Research Article

Rhizosphere Saturation With Carcinogenic Heavy Metals (Cd, Cr, Pb and Ni) and their Uptake by Crops in Urban Wastewater Irrigated Lands- A Mayday Call

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Abstract | The depletion of fresh water resources in the developing world has necessitated the use of untreated wastewater use in agriculture, posing serious health risks. In the current research study; soil, plant and water samples were collected from the areas irrigated with wastewater from two major industrial zones of Khyber Pakhtunkhwa, Pakistan i.e. Hayatabad Industrial Estate (HIE), Peshawar and Gadoon Industrial Estate (GIE), Swabi. The results showed that soil texture of both locations varied from loam to silty clay loam with silt loam being the dominant textural class. The pH was above 7 in majority of the soil samples, except for a few where the pH was slightly acidic, while EC less than 2 dS m^{-1}. The heavy metal status and its uptake by various plants irrigated with industrial wastewater were analyzed. Results of soil analysis indicated that Cd, Cr, and Pb were higher than the permissible limit for Peshawar soils with a mean value of 11.92, 25.56 and 99.6 mg kg^{-1}, respectively. The mean values of Cd, Cr, and Pb in Swabi were 8.90, 13.68 and 59.3 mg kg^{-1}, respectively, which were lower as compared to Peshawar. The values of Ni, on the contrary were higher in Swabi (61.1 mg kg^{-1}) than wastewater irrigated Peshawar soils (50.1 mg kg^{-1}). The mean values were within the permissible limits of heavy metals (Cd=0.02, Cr=1.30, Pb=2.00 and Ni=10.00 mg kg^{-1}) while some phytotoxic values of Cd and Cr in Peshawar and Ni in Swabi soils were recorded. The analysis of plant samples (cabbage, wheat, maize, spinach, common grass, *Rumex crispus* L., Okra), grown on wastewater irrigated soils, were compared which resonated with the results soil samples, indicating higher accumulation of Cd, Cr and Pb in Peshawar samples while higher Ni concentration in Swabi plant samples. It can be concluded that persistent use of untreated industrial wastewater causes accumulation of carcinogenic heavy metals in soil, indicating the need practice in situ stabilization techniques for producing safe and healthy crops.

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Introduction

In the urban and peri-urban areas of the developing countries, the anthropogenic addition of heavy metals to agricultural soils primarily results from mining activities, intended application of synthetic fertilizers, and irrigation with wastewater. Another major contributor is the extensive pesticide application and insecticides, particularly vegetables, in urban agricultural soils in developing countries (Aoyama and Tanaka, 2013).

The Environmental Protection Agencies (EPAs) of most countries around the globe have made it mandatory to pre-treat wastewater, especially the industrial discharge, before it enters the main water channels which is later used for irrigation (Kalavrouziotis, 2011). However, since wastewater treatment is a costly process and the scale of wastewater generation is enormous, wastewater treatment is seldom practiced. This direct application of untreated wastewater to crops increases the risk of heavy metals being taken up by plants and entering the food chain. The practice is more common in developing countries, where limited fresh water resources are available and financial resources for wastewater treatment are limited (Singh *et al*., 2010; Surdyk *et al*., 2010).

The direct application of untreated wastewater has led to various overlooked problems, such as the increase risk of diseases, including cancer. The International Agency for Research on Cancer has identified Cd, Cr, Pb and Ni as Group I carcinogens, among 120 elements known to cause cancer in humans (IARC, 2020). Researchers worldwide are working to find ways to minimize the entry of these metals into the food cycle by developing safe and cost-effective in situ remediation technologies that making these metals more stable in plants and less mobile.

Problems such as overpopulation, shrinking freshwater resources, climate change and the increased water requirements of high-yielding varieties have further necessitated the use of wastewater in both urban and peri-urban agriculture of industrial states globally. Since the industries are also located near big cities, the industrial wastewater is used untreated for growing crops and vegetables. The industrial wastewater contains carcinogenic elements (e.g., Cd, Cu, As, Cr, Ni, Pb, Mn, Mo and Zn etc.), many of which are heavy metals and their higher levels can be toxic to plants. The accumulation of heavy metal has been reported to build up in soil overtime (Kennish, 1992) that may be toxic to plants or may lead to bio-accumulation and cause soil deterioration (Kirkham, 1983). In a study on vegetables Khan *et al*. (2015), concluded that the high consumption of these vegetables can pose a high health risk for the consumers.

Many remediation techniques are applied as soil amendment to reduce heavy metal uptake by plants. In situ stabilization techniques are recommended for stabilizing heavy metals in agricultural soils where untreated wastewater has been applied for irrigation purpose. This reduces the heavy metal mobility in soil through the addition of a stabilization/immobilization agent. The stabilization agent changes the environmental condition enough for the element stabilization, leaching or transformation into an unavailable complex (Kumpiene *et al*., 2019). Hence, it cannot be taken up by the plant. Mulligan *et al*. (2001) have compared the use of some common stabilization techniques with soil-stabilizing agents and found that soil stabilization of metals is the most appropriate technique for crop production.

Some of the chemicals used to make the heavy metals mobile and leach them down below root zone are called chelates, i.e., Ethylenediaminetetraacetic acid (EDTA), Nitrilo-Triacetic Acid (NTA), Ethylene Diamine DiSuccinic acid (EDDS) and citric acid, hence reducing their phytotoxicity in the rhizosphere (Quartacci *et al*., 2006; Meers *et al*., 2005). This mobilization, however, may prove detrimental to the sub-surface water resources. Additionally, this ex-situ remediation technique of using chelating agents to wash out soil on large scale is not feasible because of the extent of the problem, and the cost of chemicals, hence is an unlikely solution for dealing with large areas of heavy metal contamination.

The foregoing findings indicate that various methods exist for the remediation of soils off heavy metals with some effective for one element while some effective for another. In this research study, the main aim was to target heavy metals commonly found in urban agriculture soils irrigated with untreated industrial wastewater, through sole and integrated application of various organic and inorganic amendments and natural clays in various combinations to check their ability to reduce uptake of specifically Cd, Cr, Pb and Ni by lettuce grown on a natural and spiked soils.

The addition of soil amendments showed a reduction in the phyto-toxicity of various elements while simultaneously improving the availability of depleted nutrients (Bolan *et al*., 2003). Phosphorus and humic acid, at five to ten times the recommended doses, have been used by researchers.

Amendments like phosphorous compounds have been effective in stabilizing one or two heavy metals (Melamed *et al*., 2003) while humic substances have been reported to reduce leaching of metals from the soil (Warren *et al*., 2003). Keeping in view the extensive use of wastewater for irrigation and the effectiveness of various amendments used in the past, a series of experiments were conducted to determine the best possible source, rate of amendment application and their best combinations to minimize the plant uptake of metals and enhance its phyto-stability in soil.

Materials and Methods

A survey was conducted to assess the levels of heavy metals in soils irrigated with industrial wastewater from the Gadoon Industrial Estate in District Swabi and the Hayatabad Industrial Estate in District Peshawar, of the Khyber Pakhtunkhwa province in Pakistan. Composite soil samples were collected from each site at three depths: 0–15 cm, 16–30 cm, and 31–45 cm. Plant samples of cabbage, wheat, maize, spinach, lawn grass, *Rumex crispus*, and okra (both leaves and edible parts) were also collected. In total, fifteen sites were selected across Peshawar and Swabi, and the locations were mapped using GPS to produce satellite location maps (Figures 1, 2).

Figure 1: *Site location of soil and plant samples collected from district Peshawar irrigated with untreated industrial wastewater from Hayatabad Industrial Estate, Peshawar.*

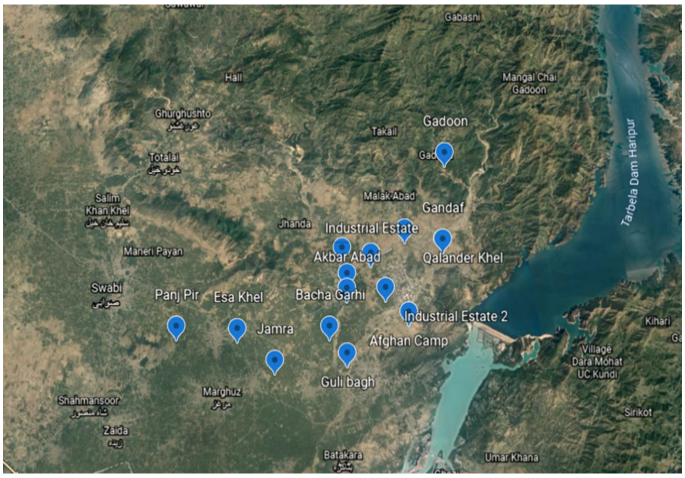

Figure 2: *Site location of soil and plant samples collected from district Swabi irrigated with untreated industrial wastewater from Gadoon Industrial Estate, Swabi.*

The AB-DTPA extractable heavy metal content (Cd, Cr, Pb, and Ni), soil texture, pH, electrical conductivity (EC), and organic matter were analyzed in all soil samples. The sites with the highest levels of heavy metal accumulation were recorded along with their GPS coordinates for potential further investigation.

Collection of soil and plant samples

Soil samples were collected using an auger from depths of 0-15 cm, 16-30 cm, and 31-45 cm at various locations in Peshawar and Swabi, focusing on sites irrigated with industrial wastewater. The samples were air-dried, ground using a wooden hammer, sieved through a 2mm sieve, and stored in plastic bags for laboratory analysis. Additionally, plants such as cabbage, wheat, maize, spinach, lawn grass, *Rumex crispus*, and okra, were collected for heavy metal analysis using the methodology of Walsh and Beaton (1977). The plant leaves were washed, oven-dried, ground with an electric grinder, labeled, and stored in capped bottles. Both soil and plant samples were analyzed for physicochemical characteristics and heavy metal concentrations.

Laboratory analysis

The following standard procedures of analysis used in the Department of Soil and Environmental Sciences, The University of Agriculture, Peshawar, Khyber Pakhtunkhwa, Pakistan, were used for the experiment.

Soil pH

Soil water suspension (1:5) was prepared by taking 5 grams soil in a conical flask and then added 25 mL distilled water. The suspension was shaken for 30 minutes on a horizontal shaker. Before determining the pH, the pH meter was calibrated using standard buffer solutions of pH 4 and pH 9. The soil pH was then measured in the suspension (McLean, 1982).

Soil EC

A 1:5 soil-water suspension was prepared for determine the electrical conductivity by using EC meter (Rhoades, 1982). The meter was calibrated using standard 0.1 N KCL solution.

Soil organic matter

One gram of soil was mixed with 10 mL of 0.5 N Potassium Dichromate ($K_2Cr_2O_7$) and 20 mL of concentrated H_2SO_4 in a conical flask. The mixture was gently shaken and allowed to react for 30 minutes. Afterward, 200 mL of distilled water was added, and the solution was filtered through filter paper (Whatman No. 40). Finally, 2-3 drops of Ortho-phenolphthalein indicator were added to the filtrate, which was then titrated against 0.5 N ferrous sulfate ($FeSO_4 \cdot 7H_2O$) until the color changed from dark green to dark brown (Nelson and Sommer, 1982).

Percent OM was calculated as follows:

$$\%OM = \frac{[(\text{mL of K2Cr2O7 x N}) - (\text{mL of FeSO4.7H2O x N})] \times 0.69}{\text{wt of Soil}}$$

AB-DTPA extractable heavy metals

A 20 mL AB-DTPA solution was added to 10 grams of soil in a 250 mL conical flask and shaken for 30 minutes. The solution was filtered through filter paper (Whatman No. 42), and the heavy metal content in the filtrate was determined using an Atomic Absorption Spectrophotometer (Soltanpour and Schawab, 1977).

Heavy metals content in plant leaves (wet digestion)

A 0.5-gram plant sample was digested with 10 mL concentrated HNO_3 and kept overnight. Subsequently, 4 mL Perchloric acid ($HClO_4$) was then added, and the sample and heated at 300 °C until the solution turned colorless. The digested solution was then diluted with distilled water to a final volume of 100 mL (Walsh and Beaton, 1977).

Statistical analysis

The data were analyzed using Statistix 8.1 and Genstat Discovery Edition 3 package (Steel and Torrie, 1980). The means were separated using least significant difference (LSD) test at 5 % level of probability.

Results and Discussion

The sampling locations included urban and peri-urban areas of the Peshawar and Swabi districts in the Khyber Pakhtunkhwa province of Pakistan. The soil, plant, and water samples collected from each location were analyzed for selected heavy metals (Cd, Cr, Pb, and Ni).

Assessment of heavy metal content (Cd, Cr, Pb and Ni) in soil and crops irrigated with wastewater in Peshawar and Swabi

Soil, plant and water samples were collected from agriculture lands with a history of wastewater irrigation around the industrial zones in Peshawar and Swabi. Fields irrigated with effluent from the Hayatabad Industrial Estate (HIE, Latitude: 33.9850 Longitude: 71.4542) in Peshawar showed elevated concentrations of Cd, Cr, and Pb, while soil irrigated with wastewater from the Gadoon Industrial Estate (GIE, Latitude: 34.1199 Longitude: 72.4699) in Swabi exhibited higher concentrations of Ni. The nitrogen content in all soil samples from both districts was found to be less than 1%. Organic matter content was also low, 12 with values below 1%. The soils were strongly calcareous in nature, containing approximately 18% lime. Phosphorus was deficient in almost all samples, whereas potassium content was generally sufficient across the samples (Table 1).

Table 1: *Extent of Heavy Metals in Irrigation Waters Polluted with Waster water from Hayatabad Industrial Estate Peshawar.*

S.	Properties	Unit	Waste water	Tubewell water
1.	pH	–	7.03 (±0.08)	7.66 (±0.13)
2.	EC	dS m^{-1}	1.49 (±0.08)	0.34 (±0.07)
3.	Cd	mg L^{-1}	0.25 (±0.04)	ND*
4.	Cr	mg L^{-1}	0.21 (±0.03)	ND
5.	Cu	mg L^{-1}	1.12 (±0.04)	0.09 (±0.04)
6.	Fe	mg L^{-1}	20.47 (±0.31)	0.14 (±0.04)
7.	Mn	mg L^{-1}	0.84 (±0.29)	0.06 (±0.08)
8.	Ni	mg L^{-1}	0.13 (±0.03)	ND
9.	Pb	mg L^{-1}	3.34 (±0.09)	0.05 (±0.18)
10.	Zn	mg L^{-1}	0.66 (±0.16)	0.07 (±0.09)

**ND = Not Detected. Values are a mean of samples taken at different intervals. Values in parenthesis indicate Standard deviation.*

Soil pH

The pH data of soil samples collected from Peshawar and Swabi are presented in Table 2. The mean pH value across both the locations in the surface soil (0-

15 cm) varied from 6.64 to 7.88 with a mean value of 7.27. The pH of 16-30 cm depth ranged from 6.50 to 7.93 with a mean value of 7.24, whereas the pH at 31-45 cm depth ranged from 6.73 to 8.11 with a mean value of 7.35. The descriptive statistics (Table 2) showed a minimum mean pH of 6.62 and a maximum pH of 7.95. The location wise pH values for the soil depths (0-45 cm) in both the districts are given in Table 6 and depth wise pH values of Peshawar are presented in Supplementary Table 8.

Table 2: *Mean pH values (0-45 cm) of soil samples in wastewater irrigated soil in urban and peri-urban areas of Peshawar and Swabi.*

Location		pH			
		0-15	16-30	31-45	Mean
Peshawar	Minimum	6.64	6.50	6.73	6.62
	Maximum	7.88	7.93	8.11	7.95
	Mean	7.27	7.24	7.35	7.29
	Std Dev.	0.35	0.39	0.38	0.37
Swabi	Minimum	7.01	7.11	6.93	7.02
	Maximum	7.75	7.88	7.82	7.77
	Mean	7.39	7.43	7.44	7.42
	Std Dev.	0.22	0.21	0.25	0.21

Table 3: *Mean pH of soil samples (0-45 cm) collected from wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

S. No.	District Peshawar		District Swabi	
	Location	Mean pH	Location	Mean pH
1.	Palusi Piran	7.51	Gandaf	7.25
2.	Palusi Regi	7.54	Industrial area	7.57
3.	Khasra 512	7.51	Afghan Camp	7.77
4.	Palusi Payan	6.94	Panj Pir	7.67
5.	IslamiaTown	7.89	Afghan Camp	7.49
6.	Pirbala	7.04	Industrial area	7.19
7.	Kafoor Dheri	6.91	Maini Maira	7.44
8.	Darmango	6.62	Mainee Mazafaat	7.14
9.	Daag Lara, Warsak	7.15	Qalander Khel	7.36
10.	Irrigation Colony	7.32	Guli Bagh	7.45
11.	Afghan Colony	7.49	Essa Khel	7.54
12.	Iqbal Colony	7.36	Jamraa	7.31
13.	Band Wala, Bhudni	7.95	Gadoon	7.02
14.	Dhery Malk, Bhudni	6.94	Bacha Garhi	7.44
15.	Dhery Malk, Bhudni	7.14	Akbar Abad	7.61

The soil samples collected from various locations of Swabi showed a mean pH value of 7.39for the top soil layer (0-15 cm), and ranged between 7.01 to 7.75. The pH of 16-30 cm depth ranged from 7.11 to 7.88 with a mean value of 7.43, whereas the pH of 31-45 cm depth ranged from 6.93 to 7.82 with a mean value of 7.44. According to the descriptive statistics (Table 5), the pH of profile (0-45 cm) varied from 7.02 to 7.77 with a mean value of 7.42.

Table 4: *Mean EC values (0-45 cm) of soil samples in wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

Location		EC (dS m^{-1})			
		0-15	16-30	31-45	Mean
Peshawar	Minimum	0.45	0.41	0.40	0.42
	Maximum	1.52	1.18	1.43	1.38
	Mean	0.92	0.78	0.76	0.82
	Std Dev.	0.31	0.22	0.25	0.25
Swabi	Minimum	0.24	0.20	0.20	0.21
	Maximum	1.71	1.64	1.62	1.66
	Mean	0.91	0.84	0.83	0.86
	Std Dev.	0.44	0.42	0.43	0.43

Table 5: *Mean EC of soil samples (0-45 cm) collected from wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

District Peshawar		District Swabi	
Location	Mean EC (dS m^{-1})	Location	Mean EC (dS m^{-1})
Palusi Piran	0.50	Gandaf	0.60
Palusi Regi	0.61	Industrial area	0.84
Khasra 512	0.42	Afghan Camp	0.55
Palusi Payan	0.77	Panj Pir	1.66
IslamiaTown	0.81	Afghan Camp	0.76
Pirbala	1.01	Industrial area	1.30
Kafoor Dheri	1.38	Maini Maira	0.21
Darmango	1.06	Mainee Mazafaat	1.36
Daag Lara, Warsak	0.80	Qalander Khel	1.13
Irrigation Colony	0.80	Guli Bagh	0.79
Afghan Colony	0.76	Essa Khel	1.13
Iqbal Colony	0.76	Jamraa	0.49
Band Wala, Bhudni	0.74	Gadoon	1.28
Dhery Malk, Bhudni	1.20	Bacha Garhi	0.38
Dhery Malk, Bhudni	0.68	Akbar Abad	0.44

The highest pH (7.95) was noted in Band wala, Bhudni and lower pH was noted in samples collected from Darmango (Table 3). Similarly, almost same trend i.e., alkaline pH (pH >7) were recorded in Swabi soils. The pH values ranged between of 7.02 and 7.77 with a mean value of 7.42. The highest pH (7.77) was noted in Afghan camp while the lowest pH value was noted in samples collected from Gadoon industrial site (Supplementary Table 8).

Table 6: *Concentration of Cd in soil samples in wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

Location		Cd (mg kg^{-1})			
		0-15	16-30	31-45	Mean
Peshawar	Minimum	5.80	3.62	3.60	3.61
	Maximum	19.34	20.56	23.46	22.01
	Mean	13.15	12.26	11.59	11.92
	Std Dev.	4.12	4.28	5.25	4.37
Swabi	Minimum	3.32	3.10	3.60	4.14
	Maximum	16.56	15.48	12.28	12.49
	Mean	9.24	9.08	8.73	8.90
	Std Dev.	2.64	4.42	2.64	2.41

It can be concluded from these results that over all pH of the surface soil was slightly lower than the subsurface soil samples that may be due to active root zone, having comparatively high organic matter as well as direct fertilizer application on surface. Wastewater samples, having slightly acidic pH may also have contributed in lowering pH of the surface as compared to the sub-surface soils. Moreover, the slight variation in pH may not be affecting the availability of metals.

Electrical conductivity

The descriptive statistic of EC values of soils collected from Peshawar and Swabi are given in Table 4 and the profile EC of specific site are given in Table 5. The details of depth wise analysis are given in Supplementary Table 9. The results showed that minimum and maximum EC in upper 0-15 cm depth was 0.45 to 1.52, respectively with a mean value of 0.92 dS m^{-1}. The EC of 16-30 cm depth ranged from 0.41 to 1.18 dS m^{-1} with a mean value of 0.78 dS m^{-1}, whereas the EC of 31-45 cm depth ranged from 0.40 to 1.43 dS m^{-1} with a mean value of 0.76 dS m^{-1}. According to the descriptive statistics (Table 4), the EC of profile when average across the depth (0-45 cm), minimum EC was 0.42 and maximum was 1.38 dS m^{-1} with a mean value of 0.82 dS m^{-1}. The detailed EC values in all the locations of Peshawar from where the samples were collected are given in Table 5.

Table 7: *Concentration of Cr in soil samples in wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

Location		Cr (mg kg^{-1})			
		0-15	16-30	31-45	Mean
Peshawar	Minimum	5.52	5.20	4.76	5.72
	Maximum	66.44	60.28	50.76	59.16
	Mean	31.20	26.93	18.55	25.56
	Std Dev.	18.06	16.28	14.65	15.64
Swabi	Minimum	4.92	3.84	3.36	7.16
	Maximum	30.10	29.44	22.00	27.18
	Mean	17.63	13.67	9.75	13.68
	Std Dev.	7.74	6.84	5.74	5.72

Table 8: *Concentration of Pb in soil samples in wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

Location		Pb (mg kg^{-1})			
		0-15	16-30	31-45	Mean
Peshawar	Minimum	69.5	62.4	60.0	61.5
	Maximum	229.9	220.6	206.5	213.6
	Mean	110.2	105.4	93.7	99.6
	Std Dev.	42.3	43.7	38.5	40.1
Swabi	Minimum	18.9	22.4	16.3	21.3
	Maximum	142.3	122.4	121.1	121.7
	Mean	66.3	61.2	57.3	59.3
	Std Dev.	28.9	34.2	29.9	29.0

Samples collected from various locations of Swabi, the mean EC value across the soil sample's locations in the top layer (0-15 cm) ranged between 0.24 to 1.71 dS m^{-1} with a mean value of 0.91 dS m^{-1}. The EC of 16-30 cm depth ranged from 0.20 to 1.64 dS m^{-1} with a mean value of 0.84 dS m^{-1}, whereas the EC of 31-45 cm depth ranged from 0.20 to 1.62 dS m^{-1} with a mean value of 0.83 dS m^{-1}. According to the descriptive statistics (Table 4), the mean EC of profile (0-45 cm) varied from 0.21 to 1.66 dS m^{-1} with a mean value of 0.86 dS m^{-1}. The detailed EC values in all the locations of Swabi from where the samples were collected are given in Table 5.

Heavy metal status of soil irrigated with industrial wastewater in Peshawar and Swabi

The proper management of the vast amount of industrial and municipal wastewater is a global challenge because untreated wastewater discharge pollutes the water bodies and irrigated soils and ultimately results in the buildup of heavy metals in soils. The status of Cd, Cr, Pb and Ni in the soils irrigated with industrial wastewater from HIE at Peshawar and GIE at Swabi are discussed in detail here under:

Cadmium concentration in soil irrigated with industrial wastewater in Peshawar and Swabi

Results of AB-DTPA extractable Cd concentration in soil is given in Table 6. The Cd concentration in Peshawar in the surface soil (0-15 cm depth) varied from 5.80 to 19.34 mg kg^{-1} with overall mean (averaged across different soil locations) value of 13.15 mg kg^{-1}, whereas, in 16-30 cm depth the Cd content varied from 3.62 to 20.56 mg kg^{-1} with a mean value of 12.26 mg kg^{-1}. Similarly, in 31-45 cm depth the AB-DTPA extractable Cd ranged from 3.60 to 23.46 mg kg^{-1} with a mean value of 11.59 mg kg^{-1}. The descriptive statistics of all the three depths (0-45 cm) indicated that the concentration of Cd ranged between 3.61 and 22.01 mg kg^{-1} with an overall mean of 11.92 mg kg^{-1}. The location wise Cd values of the 0-45 cm depth soil of the districts are given in Table 7 and depth wise Cd value of Peshawar and Swabi are given in Supplementary Table 10.

Table 9: *Concentration of Ni in soil samples in wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

Location		Ni (mg kg^{-1})			
		0-15	16-30	31-45	Mean
Peshawar	Minimum	23.7	22.0	21.3	21.7
	Maximum	116.2	115.1	95.6	105.4
	Mean	59.4	53.0	47.2	50.1
	Std Dev.	25.5	25.0	20.2	22.4
Swabi	Minimum	45.2	43.5	42.8	45.3
	Maximum	126.2	97.2	85.1	102.8
	Mean	65.1	62.5	55.6	61.1
	Std Dev.	23.4	13.6	10.4	15.2

In Swabi soils, the Cd concentration in the surface soil (0-15 cm depth) varied from 3.32 to 16.56 mg kg^{-1} with overall mean (averaged across different soil locations) value of 9.24 mg kg^{-1}, whereas, in 16-30 cm depth the value varied from 3.10 to 15.48 mg kg^{-1} with a mean value of 10.03 mg kg^{-1}. Similarly, in 31-45 cm depth the AB-DTPA extractable Cd ranged from 3.60 to 12.28 mg kg^{-1} with a mean value of 8.73 mg kg^{-1} (Table 6). The descriptive statistics of all the three depths (0-45 cm) indicated that the concentration of Cd ranged between 4.14 and 12.49 mg kg^{-1} with an overall mean of 8.90 mg kg^{-1}.

Table 10: *Mean Cd, Cr, Pb and Ni of soil samples (0-45 cm) collected from wastewater irrigated soils in urban and peri-urban areas of Peshawar and Swabi.*

S. No.	District Peshawar				
	Location	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Pb (mg kg^{-1})	Ni (mg kg^{-1})
1.	Palusi Piran	4.94	22.19	115.8	59.4
2.	Palusi Regi	14.99	32.91	194.1	79.2
3.	Khasra 512	14.26	46.03	101.2	64.5
4.	Palusi Payan	8.91	39.51	229.9	105.4
5.	IslamiaTown	8.47	5.72	69.5	57.1
6.	Pirbala	9.83	23.07	77.3	48.9
7.	Kafoor Dheri	14.83	59.16	123.8	59.4
8.	Darmango	20.39	49.12	123.2	59.0
9.	Daag Lara, Warsak	16.85	22.25	86.6	52.6
10.	Irrigation Colony	9.43	17.43	76.0	21.7
11.	Afghan Colony	15.31	13.37	77.3	26.1
12.	Iqbal Colony	11.85	12.09	103.8	27.1
13.	Band Wala, Bhudni	9.35	17.89	83.9	36.0
14.	Dhery Malk, Bhudni	14.13	7.16	99.8	27.9
15.	Dhery Malk, Bhudni	11.49	15.47	90.6	27.7

Concentration of Cr in soil irrigated with industrial wastewater in Peshawar and Swabi

Results of AB-DTPA extractable Cr concentration in soil is given in Table 7. The Cr concentration in Peshawar in the surface soil (0-15 cm depth) varied from 5.52 to 66.44 mg kg^{-1} with overall mean (averaged across different soil locations) value of 31.20 mg kg^{-1}, whereas, in 16-30 cm depth, the value varied from 5.2 to 60.28 mg kg^{-1} with a mean value of 26.93 mg kg^{-1}. Similarly, in 31-45 cm depth the AB-DTPA extractable Cr ranged from 4.76 to 50.76 mg kg^{-1} with a mean value of18.55 mg kg^{-1}.

In Swabi soils, the Cr concentration in the surface soil (0-15 cm depth) varied from 4.92 to 30.10 mg kg^{-1} with overall mean (averaged across different soil locations) value of 17.63 mg kg^{-1}, whereas, in 16-30 cm depth, the value varied from 3.84 to 29.44 mg kg^{-1} with a mean value of 13.67 mg kg^{-1} (Table 7). Similarly, in 31-45 cm depth, the AB-DTPA extractable Cr ranged from 3.36 to 22.00 mg kg^{-1} with a mean value of 9.75 mg kg^{-1}. The descriptive statistics of all the three depths (0-45 cm) indicated that the concentration of Cr ranged between 7.16 and 27.18 mg kg^{-1} with an overall mean of 13.68 mg kg^{-1}.

Table 11: *Mean Cd, Cr, Pb and Ni of soil samples (0-45 cm) collected from wastewater irrigated soils in urban and peri-urban areas of Swabi.*

S. No.	District Swabi				
	Location	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Pb (mg kg^{-1})	Ni (mg kg^{-1})
1.	Gandaf	11.07	11.32	91.9	48.9
2.	Industrial area	12.99	12.76	85.3	45.3
3.	Afghan Camp	8.93	7.16	95.9	49.0
4.	Panj Pir	5.88	8.09	55.1	53.1
5.	Afghan Camp	6.73	9.12	45.5	52.6
6.	Industrial area	13.49	27.18	142.3	92.3
7.	Maini Maira	6.97	7.84	72.0	56.9
8.	Mainee Mazafaat	7.94	9.79	64.0	58.4
9.	Qalander Khel	8.65	24.08	119.8	102.8
10.	Guli Bagh	6.50	9.12	18.9	60.8
11.	Essa Khel	11.00	16.09	26.1	57.7
12.	Jamraa	12.21	17.85	62.7	64.1
13.	Gadoon	11.00	14.19	49.4	60.1
14.	Bacha Garhi	11.37	14.91	29.9	58.2
15.	Akbar Abad	10.93	15.72	36.2	55.8

Concentration of Pb in soils irrigated with industrial wastewater in Peshawar and Swabi

Results of AB-DTPA extractable Pb concentration in soil is given in Table 8. The Pb concentration in Peshawar in the surface soil (0-15 cm depth) varied from 69.5 to 229.9 mg kg^{-1} with overall mean (averaged across different soil locations) value of 110.2 mg kg^{-1}, whereas, in 16-30 cm depth the value varied from 62.4 to 220.6 mg kg^{-1}. Similarly, in 31-45 cm depth the AB-DTPA extractable Pb ranged from 60.0 to 206.5 mg kg^{-1}. The averaged mean value for 16-30 and 31-45 were 105.4 and 93.7 mg kg^{-1}, respectively.

In case of Swabi soils, the lowest concentration of Pb was 18.9, 22.4 and 16.3 mg kg^{-1} was recorded in 0-15, 16-30 and 31-45 cm depth, respectively while the higher concentration varied from 142.3, 122.4, and 121.1 mg kg^{-1} in 0-15, 16-30 and 31-45 cm depth, respectively (Table 11). The mean values of the three depths were 66.3, 61.2 and 57.3 mg kg^{-1} for 0-15, 16-30 and 31-45 cm depths, respectively. The descriptive statistics for Swabi showed that the mean minimum and maximum Pb concentration of all the samples was 21.3 and 121.7 mg kg^{-1} while the overall mean for all the samples of Swabi was 59.3 mg kg^{-1}.

Concentration of Ni in soils irrigated with industrial wastewater in Peshawar and Swabi

Results of AB-DTPA extractable Ni concentration in soil is given in Table 9. The Ni concentration in Peshawar in the surface soil (0-15 cm depth) varied from 23.7 to 116.2 mg kg^{-1} with overall mean (averaged across different soil locations) value of 59.4 mg kg^{-1}, whereas, in 16-30 cm depth the value varied from 22.0 to 115.1 mg kg^{-1}. Similarly, in 31-45 cm depth the AB-DTPA extractable Ni ranged from 21.3 to 95.6 mg kg $^{-1}$. The averaged mean value for 16-30 and 31-45 were 53.0 and 47.2 mg kg^{-1}, respectively. In case of Swabi soils, the lowest concentration of 45.2, 43.5 and 42.8 mg kg^{-1} was recorded in 0-15, 16-30 and 31-45 cm depth, respectively. The higher concentration varied from 126.2, 97.2 and 95.6 mg kg^{-1} in 0-15, 16-30 and 31-45 cm depth, respectively.

The location wise Ni values of the 0-45 cm depth soil of the districts are given in Table 10, whereby, the highest values of Ni were 105.4 and 102.8 at Palusi Piran in Peshawar and Qalandarkhel in Swabi, respectively. Majority of the samples were beyond the permissible limits as given by Kabata-Pendias and Pendias (1985). The depth-wise Ni content of Peshawar and Swabi are given in Supplementary Table 13.

Concentration of Cd, Cr, Pb and Ni in different plant samples irrigated with industrial wastewater in Peshawar and Swabi

The results of analysis showed noticeable accumulation of heavy metals in various plants although the content of heavy metals in various plant species was different. The selected heavy metals are discussed in detail as follows.

Cadmium (Cd)

The Cd concentration in various crop/plants is given in Figure 4. It can be seen from the results that different crops/plants have different pattern of Cd uptake. The Cd content in cabbage leaf samples was 0.09 and 0.03 mg kg^{-1} on dry weight (DW) basis in Peshawar and Swabi, respectively, whereas in wheat, the Cd concentration was slightly higher than Cd content in cabbage. The same trend of Cd was noted in maize with 0.09 mg kg^{-1} in Peshawar and 0.08 mg kg^{-1} in Swabi. The Cd content in spinach leaves collected from Peshawar and Swabi was 0.06 and 0.08 mg kg^{-1} respectively on dry weight (DW) basis.

Spinach accumulated lesser Cd content than cereals as well as cabbage. Grass followed similar trend as of wheat and maize but had higher Cd content than cabbage and okra. The Cd content in *Rumex crispus* was almost similar to Cd content of spinach. In okra, the Cd in Peshawar was 0.01 mg kg^{-1} while in Swabi Cd was noted to be 0.04 mg kg^{-1}.

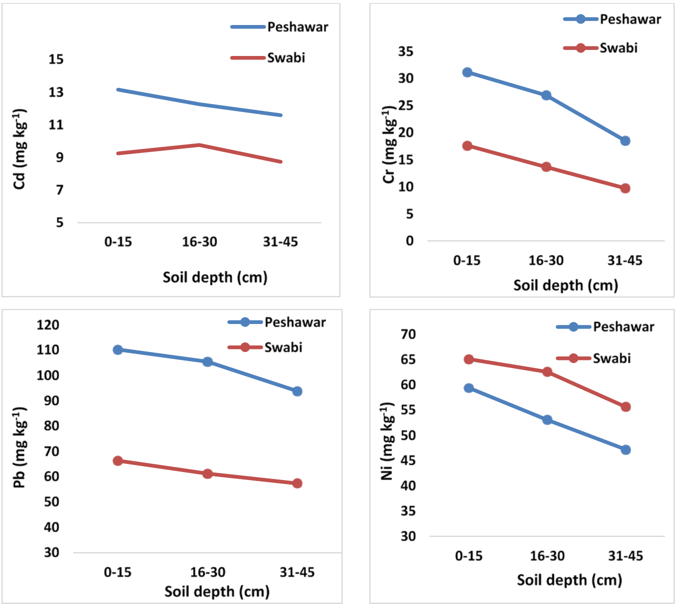

Figure 3: *Concentrations of Cd, Cr, Pb and Ni (mg kg^{-1}) in soil irrigated with industrial wastewater in Peshawar and Swabi.*

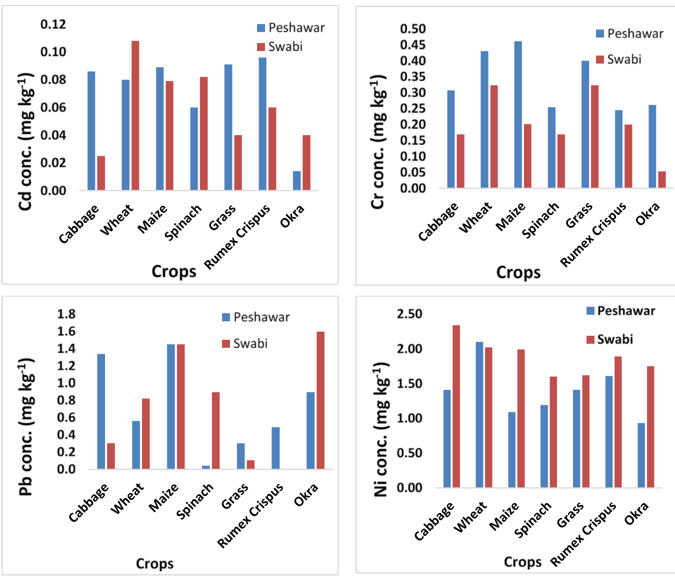

Figure 4: *Concentrations of Cd, Cr, Pb and Ni (mg kg^{-1}) in various crops irrigated with industrial wastewater in Peshawar and Swabi.*

According to the permissible limits of Cd in plants set by WHO (1996), all the cereals, grasses and vegetables accumulated Cd concentration above the permissible limit. According to Kabata-Pendias and Pendias (1985), the normal range of Cd in mature leaf tissue varies from 0.07 to 0.5 mg kg^{-1} (DW) which suggests that all the above plant samples accumulated Cd concentration within the permissible limits and may not cause toxicity in animals and human beings.

It was further noted that Cd content was higher in all the plant species collected from Peshawar sites. This may be due to higher concentration of Cd in Peshawar soil than Swabi. Overall, wheat and maize leaves accumulated higher concentration of Cd than all the other plant species.

Chromium (Cr)

The Cr concentration in various plant samples taken from various location of Peshawar and Swabi are presented in Figure 4. The concentration of Cr in cabbage leaves was recorded to be 0.31 and 0.17 mg kg^{-1} on dry weight (DW) basis in Peshawar and Swabi, respectively. Grain crops, wheat and maize accumulated the highest amount of Cr which was 0.43 and 0.46 in Peshawar, respectively while in Swabi, it was 0.32 and 0.20 mg kg^{-1}, respectively. Lawn grass samples collected from both the locations showed higher uptake of Cr which was at par with the Cr content of cereals.

Spinach and *Rumex crispus*, both leafy vegetables accumulated much lesser content of Cr in both the locations. The concentration of Cr in spinach was 0.25 and 0.17 mg kg^{-1} in Peshawar and Swabi, respectively. The samples of *Rumex crispus* collected from Peshawar accumulated 0.25 mg kg^{-1} of Cr in comparison to 0.20 mg kg^{-1} of Cr in samples collected from Swabi. Okra had the least accumulation of Cr in Swabi (0.05 mg kg^{-1}) while in samples collected from Peshawar, the concentration of Cr was 0.26 mg kg^{-1}.

Following the pattern of Cd, the plant samples taken from Peshawar had higher accumulation of Cr as compared to Swabi plant samples. The higher concentration of Cr in the soils of Peshawar may have translated into higher plant thus the Cr uptake was higher by plants in Peshawar samples. The permissible limits of Cr in plants is 1.30 mg kg^{-1} according to WHO (1996). All the plant samples had a Cr concentration lower than the permissible limits of WHO, whereas according to Kabata-Pendias and Pendias (1985), the normal range of Cr in mature leaf tissue varies from 1.0 to 5.0 mg kg^{-1} (DW).

Lead (Pb)

The Pb concentration in plant samples collected from Peshawar and Swabi is presented in Figure 4. Maize plants showed the highest tendency to accumulate

Pb in plant body in both the samples taken from Peshawar and Swabi being 1.45 mg kg^{-1} DW at both the sites. The concentration of Pb in wheat samples taken from Swabi was more than that of Peshawar being 0.82 and 0.56 mg kg^{-1}, respectively. Cabbage and okra showed a reverse trend in Peshawar and Swabi where the concentration of Pb was higher in cabbage samples of Peshawar (1.34 mg kg^{-1}) as compared to Swabi (0.30 mg kg^{-1}) while in case of okra the concentration of Pb in sample collected from Swabi had higher concentration of Pb (1.60 mg kg^{-1}) closely followed by Pb in Peshawar (0.89 mg kg^{-1}).

Leafy plants, spinach and *Rumex crispus* in addition to lawn grass showed the lowest accumulation of Pb in plant body. The concentration of Pb in spinach at Peshawar was 0.04 mg kg^{-1} while in Swabi the Pb content in spinach leaves was 0.89 mg kg^{-1}. The Pb concentration *Rumex crispus* was 0.48 and 0.01 mg kg^{-1} in Peshawar and Swabi, respectively. Lawn grass showed a low concentration in both Peshawar and Swabi, being 0.49 and 0.11 mg kg^{-1}, respectively.

It was concluded that comparatively higher concentration of Pb was noticed in samples collected from Swabi sites in comparison to Peshawar soils. This may be attributed to the excessive levels of Pb in the soil samples collected from Swabi.

The Pb concentration in cabbage leaf samples (Figure 4) collected from Peshawar and Swabi was 1.34 and 0.30 mg kg^{-1} on dry weight (DW) basis, respectively. According to the permissible limits of Pb in plants (2.00 mg kg^{-1}), set by WHO (1996), the Pb concentration was lower than the permissible limits, whereas according to Kabata-Pendias and Pendias (1985) the normal range of Pb in mature leaf tissue varies from 3 to 70 mg kg^{-1} (DW). The Pb concentration in okra, spinach, *Rumex crispus* and lawn grass is not considered phyto-toxic or excessive for animal consumption.

Nickel (Ni)

Plant Ni concentration in samples collected from Peshawar and Swabi is presented in Figure 4. The highest accumulation of Ni in plant was noted in cabbage samples collected from Swabi (2.34 mg kg^{-1}), closely followed by wheat, maize and *Rumex crispus* being 2.02, 1.99 and 1.89 mg kg^{-1}, respectively. Wheat showed a reverse trend in Peshawar where the concentration of Ni was higher in wheat samples of Peshawar (2.10 mg kg^{-1}) as compared to Swabi (2.02 mg kg^{-1}). In case of all other samples, the concentration of Ni was noted higher in Swabi than Peshawar.

Okra and maize samples collected from Peshawar showed the lowest accumulation of Ni in plant leaves. The concentration of Ni in okra leaves at Peshawar was 0.93 mg kg^{-1} while in Swabi the Ni content in maize was 1.09 mg kg^{-1}. The Ni concentration in *Rumex crispus* was 1.61 and 1.89 mg kg^{-1} in Peshawar and Swabi, respectively. Lawn grass showed a low concentration in both Peshawar and Swabi, being 1.41 and 1.62 mg kg^{-1}, respectively.

It was concluded that comparatively higher concentration of Ni was noticed in samples collected from Peshawar sites compared to Swabi soils. This may be attributed to the excessive levels of Ni in the soil samples collected from Swabi.

The Ni concentration in cabbage leaf samples (Figure 4) collected from Swabi was 2.34 mg kg^{-1} on dry weight (DW) basis. According to the permissible limits of Ni in plants (10 mg kg^{-1}), set by WHO (1996), the Ni concentration was lower than the permissible limits, whereas according to Kabata-Pendias and Pendias (1985) the normal range of Ni in mature leaf tissue varies from 3 to 70 mg kg^{-1} (DW).

Soil pH and EC levels of soil irrigated with industrial wastewater in Peshawar and Swabi

By comparing the two sites, Peshawar soil samples were having comparatively lower pH than Swabi sites and the reason partly may be the results of low pH of wastewater irrigation. Here again, the variation in pH are not significant, thus may not be contributing factor to the plant availability or extractability of metals under study. Shah *et al.* (2016) reported similar findings in their study on the command area of Warsak and Bara Canal area of district Peshawar.

Analysis of the samples showed that electrical conductivity (EC) of the soil of Peshawar ranged from 0.42 to 1.38 dS m^{-1} with an average of 0.82 dS m^{-1} (Table 5) with the highest value recorded at Kafoor Dheri site (1.38 dS m^{-1}) and the minimum EC value of 0.42 dS m^{-1} at Khasra 512. None of the samples fall in the category of salinity, thus salinity is not cropping limiting factor. The reason of low salts may be due to the installation of tile drains under the SCARP (Salinity Control and Reclamation Project) in the area. These results are in agreement with the findings of Khan and Shah (2015) who reported that the soil in the urban areas of Peshawar irrigated with wastewater mixed canal water have a mean EC value of 0.24 dS m^{-1}.

Heavy metal status of soil irrigated with industrial wastewater in Peshawar and Swabi

It was noted from these results that comparatively higher concentrations were recorded in surface soil and then decreased progressively with depth. By comparing the two locations (Figure 3), comparatively higher values were recorded in Peshawar than Swabi districts. Based on the USEPA (1999) standards for irrigation (5.0 mg L^{-1}) and WHO (1996) standard for soil (5.0-30.0 mg kg^{-1}), most of the surface soils have Cd level beyond the permissible limits that may cause health problems. The accumulation of heavy metals in soil overtime with wastewater irrigation has been also reported by Kinuthia *et al.* (2020). They reported that the concentration of Cd in the wastewater was above USEPA standards. They showed concern about public health with the use of wastewater generated by the Industrial area of Nairobi where Cd was reported to be in higher concentration than the limits set by WHO and US-EPA.

It was noted from these results that higher concentrations were recorded in surface soil and then increased progressively with depth. This can be attributed to the frequent irrigation with wastewater of the field and ploughing of the fields after every harvest. By comparing the two locations (Figure 3), comparatively higher values were recorded in Peshawar than Swabi districts. Based on the USEPA (1999) standards for irrigation (0.1 mg L^{-1}) and WHO (1996) standard for soil (8.0 mg kg^{-1}) most of the surface soils have Cr level beyond the permissible limits that may cause health problems. These results are in agreement with the findings of Mussarrat *et al.* (2007) who reported that Cr was high in 33% sewage water and 13% in canal water samples. It was argued that industries and municipal corporation must build sewers to collect and transmit the wastewater to treatment plant to curtail the addition of heavy metals into agricultural soils.

It was noted from these results that higher concentrations were recorded in surface soil and then decreased slightly with depth in Peshawar, whereas there was no change in Swabi with depth showing uniform distribution of Pb in the profile. By comparing the two locations (Figure 3), comparatively higher values were recorded in Peshawar than Swabi districts. Based on the USEPA (1999) standards for irrigation (5.0 mg L^{-1}) and WHO (1996) standard for soil (13.00 mg kg^{-1}) most of the surface soils have Pb level beyond the permissible limits that may cause health problems. Mussarat *et al.* (2007) also reported similar findings in their study wherein they collected soil and plant samples from various locations of Peshawar and analyzed for various physico-chemical properties. Rosen (2002) reported that plant require very small amounts of Pb from soil and normally the soils contain safe amount of lead for normal plant requirements. The soil content of 300 pm is generally considered safe for plant production. Higher concentrations of Pb are considered as risky for safe land husbandry and agriculture production and higher lead concentrations may lead to lead toxicity through uptake by plants. The accumulation of heavy metals in soil overtime with wastewater irrigation has been also reported by Kinuthia *et al.* (2020) in Kenya. They reported that the concentration of Pb in the wastewater was above USEPA standards. They showed concern about public health with the use of wastewater generated by the industrial area of Nairobi where Pb was reported to be in higher concentration than the limits set by WHO and US-EPA.

It was noted from the results that higher concentrations were recorded in surface soil and then decreased progressively with depth. By comparing the two locations (Figure 3), comparatively higher values were recorded in Peshawar than Swabi districts as was expected that may be due to the higher values of Ni in the wastewater generated by HIE. Based on the USEPA (1999) standards for irrigation (0.02 mg L^{-1}) and WHO (1996) standard for soil (8.1 mg kg^{-1}) most of the surface soils have Ni level beyond the permissible limits that may not be safe for humans as well as animals consuming agricultural produce. The natural concentration of Ni in soil is very low unless altered anthropogenically. The Ni pollution is mainly attributed to mining, fossil fuel combustion, electroplating and metal plating industries (Khodadoust *et al.*, 2004). While analyzing soil samples from various locations of Peshawar reported that highest concentration of Ni was found to be in areas planted with plum orchard irrigated with wastewater as compared to vegetable fields. The comparison of soil irrigated with normal soils indicate that the wastewater irrigated soils have acquired higher values of Ni. Our findings are in conformity with the findings of Nazir *et al*. (2015) who analyses soil, plant and water samples in the vicinity of Tanda dam, Kohat, Pakistan and reported accumulation of various metals in soil indicating a possible buildup.

Concentration of Cd, Cr, Pb and Ni in different plant samples irrigated with industrial wastewater in Peshawar and Swabi

Islam (2016) reported higher accumulation of Cd in maize leaves while using amendments for *in-situ* stabilization of Cd in soil. Lui *et al*. (2009) assessed the accumulation of various heavy metals, including Cd, by winter wheat in China and argued that wheat accumulated higher concentration of Cd which were very weakly transported to the edible grain portion. Atamaleki *et al*. (2021) correlated the irrigation of vegetables irrigated with wastewater and the concentration of various potentially toxic elements in plant parts. They argued that the concentration of Cd in spinach was seventh among the toxic elements and regarded spinach as a low accumulator of Cd in comparison to root vegetables. Okra is also accumulating lesser concentrations of Cd. In a study by Rasheed *et al*. (2018), two cultivars of okra were tested with high dose of Cd to check the tolerance of the species to Cd toxicity. They concluded that okra is not a good accumulator of Cd in plant part while even under Cd stress, the plant experiences oxidative burst scavenging the defense protein of the plant. Černe *et al*. (2021) used sewage sludge-based compost and biochar on the Chinese cabbage in Croatia to assess the uptake of various heavy metals including Cd and reported that the concentration of Cd in cabbage plant body was within the safe limits for human consumption.

Various researchers have analyzed various crops for elevated uptake of heavy metals from soil and assessed their chances of posing health risks. Qing *et al*. (2015) reported that cabbage accumulated substantial concentration of Cr in its leaves, however, the concentration in the edible portion was within the agreeable range. In a study by Lui *et al*. (2009), the authors reported that the Cr in wheat is not considered phyto-toxic or excessive for the human and animal consumption. The findings of Marwa *et al*. (2012) resonate with the finding of this study. Spinach leaf Cr content is also within the limit as reported by Sharma *et al*. (2005).

A number of studies have reported that the concentrations of Ni in plants grown on soils irrigated with wastewater have different effect on different crops because of the tendency of various crop to resist the uptake of unwanted metals. Yang *et al*. (1996), for example, reported that concentration of Ni in leaves of cabbage plant cannot be considered phyto-toxic or excessive for the human and animal consumption, if consumed for a short period of time. However, the risk increased if the small concentrations are added up and stored in the human or animal body causing the magnification effect which can result in carcinogenicity.

Ali *et al*. (2021) amended Ni-contaminated soil with various organic amendments to ascertain their effect on immobilization of Ni sown with spinach. They concluded that spinach grown on contaminated soils accumulated higher Ni concentrations.

Conclusions and Recommendations

The problem of heavy metal pollution of the wastewater irrigated soil of urban areas of big cities, primarily the industrial wastewater irrigated fields, is significantly higher that may be causing heavy metal bio-accumulation and bio-magnification in the food chain. Resultantly, the cases of cancers in humans are increasing. The following conclusion is derived from the present study:

Peshawar showed higher levels of Cd, Cr, and Pb, while Swabi soils had elevated Ni concentrations, with surface soils (0-15 cm) containing higher metal levels that decreased with depth. Despite most mean values being within permissible limits, areas near industries exceeded these limits. Plant analysis reflected soil data, with wheat and maize accumulating more Cd and Cr, and okra, maize, wheat, and spinach showing higher Pb levels, particularly in Swabi. Ni accumulation was higher in Swabi plants, especially in cabbage, while Peshawar plants had lower Ni levels.

Based upon the conclusion, the study recommends that agricultural lands irrigated with industrial wastewater, particularly those near industrial zones in Peshawar and Swabi, be treated with soil amendments such as Triple Superphosphate (TSP) and Humic Acid (HA) thereby mitigating potential health risks associated with heavy metal bioaccumulation in the food chain. This study also recommends further experimentation on the heavy metals buildup in soil over a long period of time.

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Novelty Statement

This study uniquely compares heavy metal accumulation in soils and crops irrigated with untreated industrial wastewater from two different industrial zones i.e. Hayatabad (Peshawar) and Gadoon (Swabi) of Khyber Pakhtunkhwa, Pakistan

Author's Contribution

Farmanullah Khan: Conducted the field and laboratory activities and manuscript writeup.
Mohammad Jamal Khan: Supervised the research and edited the manuscript.
Dost Muhammad: Helped in supervision of the laboratory operations and research work.

Supplementary material
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Generative AI or AI-assisted Technology Statement
The authors declare that no Genrative AI was used in the creation of this manuscript.

Conflict of interest
The authors have declared no conflict of interest.

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