal transfer factor (MTF) was computed as the ratio of metal concentrations in plants (on dry weight basis) to metal concentrations in soil. The MTF was calculated using the formula such as:

$$\mathrm{MTF} = \frac{C\mathrm{plants}}{C\mathrm{soil}} \tag{i}$$

where C_{plant} and C_{soil} represent the heavy metals concentration in extracts of plants and soil on dry weight basis, respectively.

2.6.2. Daily intake of metals

The average daily intake of food crops both for adults and for children was calculated from the data obtained during questionnaire survey. The respondents were asked for full detail of their diet for week. The daily intake of metals (DIM) was determined by the following equation:

$$\mathrm{DIM} = \frac{C_{\mathrm{metals}} \times C_{\mathrm{factors}} \times D_{\mathrm{food\,intake}}}{B_{\mathrm{average\,weight}}} \tag{ii}$$

where C_{metal}, C_{factor}, $D_{\mathrm{food\,intake}}$ and $B_{\mathrm{average\,weight}}$ represent the heavy metal concentrations in plants (mg/kg), conversion factor, daily intake of vegetables and average body weight, respectively. Fresh to dry weight conversion factor (0.085) was used for these food crops. The average daily food crops intakes for adults and children were calculated to be 0.250 and 0.165 kg/person/day, respectively, based on the data obtained during questionnaire survey. Both male and female adults (18–60 years) and children (5–17 years) were considered for questionnaire survey. The average adult and child body weights were considered to be 73 and 32.7 kg, respectively.

2.6.3. Risk assessment

Health risk indices (HRIs) for intake of Zn, Cd, Pb, Ni, Cu, Cr and Mn through the consumption of contaminated food crops were calculated using the following equations adopted from Khan et al. [2].

$$\mathrm{HRI} = \frac{\mathrm{DIM}}{\mathrm{RfD}} \tag{iii}$$

where HRI is the human risk index through the consumption of vegetables, DIM is the daily intake of metal (mg metal/kg body weight/day) and RfD is the reference dose. The RfD values for Zn, Cd, Pb, Ni, Cu, Cr and Mn were 0.30, 0.001, 0.004, 0.02, 0.04, 1.5 and 0.033 mg/kg bw/day, respectively [15–17].

2.6.4. Statistical analysis of the data

The data were statistically analyzed using SPSS software for window version-16. ANOVA and Cluster Analysis (CA) statistical techniques were applied for the determination of significant difference among vegetables samples and their classification based on the metals contents.

3. Results

3.1. Soil fractionation

Fig. 2 summarizes available fractions of heavy metals in soil samples collected from wastewater irrigated, background and control sites, while complete fraction speciation of metals is listed in Table 1. The data show that the phytoavailable fraction of Zn in the polluted soil was 40.94 mg/kg which was significantly higher as compared to background (10.08 mg/kg) and control soils (4.1 mg/kg). Phytoavailable Cd concentration was 0.87, 0.11 and

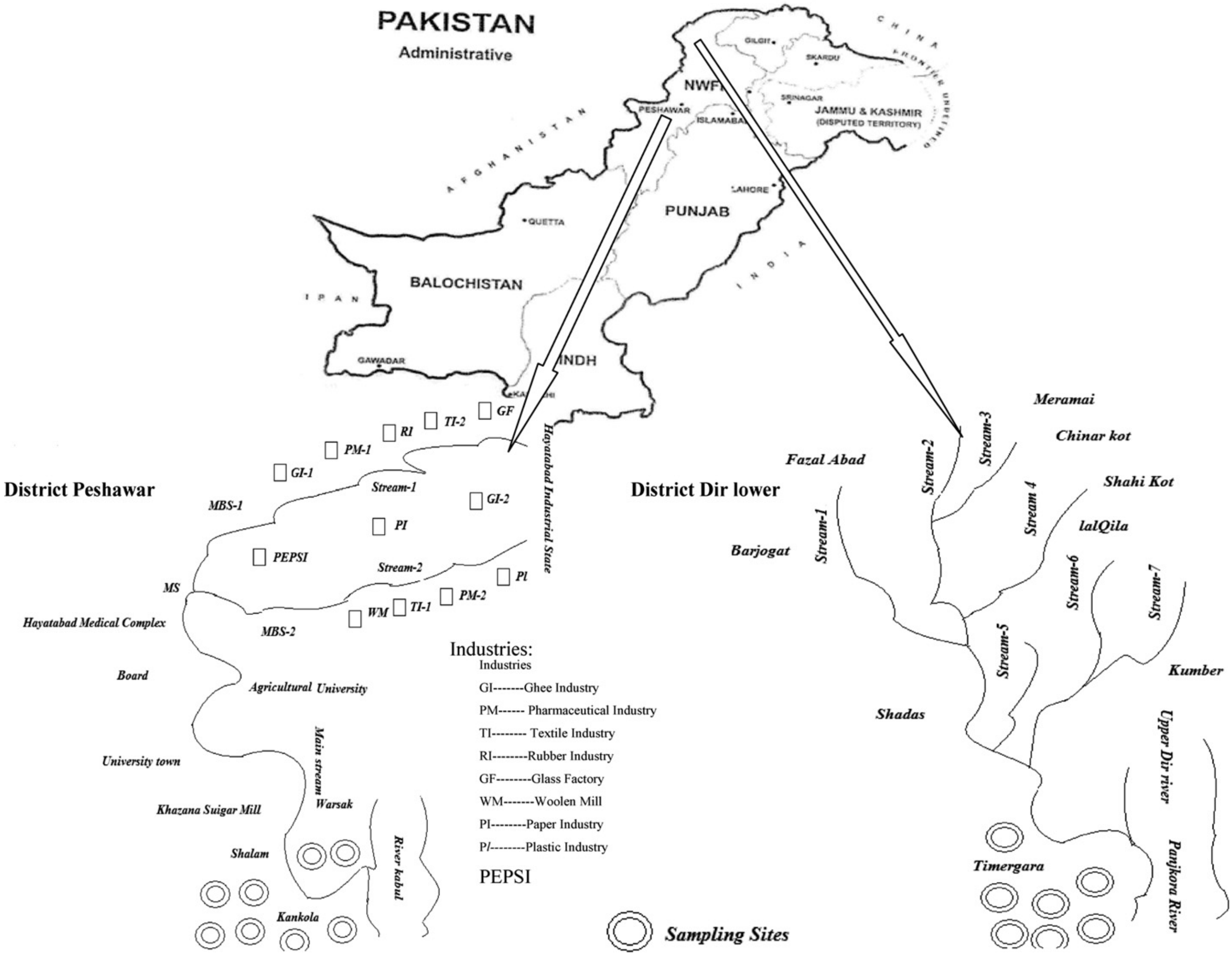

Fig. 1. Location map of the samples collection points in the polluted area and control area.

0.1 mg/kg in wastewater irrigated, background and control soils, respectively. Pb phytoavailable concentration was 0.4 mg/kg in wastewater irrigated, 0.30 mg/kg in background and 0.13 mg/kg in control soils. Similarly, Ni bioavailable concentration was 10.54, 3.54 and 1.26 mg/kg in wastewater irrigated, background and control soils, respectively. In wastewater irrigated soil, the Cu phytoavailable concentration was 20.84 mg/kg, while 13.03 mg/kg in background soil and 4.69 mg/kg in control soil. Furthermore, the Cr phytoavailable concentration was 1.65 mg/kg in the wastewater irrigated soil, 1.28 mg/kg in background and 0.2 mg/kg in

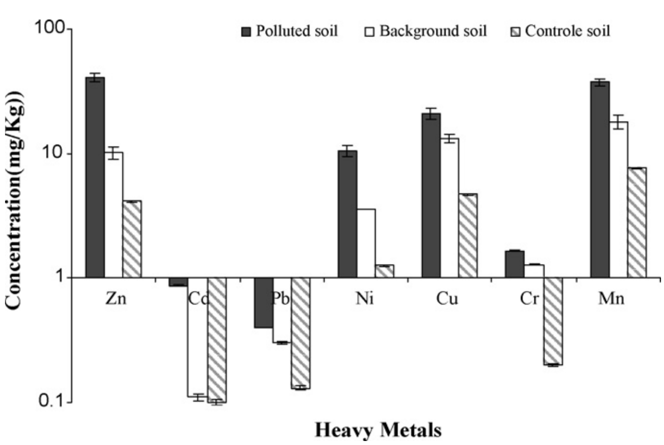

Fig. 2. Phytoavailable concentrations of different heavy metals in soils collected from wastewater irrigated, background and control areas (error bars indicate standard deviation).

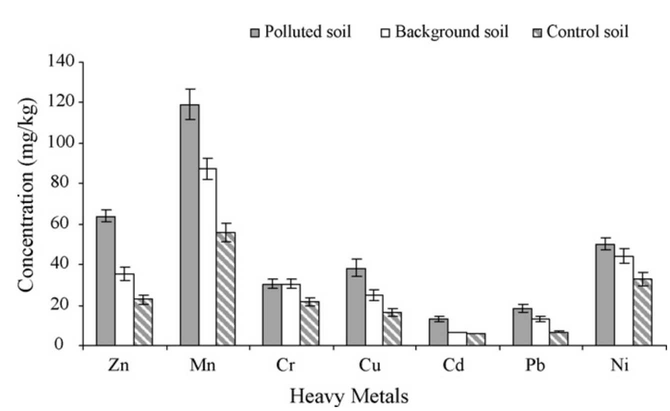

Fig. 3. Total heavy metals content of soils collected from wastewater irrigated, background and control areas (error bars indicate standard deviation).

Table 1
Mean values (mg/kg) of different fractions of heavy metals in soils collected from study areas.

Fractions	Zn	Cd	Pb	Ni	Cu	Cr	Mn
Polluted soil							
Water soluble + exchangeable	15.50 (24.21)	0.06 (0.50)	0.21 (1.40)	5.12 (9.42)	8.32 (21.68)	0.31 (1.02)	12.56 (10.53)
Pb displaceable	14.92 (23.31)	0.03 (0.25)	0.11 (0.73)	4.11 (7.57)	7.12 (18.56)	0.08 (0.26)	14.1 (11.82)
Acid soluble	10.52 (16.43)	0.78 (6.50)	0.32 (2.13)	1.31 (2.41)	5.40 (14.07)	1.26 (4.24)	10.8 (9.06)
Organically bound	8.11 (12.66)	0.02 (0.16)	0.05 (0.33)	0.72 (1.34)	0.93 (2.42)	8.32 (27.72)	7.9 (6.62)
Mn-oxide occluded	2.42 (3.78)	0.54 (4.59)	5.61 (37.41)	10.3 (18.92)	0.11 (0.28)	6.72 (22.47)	6.4 (5.37)
Fe-oxide occluded	5.34 (8.34)	5.54 (46.24)	2.60 (14.17)	4.51 (7.87)	4.00 (10.42)	3.2 (10.71)	6.2 (5.20)
Residual	6.42 (10.03)	5.01 (41.81)	6.10 (40.66)	28.2 (49.24)	11.7 (30.50)	10(32.84)	60(50.32)
Background soil							
Water soluble + exchangeable	1.91 (5.39)	0.01 (0.16)	0.07 (0.64)	2.09 (4.44)	0.42 (1.68)	0.10 (0.33)	3.45 (3.95)
Pb displaceable	4.75 (13.41)	0.03 (0.49)	0.01 (0.09)	1.2 (2.55)	6.4 (25.64)	0.08 (0.26)	8.32 (9.52)
Acid soluble	3.42 (9.65)	0.07 (1.15)	0.22 (2.05)	0.25 (0.53)	6.21 (24.87)	1.10 (3.61)	6.31 (7.23)
Organically bound	7.21 (20.36)	0.12 (1.90)	0.01 (0.09)	0.52 (1.4)	0.11 (0.44)	6.31 (21.22)	6.31 (7.23)
Mn-oxide occluded	0.35 (0.98)	0.32 (5.26)	2.40 (22.41)	12.03 (25.57)	0.05 (0.20)	5.23 (17.59)	6.32 (7.24)
Fe-oxide occluded	4.72 (34.76)	2.22 (36.53)	0.77 (7.24)	1.92 (4.08)	1.99 (7.97)	2.91 (9.76)	5.91 (6.760
Residual	12.31 (34.76)	3.31 (54.44)	7.20 (67.41)	29.02 (61.71)	9.23 (36.98)	14(47.09)	50(57.25)
Control soil							
Water soluble + exchangeable	0.58 (2.54)	0.02 (0.35)	0.04 (0.60)	1.09 (3.33)	0.19 (1.17)	0.05 (0.23)	1.97 (3.51)
Pb displaceable	2.20 (9.62)	0.03 (0.53)	0.07 (1.12)	0.09 (0.27)	4.45 (27.43)	0.02 (0.08)	0.33 (0.58)
Acid soluble	1.32 (5.77)	0.05 (0.89)	0.02 (0.32)	0.08 (0.24)	0.05 (0.31)	0.75 (3.26)	5.32 (9.49)
Organically bound	3.32 (14.51)	0.11 (1.97)	0.15 (2.42)	0.10 (0.30)	0.07 (0.43)	2.33 (10.09)	1.21 (2.16)
Mn-oxide occluded	0.07 (0.30)	0.81 (14.56)	1.22 (19.56)	8.55 (26.17)	0.03 (0.18)	6.51 (28.02)	5.98 (10.67)
Fe-oxide occluded	4.52 (19.76)	0.32 (5.73)	0.55 (8.82)	0.53 (1.65)	0.93 (5.73)	3.42 (14.81)	6.32 (11.28)
Residual	10.22 (44.68)	4.22 (75.89)	4.20 (67.20)	22.23 (68.04)	10.20 (62.88)	10(43.32)	34(6.07)

Values in parenthesis indicate percentage of total metal content in soil.

Table 2
MTF for heavy metals in vegetables grown in wastewater irrigated soil.

	Zn	Cd	Pb	Ni	Cu	Cr	Mn
Brassica rapa	1.693	0.004	0.014	1.167	1.459	0.068	1.136
Spinacia oleracae L.	3.033	0.005	0.007	1.267	0.944	0.065	1.131
B. oleracae botrytis	1.158	0.007	0.015	1.011	1.262	0.059	0.635
Pisum sativum	1.914	0.008	0.014	1.067	1.426	0.050	0.771
Lycopersicum esculantum	1.540	0.004	0.013	1.327	1.630	0.072	1.208
B. Compestris	1.271	0.003	0.011	0.933	1.371	0.058	1.261
Hebiscus esculantus	1.849	0.015	0.014	1.080	1.427	0.050	0.622
B. oleracae capitita	1.070	0.005	0.005	1.049	1.596	0.053	0.518
Triticum aesativum L. (grain)	1.100	0.003	0.009	1.007	1.187	0.042	0.898
Mentha vridis	1.133	0.009	0.014	0.565	1.732	0.063	1.003
Coriandum sativum	3.006	0.006	0.015	0.926	1.706	0.030	1.310
Oryza sativa L. (grain)	1.225	0.006	0.013	1.129	1.703	0.025	0.559
Lactuca sativa	1.048	0.004	0.008	0.911	1.528	0.047	1.212
Portulaca oleracae	2.599	0.008	0.011	1.045	1.959	0.032	0.588
Allium sativum	1.237	0.009	0.007	0.645	1.581	0.054	1.224
Allium	1.191	0.006	0.013	1.109	1.760	0.057	0.872
Daucus carota	2.287	0.005	0.007	0.984	1.419	0.066	1.248
Malva neglecta	4.505	0.003	0.014	0.590	1.610	0.056	0.733
Solanum tuberosum	4.627	0.009	0.011	1.229	2.052	0.069	0.808
Zea mays L.	0.599	0.003	0.011	0.930	1.208	0.048	0.733

control soils. Mn phytoavailable concentration was 37.46 mg/kg in the wastewater irrigated soil, 18.08 mg/kg in background and 7.62 mg/kg in control soils. The total metal contents of the soil of the selected sites are also shown in Fig. 3 (Supplementary materials, Table 1).

Table 3
Classification of food crops grown on wastewater irrigated soil using cluster analysis.

Group No.	Food crops
1	*Brassica compestris*, *Allium sativum*, *Lactuca sativa*, *B. rapa*, *Lycopersicum esculantum*
2	*Triticum aesativum* L., *Allium*, *Mentha viridis*, *B. oleracae botrytis*, *B. oleracae capitita*, *Zea mays* L.
3	*Oryza sativa* L.
4	*Pisum sativum*, *Hebiscus esculantum*, *Portulaca oleracae*
5	*Spinacia oleracae* L., *Coriandum sativum*, *Daucus carota*
6	*Malva neglecta*, *Solanum tuberosum*

3.2. Heavy metals in food crops

Mean concentrations of heavy metals in the edible parts of food crops grown on wastewater irrigated soil, background and control areas along with WHO/FAO permissible limits are shown in Fig. 4 and detailed data are listed in Supplementary materials (Tables 2 and 3).

The maximum permissible limits for Zn, Cd, Pb, Ni, Cu, Cr and Mn are 100, 0.1, 0.3, 67, 73, 2.3 and 500, respectively, on dry weight basis. Zn concentrations ranged from 38.38 to 296.29 mg/kg in food crops grown on wastewater irrigated soil, 32.23–95.44 mg/kg in background and 30.53–89.34 mg/kg in control soils. *Brassica rapa*, *Spinacia oleracae* L., *Pisum sativum*, *Hebiscus esculantum*, *Coriandum sativum*, *Portulaca oleracae*, *Daucus carota*, *Mentha viridis* and *Solanum tuberosum* accumulated significantly higher concentration of Zn as compared to background and control areas. The Zn concentrations in these food plants exceeded the permissible limits set by WHO/FAO. Cd concentrations ranged from 0.04 to 0.20 mg/kg in

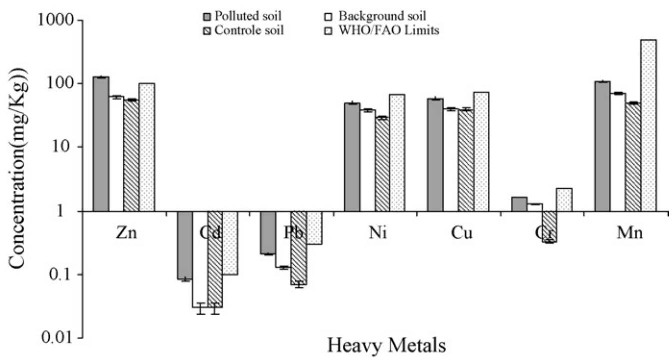

Fig. 4. Comparative plot of mean heavy metals concentration of 20 food crops from wastewater irrigated, background, and control area vs. WHO/FAO safe limits (error bars indicate standard deviation).

Table 4
Classification of food crops grown on control soil using cluster analysis.

Group No.	Food Crops
1	*B. oleracae botrytis*, *Hebiscus esculantum*, *Daucus carota*, *Lactuca sativa*, *B. oleracae capitita*, *Allium*, *B. compestris*, *Allium staivum*
2	*Solanum tuberosum*
3	*Portulaca oleracae*, *Malva neglecta*, *Pisum sativum*
4	*Zea mays* L.
5	*Spincia oleracae* L., *Lycpersicum esculantum*, *B. rapa*, *Coriandum sativum*
6	*Triticum aesativum*, *Mentha viridis*, *Oryza sativa* L.

wastewater irrigated food crops, 0.01–0.07 mg/kg in background and 0.01–0.06 mg/kg in control areas. Cd concentrations in *Mentha viridis*, *Allium sativum*, *Portulaca oleracae*, *Solanum tuberosum* and *Pisum sativum* exceeded the permissible limit set by WHO and FAO. Similarly, the concentrations of Pb ranged from 0.1 to 0.28 mg/kg in wastewater irrigated food crops, 0.07–0.25 mg/kg in background and 0.06–0.24 mg/kg in control soils. Pb concentrations found in *Hebiscus esculantum*, *B. oleracae botrytis*, *C. sativum*, *Mentha viridis*, *Pisum sativum*, *B. rapa* and *Malva neglecta* plants were higher than permissible limit. Ni concentrations ranged from 29.55 to 66.46 mg/kg in food crops grown in wastewater irrigated soil, 18.24–58.26 mg/kg in background and 17.47–56.65 mg/kg in control soils. Cu concentrations ranged from 36.22 to 78.72 mg/kg in wastewater irrigated food crops, 20.21–66.34 mg/kg in background and 18.22–63.42 mg/kg in control soils. Only in two species such as *Solanum tuberosum* and *Portulaca oleracae*, Cu concentrations were exceeded the permissible limit. Cr concentrations ranged from 0.98 to 2.10 mg/kg in wastewater irrigated food crops, 0.79–1.92 mg/kg in background and 0.77–1.75 mg/kg in control soils. Mn concentrations ranged from 61.86 to 156.24 mg/kg in food crops grown on wastewater irrigated soil, 16.14–102.22 mg/kg in background and 13.03–98.56 mg/kg in control soils.

3.3. Heavy metals transfer from soil to plants

Table 2 summarizes the MTF values for selected metals in different food crops collected from the study areas. The MTF for plants irrigated with wastewater ranged from 0.59–4.62, 0.003–0.015, 0.005–0.015, 0.56–1.32, 0.944–2.05, 0.05–0.072, 0.51–1.31 for Zn, Cd, Pb, Ni, Cu, Cr and Mn, respectively. Zn transfer factor was high-

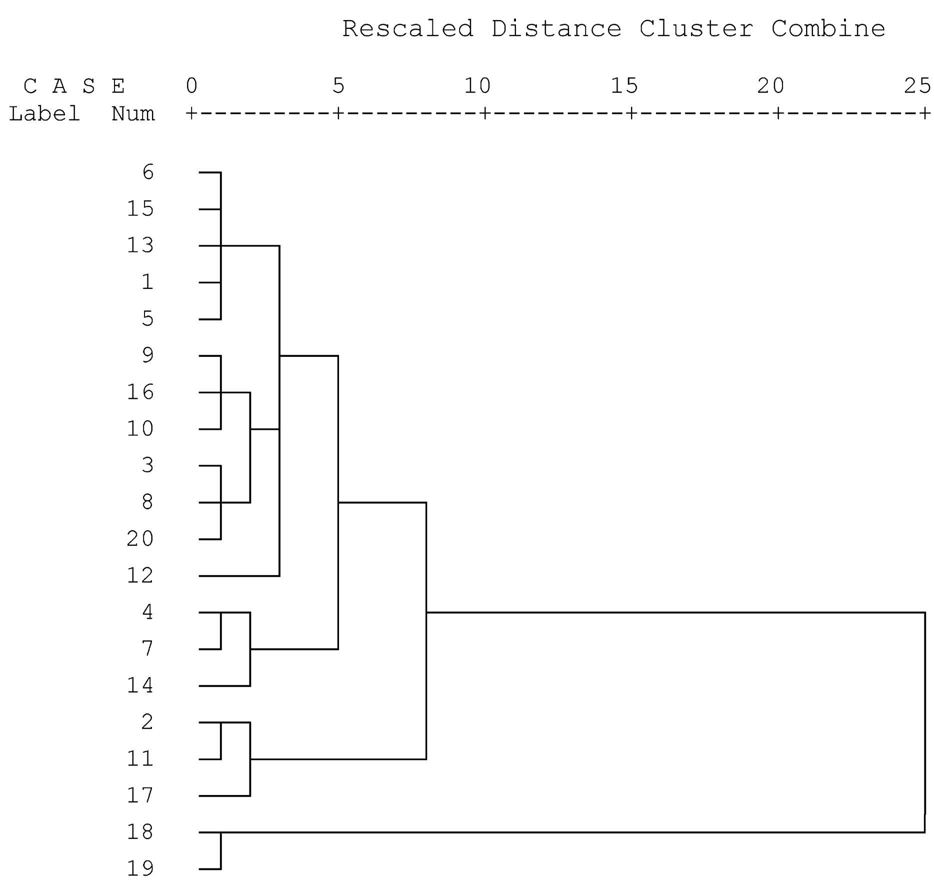

Fig. 5. Dendogram for the classification of food crops grown in wastewater irrigated soil.

Table 5
DIM and HRI for individual heavy metals caused by the consumption of different selected vegetables grown on wastewater irrigated soil.

Vegetables	Individuals		Zn	Cd	Pb	Ni	Cu	Cr	Mn
Brassica rapa	Adults	DIM	3.1E−2	1.7E−5	7.5E−5	1.7E−2	1.6E−2	6.1E−4	3.9E−2
		HRI	1.0E−1	1.7E−2	1.8E−2	8.5E−1	4.0E−1	4.0E−4	1.3
	Children	DIM	3.1E−2	1.7E−5	7.4E−5	1.6E−2	1.6E−2	6.0E−4	3.8E−2
		HRI	1.0E−1	1.7E−2	1.8E−2	8.3E−1	4.0E−1	4.0E−4	1.2
Spinacia oleracae L.	Adults	DIM	5.6E−2	2.0E−5	9.8E−5	1.8E−2	1.0E−2	5.7E−4	3.9E−2
		HRI	1.8E−1	2.0E−2	2.4E−2	9.2E−1	2.6E−1	3.8E−4	1.3
	Children	DIM	5.5E−2	2.0E−5	9.7E−5	1.8E−2	1.0E−2	5.6E−4	3.8E−2
		HRI	1.8E−1	2.0E−2	2.4E−2	9.0E−1	2.5E−1	3.7E−4	1.28
B. oleracae botrytis	Adults	DIM	2.1E−2	3.7E−5	8.1E−5	1.4E−2	1.4E−2	5.3E−4	2.2E−2
		HRI	7.1E−1	3.7E−2	2.0E−2	7.3E−1	3.5E−1	3.5E−4	7.3E−1
	Children	DIM	2.1E−2	3.7E−5	8.0E−5	1.4E−2	1.3E−2	5.2E−4	2.1E−2
		HRI	7.0E−2	3.7E−2	2.0E−2	7.2E−1	3.4E−1	3.4E−4	7.2E−1
Pisum sativum	Adults	DIM	3.5E−2	3.2E−5	1.0E−4	1.5E−2	1.5E−2	4.4E−4	2.6E−2
		HRI	1.1E−1	3.2E−2	2.6E−2	7.7E−1	3.9E−1	2.9E−4	8.9E−1
	Children	DIM	3.5E−2	3.1E−5	1.0E−4	1.5E−2	1.5E−2	4.3E−4	2.6E−2
		HRI	1.1E−1	3.1E−2	2.6E−2	7.6E−1	3.9E−1	2.9E−4	8.7E−1
Lycopersicum esculantum	Adults	DIM	2.8E−2	1.7E−5	1.8E−4	1.9E−2	1.8E−2	6.4E−4	4.1E−2
		HRI	9.5E−2	1.7E−2	4.6E−2	9.6E−1	4.5E−1	4.2E−4	1.3
	Children	DIM	2.8E−2	1.7E−5	1.8E−4	1.9E−2	1.7E−2	6.2E−4	4.1E−2
		HRI	9.4E−2	1.7E−2	4.5E−2	9.5E−1	4.4E−1	4.1E−4	1.31
B. Compestris	Adults	DIM	2.3E−2	1.1E−5	6.4E−5	1.3E−2	1.5E−2	5.1E−4	4.3E−2
		HRI	7.8E−2	1.1E−2	1.6E−2	6.8E−1	3.8E−1	3.4E−4	1.4
	Children	DIM	2.3E−2	1.1E−5	6.2E−5	1.3E−2	1.5E−2	5.0E−4	4.3E−2
		HRI	7.7E−2	1.1E−2	1.5E−2	6.6E−1	3.7E−1	3.3E−4	1.4
Hebiscus esculantus	Adults	DIM	3.4E−2	5.8E−5	7.59E−5	1.5E−2	1.5E−2	4.5E−4	2.1E−2
		HRI	1.1E−1	5.8E−2	1.8E−2	7.8E−1	3.9E−1	3.0E−4	7.2E−1
	Children	DIM	3.3E−2	5.7E−5	7.4E−5	1.5E−2	1.5E−2	4.4E−4	2.1E−2
		HRI	1.1E−1	5.7E−2	1.8E−2	7.7E−1	3.9E−1	2.9E−4	7.0E−1
B. oleracae capitita	Adults	DIM	1.9E−2	2.0E−5	8.7E−5	1.5E−2	1.7E−2	4.7E−4	1.8E−2
		HRI	6.6E−2	2.0E−2	7.1E−3	7.6E−1	4.4E−1	3.1E−4	6.0E−1
	Children	DIM	1.9E−2	2.0E−5	8.5E−5	1.5E−2	1.7E−2	4.6E−4	1.7E−2
		HRI	6.5E−2	2.0E−2	2.1E−2	7.5E−1	4.3E−1	3.1E−4	5.8E−1
Triticum aesativum L.	Adults	DIM	2.0E−2	1.1E−5	5.2E−5	1.4E−2	1.3E−2	3.7E−4	3.1E−2
		HRI	6.8E−2	1.1E−2	1.3E−2	7.3E−1	3.3E−1	2.4E−4	1.0
	Children	DIM	2.0E−2	1.1E−5	5.1E−5	1.4E−2	1.3E−2	3.6E−4	3.0E−2
		HRI	6.7E−2	1.1E−2	1.2E−2	7.2E−1	3.2E−1	2.4E−4	1.0
Mentha vridis	Adults	DIM	2.1E−2	4.6E−5	7.8E−5	8.2E−3	1.9E−2	5.6E−4	3.4E−2
		HRI	7.0E−2	4.6E−2	1.9E−2	4.1E−1	4.8E−1	3.7E−4	1.1
	Children	DIM	2.0E−2	4.0E−5	7.7E−5	8.0E−3	1.9E−2	5.5E−4	3.4E−2
		HRI	6.9E−2	4.5E−2	1.9E−2	4.0E−1	4.7E−1	3.6E−4	1.1
Coriandum sativum	Adults	DIM	5.5E−2	2.6E−5	8.1E−5	1.3E−2	1.9E−2	2.7E−4	4.5E−2
		HRI	1.8E−1	2.6E−2	2.0E−2	6.7E−1	4.7E−1	1.8E−4	1.5
	Children	DIM	5.5E−2	2.5E−5	8.0E−5	1.3E−2	1.8E−2	2.6E−4	4.4E−2
		HRI	1.8E−1	2.5E−2	2.0E−2	6.6E−1	4.6E−1	1.7E−4	1.4
Oryza sativa L.	Adults	DIM	2.2E−2	5.8E−5	6.9E−5	1.6E−2	1.9E−2	2.2E−4	1.9E−2
		HRI	7.6E−2	5.8E−2	1.7E−2	8.2E−1	4.7E−1	1.5E−4	6.4E−1
	Children	DIM	2.2E−2	5.7E−5	6.8E−5	1.6E−2	1.8E−2	2.2E−4	1.9E−2
		HRI	7.4E−2	5.7E−2	1.7E−2	8.0E−1	4.6E−1	1.4E−4	6.3E−1
Lactuca sativa	Adults	DIM	1.9E−2	1.7E−5	4.6E−5	1.3E−2	1.7E−2	4.2E−4	4.2E−2
		HRI	6.5E−2	1.7E−2	1.1E−2	6.6E−1	4.2E−1	2.8E−4	1.4
	Children	DIM	1.9E−2	1.7E−5	4.5E−5	1.3E−2	1.6E−2	4.1E−4	4.1E−2
		HRI	6.3E−2	1.7E−2	1.1E−2	6.5E−1	4.1E−1	2.7E−4	1.3
Portulaca oleracae	Adults	DIM	4.8E−2	3.7E−5	9.0E−5	1.5E−2	2.1E−2	2.8E−4	2.0E−2
		HRI	1.6E−1	3.7E−2	2.2E−2	7.6E−1	5.4E−1	1.9E−4	6.8E−1
	Children	DIM	4.7E−2	3.7E−5	8.8E−5	1.4E−2	2.1E−2	2.8E−4	2.0E−2
		HRI	1.5E−1	3.7E−2	2.2E−2	7.4E−1	5.3E−1	1.8E−4	6.6E−1
Allium sativum	Adults	DIM	2.3E−2	3.4E−5	1.5E−4	9.4E−3	1.7E−2	4.8E−4	4.2E−2
		HRI	7.6E−2	3.4E−2	9.8E−3	4.7E−1	4.4E−1	3.2E−4	1.4
	Children	DIM	2.2E−2	3.4E−5	1.5E−4	9.2E−3	1.7E−2	4.7E−4	4.1E−2
		HRI	7.5E−2	3.4E−2	3.7E−2	4.6E−1	4.3E−1	3.1E−4	1.3
Allium	Adults	DIM	2.2E−2	2.6E−5	7.2E−5	1.6E−2	1.9E−2	5.0E−4	3.0E−2
		HRI	7.3E−2	2.6E−2	1.8E−2	8.0E−1	4.9E−1	3.4E−4	1.0
	Children	DIM	2.1E−2	2.5E−5	7.1E−5	1.5E−2	1.9E−2	5.0E−4	2.9E−2
		HRI	7.2E−2	2.5E−2	1.7E−2	7.9E−1	4.8E−1	3.3E−4	9.7E−1

Table 5 (*Continued*)

Vegetables	Individuals		Zn	Cd	Pb	Ni	Cu	Cr	Mn
Daucus carota	Adults	DIM	4.2E−2	3.2E−5	3.7E−5	1.4E−2	1.5E−2	5.8E−4	4.3E−2
		HRI	1.4E−1	3.2E−2	9.4E−3	7.1E−1	3.9E−1	3.9E−4	1.4
	Children	DIM	4.1E−2	3.1E−5	3.7E−5	1.4E−2	1.5E−2	5.7E−4	4.2E−2
		HRI	1.3E−1	3.1E−2	9.2E−3	7.0E−1	3.8E−1	3.8E−4	1.4
Malva neglecta	Adults	DIM	8.3E−2	1.1E−5	7.5E−5	8.6E−3	1.7E−2	5.0E−4	2.5E−2
		HRI	2.7E−2	1.1E−2	1.8E−2	4.3E−1	4.4E−1	3.3E−4	8.4E−1
	Children	DIM	8.2E−2	1.1E−5	7.4E−5	8.4E−3	1.7E−2	4.9E−4	2.4E−2
		HRI	2.7E−1	1.1E−2	1.8E−2	4.2E−1	4.4E−1	3.3E−4	8.3E−1
Solanum tuberosum	Adults	DIM	8.6E−2	6.1E−5	1.5E−4	1.7E−2	2.2E−2	6.1E−4	2.8E−2
		HRI	2.8E−1	6.1E−2	3.7E−2	8.9E−1	5.7E−1	4.0E−4	9.3E−1
	Children	DIM	8.4E−2	6.0E−5	1.4E−4	1.7E−2	2.2E−2	6.0E−4	2.7E−2
		HRI	2.8E−1	6.0E−2	3.7E−2	8.7E−1	5.6E−1	4.0E−4	9.1E−1
Zea mays L.	Adults	DIM	1.1E−2	1.4E−5	6.1E−5	1.3E−2	1.3E−2	4.3E−4	2.5E−2
		HRI	3.7E−2	1.4E−2	1.5E−2	6.7E−1	3.3E−1	2.8E−4	8.4E−1
	Children	DIM	1.0E−2	1.4E−5	6.0E−5	1.3E−2	1.3E−2	4.2E−4	2.5E−2
		HRI	3.6E−2	1.4E−2	1.5E−2	6.6E−1	3.3E−1	2.8E−4	8.3E−1

est (4.62) for *Solanum tuberosum* followed by *Malva neglecta* (4.50), *Spinacia oleracae* L. (3.03), *C. sativum* (3.00), *Portulaca oleracae* (2.59) and *D. carota* (2.28). The trend of MTF for heavy metals in different food crops species grown on wastewater irrigated soil was in order of Zn > Cu > Ni > Mn > Cr > Pb > Cd.

In case of vegetables collected from background and control areas the MTF for Zn, Cd, Pb, Ni, Cu, Cr and Mn ranged from 1.12–3.9, 0.001–0.18, 0.007–0.035, 0.54–1.76, 1.12–3.90, 0.03–0.08, 0.23–1.75, respectively. Highest MTF value (3.90) for Zn was found in *Malva neglecta* followed by *B. rapa* (3.87), *C. sativum* (3.70), *Portulaca oleracae* (3.25), *Spinacia oleracae* L. (3.16) and *Solanum tuberosum* (3.16). The highest MTF value (3.9) for Cu was found in *Pisum sativum* followed by *C. sativum* (3.30), *B. oleracae capitita* (3.22), *Allium* (3.03), *A. sativum* (3.17) and *Solanum tuberosum* (3.11). No significant difference was observed in the trends of MTF for heavy metals in food crops grown in background and control areas.

3.4. Cluster analysis

Cluster analysis (CA) using complete linkage method was applied to classify the vegetables of similar nature on the basis of metals as variables into different groups. In case of wastewater irrigated and control soils, CA classified the food crops into 6 groups as shown in Figs. 5 and 6 and Tables 3 and 4.

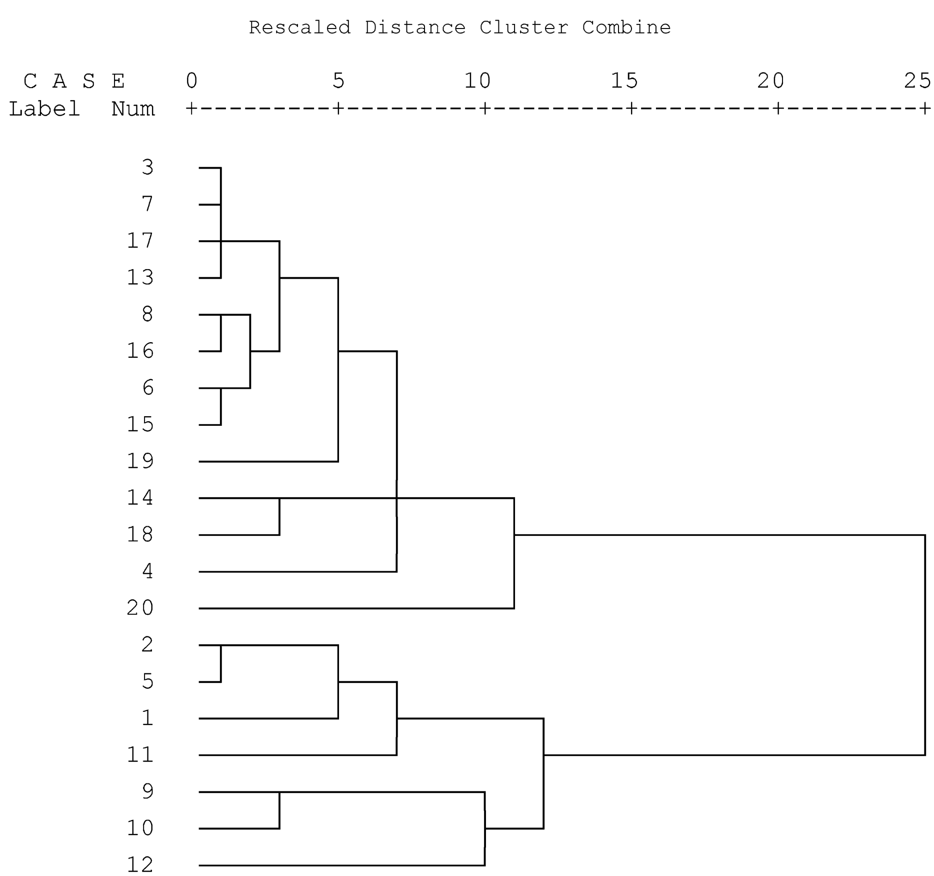

Fig. 6. Dendogram for the classification of food crops grown in control area.

Table 6
DIM and HRI for individual heavy metals caused by the consumption of different selected vegetables grown on control area.

Vegetables	Individuals		Zn	Cd	Pb	Ni	Cu	Cr	Mn
Brassica rapa	Adults	DIM	2.5E−2	–	6.6E−5	1.5E−2	5.3E−3	3.2E−4	2.1E−2
		HRI	8.5E−2	–	1.6E−2	7.7E−1	1.3E−1	2.1E−4	7.1E−1
	Children	DIM	2.5E−2	–	6.5E−5	1.5E−2	5.2E−3	3.2E−4	2.0E−2
		HRI	8.4E−2	–	1.6E−2	7.6E−1	1.3E−1	2.1E−4	6.9E−1
Spinacia oleracae L.	Adults	DIM	2.1E−2	5.8E−6	5.5E−5	1.4E−2	9.1E−3	4.4E−4	2.5E−2
		HRI	7.0E−2	5.8E−3	1.3E−2	7.3E−1	2.2E−1	2.9E−4	8.5E−1
	Children	DIM	2.0E−2	5.7−6	5.4E−5	1.4E−2	8.9E−3	4.3E−4	2.5E−2
		HRI	6.9E−2	5.7E−3	1.3E−2	7.2E−1	2.2E−1	2.9E−4	8.4E−1
B. oleracae botrytis	Adults	DIM	1.8E−2	–	5.8E−5	1.0E−2	1.0E−2	2.6E−4	7.3E−3
		HRI	6.2E−2	–	1.4E−2	5.4E−1	2.5E−1	1.7E−4	2.4E−1
	Children	DIM	1.8E−2	–	5.7E−5	1.0E−2	1.0E−2	2.6E−4	7.2E−3
		HRI	6.1E−2	–	1.4E−2	5.3E−1	2.5E−1	1.7E−4	2.4E−1
Pisum sativum	Adults	DIM	1.8E−2	5.8−6	2.6E−5	1.2E−2	1.8E−2	2.2E−4	1.4E−2
		HRI	6.2E−2	5.8E−3	6.5E−3	6.0E−1	4.6E−1	1.4E−4	4.9E−1
	Children	DIM	1.8E−2	5.7−6	2.5E−5	1.1E−2	1.8E−2	2.2E−4	1.4E−2
		HRI	6.1E−2	5.7E−3	6.4E−3	5.9E−1	4.5E−1	1.4E−4	4.8E−1
Lycopersicum esculantum	Adults	DIM	1.9E−2	2.9−6	6.1E−5	1.6E−2	1.1E−2	4.1E−4	2.4E−2
		HRI	6.3E−2	2.9E−3	1.5E−2	8.2E−1	2.8E−1	2.7E−4	8.2E−1
	Children	DIM	1.8E−2	2.8−6	6.0E−5	1.6E−2	1.1E−2	4.0E−4	2.4E−2
		HRI	6.2E−2	2.8E−3	1.5E−2	8.0E−1	2.8E−1	2.7E−4	8.1E−1
B. Compestris	Adults	DIM	1.5E−2	1.4E−5	4.3E−5	8.2E−3	1.2E−2	4.7E−4	6.8E−3
		HRI	5.2E−2	1.4E−2	1.0E−2	4.1E−1	3.0E−1	3.1E−4	2.2E−1
	Children	DIM	1.5E−2	1.4E−5	4.2E−5	8.1E−3	1.1E−2	4.6E−4	6.7E−3
		HRI	5.1E−2	1.4E−1	1.0E−2	4.0E−1	2.9E−1	3.0E−4	2.2E−1
Hebiscus esculantus	Adults	DIM	1.9E−2	3.0E−4	6.6E−5	1.3E−2	1.0E−2	4.8E−4	6.6E−3
		HRI	6.6E−2	3.0E−1	1.6E−2	6.5E−1	2.7E−1	3.2E−4	2.2E−1
	Children	DIM	1.9E−2	3.0E−4	6.5E−5	1.2E−2	1.0E−2	4.7E−4	6.5E−3
		HRI	6.5E−2	3.0E−1	1.6E−2	6.3E−1	2.6E−1	3.1E−4	2.1E−1
B. oleracae capitita	Adults	DIM	1.3E−2	–	4.9E−5	1.1E−2	1.5E−2	2.4E−4	5.5E−3
		HRI	4.4E−2	–	1.2E−2	5.6E−1	3.8E−1	1.6E−4	1.8E−1
	Children	DIM	1.3E−2	–	4.8E−5	1.1E−2	1.4E−2	2.3E−4	5.4E−3
		HRI	4.4E−2	–	1.2E−2	5.5E−1	3.7E−1	1.5E−4	1.8E−1
Triticum aesativum L.	Adults	DIM	1.5E−2	–	2.3E−5	1.1E−2	5.3E−3	4.1E−4	2.2E−2
		HRI	5.0E−2	–	5.8E−2	5.8E−1	1.3E−1	2.7E−4	7.3E−1
	Children	DIM	1.4E−2	–	2.2E−5	1.1E−2	5.2E−3	4.1E−4	2.1E−2
		HRI	4.9E−2	–	5.7E−3	5.7E−1	1.3E−1	2.7E−4	7.2E−1
Mentha vridis	Adults	DIM	1.2E−2	1.7E−5	6.9E−5	6.9E−3	6.5E−3	5.0E−4	2.6E−2
		HRI	4.3E−2	1.7E−2	1.7E−2	3.4E−1	1.6E−1	3.3E−4	8.7E−1
	Children	DIM	1.2E−2	1.7E−5	6.8E−5	6.7E−3	6.4E−3	4.9E−4	2.5E−2
		HRI	4.2E−2	1.7E−2	1.7E−2	3.3E−1	1.6E−1	3.3E−4	8.5E−1
Coriandum sativum	Adults	DIM	2.4E−2	–	2.6E−5	1.1E−2	1.5E−2	3.5E−4	2.7E−2
		HRI	8.2E−2	–	6.5E−3	5.6E−1	3.9E−1	2.3E−4	9.2E−1
	Children	DIM	2.4E−2	–	2.5E−5	1.1E−2	1.5E−2	3.4E−4	2.7E−2
		HRI	8.0E−2	–	6.4E−3	5.5E−1	3.8E−1	2.3E−4	9.0E−1
Oryza sativa L.	Adults	DIM	8.8E−3	8.7−6	3.2E−5	1.6E−2	1.2E−2	2.5E−4	2.8E−2
		HRI	2.9E−2	8.7E−3	8.0E−3	8.2E−1	3.1E−1	1.7E−4	9.5E−1
	Children	DIM	8.7E−3	8.5−6	3.1E−5	1.6E−2	1.2E−2	2.5E−4	2.8E−2
		HRI	2.9E−2	8.5E−3	7.8E−3	8.0E−1	3.1E−1	1.6E−4	9.3E−1
Lactuca sativa	Adults	DIM	1.6E−2	–	1.7E−5	1.3E−2	9.6E−3	5.0E−4	9.8E−3
		HRI	5.4E−2	–	4.3E−3	6.6E−1	2.4E−1	3.4E−4	3.2E−1
	Children	DIM	1.6E−2	–	1.7E−5	1.3E−2	9.4E−3	5.0E−4	9.6E−3
		HRI	5.4E−2	–	4.2E−3	6.5E−1	2.3E−1	3.3E−4	3.2E−1
Portulaca oleracae	Adults	DIM	2.1E−2	2.0E−5	2.3E−5	6.3E−3	1.3E−2	3.2E−4	8.1E−3
		HRI	7.2E−2	2.0E−2	5.8E−3	3.1E−1	3.3E−1	2.1E−4	2.7E−1
	Children	DIM	2.1E−2	2.0E−5	2.2E−5	6.1E−3	1.3E−2	3.1E−4	8.0E−3
		HRI	7.0E−2	2.0E−2	5.7E−3	3.0E−1	3.3E−1	2.1E−4	2.6E−1
Allium sativum	Adults	DIM	1.5E−2	1.1E−5	3.4E−5	7.3E−3	1.5E−2	3.7E−4	9.0E−3
		HRI	5.0E−2	1.1E−2	8.7E−3	3.6E−1	3.7E−1	2.5E−4	3.0E−1
	Children	DIM	1.4E−2	1.1E−5	3.4E−5	7.0E−3	1.4E−2	3.7E−4	8.8E−3
		HRI	4.9E−2	1.1E−2	8.5E−3	3.5E−1	3.6E−1	2.4E−4	2.9E−1
Allium	Adults	DIM	1.6E−2	2.9−6	1.7E−5	1.1E−2	1.4E−2	4.4E−4	7.6E−3
		HRI	5.5E−2	2.9E−3	4.3E−3	5.7E−1	3.5E−1	2.9E−4	2.5E−1
	Children	DIM	1.6E−2	2.8−6	1.7E−5	1.1E−2	1.4E−2	4.4E−4	7.5E−3
		HRI	5.4E−2	2.8E−3	4.2E−3	5.6E−1	3.5E−1	2.9E−4	2.5E−1
Daucus carota	Adults	DIM	1.8E−2	8.7−6	1.4E−5	8.8E−3	1.0E−2	3.8E−4	9.5E−3
		HRI	6.2E−2	8.7E−3	3.6E−3	4.4E−1	2.5E−1	2.5E−4	3.1E−1
	Children	DIM	1.8E−2	8.5−6	1.4E−5	8.6E−3	9.9E−3	3.7E−4	9.3E−3
		HRI	6.1E−2	8.5E−3	3.5E−3	4.3E−1	2.4E−1	2.5E−4	3.1E−1

Table 6 (*Continued*)

Vegetables	Individuals		Zn	Cd	Pb	Ni	Cu	Cr	Mn
Malva neglecta	Adults	DIM	2.6E−2	–	3.7E−5	5.0E−3	1.3E−2	2.2E−4	1.2E−2
		HRI	8.6E−2	–	9.4E−3	2.5E−1	3.3E−1	1.5E−4	4.2E−1
	Children	DIM	2.5E−2	–	3.7E−5	4.9E−3	1.3E−2	2.2E−4	1.2E−2
		HRI	8.5E−2	–	9.2E−3	2.4E−1	3.2E−1	1.4E−4	4.1E−1
Solanum tuberosum	Adults	DIM	2.1E−2	1.7E−5	5.5E−5	1.4E−2	1.4E−2	4.8E−4	3.7E−3
		HRI	7.0E−2	1.7E−2	1.3E−2	7.2E−1	3.6E−1	3.2E−4	1.2E−1
	Children	DIM	2.0E−2	1.7−6	5.4E−5	1.4E−2	1.4E−2	4.7E−4	3.7E−3
		HRI	6.9E−2	1.7E−2	1.3E−2	7.0E−1	3.6E−1	3.1E−4	1.2E−1
Zea mays L.	Adults	DIM	8.3E−3	–	1.7E−5	9.4E−3	7.7E−3	3.8E−4	1.0E−2
		HRI	2.7E−2	–	4.3E−3	4.7E−1	1.9E−1	2.5E−4	3.5E−1
	Children	DIM	8.1E−3	–	1.7E−5	9.2E−3	7.5E−3	3.7E−4	1.0E−2
		HRI	2.7E−2	–	4.2E−3	4.6E−1	1.8E−1	2.5E−4	3.4E−1

3.5. DIM through food and human health risk

The estimated DIM and HRI values are listed in Tables 5 and 6 for both children and adults. The data indicate that the DIM values for metals were higher for vegetables obtained from wastewater irrigated area as compared to background and control areas (data not shown here). The highest intake of Cd, Pb and Cr was found for all these vegetables, while lowest intake for Zn, Ni, Cu and Mn.

In case of wastewater irrigated area, the HRI for Zn, Cd, Pb, Ni, Cu, Cr and Mn ranged from 7.6E−2 to 1.0E−1, 5.8E−2 to 1.1E−2, 9.8E−3 to 1.1E−2, 9.6E−1 to 4.1E−1, 5.7E−1 to 2.6E−1, 4.2E−4 to 1.5E−4 and 9.3E−1 to 0 1.4, respectively. for adults and from 9.4E−2 to 1.1E−1, 3.5E−2 to 1.7E−2, 3.8E−2 to 1.8E−2, 9.8E−1 to 4.0E−1, 5.6E−1 to 2.5E−1, 4.1E−4 to 1.4E−4 and 9.7E−1 to 1.4, respectively, for children. In case of control area, the HRI for Zn, Cd, Pb, Ni, Cu, Cr and Mn ranged from 8.6E−2 to 2.7E−2, 8.7E−3 to 3.0E−1, 9.4E−3 to 1.2E−2, 8.2E−1 to 4.1E−1, 4.6E−1 to 1.3E−1, 3.4E−4 to 1.4E−4 and 9.5E−1 to 1.2E−1, respectively, for adults, while ranged from 8.5E−2 to 2.7E−2, 8.5E−3 to 1.1E−2, 9.2E−3 to 1.0E−2, 8.0E−1 to 2.4E−1, 3.8E−1 to 1.3E−1, 3.3E−4 to 1.4E−1 and 9.3E−1 to 1.2E−1, respectively, for children.

4. Discussions

Continuous application of wastewater leads to the enrichment of soil with heavy metals. Oxidation state, phase and form of heavy metals strongly affect their bioavailability. Chemical extraction techniques provide a well established mean of identification and characterization of different fractions of heavy metals in soil [18–20]. Fig. 2 shows that metal bioavailable fraction was higher in wastewater irrigated soil as compared to background and control soils. Zn, Cu and Mn have shown high concentrations in the available pool in the present study and can be attributed to the reduction in soil pH into moderately acidic conditions as well as increase in organic contents due to continuous use of wastewater. Long-term application of wastewater resulted an increase in organic carbon and reduction in soil pH which might result in the remobilization of metal pool to more mobile fraction. Based on the fractionation study, the metals can be arranged in the decreasing order of bioavailability Cu > Zn > Ni > Cd > Cr > Pb. The data indicate that the total metal concentrations were higher in wastewater irrigated soil as compared to background and control soils.

The heavy metals accumulation by food crops can cause a serious health concern due to potential public health risks. In this study, the contamination of soil with heavy metals was due to wastewater irrigation and possible atmospheric deposition. One way ANOVA was used to compare the metal concentrations in wastewater irrigated soil with the control and background sites. The data show a significantly higher concentration ($p \geq 0.001$) in wastewater irrigated soil as compared to control soil, indicating that heavy metal concentrations were increased due to the application of wastewater. These results are in agreement with the previous studies [21–23]. Though there was a grade variation in the heavy metal concentrations of the wastewater irrigated, background and control soils but were found within permissible limits set by WHO/FAO except for Zn.

Previous studies [24,25] have indicated that the vegetables grown on wastewater irrigated soil have accumulated high concentration of heavy metals. The present study also indicates that higher concentrations of metals accumulated in vegetables grown on wastewater irrigated soil. All the plants grown on wastewater irrigated soil were contaminated with these heavy metals. In most of the food crops, Zn concentration exceeded the permissible limits set by WHO/FAO. Other heavy metals such as Cd, Pb, Ni, Cu, Cr and Mn were found within permissible limits. In case of food crops grown in background and control areas, these heavy metal concentrations were found within the limits set by WHO/FAO. Using ANOVA to know the differences in vegetables based on their metal contents it showed no statistical difference ($p = 0.99$). In order to classify the vegetables of similar nature CA was applied that grouped the vegetables into 6 groups in case of polluted, background and control areas.

Soil to plant transfer factor is the key component of human exposure to metals through food chain. In order to investigate HRI for selected metals, it is essential to assess MTF. MTF varied greatly for metals in different vegetables and was found higher for Zn, Ni and Mn (Table 2). The high MTF values were found for Zn, Cu, Ni and Mn for leafy vegetables. MTF values were lower than those reported in the literature for food crops [26]. The decrease in MTF values with increasing total metal concentrations in soil indicated an inverse relationship between transfer factor and total metal concentrations as reported for vegetables [27].

For assessing health risk associated with any chemical pollutant, it is necessary to estimate the level of exposure by quantifying the route of exposure of pollutant to target organism. Among different pathways of human exposure, food chain is one of the most important routes. In the study area food crops were contaminated with the heavy metals and consumption of these contaminated food crops can cause human health risks. The food crops were sold in the urban market therefore, the average metal concentrations were used for the calculation of HRI. The data indicate that HRI values were >1, for most of the other metals except Mn, particularly for plants grown on wastewater irrigated soil. In some food crops, HRI was found to be higher like *B. rapa*, *Spinacia oleracae* L., *Lycopersicum esculantum*, *Brassica compestris*, *Mentha viridis*, *C. sativum*, *Lactuca sativa* and *A. sativum*. These vegetable consumption poses a possible health risk regarding Mn intake, while safe with respect to other metals. HRI values for metals were >1 in case of vegetable grown on control area and found to be risk free and generally assumed to be safe.

The oral reference dose for Zn, Cd, Pb, Ni, Cu, Cr and Mn are 3E−1, 1E−1, 4E−3, 2E−2, 4E−2, 1.5E−0, and 3.3E−2 mg/kg/day, respectively (US-EPA, IRIS). The estimated dietary intake of Zn, Cd, Pb, Ni, Cu, and Cr were below the tolerable limits. DIM values for metals through the consumption of vegetables in case of wastewater irrigated and control areas were less than the tolerable limits. The daily intake values for metals both for adults and for children through the consumption of vegetables were less than the limits of RfD limits set by US-EPA IRIS. The findings regarding DIM and HRI in this study suggest that *B. oleracae botrytis*, *Pisum sativum*, *Hebiscus esculantum*, *Triticum aesativum* L., *Oryza sativa* L., *Portulavca oleracae*, *Allium*, *D. carota*, *Malva neglecta*, *B. oleracae capitita*, *Solanum tuberosum* and *Zea mays* L. grown on wastewater irrigated soil were nearly free of any risk but a few species *B. rapa*, *Spinacia oleracae* L., *Lycopersicum esculantum*, *Mentha viridis*, *C. sativum*, and *Lactuca sativa* pose risk with regard to Mn pollution. In case of background and control areas these vegetable were totally risk free.

5. Conclusion

Long-term wastewater irrigation of the soil has caused a substantial build up of heavy metals in the soil as compared to background and control soils, where stream water is used for irrigation. The sequential extraction study suggested that these soils were strongly enriched with Cu, Zn, Mn and Ni. As a result, the vegetables grown in the contaminated soil also showed elevated levels of individual metal. The soil metal concentrations were found within WHO/FAO limits in all study areas. HRI values indicated that vegetables grown on background and control areas were free of any risk for the consumers but in case of wastewater irrigated soil *B. rapa*, *Spinacia oleracae* L., *Lycopersicum esculantum*, *Mentha viridis*, *C. sativum*, *Lactuca sativa* can pose risks, particularly with high concentration of Mn.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.03.047.

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