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Heavy metal status of soil and vegetables grown on peri-urban area of Lahore district

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Abstract

Use of wastewater for growing vegetables has become a common practice around big cities. Wastewater contains organic material and inorganic elements essential for plant growth but also contain heavy metals which may be lethal for animals and humans if their concentration increases than permissible limit. To monitor this situation, a survey was conducted to ascertain the addition of heavy metals into agricultural fields through wastewater irrigation and their translocation in to the edible parts of the vegetables. For this purpose, during year 2009-10, 25 sewage water, 76 soil, 40 leaf and 30 vegetable samples (tomato, spinach, carrot and cauliflower) were taken from peri-urban area of Lahore district. These samples were analyzed for Zn, Cu, Fe, Mn, Pb, Cd and Ni contents. The analysis showed that in wastewater concentration of Cu (100 %), Mn (72 %), Ni (32 %) and Cd (44%) were higher than the safe limits while Zn, Fe and Pb concentration was below permissible limits. In soil DTPA extractable concentration of Zn, Cu, Fe, Mn, Pb, Ni and Cd was in safe limit and ranged between 1.30-8.02, 1.06 - 5.42, 8.60-35.03, 8.7-30.07, 2.11-30.86, 0.28-1.76 and 0.05-0.52 mg kg⁻¹ respectively. In vegetable, 100 % leaf and fruit samples were contaminated and accumulation of heavy metals was higher than the WHO/FAO recommended permissible limits.

Key words: Heavy metals, sewage water, soil, vegetables, peri-urban area

Introduction

Water is required by all living things for their survival and existence on this planet. Of the total available water, about 6% water is used for domestic, 3% for industrial and 90% of available water is used for irrigation purposes. In Pakistan there is shortage of surface water supply. This shortage is being compensated by the conjunctive use of ground water for irrigation to grow cereals and use of urban wastewater (sewage and industrial effluents) for growing vegetables especially in areas around cities (Lone, 1995). Use of wastewater for irrigation gives good crop yields because it contains large amount of organic material and inorganic elements essential for proper growth and development of crops (Mitra and Gupta, 1999). The heavy metals which have been identified from different industrial effluents are Cr, Cd, Cu, Pb, Ni, Zn, Co, Mg, Fe and As (Asaolu, 1995). Some of the heavy metals are essential for proper plant growth but the others are not essential so after accumulating in the soil they could be transferred to food chain and caused harmful effects (Ghafoor et al., 1995; Malla et al., 2007). Elements like Fe, Mn, Co, Cu and Ni are essential and their permissible limits are quite low but in wastewater they are present in concentrations higher than their permissible limits and show toxic effects on biological system.

Heavy metals are harmful because of their nonbiodegradable nature, long biological half-lives and their potential to accumulate in different body parts. Most of the heavy metals are extremely toxic because of their solubility in water. Even low concentrations of heavy metals have damaging effects to man and animals because there is no established mechanism for their elimination from the body. Nowadays heavy metals are ubiquitous because of their excessive use in industrial applications so wastewater contains substantial amounts of toxic heavy metals, which create problems (Singh et al., 2004; Chen et al., 2005). In human, heavy metals can directly damage mental and neurological function, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes. Systems in which toxic elements can induce impairment include the blood and cardiovascular, detoxification pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive, and urinary (Greenwood and Earnshaw, 1986).

Irrigation of agriculture soils through wastewater may not only result in soil contamination, but also affect food quality and safety (Muchuweti *et al.*, 2006). In plants heavy metal toxicity is the result of complex interaction of major toxic ions with other essential or non-essential ions. These metals reduce the activity of hydrolysis viz., α amylase, phosphatase, RNAse and proteins. They interfere in the enzyme action by replacing metal ions from the

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metaloenzymes. Among heavy metals, cadmium shows severe effect on seedling length and dry weight (Raza et al., 2013), reduces photosystem II activity, causes structural change in chloroplast and thus reduces photosynthesis, availability of carbon dioxide, lowers stomatal conductance, reduces total lipids, glycolipids and neutral lipids, interfere with membrane permeability and reduces respiration in leaves (Agarwal, 2002). Toxic level of Pb inhibits germination, reduces rate of photosynthesis, transpiration, gaseous exchange in leaves and total chlorophyll production by altering relative proportion of chlorophyll a and chlorophyll b. Similarly, toxic levels of nickel and chromium show drastic effect on dry matter production and vield (Agarwal, 2002). Keeping in view the above mentioned facts, this survey was conducted to evaluate heavy metals in wastewater, soil and vegetables grown around Lahore district.

Materials and Methods

Sample Collection and preparation

The survey was conducted around peri-urban area of Lahore during 2009-2010. In these areas wastewater (sewage & industrial) was used by farmers for raising vegetables. In the field, soil samples were collected from two depths (0-15 cm and 15-30 cm), by using spiral auger of 2.5 cm diameter. Soil samples from the farmer's fields were randomly collected and bulked together to form a composite sample and transported to the laboratory. Samples were air-dried, crushed, passed through 2 mm mesh sieve and stored in plastic jars.

Vegetables (spinach, *Amaranthus caudatus;* carrot, *Daucus carota; cauliflower, Brassica oleracea*; and tomato, *Lycopersicon sculenetum) samples were* collected randomly in triplicate from the same field. In laboratory, vegetables were washed with distilled water to remove soil particles, sun dried, crushed and ground for heavy metals determination.

The sampling of wastewater was done from water courses of same field from where the soil and vegetable samples were collected so that the quality of irrigation water may be monitored which was being applied to the field rather than at drains/outlets of pumping stations. Samples were collected in plastic bottles containing 2 mL concentrated nitric acid to avoid microbial activity during storage. Total 25 wastewater, 76 soil and 70 vegetable samples were collected for heavy metal determination.

Soil, water and plant analysis

To estimate heavy metals concentration, 25 g dried soil sample was mixed with 50 mL of DTPA (diethylene triamin penta acetic acid) extracting solution at pH 7.3 and kept on a reciprocal shaker at 120 rpm for 2 h. The aliquot was centrifuged at 5000 rpm for 5 min and supernatants were collected for heavy metal determination (Lindsay and Norvell, 1978).

Heavy metal concentrations in vegetable samples were estimated by digesting with tri-acid mixture (HNO₃ + $HClO_4 + H_2SO_4$; 5: 2: 1). The digested samples were cooled and filtered through Whatman No.42 filter paper and volumes were made up to 100 ml using distilled water.

Wastewater samples were analyzed by method of AOAC (1984).

Heavy metal (Zn, Cu, Fe, Mn, Pb, Ni and Cd) concentrations in wastewater, soil and vegetable samples were estimated on Atomic Absorption Spectrophotometer (Shimadzhu-7000, Japan) by using respective hallow cathode lamp.

Results and Discussion

Wastewater analysis

In Pakistan, the farmers are blindly using untreated sewage/industrial water for vegetable production especially in peri-urban areas. In present survey sewage/industrial wastewater samples from twenty five different localities of Lahore district were analyzed for heavy metal concentration. The results regarding heavy metal content in sewage/industrial water are presented in Table 1. The obtained results showed that in sewage/industrial water samples, the concentration of Zn, Cu, Fe, Mn, Pb, Cd and Ni in the sewage/industrial water ranged from 0.1 - 1.07, 0.24 - 1.65, 0.27 - 0.94, 0.19 - 1.65, 0.03 - 0.65, 0.001 - 0.21 and 0.01 - 0.23 ml L⁻¹ with an average values of 0.58 ± 0.28 , 0.94 ± 0.38 , 0.60 ± 0.19 , 0.94 ± 0.35 , 0.34 ± 0.18 , 0.10 ± 0.009 and 0.12 ± 0.06 mL L^{-1} . These results clearly exhibited that 100, 72, 32 and 44% wastewater samples had concentration of Cu, Mn, Ni and Cd above the safe limits whereas Zn, Fe and Pb contents were below the safe limits. Constant use of such sewage/industrial water for irrigation over longer period may cause buildup of heavy metals up to toxic levels for plant and animal health (Kirkhan, 1983). Elevated levels of heavy metals in sewage water were also investigated by other scientists in Pakistan and they found excessive concentration of Cu, Mn, Pb and Cd in sewage water samples from Peshawar (Ehsan et al., 2011) and Jagtap et al. (2010) reported higher contents of Zn, Cu, Pb, Ni, Cd and Cr in wastewater samples from Rawalpindi Area. Ensink et al. (2007) found same results in industrial water of Faisalabad and Lone et al. (2003) in sewage water of Attok area.

Element	Range	Avgerage	Standard Deviation	Samples above safe limit (%)	WHO safe limits (ml L ⁻¹)
Zn	0.1-1.07	0.58	0.28	-	2.0
Cu	0.24-1.65	0.94	0.38	100	0.2
Fe	0.27-0.94	0.60	0.19	-	-
Mn	0.19-1.65	0.92	0.35	72	0.2
Pb	0.03-0.65	0.34	0.18	-	5
Ni	0.01-0.23	0.12	0.06	32	0.2
Cd	0.001- 0.21	0.10	0.009	44	0.01

Table 1: Heavy metal concentration of wastewater used for irrigation (ml L⁻¹)

* (WHO, 2007) (number of samples 25)

Table 2: Heavy metal status of fields receiving wastewater (mg kg-¹)

			Soil D	epth (cm)			Safa
Flomont	0-15 cm			15-30 cm			- Safe
Element	Range	Average	STDV	Range	Average	STDV	- limits*
Zn	1.58 - 8.02	5.33	1.99	1.30 - 7.70	4.04	2.04	300
Cu	1.16 - 5.42	3.41	1.19	1.06 - 4.23	1.96	0.77	140
Fe	8.89 - 35.03	19.54	6.56	8.6 - 28.76	14.94	5.13	-
Mn	9.12 - 30.08	18.11	4.84	8.7 - 24.87	14.19	4.13	-
Pb	4.78 - 30.86	14.99	5.78	2.11 - 22.75	11.19	4.61	300
Ni	0.68 - 1.76	1.15	0.27	0.28 - 1.68	1.00	0.30	75
Cd	0.098 - 0.52	0.29	0.11	0.05 - 0.41	0.21	0.09	3

*(WHO, 2007) (Number of samples 76)

Soil Analysis

DTPA extractable heavy metals concentration of soil samples, collected from the same point where the water samples were collected is presented in Table 2. The results showed that Zn, Cu, Fe, Mn, Pb, Ni and Cd content in upper layer of soil ranged from 1.58-8.02, 1.16-5.42, 8.89- 35.03, 9.12- 30.08, 4.78- 30.86, 0.68- 1.76 and 0.098- 0.52 mg kg⁻¹, respectively, with an average value of 5.33 ± 1.99 , 3.41 ± 1.19 , 19.54 ± 6.56 , 14.99 ± 5.78 , 16.48 ± 5.66 , 1.15 ± 0.27 , 0.29 ± 0.11 mg kg⁻¹. According to the WHO (1996) and FAO (1985) limits, all soil samples were in safe range. It is interesting that heavy metal content of wastewater were high whereas their concentration in soil was low. This might be due to the insolubility of metals because of high soil pH. Factors like soil pH, amount of organic matter, redox potential of soil and rate of addition of metals mainly affect their adsorption and retention in soil (McBride, 1994). Similar results were reported by Khan et al. (1992) and Butt et al. (2005) in Faisalabad city Jawahar and Javed (1997) in Sheikhupura and Maredke area while Mian and Ahmad (1997) reported the same trend in Rawalpindi area.

Plant Analysis

Vegetables are used for common human nutrition and the edible portions of different vegetables varied. Some vegetables are consumed as leaf like spinach, coriander whereas other are used as fruit or root like carrot, tomato and cauliflower. Therefore the concentration of heavy metals was investigated in both leaf and fruit of vegetables. The results presented in Table 3 showed that Zn, Cu, Fe, Mn, Pb, Ni and Cd contents of vegetable leaves ranged from 38.4-153.2, 12.2-199.3, 164.7-586.1, 26.9-151.7, 30.8- 97.2, 10.3- 35.5 and 2.9- 10.3 mg kg⁻¹, respectively, with average values of 95.8 ± 31.61 , $55.75 \pm$ 42.57, 250.5 \pm 96.79, 89.3 \pm 22.07, 64.0 \pm 15.02, 22.9 \pm 7.29 and 6.6 \pm 1.29 mg kg⁻¹. It was revealed from the results that all vegetable leaf samples have heavy metal concentration higher than the permissible limits set by the WHO, 1996. The uptake of heavy metal by vegetables is not only affected by plant species and physicochemical characteristics of soil but temperature and rain fall also exert substantial effect. Farid et al. (2003) collected spinach, bitter gourd, okra, pumpkin and egg plant samples and observed that they were contaminated with heavy metals similarly Ronag et al. (2005) collected spinach and turnip samples from market and found that these vegetables were unsafe for eating due to higher heavy metal concentration.

Vegetable fruit samples were also analyzed to assess their heavy metal concentration and results are given in Table 4. The heavy metal contents in vegetable fruit samples ranged from Zn, 35- 55; Cu, 10.7- 179.8; Fe, 152.6 -287.5; Mn, 30.8- 125.7; Pb, 18.9- 84.6; Ni, 9.4-35.8 and Cd, 1.2- 9.87 mg kg⁻¹. The content of heavy metals in all vegetable fruit samples were above the

Element	Zn	Cu	Fe	Mn	Pb	Ni	Cd
				Spinach			
Range	70.6-153.2	37-199.3	161-586	59.4-152	42-97.2	26.7-35	4.8-10.3
Average	108.4	93.15	332.40	86.19	64.62	30.21	6.47
SD	30.77	59.07	151.23	28.38	15.99	2.92	1.57
				Cauliflower			
Range	38.9-121.3	12.3-45.8	98 - 370	37.4-75.3	36-68.4	12 - 35	3.9-6.5
Average	81.19	25.46	183.13	56.96	58.45	19.47	5.15
SD	25.16	11.59	100.52	10.65	9.15	6.15	0.80
				Carrot			
Range	43.1-121.8	19.6-45.6	110-453	47.6-95.8	49-78.4	10-34.7	3.8-7.7
Average	82.62	25.82	241.96	67.22	59.92	22.0	5.22
SD	25.13	7.92	119.5	15.01	8.94	8.67	1.13
				Tomato			
Range	38.4-119.7	12.2-31.1	61-227	26.9-86.4	31-59	10 - 29	2.9-5.7
Average	57.26	18.0	104.83	55.61	41.94	19.82	4.62
STDV	24.47	5.75	57.63	17.38	7.93	4.98	0.86
	eavy metal accur	nulation in edibl	e portion of ve	getables (mg k	g ⁻¹)		
	eavy metal accur Zn		e portion of ve Fe	getables (mg k Mn	g ⁻¹) Pb	Ni	Cd
Table 4: He		nulation in edibl	-		<i>。</i> ,	Ni	Cd
Table 4: Ho Element	Zn	nulation in edibl	-	Mn	<i>。</i> ,	Ni 9.87-34.6	
Table 4: He		nulation in edibl Cu	Fe	Mn Cauliflower	Pb		Cd 1.5-6.7 5.17
Table 4: Ho Element Range	Zn 35 - 55	nulation in edibl Cu 15.2 – 35.6	Fe 52 -165	Mn Cauliflower 34.9- 63	Pb 28.7-45.9	9.87-34.6	1.5-6.7
Table 4: Ho Element Range Average	Zn 35 - 55 41.43	nulation in edibl Cu 15.2 – 35.6 22.68	Fe 52 -165 107	Mn Cauliflower 34.9- 63 49.15	Pb 28.7-45.9 36.09	9.87-34.6 18.42	1.5-6.7 5.17
Table 4: Ho Element Range Average	Zn 35 - 55 41.43	nulation in edibl Cu 15.2 – 35.6 22.68	Fe 52 -165 107	Mn Cauliflower 34.9- 63 49.15 9.84	Pb 28.7-45.9 36.09	9.87-34.6 18.42	1.5-6.7 5.17 1.44
Table 4: Ho Element Range Average STDV	Zn 35 - 55 41.43 6.50	nulation in edibl Cu 15.2 – 35.6 22.68 6.19	Fe 52 -165 107 40.35	Mn Cauliflower 34.9-63 49.15 9.84 Carrot	Pb 28.7-45.9 36.09 5.18	9.87-34.6 18.42 6.87	1.5-6.7 5.17 1.44
Table 4: Ho Element Range Average STDV Range	Zn 35 - 55 41.43 6.50 45.8-95.1	nulation in edibl Cu 15.2 - 35.6 22.68 6.19 23.3-179.8	Fe 52 -165 107 40.35 103 -287	Mn Cauliflower 34.9-63 49.15 9.84 Carrot 50 -125	Pb 28.7-45.9 36.09 5.18 41.6-84.6	9.87-34.6 18.42 6.87 13.9-35.8	1.5-6.7 5.17 1.44 5.2-9.9
Table 4: Ho Element Range Average STDV Range Average	Zn 35 - 55 41.43 6.50 45.8-95.1 61.30	nulation in edibl Cu 15.2 - 35.6 22.68 6.19 23.3-179.8 41.16	Fe 52 -165 107 40.35 103 -287 190.7	Mn Cauliflower 34.9-63 49.15 9.84 Carrot 50 -125 80.25	Pb 28.7-45.9 36.09 5.18 41.6-84.6 57.90	9.87-34.6 18.42 6.87 13.9-35.8 22.04	1.5-6.7 5.17 1.44 5.2-9.9 6.58
Table 4: He Element Range Average STDV Range Average SD	Zn 35 - 55 41.43 6.50 45.8-95.1 61.30	nulation in edibl Cu 15.2 - 35.6 22.68 6.19 23.3-179.8 41.16	Fe 52 -165 107 40.35 103 -287 190.7	Mn Cauliflower 34.9-63 49.15 9.84 Carrot 50-125 80.25 24.42	Pb 28.7-45.9 36.09 5.18 41.6-84.6 57.90	9.87-34.6 18.42 6.87 13.9-35.8 22.04	1.5-6.7 5.17 1.44 5.2-9.9 6.58 1.56
Table 4: Ho Element Range Average STDV Range Average	Zn 35 - 55 41.43 6.50 45.8-95.1 61.30 14.23	nulation in edibl Cu 15.2 - 35.6 22.68 6.19 23.3-179.8 41.16 48.80	Fe 52 -165 107 40.35 103 -287 190.7 58.98	Mn Cauliflower 34.9-63 49.15 9.84 Carrot 50 -125 80.25 24.42 Tomato	Pb 28.7-45.9 36.09 5.18 41.6-84.6 57.90 13.85	9.87-34.6 18.42 6.87 13.9-35.8 22.04 7.07	1.5-6.7 5.17 1.44 5.2-9.9 6.58

Table 3: Heavy metal accumulation in leaves of vegetables (mg kg⁻¹)

critical limits (WHO, 1996 and Asaolu, 1995). Similar results were reported by many scientists. Ahsan *et al.* (2011) investigated heavy metal contents in edible portion of vegetables and found that Zn, Cu, Pb, Ni, Cd and Cr contents were higher than the safe limits. Arora *et al.* (2008) have reported the buildup of heavy metal in edible portion of vegetable. Liu *et al.* (2006) and Barman *et al.* (2000) also reported excessive concentration of heavy metals in edible portion of vegetables.

Conclusion

This study was conducted to investigate the heavy metals content in soil and vegetable receiving wastewater around Lahore district. The results indicated that in wastewater the contents of Cu, Mn, Ni and Cd were higher than the safe limits. The accumulation of heavy metals in soil samples were lower than the permissible limits but in vegetables, the content of Zn, Cu, Fe, Mn, Pb, Ni and Cd were higher than the critical limits. It indicated that heavy metals may be absorbed directly from wastewater whereas their accumulation in soil is relatively slow. The accumulation of heavy metals was more in leaf than fruit.

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