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Original Research

Assessment of Heavy Metals in Wheat Plants Irrigated with Contaminated Wastewater

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Abstract

Untreated discharges from industrial, domestic, and storm waters, agricultural runoff, and other sources significantly affect the quality of irrigation water both on short- and long-term basis. The present study deals with the assessment of heavy metals in irrigation wastewater, soils, and wheat grains irrigated with contaminated water from municipal sources in Abbottabad, Pakistan. The concentrations of most of the metals were found above the threshold limits for irrigation water and food set by international regulations. The concentrations of metals in wheat grains showed a decreasing order of Zn>Fe>Mn>Cu>Pb>Cd>Ni>Cr in samples collected from areas irrigated with municipal wastewater. Grains were found to accumulate in Cr, Ni, and Fe metals, which were beyond recommended dietary limits. It is recommended that treatment facility must be installed to reduce heavy metals and turbidity of the wastewater being used for downstream irrigation.

Keywords: dietary toxicity, heavy metal assessment, soil, wastewater, wheat grains (*Triticum aestivum* L.)

Introduction

The growing dearth of water has threatened profitable development, quality of the environment, sustainable human livelihood, and a multitude of other public goals in many developing Asian and African regions. Unchecked growth of the urban population, particularly in developing countries, places an enormous pressure on water and land resources. Wastewater is increasingly being used for agricultural irrigation in urban and peri-urban areas. It also is used in distant rural areas downstream of very large cities. It drives significant economic activity, particularly those of farmers, and largely changes the hydrology and water quality of natural water bodies. There are serious drawbacks of using wastewater without ample safeguards for human health and the environment [1].

Globally, around 20 million ha of land are irrigated with municipal wastewater (raw, diluted, or treated). This figure is likely to increase noticeably over the next few decades in response to growing levels of water stress in inhabited catchments. Wastewater irrigation is relevant to major global development objectives, most notably Goal 7 of the priority targets of the United Nations Millennium Development Goals (UNMDG). Sustainable and safe wastewater use can support the achievement of these goals by preserving valuable freshwater. Furthermore, reclamation and reuse leads to reduced discharge of wastewater to the ambient environment, particularly to sensitive coastal ecosystems [2].

Many industrial plants in developing countries operate without any, or a nominal wastewater treatment and routinely discharge their waste into drains that either contaminate rivers and streams or add to the contaminant load of sewage sludge [3]. Contaminants from industrial, urban, and agricultural sources may enter the food chain in addition to the low water quality of the area [4]. The heavy metals contamination of agricultural soils and crops is causing concerns due to the probable effects on food production and

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human health in affected areas. Heavy metals are ubiquitous in the environment as a result of both natural and anthropogenic behavior, and humans are exposed to them through various pathways [5]. Solid waste disposal, wastewater irrigation, sludge applications, and industrial actions are the major sources of soil heavy metals pollution, and an increased metal uptake by food crops grown on such contaminated soils is not uncommon [6]. In general, wastewater use provides substantial amounts of potentially toxic heavy metals, which are creating problems for agricultural production [7]. Extreme accumulation of heavy metals in agricultural soils through wastewater irrigation may not only result in soil contamination but also lead to elevated heavy metal up-take by crops, threatening food quality and safety [8]. The dietary toxicity of heavy metals in vegetables and food crops were reviewed by Islam et al. [9]. Wastewater irrigation is a widespread practice around the globe [10-13]. Especially for vegetables cultivated in wastewater, irrigated soils take up heavy metals in large quantities, causing potential health risks to consumers [9, 14, 15].

Wheat (*Triticum aestivum* L.) is the most important crop worldwide, followed by coarse grains and rice. In Pakistan, wheat is a staple grown across some 8,069,000 ha. According to the Pakistan Agricultural Research Council (PARC), per capita wheat consumption of the country is 120 kg per year – among the highest in the world [16]. The aim of the present study was the assessment of heavy metals in irrigation wastewater, soil, and wheat grown under the influence of that contaminated wastewater.

Materials and Methods

Study Area

The Abbottabad district is spread over an area of about 5,094 km^2 and is located in the Khyber Pakhtun Khwa (KPK) province of Pakistan. Abbottabad is situated in the Orash Valley, lying between 34º09′N latitude and 73º13′E longitude at an altitude of 4,120 feet. Abbottabad is bordered by Mansehra District to the north, Muzaffarabad District to the east, Rawalpindi District to the south, and the Haripur District to the west.

Streams of Abbottabad

The most important streams of the Abbottabad District are Harno and Daur. The Daur River has numerous tributaries including the perennial streams flowing year-round, these are called *kathas* locally and the seasonal ones are called *Kassies* [17]. Mandroch stream is one of the major tributaries of the Daur River, which drains most of the Abbottabad city area.

Drainage System of Abbottabad

Untreated discharge of pollutants from domestic sewers, storm water discharges, industrial sources, and agricultural runoff to water resources exert significant short- and long-term harmful effects on the quality of irrigation water and the subsequent food produced. It is a common practice for people living along the river catchments in Pakistan to discharge their wastewater into streams/rivers. The Sarhad Provincial Conservation Strategy (SPCS) requires proper sewage networks, drainage systems, and wastewater treatment facilities, which are completely lacking in KPK cities [18]. Rural areas are even more poorly equipped to deal with wastewater and solid waste disposal. In urban areas of Abbottabad, the problem of municipal waste is critical. Households, hospitals, hotels, restaurants, and small business in Abbottabad discharge wastewater into open drains that run through residential areas and thus create a serious threat to sustainability. The wastewater disposal infrastructure is no longer able to cope with this pressure, and most of the untreated wastewater enters the streams/rivers used for irrigation and other purposes. Illegal townships that have sprung up as a result of urbanization put additional pressure on already fragile municipal services.

Sampling of Irrigation Water, Soil, and Wheat Grains

The present study was conducted in the Mandroach and Daur streams, which originate from Mandroach village, passing through Dhamtor, Takia camp Abbottabad; later they join with Thandiani Nullah at Hronoi point, leading toward Havelian Bridge, extending toward Serai Saleh, and finally terminating in Tarbela Lake (a water reservoir on the Indus River). Wastewater samples used for irrigation were collected at six random places from the study area during the months of September to March (period of wheat crop sowing and irrigation). Three grab water samples at a mutual distance of about 1 km, collected from each sampling point. Water samples were collected in acidified HDPE bottles, pre-cleaned with HCl (10% v/v), and transferred to the laboratory for heavy metal analysis. Soil samples (0-20 cm depth) were collected randomly from the agricultural land irrigated with mixed wastewater and packed into polythene bags and brought to the laboratory for further analysis.

For soil sampling, three random wheat fields were selected and six random soil samples at a mutual distance of about 10 feet were collected from the surface for the same time period when water samples were collected. Three random sub-surface soil samples were collected from each sampling point. The soil samples were oven dried overnight at 105ºC, gently ground and sieved to 2 mm mesh size, homogenized, and used for heavy metal analyses. At harvest time, 10 wheat grain samples were randomly collected from each field and washed with distilled water to eliminate the adhered soil and other contaminants. The wheat grain samples were oven dried for 48 h at 70ºC and then ground to pass a 1.0 mm sieve for determination of heavy metal contents. The results of various analyses were presented as means of all samples. The rain events were avoided and sampling was not done until three days after the rain.

Water Physico-Chemical Parameters

Wastewater samples were filtered before final analysis to remove any solid particles and were analyzed according to standard methods of water and wastewater analysis [19]. A 5 g (dry weight) sample of wheat grains was crushed in a mortar and ashed in a muffle furnace at 450ºC for 6 h. After the samples turned to white ash, all the samples were digested completely with 5.0 mL of concentrated HNO_3, filtered, transferred into a 25 mL container, and brought to volume with ultra-pure water. Analytical blank samples also were prepared in the same way without any sample contents.

Soil Characteristics

The dried and sieved soil samples also were digested in a mixture of HNO_3:H_2O_2 in the same manner (USEPA). Soil samples were analyzed according to Moreno et al. [20] and Bollen et al. [21].

Plant Analysis

Wheat grains were ground sieved (< 2 mm) and stored in polythene zipper bags for later analysis. Wheat grains were analyzed according to [22]. All the samples (water, soil, wheat grains) were measured in a Perkin-Elmer AAnalyst 700 graphite furnace atomic absorption spectrophotometer for heavy metal determination.

Quality Assurance

At least one laboratory blank was analyzed with each set of five environmental samples. In general, environmental concentrations within twice the values observed in the associated laboratory reagent blanks were reported as less than the reporting level. A field quality-assurance protocol was used to determine the effect, if any, of field equipment and procedures on the concentrations of contaminants in water samples. Field blanks were subject to the same sample processing, handling, and equipment as the stream samples. The quality was further assured by randomization, replication, and comparison with international standard values.

Results and Discussion

Physico-Chemical Characteristics of Wastewater and Heavy Metal Contents

The contaminated water used for irrigation was analyzed for temperature, turbidity, chemical oxygen demand (COD), dissolved oxygen (DO), pH, electrical conductivity (EC), total dissolved solids (TDS), anions (NO_3^-, SO_4^{2-}, Cl^-), and heavy metals (Cr, Cu, Cd, Fe, Mn, Ni, Pb and Zn). The results revealed that COD, NO_3^-, SO_4^{2-}, Cr, Zn, Ni, Cd, and Pb were found higher than the permissible limits given by the National Standards for Drinking Water Quality, Pakistan (NSDWQ-Pak), the EU, and irrigation water by the US [23] (Table 1). The results of a few similar studies are reported in Table 2 [24, 25].

Soil Heavy Metal Concentrations

After comparison with various standard values, it was evident that all soil samples were contaminated with various heavy metals (Table 3). Moreover, the EC values of various soil samples were found to be in the range of 447~492 μS/cm. These findings can be explained by the fact that water at these sites contained heavy metals above permissible limits. These sites have been receiving polluted wastewater from Abbottabad city. The most prevalent heavy metals found in soil being irrigated were found to be zinc, copper, manganese, and lead (Table 3).

Elemental Concentration in Wheat Grains

Table 3 reports the results of heavy metals in wheat grains/flour; moreover, reference results of similar previous studies also have been reported from various regions where crops were irrigated with fresh water, wastewater, and or amendments with sewage sludge or solid waste. The reference values from international regulations (EC, FAO/WHO) also are reported in Table 3.

Copper (Cu)

Copper is an essential trace element in plants and animals [26]. The human body contains Cu at a level of about 1.4 to 2.1 mg per kg of body mass. The recommended dietary allowance (RDA) of Cu in normal healthy adults is quoted as 0.97 to 3.0 mg/day. Cu is absorbed in the gut, which facilitates iron uptake. Its deficiency can produce anemia-like symptoms, neutropenia, bone abnormalities, increased incidence of infections, and abnormalities in glucose and cholesterol metabolism [26]. The maximum admissible concentration of Cu should be 3 mg/kg (DW) in wheat set by the EC and FAO/WHO. In the present study the concentration of Cu in wheat grains was found to be in the range of 3.1-5.1 mg/kg (DW) with mean value of 4.1 mg/Kg (DW). Average value was higher than the permissible limit and it was also higher than the value reported (0.42 mg/kg) by Hussain et al. [26] from the same region, but quite lower than the values given by Jamali et al. [24] (11.8 mg/kg). Cu is the most reported element in elemental analysis of wheat grains [24]. Most of the studies reported higher Cu content in wheat grains, ranging from 4.21-23.73 mg/kg (DW) (Table 3) in soils that received a high metal load through the application of contaminated sewage sludge/wastewater/pond sediments, etc. [24]. Diverse values for Cu concentration also have been reported in wheat flour, ranging from 0.002 to 3.87 mg/kg (DW) of different countries, the lowest in Nigeria and the highest in Pakistan [24].

Iron (Fe)

Iron is a necessary element found in nearly all living organisms considered at the border between macro and

Table 1. Average values of water quality parameters of irrigation water, along with standard limits of drinking water by NSDWQ-Pak and the EU, and irrigation water by the US [23].

S. No.	Parameters	Present study (Mean)	NSDWQ Pak	EU drinking water standards	US irrigation water quality
1.	Temp (ºC)	18±0.50	–	–	–
2.	pH	7.2±0.10	6.5-8.5	6.5-8.5	6.5-8.4
3.	EC (µs/cm)	719±9.13	–	2500	<700
4.	DO (mg/L)	5.6±0.12	–	5.0	4.0-6.0
5.	TDS (mg/L	577.8±15.1	<1000	–	<450
6.	Turbidity (NTU)	41.7±5.22	<5	–	–
7.	COD (mg/L)	116±2.31	–	–	–
8.	Nitrate (mg/L)	55.3±0.52	50	50	–
9.	Sulfate (mg/L)	265.7±9.3	–	250	–
10.	Chloride (mg/L)	196.5±11.1	<250	250	<140
11.	Cr (mg/L)	0.1±0.01	0.05	0.05	0.1
12.	Cu (mg/L)	0.5±.0.01	2	2	0.2
13.	Fe (mg/L)	1.1±0.01	–	0.2	5.0
14.	Ni (mg/L)	0.05±0.01	0.02	–	0.2
15.	Cd (mg/L)	0.03±0.01	0.01	0.005	0.01
16.	Pb (mg/L)	0.25±0.01	0.05	0.01	5.0
17.	Zn (mg/L)	7.2±0.11	5	–	2
18.	Mn (mg/L)	0.5±0.11	>0.5	–	0.2

Table 2. Heavy metal concentrations in soil irrigated with contaminated water (mg/kg dried weight basis) and the maximum admissible concentrations of toxic metals in soils from the US, UK, and EU.

HM	This study (range)/mean	Previous studies (Pakistan) [24]	Previous studies (India) [25]	USA	UK	EU
Cd	(0.5-3.5)/2.8	2.4±0.18	10±0.76	20	3	1-3
Cr	(0.2-5.8)/4.2	2.9±0.33	313±10.1	1500	400	100-150
Cu	(1.5-39)/28	39.2±2.1	40.83±2.3	750	135	50-140
Ni	0.8-12.5)/7.5	36.0±1.2	42.24±3.3	210	75	30-75
Pb	(10.5-25.2)/15.6	75.5±4.3	30.81±2.2	150	300	50-300
Zn	(25-175) /135	235±7.2	143±4.2	1400	300	150-300
Mn	(2.5-31.5)/25.5	–	1352±10	–	–	–
Fe	(25-315)/270	–	1392±12	–	–	–

micro-elements of living organisms. Iron-containing enzymes and proteins often contain heme prosthetic groups that participate in many biological oxidations and in transport. Fe is a less studied element in wheat grain analysis. Average Fe content in current studies was found to be 28.5 mg/kg – lower than most studies but higher than the value reported [26] from the same region, as well as the permissible limit of 20 mg/kg. The variation in Fe content ranged from 7.28 to 93.6 mg/kg, the highest of all cases [24] being found in Uttar Pradesh, India (Table 3). From the same location [25] the reported Fe content of 90.16 mg/kg was consequent to industrial effluent as the main cause of higher Fe concentration in soil (1,392 mg/kg, Table 2), which ultimately resulted in high metal content in wheat grains. Higher Fe value (47.7 mg/kg) also was found in wheat grain where no soil amendments were made; however, the soil was affected by urbanization and industrialization of Cordoba, Argentina [28]. Similar results for Fe (30.04-47.7 mg/kg) were reported [29] from Serbia for different varieties of wheat grains.

Table 3. Comparison of heavy metals in wheat grains grown in soil with and without amendments.

S No.	Matrix/soil amended with	Country	Cu	Fe	Zn	Mn	Ni	Cr	Cd	Pb	References
1.	Tolerance limit (mg/kg dry weight)		3 [d]	20 [d]	27.4 [d]	2 [d]	1.63 [d]	0.02 [d]	0.2 [e]	0.2 [e]	[52]
2.	Wheat flour /different local varieties [a]	Calabar, Nigeria	0.002	0.04	0.019	–	0.006	0.012	0.002	–	[53]
3.	Wheat flour /different local varieties [a]	Sindh, Pakistan	3.87	–	–	38.1	1.07	0.3	0.66	1.03	[48]
4.	Wheat flour [b]	Sweden	1.7	–	7.6	6.2	–	–	0.029	–	[54]
5.	Wheat grain /long-term soil fertility experiments [b]	Sweden	3.51	30.33	27.35	33.26	0.24	0.022	0.038	0.018	[46]
6.	Wheat grain/no amendments	Cordoba, Argentina	3.79	47.7	29.2	49.8	0.24	0.54	0.017	0.088	[28]
7.	Wheat grain/no amendments	Italy	3.5	–	34	–	–	–	0.042	0.015	[24]
8.	Wheat grain/no amendments, different local varieties [a]	Serbia	4.65	49.36	24.13	–	–	–	0.1	1.7	[29]
9.	Wheat grain/pond sediment	West Bengal, India	23.73	–	39.38	–	0.18	0.36	1.18	16.8	[42]
10.	Wheat grain/industrial contaminated soil	Kunshan, China	5.229	–	27.78	–	0.148	0.1	0.055	0.177	[55]
11.	Wheat grain/industrial contaminated soil	Baiyin, China	4.72	–	38.02	–	–	–	0.23	1.03	[47]
12.	Wheat grain/(farmyard manure + compost)	Tunisia, Italy	3.6	–	9.51	–	–	–	0.85	–	[44]
13.	Durum wheat grain/Controlled green house, sewage sludge and fertilizers [c]	Paris, France	8.42	–	132.3	–	–	1.2	0.05	12.36	[31]
14.	Wheat grain/sewage sludge	Isfahan, Iran	4.9	–	38.5	–	–	–	0.8	–	[43]
15.	Wheat grain/wastewater	Konya, Turkey	4.21	–	22.31	38.42	9.92	5.47	–	1.63	[34]
16.	Wheat grain/sewage irrigated soil	Beijing, China	6.09	–	52.38	–	–	4.62	0.04	0.19	[30]
17.	Wheat grain /industrial effluent	Uttar Pradesh, India	5.6	93.6	28	–	4.2	8.0	0.8	9.2	[26]
18.	Wheat grain/industrial effluent	Uttar Pradesh, India	5.06	90.16	28.26	18.43	4.12	8.16	1.06	8.06	[25]
19.	Wheat grain/industrial effluent	Peshawar, Pakistan	0.42	7.82	3.01	4.15	0.09	0.01	–	0.12	[26]
20.	Wheat grain/controlled greenhouse domestic sewage sludge	Jamshoro, Pakistan	11.8	–	133	–	6.2	0.17	0.89	22.6	[24]
21.	Wheat grain/mixed wastewater-contaminated soil	KPK, Pakistan	4.1	28.5	35.3	4.9	0.2	0.05	0.28	0.35	Present study

[a] maximum reported values
[b] means of 15-year data
[c] results shown for sludge only
[d] FAO/WHO
[e] EC

Zinc (Zn)

Like copper, Zn is the most studied element in wheat grains, and it ranges from a few milligrams to hundreds of milligrams/kg. In the current study, the value of Zn was found to be 35.3 mg/kg, which was higher than the values reported from the same region (3.01 mg/kg) [26] and far lower than the values given by Jamali et al. [24] (133 mg/kg). The variation in the values is possibly due to the input of these metals into the soil by different routes. Higher values have been reported [30] during assessment of the potential health risk for inhabitants in a sewage-irrigated area from Beijing, China, i.e. 52.38 mg/kg of Zn in wheat grown on swage irrigated soil. Excessive higher value of 132.3 mg/kg has been reported [31] from Durum wheat grown in a greenhouse in sewage irrigated soil in Italy. It was concluded that the organically bound metals in biosolids are less available than more mobile metal salts found in commercial fertilizers. It is evident from Table 3 that despite the heavy metal load contributed by effected/amended soils (wastewater/sludge, etc.), the concentration of Zn was almost the same comparatively with soil without amendments.

Manganese (Mn)

Mn is a component of the antioxidant enzyme superoxide dismutase (SOD) which helps fight free radicals [32]. Mn compounds are less toxic than those of other common metals such as nickel and copper. However, exposure to manganese dusts and fumes should not exceed the ceiling value of 5 mg/m^3, even for short periods because of its toxicity level. Manganese poisoning has been linked to impaired motor skills and cognitive disorders [32]. The concentration value of 4.9 mg/kg Mn was found in current studies in wheat grains similar to those reported earlier by Hussain et al. [26] from the same region (4.15 mg/kg). However, this value is lower than 18.43 mg/kg, which was previously reported [25]. It was further postulated as the plant uptake ratio (the ratio of metals between soil and plants) for wheat plants was found <1, the wheat plants should not be considered as metal accumulators [26]. Most of the Mn concentration values in wheat grains (Table 3) were quite a bit higher than either of the values cited above. The concentration of Mn in wheat flour from Sweden was lower (6.2 mg/kg) than the value reported from Pakistan (i.e 38.1 mg/kg) [26].

Nickel (Ni)

There is not much available information on the effects of nickel upon organisms other than humans. Wheat and wheat products and many vegetables contain intermediate levels of Ni (0.2-2.0 µg/g dry basis) [33]. According to FAO/WHO, the Ni tolerance limit in wheat grains is 1.6 mg/kg. Our current finding of Ni in wheat grain is 0.2 mg/kg, which is under the permissible limit; however, this value is far lower than the 6.2 mg/kg in previous reports [24] from the same country. A very high value of 9.92 mg/kg Ni has been reported from Konya, Turkey by Karatas et al. [34], in which the soil has been irrigated by the wastewater. Similar results were reported [25, 27] from the same region of Uttar Pradesh, India. However, the Ni values (4.2 and 4.12 mg/kg) were lower than Konya, Turkey, but still higher than rest of results shown in Table 3.

Chromium (Cr)

Chromium has no verified biological role and has been classified as not essential for mammals [35]. In the United States the dietary guidelines for daily Cr uptake have been lowered from 50-200 µg for an adult to 35 µg (adult male) and 25 µg (adult female) [36]. The bioavailability of mineral nutrients is primarily determined by the efficiency of absorption from the gut into the blood [37]. Factors that may influence the uptake of metals such as Cr from ingested food include the chemical form of the mineral in food, its interaction with food ligands, the redox activity of food components, interaction with other minerals, the physiological status of the consumer, and the composition of the food or meal [37].

The Cr content in wheat grains was found to be higher than the permissible limit of 0.02 mg/kg in almost all cases reported in Table 3. Higher values have been reported [25, 27] from Uttar Pradesh (8.16 and 8.0 mg/kg). The results of the present study were in accordance with the previous reports [30, 31, 34]. The Cr concentration in wheat grain (0.05 mg/kg) as determined in the present study is similar to that of Chandra et al., [25] in which soil contained higher content of Cr than the wheat grain. However, Cr content in the present study was far lower in both soil (4.2 mg/kg) and wheat grain. Zarcinas et al. [4] pointed out that the natural levels of As, Cr, and Ni in many Southeast Asian soils is significantly higher than European soils, and therefore exceeds soil contamination guideline values in many European countries. This highlights the dilemma in extrapolating data across regions and emphasizes the need to establish metal contamination guideline values for individual regions.

Cadmium (Cd)

Cadmium is taken up through the roots of plants to edible leaves, fruits, and seeds. It accumulates in animal milk and fatty tissues [38]. Cadmium, usually added to the soil as an impurity of phosphatic fertilizer, is the heavy metal of most concern. Its transfer from soil to the edible portions of agricultural food crops is significantly greater than for other contaminant elements [39]. Cadmium also may be detrimental to soil microbial populations [40]; the cumulative addition of Cd via phosphatic fertilizers and especially industrial wastes may have a detrimental effect on soil microorganisms. The toxic effects of heavy metals (especially Cd) of wheat indicate that heavy metals inhibit root and shoot growth and also induce oxidative stress and lipid peroxidation [41]. Bermudez et al. [28] pointed out that the concentration of Cd in wheat grain was dependent on soil pH being one of the major factors controlling Cd mobilization and uptake by plants. A higher concentration than the international regulations of Cd has been reported [24, 25, 42] (0.89 mg/kg). The Cd concentration of 0.28 mg/kg found in the present study was similar to the mean reported value (0.23 mg/kg) [47], and both were slightly above the regulation of 0.2 mg/kg. Similar results were shown by earlier reports [27, 43, 44]. In all these cases, the soils were either irrigated by wastewater or amended by sludge. However, the value of Cd concentration in wheat grains is under the regulation where soil is not amended with sludge or wastewater [28, 45, 46]. The Cd concentration in wheat flour from Sweden and Nigeria was found be lower than the regulations; whereas, the flour from Pakistan contained higher concentrations of 0.66 mg/kg [48].

Lead (Pb)

The bans on leaded gasoline and paint have reduced its exposure [49]. Pb dietary exposure ranges from 0.36 to 1.24, up to 2.43 μg/kg body weight/day in average adult consumers in Europe. High Pb concentrations reduce the growth, biomass and total chlorophyll content of plants [50]. Consumption of Grains as part of a diet may contribute to increased blood Pb levels with increased risk of anemia and neurological disorders [51].

The Pb concentration in wheat grains reported by most authors is high, ranging from 0.015 to 22.6 mg/kg (Table 3). The concentration value of Pb in our current study was found to be 0.35 mg/kg, unlike the reported values [24, 48] but similar to Hussain et al. [26] from the same country (22.6 and 0.12 mg/kg, respectively). A higher concentration of lead (>1 mg/kg) in wheat grain also was reported [25, 27, 31, 42, 47], where soil was irrigated by wastewater or amended by sludge (Table 3). Despite the higher Pb concentration in soil (15.6 mg/kg) in current findings; the value of Pb in grains seemed to be low, indicating its lower bioavailability in soils. Gupta and Gupta [51] concluded that the increment of total soil heavy metals contents (Cd, Pb, Zn, Cu) could enhance grain Cd accumulation and the increment of total soil Zn content may lower Pb accumulation in grain.

Conclusions

The present study involved an analysis of heavy metal concentrations in wheat grains grown in soils irrigated with municipal wastewater. Most of the metals found in wheat grains were higher than the international regulations. There are no established tolerable or safe limits available for heavy metals in irrigation water, soil, and food crops in Pakistan. Zn, Cu, and Cd in irrigation water in the current study were found above the US irrigation water quality, whereas Cr, Fe, Ni, Pb, and Mn were under the safe limits. Regular monitoring of these toxic heavy metals from industrial and domestic effluents, irrigation waters, and in crops is essential to preventing their excessive accumulation in the food chain. It is recommended that municipal wastewater treatment must be carried out prior to irrigating crops like wheat to avoid soil and dietary toxicity of heavy metals.

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References

1. SCOTT C., FARUQUI N.I., RASCHID L. (Eds). Wastewater Use in Irrigated Agriculture Confronting the Livelihood and Environmental Realities, CABI Publishing, IWMI, IDRC **2004** (http://web.idrc.ca/en/ev-31595-201-1-DO_TOPIC.html)
2. ANDERSON J. The environmental benefits of water recycling and reuse. Water Sci. Technol. **3**, 1, **2003**.
3. ZEB S., MALIK A. H., WASEEM, A., MAHMOOD Q. Water quality assessment of Siran River, Pakistan. Int. J. Phys. Sci. **6**, 7789, **2011**.
4. KHALID A., MALIK A. H., WASEEM A., ZAHRA S., MURTAZA G. Qualitative and quantitative analysis of drinking water samples of different localities in District Abbottabad, Pakistan. Int. J. Phys. Sci. **6**, 7480, **2011**.
5. WILSON B., PYATT F.B. Heavy metal dispersion, persistence, and bioaccumulation around an ancient copper mine situated in Anglesey. UK. Ecotox. Environ. Safe. **66**, 224, **2007**.
6. UMAR M., WASEEM A., SABIR M. A., KASSI A.M., KHAN A. S. The Impact of Geology of Recharge Areas on Groundwater Quality: A Case Study of Zhob River Basin, Pakistan. Clean- Soil Air Water. DOI: 10.1002/clen.201100581. **2012**.
7. SINGH K.P., MOHAN D., SINHA S., DALWANI R. Impact assessment of treated/untreated wastewater toxicants discharged by sewage treatment plants on health, agricultural, and environmental quality in the wastewater disposal area. Chemosphere. **55**, 227, **2004**.
8. MUCHUWETI M., BIRKETT J.W., CHINYANGA E., ZVAUYA R., SCRIMSHAW M.D. J. N. Lester. Heavy metal content of vegetables irrigated with mixture of wastewater and sewage sludge in Zimbabwe: implications for human health. Agr. Ecosyst. Environ. **112**, 41, **2006**.
9. ISLAM E, XIAO-E Y, ZHEN-LI H, QAISAR M. Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. J Zhejiang Univ. Sci. B. **8**, 1, **2007**.
10. LIU W.H., ZHAO J.Z., OUYANG Z.Y., SÖDERLUND L., LIU G.H. Impacts of sewage irrigation on heavy metals distribution and contamination in Beijing, China. Environ. Int. **31**, 805, **2005**.
11. MAPANDA F., MANGWAYANA E.N., NYAMANGARA J., GILLER K.E. The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. Agr. Ecosyst. Environ. **107**, 151, **2005**.
12. RATTAN R.K., DATTA S.P., CHHONKAR P.K., SURIBABU K., SINGH A.K. Long-term impact of irrigation with sewage effluents on heavy metal con-tent in soils, crops and groundwater-a case study. Agr. Ecosyst. Environ. **109**, 310, **2005**.
13. ROTHENBERG S.E., DU X., ZHU Y.G., JAY J.A. The impact of sewage irrigation on the uptake of mercury in corn plants (*Zea mays*) from suburban Beijing. Environ. Pollut. **149**, 246, **2007**.

14. PERVEEN S., IHSANULLAH I., SHAH Z., NAZIF,SHAH W.S.S., SHAH H. Study on accumulation of heavy metals in vegetables receiving sewage water. J. Chem. Soc. Pak. **33**, 220, **2011**.
15. GHOSH A.K., BHATT M.A., AGRAWAL H.P. Effect of long-term application of treated sewage water on heavy metal accumulation in vegetables grown in Northern India. Environ. Monit. Assess. **184**, 1025, **2012**.
16. PARC, Pakistan Agricultural Research Council, "Wheat Research and Development in Pakistan," Islamabad, **1989**.
17. ERRA District Profile, Abbottabad Earthquake Reconstruction and Rehabilitation Authority, July **2007**. Available from: http://www.erra.pk/Reports/KMC/AbbottabadProfile200907.pdf
18. SPCS: Sarhad Provincial Conservation Strategy Support (GoNWFP, IUCN **1996**). Available from: http://cmsdata.iucn.org/downloads/spcs.pdf
19. American Public Health Association Inc. (APHA), Standard Methods for the Examination of Water and Wastewater, 21st ed. New York, USA. **2005**.
20. MORENO F.N., ANDERSON C.W.N., STEWART R.B., ROBINSON B.H. Mercury volatilisation and phytoextraction from base-metal mine tailings. Environ. Pollut. **136**, 341, **2005**.
21. BOLLEN A., WENKE A., BIESTER H. Mercury Speciation Analyses in $HgCl_2$-Contaminated Soils and Groundwater-Implications for Risk Assessment and Remediation strategies. Water Res. **8**, 345, **2007**.
22. ULLRICH M.S., IIYUSHCHENKO M.A., USKOV G.A., Tanton T.W. Mercury Distribution and Transport in a contaminated River System in Kazakhistan and Associated Impacts on Aquatic Biota. Applied Geochem. **384**, 333, **2007**.
23. RADOJEVIC M., BASHKIN V.N. Practical Environmental Analysis (2nd Ed) RSC Publishing, UK, **2010**.
24. JAMALI M.K., KAZI T.G., ARAIN M.B., AFRIDI H.I., JALBANI N., KANDHRO G.A., SHAH A.Q., BAIG J.A. Heavy metal accumulation in different varieties of wheat (*Triticum aestivum* L.) grown in soil amended with domestic sewage sludge. J. Hazard. Mater. **164**, 1386, **2009**.
25. CHANDRA R., BHARAGAVA R.N., YADAV S., MOHAN D. Accumulation and distribution of toxic metals in wheat (*Triticum aestivum* L.) and Indian mustard (*Brassica campestris* L.) irrigated with distillery and tannery effluents. J. Hazard. Mater. **162**, 1514, **2009**.
26. HUSSAIN I., KHAN M.A., ALI J. Comparative Studies of Heavy Metals in Wheat Growing in Different Environmental Conditions. J. Chem. Soc. Pak. **33**, 499, **2011**.
27. BARMAN S.C., SAHU R.K., BHARGAVA S.K., CHATERJEE C. Distribution of heavy metals in wheat, mustard, and weed grown in field irrigated with industrial effluents. Bull. Environ. Contam. Toxicol. **64,** 489, **2000**.
28. BERMUDEZ G.M., JASAN S., PLÁ R., PIGNATA M.L. Heavy metal and trace element concentrations in wheat grains: Assessment of potential non-carcinogenic health hazard through their consumption. J. Hazard. Mater. **193**, 264, **2011**.
29. STEFANOVIC V.C., FILIPOVIĆ N.K., JOVANOVIC B.M. Undesirable metals content in wheat of different wheat varieties. APTEFF. **39**, 69, **2008**.
30. ZHU Y.E., ZHAO Y., SUN K., CHEN Z.F., QIAO J.J., Y.Q. J.I. Heavy metals in wheat grain and soil: assessment of the potential health risk for inhabitants in a sewage-irrigated area of Beijing, China. Fresen. Environ. Bull. **20**, 1109, **2011**.
31. FROST H.L., KETCHUM L.H. Trace metal concentration in durum wheat from application of sewage sludge and commercial fertilizer. Adv. Environ. Res. **4**, 347, **2000**.
32. The Nutrition Note Book. Available from: http://www.springboard4health.com/notebook/min_manganese.html
33. SOLOMONS N.W., VITERI F., SHULER T.R., NIELSEN F.H. Bioavailability of nickel in man: effects of foods and chemically-defined dietary constituents on the absorption of inorganic nickel. J. Nutr. **112**, 39, **1982**.
34. KARATAS M., DURSUN S., GULER E., OZDEMIR C., ARGUN M.E. Heavy Metal Accumulation in Wheat Plants Irrigated by Waste Water. Cellulose Chem. Technol. **40**, 575, **2006**.
35. DI-BONA K.R., LOVE S., RHODES N.R., MCADORY D., SINHA S.H., KERN N., KENT J., STRICKLAND J., WILSON A., BEAIRD J., RAMAGE J., RASCO J.F., VINCENT J.B. Chromium is not an essential trace element for mammals: effects of a "low-chromium" diet. J. Biol. Inorg. Chem. **16**, 381, **2011**.
36. VINCENT J.B. Recent advances in the nutritional biochemistry of trivalent chromium. Proceedings of the Nutrition Society. **63**, 41, **2007**.
37. MUTUMA S, AMUNA P, SHUKLA H, SUMAR S. Chromium in food, nutrition and health – an introduction. Nutrition & Food Science **99**, 81, **1999**.
38. KANETA M., HIKICHI H., ENDO S., SUGIYAMA N. Chemical form of cadmium (and other heavy metals) in rice and wheat plants. Environ. Health Persp. **65**, 33, **1986**.
39. MCLAUGHLIN M.J., TILLER K.G., NAIDU R., STEVENS D.P. Review: the behaviour and environmental impact of contaminants in fertilisers. Aust. J. Soil. Res. **34**, 1, **1996**.
40. CHAUDRI A.M., MCGRATH S.P., GILLER K.E. Survival of the indigenous population of *Rhizobium leguminosarum* biovar *trifolii in* soil spiked with Cd, Zn, Cu and Ni salts. Soil Biol. Biochem. **24**, 1992, **625**.
41. CAILIN G.E., YAN D., ZEGANG W., DINGZHEN W., YULONG W., QI S., SHISHI L. Responses of wheat seedlings to cadmium, mercury and trichlorobenzene stresses. J. Environ. Sci. **21**, 806, **2009**.
42. KARAK T., BHATTACHARYYA P. Heavy metal accumulation in soil amended with roadside pond sediment and uptake by winter wheat (*Triticum aestivum* L. cv. PBW 343). TheScientificWorldJOURNAL **10**, 2314, **2010**.
43. KARAMI M., AFYUNI M., REZAINEJAD Y., SCHULIN R. Heavy metal uptake by wheat from a sewage sludge-amended calcareous soil. Nutr. Cycl. Agroecosyst. **83**, 51, **2009**.
44. A. LAKHDAR, W. ACHIBA, F. MONTEMURRO, N. JEDIDI, C. ABDELLY. Effect of municipal solid waste compost and farmyard manure application on heavy metal uptake in wheat. Commun. Soil Sci. Plan. **40**, 3524, **2009**.
45. CONTI, M.E. CUBADDA F., CARCEA M., Trace metals in soft and durum wheat from Italy. Food Addit. Contam. **17**, 45, **2000**.
46. KIRCHMANN H., MATTSSON L. ERIKSSON J. Trace element concentration in wheat grain: results from the Swedish long-term soil fertility experiments and national monitoring program. Environ. Geochem. Health. **31**, 561, **2009**.
47. NAN Z., ZHAO C., JIJUN LI., CHEN F., SUN W. Relations between soil properties and selected heavy metal concentrations in spring wheat (*Triticum aestivum* L.) grown in contaminated soils. Water Air Soil Poll. **133**, 205, **2002**.

48. SHAR G.Q., KAZI T.G., JAKHRANI M.A., SAHITO S.R., MEMON M.A. Determination of seven heavy metals, cadmium, cobalt, chromium, nickel, lead, copper and manganese in wheat flour samples by flame atomic absorption spectrometry. J. Chem. Soc. Pakistan **24**, 265, **2002**.
49. ATSDR 1993, Agency for Toxic Substances and Disease Registry. April **1993**. URL: Available from: http://atsdr1.atsdr.cdc.gov:8080/tfacts13.html
50. CHANATACHON S., KRUATRACHUE M., POKETHITIYOOK P., TANTANASARIT S., UPATHAM S., SOONTJORNSARATHOOL V. Phytoextraction of lead from contaminated soil by vetiver grass (*Vetiver* sp.). In: Proceedings of the 17th World Congress of Soil Science, Paper No. 2308, Bangkok, August 14-21, **2002**.
51. GUPTA U.C., GUPTA S.C. Trace element toxicity relationships to crop production and livestock and human health: implication for management. Commun. Soil Sci. Plant Anal. **29**, 1491, **1998**.
52. FAO/WHO, Contaminants, Codex Alimentarius, vol. XVII, Edition 1, FAO/WHO, Codex Alimentarius Commission, Rome, **1984**.
53. CHRISTOPHER E., INIAMA G., OSABOR V., ETIUMA R., OCHELEBE M. A. Comparative evaluation of heavy metals in commercial wheat flours sold in Calabar-Nigeria Pakistan. J. Nutr. **8**, 585, **2009**.
54. JORHEM L., SUNDSTROM B., ENGMAN J. Cadmium and other metals in Swedish wheat and rye flours: longitudinal study. J. AOAC Int. **84**,1984, **2001**.
55. HUANG M., ZHOUB S., SUN B., ZHAO Q. Heavy metals in wheat grain: assessment of potential health risk for inhabitants in Kunshan, China. Sci. Total Environ. **405**, 54, **2008**.