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ACCUMULATION OF METALS AND METALLOIDS IN TURNIP (*BRASSICA RAPA* L.) IRRIGATED WITH DOMESTIC WASTEWATER IN THE PERI-URBAN AREAS OF KHUSHAB CITY, PAKISTAN

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Abstract

Accumulation of different metals and metalloids was assessed in a potential vegetable crop, turnip (*Brassica rapa* L.) irrigated with domestic wastewater in the peri-urban areas of Khushab City, Pakistan. Two sites at a distance of 15 km radius were selected for this study. The levels of different metals and metalloids such as Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd and Pb, at site-I were 0.06, 15.8, 34.4, 13.5, 1.95, 3.15, 4.25, 41.5, 1.68, 4.79, 8.76, and 27.5 mg kg^{-1}, whereas those at site-II were 0.07, 23.7,41.9, 20.2, 3.70, 3.63, 9.64, 47.08, 2.73, 5.85, 19.09 and 33.85 mg kg^{-1}, respectively. In general, the metal and metalloid concentrations were higher at site-II than those found at site-I, except Cd. The concentrations (mg kg^{-1}) of metals and metalloids in the vegetable at site-I following the order of arrangement in the case of soil were, 9.07, 33.66, 28.48, 0.49, 7.64, 18.73, 35.79, 2.53, 0.41, 6.8, 0.58 and 7.28 mg/kg, whereas those at site-II were 17.09, 49.23, 42.05,0.77, 9.95, 15.10, 55.5, 5.21, 0.63, 16.1, 0.66 and 12.6 mg/kg, respectively. At both sites the levels of metals in the vegetable were below the permissible level except those of Mn, Ni, Zn, Mo and Pb. At both sites, the transfer factor ranged from 0.03-216.3 mg kg^{-1} with Cr having the highest transfer factor. The metal pollution index in soil was in the following order: Cd > Ni > Se > Zn > Mn > Co > Cr > Pb > Mo > Fe > Cu > As and in the vegetables as Mo > As > Cr > Pb > Zn > Co > Se > Fe > Mn > Ni > Cd > Cu, respectively.

Introduction

Accumulation of metals in soils, waters, as well as environment takes place mainly due to anthropogenic activities such as industry, mining, and agriculture. However, agriculture in peri-urban mainly depends on irrigation with domestic wastewater enriched with different types of metals (Amman *et al*., 2002). In most of peri-urban areas of Pakistan, metals present in wastewaters are not usually removed so such types of waters when used for irrigation contaminate both soils and plants growing there. Thus, it is naïve to expect that vegetables and other crops grown in peri-urban areas accumulate considerable amount of metals and hence they pose high health risk to humans and animals consuming such metal-contaminated crops. When ingested by humans, heavy metals such as Cu, Hg, Pb, Zn, As and Al, cause a variety of diseases such as gastro-intestinal malfunctioning, vomiting, pneumonia, depression etc. Similarly, Cd is known to cause lung diseases such as bronchiolitis, alveolitis and emphysema as well as subchronic breathing (Anon., 2002; Young *et al*., 2005). Furthermore, presence of excessive amount of Zn can impair growth and reproduction (Nolan *et al*., 2003).

A variety of vegetables are usually grown in peri-urban areas because of the reason that their transport to vegetable market is very convenient. Of these peri-urban vegetables, turnip (*Brassica rapa*) is a very popular winter vegetable which is grown on large areas. It is highly likely that this vegetable accumulates considerable amount of heavy metals. Thus, the aim of the present research was to appraise the metal contents (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd and Pb) in soil and the vegetable (turnip) grown in the areas treated with sewage water, and determine whether or not this vegetable is suitable for human consumption.

Materials and Methods

Study area sample collection and preparation: The present study was conducted in the peri-urban areas of Khushab. City, Punjab, Pakistan. The study area is located at the coordinates 32.30 °N 72.34 °E, situated on the exact bank of the Jhelum River. The samples of soil and turnip (*Brassica rapa* L.) from the two different sites of Namy Vally and Kurar from the study area irrigated with domestic wastewater. Site-I, Namy Vally, is located at 15 km radius and site-II, Kurar, at 28 km radius from the Khushab city. The sampling was done in the month of November and December 2012. Five replicates of turnip and soil were collected from each of two different sites. The samples were dried in an oven at 72°C for 4 to 5 days and ground into small powder. Ground samples (each 1 g) were digested in an acid mixture (H_2O_2 and H_2SO_4 2:1 ratio) and the digested samples were filtered through Whatman filter paper # 42 and made the final volume of the sample to 50 ml with double distilled water.

Analysis of metals and metalloids: After wet digestion, the vegetable and soil samples were subjected to metal analysis using an atomic absorption spectrophotometer. The metals and metalloids analyzed were Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd and Pb.

Quality assurance: For ensuring the reliability of observed results, some standard quality assurance measures were performed such as handling the samples cautiously, use of double distilled water for dilution and solution preparations, clear-cut cleaning of glassware, etc. Standard solutions were prepared precisely.

Statistical analysis: For statistical analysis of data of each metal, the SPSS software version 20 was used. One-way analysis of variance was applied for soil and vegetable data. Correlation among the values of the soil and vegetable was also employed. The significance differences among mean values were worked out at 0.001, 0.01 and 0.05 probability levels as recommended by Steel & Torrie (1980).

Bioconcentration factor: Bioconcentration factor was examined to assess the risk and associated hazards due to wastewater irrigation and metal accumulation in the edible portion of the vegetable (Cui *et al.,* 2004).

$$\text{Bioconcentration factor} = \frac{\text{Concentration of metal in vegetable}}{\text{Concentration of metal in soil}}$$

Pollution load index (PLI): Metal concentrations have been estimated at each site by the pollution load index (Liu *et al*., 2005).

$$\text{PLI} = \frac{\text{Metal concentration in investigated soil}}{\text{Reference value of the metal in soil}}$$

Results

Analysis of variance of the soil metals showed that the sites differed significantly for Cr, Mn, Fe, Co, Ni, Zn, As, Se, Cd and Pb, but they did not differ for Cu and Mo (Table 1). While in the case of vegetable, the sites differed significantly except for Ni and Cu (Table 2).

Table 1. One-way ANOVA for metal concentration in soil at two different sites.

Metals and metalloids	Site
Cr	0.001***
Mn	107.9***
Fe	107.4 **
Co	75.06***
Ni	5.239***
Cu	1.258ns
Zn	8.692***
As	54.53*
Se	2.051***
Mo	3.75ns
Cd	183.85***
Pb	72.78*

*** = Significant at 0.001 ****** = Significant at 0.01
***** = Significant at 0.05 ns = Non-significant

Table 2. One-way ANOVA for metal concentration in the vegetable at two different sites.

Metals and metalloids	Site
Cr	117.19***
Mn	501.83 ***
Fe	626.21**
Co	0.203***
Ni	9.654ns
Cu	23.73ns
Zn	651.8***
As	12.02***
Se	0.12***
Mo	148.9***
Cd	0.169**
Pb	54.5**

*** = Significant at 0.001 ****** = Significant at 0.01
***** = Significant at 0.05 ns = Non-significant

Metal and metalloid concentrations (mg kg^{-1}) in soil samples: The concentrations of metals and metalloids were higher at site-II than those determined at site-I. The levels of metals and metalloids at both sites in the soil irrigated with canal and sewage water were found below the permissible level (USEPA, 1997) except those of As and Cd. The concentrations (mg kg^{-1}) of metals and metalloids at site-I were: Cr (0.06), Mn (15.8), Fe (34.4), Co (13.5), Ni (1.95), Cu (3.15), Zn (4.25), As (41.5), Se (1.68), Mo (4.79), Cd (8.76) and Pb (27.5) , respectively, whereas at site-II the concentrations observed were Cr (0.07), Mn (23.7), Fe (41.9), Co (20.2), Ni (3.70), Cu (3.63), Zn (9.64), As (47.08), Se (2.73), Mo (5.85), Cd (19.09) and Pb (33.85) mg kg^{-1}, respectively (Table 1). The order of accumulation of metals and metalloids in soil at both sites was: As> Fe> Pb> Mn> Co> Cd > Zn> Mo > Ni> Cu > Se> Cr. (Table 3).

Metal and metalloid concentrations (mg kg^{-1}) in vegetable samples: Except Cu, the levels of metals and metalloids at site-II were higher in *Brassica rapa* than those at site-I. At both sites, the concentrations of metals and metalloids in the vegetable samples irrigated with canal and sewage water were found to be below the permissible level except Mn, Ni, Zn, Mo,Cd and Pb (Anon., 1996). The observed values for different metals and metalloids at site-I were: Cr (9.07), Mn (33.66), Fe (28.48), Co (0.49), Ni (7.64), Cu (18.73), Zn (35.79), As (2.53), Se (0.41), Mo (6.8), Cd (0.58) and Pb (7.28) mg/kg, respectively whereas at site-II were: Cr (17.09), Mn (49.23), Fe (42.05), Co (0.77), Ni (9.95), Cu (15.10), Zn (55.5), As (5.21), Se (0.63), Mo (16.1), Cd (0.66) and Pb (12.6) mg/kg, respectively. The order of accumulation of metals and metalloids in the soil at site-I was: Zn> Mn> Fe> Cr> Mo > Pb > Cu > Ni > As > Co > Cd > Se (Table 4).

Bioconcentration factor for vegetable/soil system: The average of bio-concentration factor was estimated as the concentrations of metals and metalloids in the edible portion of the vegetable associated with the concentrations in soil. Its concentration varied from 0.03-216.3 mg kg^{-1} (Table 5). At site-I, the sequence was: Cr (143.1) > Zn (8.40) > Cu (5.93) > Ni (3.90) > Mn (2.11) > Mo (1.41) > Fe (0.82) > Pb (0.264) > Se (0.248) > Cd (0.066) > As (0.06) > Co (0.036) while at site-II it was: Cr (216.3) > Zn (8.53) > Cu (4.15) > Mo (2.76) > Ni (2.68) > Mn (2.07) > Fe (1.01) > Pb (0.374) > Se (0.233) > As (0.11) > Co (0.038) > Cd (0.03).

Correlation between soil and vegetable metal levels: Correlations for Cr (r =0.675*), Mn (r =0.844**), Co (r =0.697*), Zn (r =0.895**), As (r = 0.755*), Se (r = 0.701*) and Pb (r =0.819**) were positive and significant between the vegetable and the soil, while that for Fe (r =0.628), Ni (r = 0.629), Mo (r =0.402) and Cd (r = 0.568) was non-significant. The correlation for Cu (r = -0.582) between the vegetable and the soil was negative (Table 6).

Pollution load index for metals and metalloids in the soil and vegetable: Metal pollution index in soil ranged in following sequence : Cd (2.179) > Ni (1.891) > Se (1.620) > Zn (1.528) > Mn (1.495) > Co (1.493) > Cr (1.246) > Pb (1.229) > Mo (1.221) > Fe (1.217) > Cu (1.151) > As (1.133) and in the vegetable the sequence observed was Mo (2.379) > As (2.059) > Cr (1.884) > Pb (1.74) > Zn (1.551) > Co (1.549) > Se (1.518) > Fe (1.476) > Mn (1.462) > Ni (1.301) > Cd (1.151) > Cu (0.806), respectively (Table 7).

Table 3. Metal and metalloid concentrations (mg kg^{-1}) in soil samples of two sites of Khushab city.

Metals and metalloids	Sampling sites		Permissible maximum limit (mg kg^{-1})
	Site-I (means ± S.E)	Site-II (means ± S.E)	
Cr	0.06 ± 0.004	0.07 ± 0.003	400
Mn	15.8 ± 0.51	23.7 ± 0.90	80
Fe	34.4 ± 2.02	41.9 ± 1.53	21000
Co	13.5 ± 0.69	20.2 ± 1.54	40
Ni	1.95 ± 0.14	3.70 ± 0.33	300
Cu	3.15 ± 0.26	3.63 ± 0.29	3
Zn	4.25 ± 0.35	6.50 ± 0.27	65
As	41.5 ± 1.64	47.08 ± 1.06	50
Se	1.68 ± 0.03	2.73 ± 0.25	50
Mo	4.79 ± 0.51	5.85 ± 0.48	40
Cd	8.76 ± 0.86	19.09 ± 1.66	200
Pb	27.5 ± 0.69	33.85 ± 2.29	3

Table 4. Metal and metalloid concentrations (mg kg^{-1}) in vegetable samples of two sites of Khushab city.

Metals and metalloids	Sampling sites		Permissible maximum limit (mg kg^{-1})
	Site-I (means ± S.E)	Site-II (means ± S.E)	
Cr	9.07 ± 1.33	17.09 ± 1.31	50
Mn	33.66 ± 2.22	49.23 ± 3.97	30
Fe	28.48 ± 3.05	42.05 ± 4.45	1000
Co	0.49 ± 0.05	0.77 ± 0.04	1
Ni	7.64 ± 0.63	9.95 ± 1.22	2
Cu	18.73 ± 1.28	15.1 ± 1.42	20
Zn	35.79 ± 0.95	55.5 ± 4.69	50
As	2.53 ± 0.17	5.21 ± 0.60	7
Se	0.41 ± 0.04	0.63 ± 0.05	-
Mo	6.8 ± 0.79	16.1 ± 1.12	5
Cd	0.58 ± 0.05	0.66 ± 0.07	0.5
Pb	7.26 ± 0.7	12.6 ± 1.45	10

Table 5. Bioconcentration factor for vegetable/soil system.

Study sites	Bioconcentration factor											
	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Pb
Site-I	143.1	2.11	0.82	0.036	3.90	5.93	8.40	0.06	0.248	1.41	0.066	0.264
Site-II	216.3	2.07	1.01	0.038	2.68	4.15	8.53	0.11	0.233	2.76	0.03	0.374

Table 6. Correlation between soil and vegetable metal levels.

Metals and metalloids	Cr	Mn	Fe	Co	Ni	Cu
Soil-vegetable	0.675*	0.844**	0.628	0.697*	0.629	-0.582
Metals and metalloids	Zn	As	Se	Mo	Cd	Pb
Soil-vegetable	0.895**	0.755*	0.701*	0.402	0.568	0.819**

Table 7. Pollution load index for metals and metalloids in the soil and vegetable.

Metals/ metalloids	Pollution load index											
	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Pb
Soil	1.246	1.495	1.217	1.493	1.891	1.151	1.528	1.133	1.620	1.221	2.179	1.229
Vegetables	1.884	1.462	1.476	1.549	1.301	0.806	1.551	2.059	1.518	2.379	1.131	1.74

Discussion

The levels of metals and metalloids in the soil at both sites irrigated with canal and sewage water were found below the permissible levels (USEPA, 1997) except As and Cd. Similar conclusions were established by Khan *et al*., (1992) and Butt *et al*., (2005) in the peri-urban areas of Faisalabad city. Significant differences between the two sites were found in terms of soil for Cr, Mn, Fe, Co, Ni, Zn, As, Se, Cd and Pb, but they did not differ for Cu and Mo. In the current study soil was heavily loaded with As and Fe whereas the concentration of Cr was too low. At both sites, the concentrations of metals and metalloids in the vegetable samples irrigated with canal and sewage water were found to be below the permissible level except Mn, Ni, Zn, Mo and Pb set by WHO Standards (Anon., 1996).

In the case of vegetable, the sites differed significantly except for Ni and Cu. At both sites, the concentrations of metals and metalloids in the vegetable samples irrigated with canal and sewage water were found to be below the permissible level except Mn, Ni, Zn, Mo and Pb (Anon., 1996). In the current study vegetables were heavily loaded with Zn whereas the concentration of Se was too low. The edible portion of the vegetable samples had metal concentrations which were above the critical limits (Anon., 1996). The levels of Cd and Mn in the vegetable irrigated with city effluents were higher than those reported by Murtaza *et al*., (2003). Previous researchers have reported higher content of heavy metals in the edible portions of vegetables such as radish, spinach, turnip, brinjal, cauliflower and carrot grown under wastewater irrigation as contrast to those grown in canal water irrigation (Arora *et al*., 2008; Liu *et al*., 2006 and Barman *et al*., 2000).

Transfer factors (TF) of heavy metals calculated as the proportion of the amount of a heavy metal absorbed in a plant to the amount of heavy metal in soil, measures the differences in bioavailability of heavy metals to vegetables or to recognize the efficiency of a vegetable species to accumulate a heavy metal (Uwah *et al*., 2011). The transfer factors observed for different metals ranged between 0.05 and 0.28 as shown by Rusu (2005), while the values observed in the present study are much higher (4.15-5.93) than those described by Rusu (2005).

There was a direct positive correlation between Zn and Pb levels in soils with those in the vegetable. In numerous areas of Dar Es Salaam, Africa, where analysis for Pb, Cd, Cr, Zn, Ni and Cu was examined, a direct positive correlation between Zn and Pb levels in soils with those in vegetables was observed (Othman, 2001). Sinha *et al*., (2006) have also established positive and negative correlations between heavy metal absorptions of plants and soil, which may be due to numerous relationships among heavy metals for uptake in the plants (An *et al*., 2004).

The pollution load index (PLI) was worked out for distinguishing pollution which allows evaluation levels of toxic waste among sites and at various phases (Tomlinson *et al*., 1980). The PLI is considered as a concentration factor of heavy metal with relation to the surrounding soil concentration. In the present investigation metal pollution index in soil ranged in following sequence : Cd > Ni > Se > Zn > Mn > Co > Cr > Pb > Mo > Fe > Cu > As and in the vegetable the sequence observed was Mo > As > Cr > Pb > Zn > Co > Se > Fe > Mn > Ni > Cd > Cu. The PLI was greater than 1 in both soil and turnip except Cu of vegetable. Higher values of PLI might be due to anthropogenic activities, municipal waste water, industrial and domestic waste.

Conclusion

Soil is an important constituent of biosphere so any change in soil may affect environment as well as human health. The results of the present investigation suggested that metals and metalloids are transferred from soil and accumulated in vegetable at higher level to become responsible for heavy metal contamination of vegetables. The intake of vegetable may cause health hazardous effects in human. Direct action must be taken to monitor the environmental quality by standard monitoring of metals and metalloids in soil.

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