

## Characterization of heavy metal in soils as affected by long-term irrigation with industrial wastewater

Bushra Haroon, An Ping, Arshid Pervez, Faridullah and Muhammad Irshad

### ABSTRACT

Investigation of heavy metals (HM) fractions in soils irrigated with wastewater (WW) would ascertain their bioavailability and contamination level in soils. This study investigated HM fractions in soils after long-term WW irrigation. WW irrigation profoundly affected HM fractions in soil. The ranges of HM concentrations in soils irrigated with WW were apparently wide. All fractions were significantly higher in the fields irrigated with industrial WW than rain-fed fields. HM concentrations varied in the soils as  $Pb > Cu > Ni > Zn > Fe > Cd > Mn$  after WW irrigation. In rainfed fields, HM concentrations differed in soils as  $Fe > Zn > Mn > Pb > Cd > Cu > Ni$ . The HM fractions were dominant in the residual form followed by oxides bound and carbonate associated fractions in WW-irrigated soils. Lower contents of HM in the soil were obtained in the exchangeable fraction. WW irrigation resulted in the transformation of HM into different fractions as residual > oxide associated > carbonate associated > organically bound > exchangeable form. Repeated WW irrigation increased pH values of the soils. The higher EC of soil indicated an accumulation of salts in the soils due to WW irrigation. Mitigation of HM contamination in Hattar industrial effluent is required before irrigation.

**Key words** | farmers' fields, fractionation, heavy metals, wastewater irrigation

**Bushra Haroon**  
**Arshid Pervez**  
**Faridullah**

**Muhammad Irshad** (corresponding author)  
Department of Environmental Sciences,  
COMSATS University Islamabad,  
Abbottabad Campus,  
Pakistan  
E-mail: [mirshad@ciit.net.pk](mailto:mirshad@ciit.net.pk)

**An Ping**  
**Muhammad Irshad**  
Arid Land Research Center,  
Tottori University,  
Tottori City, Hamasaka Cho,  
Japan

### INTRODUCTION

Heavy metal (HM) contamination of agricultural soils and vegetation is a worldwide ecological problem. The application of domestic and industrial effluents to agricultural fields is a common practice in Pakistan (Lone *et al.* 2000; Ensink *et al.* 2004). Effluent from city sewage and industrial wastewater (WW) can have a greater impact on irrigation water quality. These effluents have been considered as a rich source of organic matter (OM) and appreciable amounts of plant nutrients. Wastewater originated from industrial estates contains toxic substances such as HM, recalcitrant organics and other undesirable pollutants which may accumulate in the edible parts of food crops and pose serious threats to human life. These are hazardous

to water resources, agriculture, ecosystems and the human population (Gray *et al.* 2006). Wastewater contains HM which may be lethal for animals and humans if their concentrations exceed the permissible limits (Noureen *et al.* 2015). Heavy metal contamination of agricultural soils has also become a significant environmental problem (Chand *et al.* 2012). Wastewater irrigation, solid waste disposal, sludge applications, vehicular exhaust and industrial activities are the most important sources of HM contamination of soil and food crops grown on contaminated soils (Singh & Kalamdhad 2013). Mapanda *et al.* (2005) also reported that wastewater irrigation caused HM accumulation in soil. Research reports on the assessment of HM in WW, their accumulation in soils and uptake by plants, especially in the Hattar area, have been reported (Hussain 2000, 2010; Sial *et al.* 2005; Sial *et al.* 2006; Aziz 2007). There is consensus that the quality of food production remains a major

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

doi: 10.2166/wrd.2018.008

concern for crops cultivated in polluted soils. (Chiroma *et al.* 2003). The understanding of the behavior of HM in soil-plant systems seems to be particularly significant. There is considerable variability of uptake of HM by plants depending on soil properties (Nyles & Ray 1999). HM have been reported in crops grown in abandoned polluted areas (Ihenyen 1991; Jeanne & Sidle 1991; Okoronkwo *et al.* 2005).

Noureen *et al.* (2015) reported that vegetable crops have been contaminated with HM in the Hattar areas, Pakistan, and extractable HM in soils exceeded the prescribed limits. Food chain contamination is one of the major routes for entry of HM into the animal system, therefore, monitoring the available pools of metals in contaminated soils has generated huge interest (Datta *et al.* 2000; Yadav *et al.* 2002). HM, once accumulated in soils, are generally difficult to remove (Smith *et al.* 1996). Therefore, efforts are made to immobilize the metal concentrations in soils so that the accumulated HM may be curtailed to prevent them entering the food chain, contaminating surface or underground water. Several studies have been carried out on the impacts of wastewater irrigation on the accumulation of HM in soil and plant systems around the world (Noureen *et al.* 2015). Reports on heavy metal pollution in soil-water-plant systems in the vicinity of Hattar industrial estate of Haripur-Pakistan, where farmers have been irrigating their fields for several years, are insufficient and scanty (Noureen *et al.* 2015). Studies on the fractionation of HM in long-term WW-irrigated soils are also poorly documented. Therefore, the study was aimed at characterizing the HM in soils of arable fields in the Hattar area after long-term irrigation with industrial WW.

## MATERIALS AND METHODS

A field study was conducted in the farmers' fields to determine the severity of HM pollution in the soils irrigated with Hattar industrial wastewater (WW) for longer periods. Wastewater irrigation has been practiced over many years (>15 years) in these areas. The wastewater originated from the Hattar industrial estate of Haripur, Pakistan. The chemical composition of wastewater is given in Table 1. Soil samples (0–20 cm) were collected randomly

**Table 1** | Average values of water quality parameters of wastewater used for irrigation, along with standard limits of drinking water by NSDWQ-Pak and irrigation water by the USA (Radojevic & Bashkin 2010)

Parameters	Unit	Present study (mean)	NSDWQ Pak	US irrigation water quality
pH	–	9.20 ± 0.3	6.5–8.5	6.5–8.4
EC	µS cm <sup>-1</sup>	1,124 ± 26	–	<700
COD	mg L <sup>-1</sup>	459 ± 14	–	–
Pb	mg L <sup>-1</sup>	2.50 ± 0.31	0.05	5.0
Ni	mg L <sup>-1</sup>	1.64 ± 0.23	0.02	0.2
Mn	mg L <sup>-1</sup>	0.98 ± 0.14	>0.5	0.2
Fe	mg L <sup>-1</sup>	0.72 ± 0.1	–	5.0
Zn	mg L <sup>-1</sup>	1.51 ± 0.1	5.0	2.0
Cu	mg L <sup>-1</sup>	0.81 ± 0.02	2.0	0.2
Cd	mg L <sup>-1</sup>	0.32 ± 0.02	0.01	0.01
K	mg L <sup>-1</sup>	0.72 ± 0.10	–	–
Ca	mg L <sup>-1</sup>	4.10 ± 0.31	–	–
Mg	mg L <sup>-1</sup>	0.91 ± 0.02	–	–
Na	mg L <sup>-1</sup>	6.81 ± 0.42	–	–

from four adjacent fields irrigated with WW and four nearby non-irrigated (rainfed) arable fields. These fields were located in the adjoining area. The major agronomic practices, for instance method of cultivation, cropping pattern, fertilization etc., were observed and reported by the farmers as identical. Soil samples were collected from an area of 20 × 20 m<sup>2</sup> as composite samples after thoroughly mixing in plastic bags. Soil samples were analyzed for physico-chemical properties (texture, OM, pH and cation exchange capacity (CEC), HM fractions). Total carbon content was measured by using a dry combustion method (Nelson & Sommers 1982). Total OM content was calculated by multiplying the total carbon values by 1.72 (Nelson & Sommers 1982). The pH of compost suspension with soil:water at the ratio of 1:5 was measured by using a pH meter (HANNA HI 8520). Electrical conductivity (EC) of the soil suspension was determined with an EC meter (4320 JENWAY). Soil texture was determined using a pipette method (Gee & Bauder 1986). Five grams of soil sample was shaken with 25 mL of 1 M ammonium acetate (NH<sub>4</sub>OAc) for 1 h, then centrifuged and filtered to determine exchangeable elements (Ca, Mg, K, Na) using an atomic absorption spectrophotometer (AAS). HM in soils

were fractionated by a modified procedure of Amacher (1996). Soil samples (5 g) were sequentially fractionated into: (i) exchangeable metals (including water soluble) extracted with  $0.1 \text{ mol L}^{-1} \text{ Mg}(\text{NO}_3)_2$  (shaking for 2 h at 80 cycles/min); (ii) carbonate associated metals extraction with  $1 \text{ mol L}^{-1}$  sodium acetate at pH 5 (shaking for 5 h at 80 cycles/min); (iii) oxide associated metals extraction with  $0.2 \text{ mol L}^{-1}$  ammonium oxalate ( $0.2 \text{ mol L}^{-1}$  oxalic acid +  $0.1 \text{ mol L}^{-1}$  ascorbic acid) at pH 3.3 (in a boiling water bath for 30 min); (iv) organically bound associated metals extraction with 30%  $\text{H}_2\text{O}_2$  at pH 2 (in a boiling water bath for 30 min); and (v) the residual metals extraction by digestion with nitric acid and perchloric acid. After each successive extraction, the supernatant solution was centrifuged and then filtered. Heavy metal contents were determined using AAS. A complete weight balance system was used to determine the amounts of metal extracted by each extraction. Taking into account the volume of water carried over in the next extraction, each metal fraction was corrected for the aqueous phase elements in lieu of washing the sample with deionized water after centrifugation. Industrial wastewater samples collected from the drain (used for irrigation) were also analyzed for chemical properties (Table 1).

### Statistical analysis

The data were statistically analyzed using the Stat View software. Means of HM fractions were separated using Fisher's least significant difference (LSD) test at  $P$  value  $< 0.05$ .

## RESULTS AND DISCUSSION

Soil sampled from agricultural fields irrigated with wastewater (WW) exhibited higher values of CEC, OM, EC and pH as compared to the rainfed fields (Table 2). This showed that WW irrigation for longer periods profoundly affected the soil chemical composition. The texture of the soils remained unchanged after WW irrigation. The study revealed that WW irrigation increased the pH values of soils. The pH of the WW-irrigated fields ranged from 7.6 to 8.7 whereas its values ranged from 6.4 to 7.1 in the rainfed fields. The EC of soils ranged from 554 to  $728 \mu\text{S m}^{-1}$  in WW-irrigated fields whereas in the non-irrigated fields the EC values ranged from 182 to  $368 \mu\text{S m}^{-1}$ . Elevated EC values indicated that the use of industrial WW for irrigation can lead to an accumulation of salts in the soils. Total carbon was achieved between 2.2 and 4.2% in the WW-irrigated fields. Carbon contents were lower in the non-irrigated fields, i.e. in the range of 1.2–2.1%.

The results showed that HM fractions were significantly ( $P < 0.05$ ) higher in fields irrigated with industrial WW as compared to the rain-fed fields. The metal pollution of soils in Hattar showed that the area is highly contaminated. Schmidt (1997) also reported that HM were present in higher concentrations in WW. Irrespective of the fraction, HM concentrations varied in the order of  $\text{Pb} > \text{Cu} > \text{Ni} > \text{Zn} > \text{Fe} > \text{Cd} > \text{Mn}$  in the soil after long-term irrigation with WW. This is likely due to the higher concentration of Pb, Cu, Ni and Zn than those of the other HM in the WW. In rainfed fields the HM concentrations differed in soils as  $\text{Fe} >$

**Table 2** | Changes in soil properties in soil of wastewater irrigated fields

Waterwater (WW) irrigation	Sampling field	pH	EC ( $\mu\text{S cm}^{-1}$ )	Total C ( $\text{g kg}^{-1}$ )	OM ( $\text{g kg}^{-1}$ )	Clay (%)	Silt (%)	Sand (%)	CEC ( $\text{mg kg}^{-1}$ )
WW-irrigated	Field 1	7.6	654	31	57.3	7.5	10	82.5	302
	Field 2	8.2	610	34	58.5	10	5	85	235
	Field 3	8.7	728	42	72.2	5	7.5	87.5	276
	Field 4	7.9	554	22	37.8	5	5	90	192
	Mean	8.1	636.5	32.2	56.3	6.8	6.8	86.2	251
Rainfed	Field 1	7.0	328	21	36.1	10	5	95	187
	Field 2	6.8	220	16	27.5	5	2.5	92.5	177
	Field 3	6.4	182	15	25.8	7	8	95	129
	Field 4	7.1	368	12	20.6	15	5	80	125
	Mean	6.8	274.5	16	27.5	9.2	5.1	90.6	155
LSD (0.05)		0.2	3.4	0.3	3.5	0.6	0.4	1.2	3.6

Zn > Mn > Pb > Cd > Cu > Ni. Heavy metal fractions differed in the order of residual metal > oxide associated metal > carbonate associated metal > organically bound metal > exchangeable metal. HM predominantly appeared in the residual form followed by oxide associated form and carbonate associated form. The residual fractions in the most HM were predominant in WW-irrigated soils, which may reflect the geological distribution in the study sites. The residual fraction is the most stable fraction in soils and it is affected by the parent material, soil properties and climate condition (Han 2007). An increase in soil HM in organic fraction was likely due to the increase in soil OM content through long-term WW irrigation. Soil OM has a higher affinity for HM adsorption (Han 2007). Singh *et al.* (2009) reported that the availability of nutrients and other metals were greatly affected by the physicochemical properties of soil.

### Lead (Pb)

Pb concentration was apparently highest among the HM in the WW-irrigated soils (Table 3). The extractability of Pb varied considerably depending on WW irrigation. The concentration of Pb was varied with WW irrigation. Exchangeable Pb ranged from 28 to 72 mg kg<sup>-1</sup> among the sampling sites irrigated with WW. In the rainfed sites the concentration of exchangeable Pb varied from 0.001 to 0.01 mg kg<sup>-1</sup>. Carbonate associated Pb ranged from 123 to 283 mg kg<sup>-1</sup> in the fields irrigated with WW. The Pb concentrations associated with carbonate were found to be between

3.4 and 6.7 mg kg<sup>-1</sup> in the rainfed fields. Oxide associated Pb was higher in field 2 (410 mg kg<sup>-1</sup>) and lowest in field 4 (286 mg kg<sup>-1</sup>) after WW irrigation. The rainfed fields gave significantly lower concentration of oxide associated Pb. Organically bound Pb ranged from 76 to 102 mg kg<sup>-1</sup> in the WW irrigated fields whereas Pb concentrations varied minutely from 0.01 to 0.06 mg kg<sup>-1</sup>. Lead was found to be dominant in the residual form which ranged from 398 to 582 mg kg<sup>-1</sup> in the long-term WW-irrigated fields. In the rainfed sites the residual form of Pb ranged from 44 to 82 mg kg<sup>-1</sup>. The higher concentrations exceeding admissible levels of metals in cultivable soils may pose a potential risk of HM to the food chain and may restrict the cultivation of crops. Fractionation of HM in soil may help to assess the available metal fractions and the risk of mobilization of metals bound to particular soil constituents (Narwal & Singh 1998). Noreen *et al.* (2015) reported concentrations of Pb in brassica (128.2 mg kg<sup>-1</sup>), spinach (107.3 mg kg<sup>-1</sup>), coriander (98.7 mg kg<sup>-1</sup>) and radish (103.2 mg kg<sup>-1</sup>) in the Hattar area where wastewater has been used for irrigation. The Pb content in these vegetables significantly exceeded the maximum permissible limits of WHO (1992).

### Nickel (Ni)

Long-term WW irrigation on agricultural lands significantly increases the concentration of Ni in soils (Table 4). The Ni forms in WW treated soils were residual > oxide associated > carbonate associated > organically bound > exchangeable form. Among the WW-irrigated fields, the

**Table 3** | Fractionation of Pb (mg kg<sup>-1</sup>) in soil of wastewater irrigated fields

Wastewater (WW) irrigation	Sampling field	Exch. Pb	Carbonate Pb	Oxide Pb	Organic-Pb	Residual-Pb
WW-irrigated	Field 1	58	194	364	96	434
	Field 2	72	283	410	102	568
	Field 3	32	168	342	85	582
	Field 4	28	123	286	76	398
	Mean	47.5	192	350	89	495
Rainfed	Field 1	0.005	6.7	22.1	0.06	62.5
	Field 2	0.006	3.4	16.4	0.07	44.8
	Field 3	0.008	5.7	28.4	0.05	82.1
	Field 4	0.001	4.8	32.6	0.01	45.1
	Mean	0.004	5.15	24.8	0.04	58.6
	LSD (0.05)	0.001	0.1	1.2	0.001	2.6

**Table 4** | Fractionation of Ni ( $\text{mg kg}^{-1}$ ) in soil of wastewater irrigated fields

Wastewater (WW) irrigation	Sampling field	Exch. Ni	Carbonate Ni	Oxide Ni	Organic Ni	Residual Ni
WW-irrigated	Field 1	6.2	32.6	98.5	16.7	268.1
	Field 2	10.5	22.4	92.8	11.6	254.3
	Field 3	2.4	43.8	82.6	21.5	295.6
	Field 4	5.8	48.5	62.1	15.7	198.1
	Mean	6.2	36.8	84	16.3	254.0
Rainfed	Field 1	0.003	0.6	6.1	0.08	20
	Field 2	0.005	0.8	2.1	0.04	10.6
	Field 3	0.004	0.6	8.2	0.06	21.5
	Field 4	0.009	0.8	4.8	0.03	16.5
	Mean	0.004	0.7	5.3	0.06	17.1
	LSD (0.05)	0.001	0.2	0.5	0.01	1.2

residual form of Ni was highest in field 3 ( $295 \text{ mg kg}^{-1}$ ) and lowest in field 4 ( $198 \text{ mg kg}^{-1}$ ). Residual Ni ranged from 10 to  $21 \text{ mg kg}^{-1}$  in the rainfed fields. Oxide bound Ni ranged from 62 to  $92 \text{ mg kg}^{-1}$  in the irrigated fields and from 2 to  $8 \text{ mg kg}^{-1}$  in the rainfed fields. Carbonate bound Ni ranged from 62 to  $92 \text{ mg kg}^{-1}$  in the WW applied fields and in the rainfed fields the carbonate form of Ni remained similar among the fields ( $0.6\text{--}0.8 \text{ mg kg}^{-1}$ ). Organically bound Ni and exchangeable Ni ranged from  $11.6$  to  $21.5 \text{ mg kg}^{-1}$  and from  $2.4$  to  $10.5 \text{ mg kg}^{-1}$  in the WW-irrigated fields, respectively. These forms of Ni were found in very minute amounts in the rainfed sites when compared with the standard values. Dougherty & Hall (1995) reported that the long-term application of WW to agricultural land resulted in HM contamination in soils. Masona *et al.* (2011) reported that long-term irrigation with WW on agricultural lands significantly increased HM concentrations

in soils, and accumulated HM in maize plants. A regular assessment of soil in the study area should be carried out to avoid the excessive build-up of HM in soils to safeguard the environment and the health of the people who consume the crops grown over these lands.

### Manganese (Mn)

Manganese fraction was affected by the irrigation with industrial WW (Table 5). In soils sampled from the fields irrigated with WW, the average concentrations of residual Mn was  $159.5 \text{ mg kg}^{-1}$ , oxide bound Mn was  $72.5 \text{ mg kg}^{-1}$ , carbonate associated Mn was  $34 \text{ mg kg}^{-1}$ , organically bound Mn was  $13 \text{ mg kg}^{-1}$  and the exchangeable form of Mn was  $2.3 \text{ mg kg}^{-1}$ . Among the rainfed fields (non-irrigated), the average concentrations of residual Mn was  $66 \text{ mg kg}^{-1}$ , oxide bound Mn was  $22 \text{ mg kg}^{-1}$ , carbonate

**Table 5** | Fractionation of Mn ( $\text{mg kg}^{-1}$ ) in soil of wastewater irrigated fields

Wastewater (WW) irrigation	Sampling field	Exch. Mn	Carbonate Mn	Oxide Mn	Organic Mn	Residual Mn
WW- irrigated	Field 1	4.8	36.8	68	17.8	164
	Field 2	1.6	24.7	54	14.6	138
	Field 3	0.8	32.7	96	11.6	182
	Field 4	2.1	41.5	72	9.2	154
	Mean	2.32	33.9	72.5	13.3	159.5
Rainfed	Field 1	0.001	6.1	36.5	0.005	86.1
	Field 2	0.001	2.1	22.8	0.008	80.2
	Field 3	traces	4.1	11.2	0.009	43.1
	Field 4	traces	5.8	18.5	0.001	54.2
	Mean	0.001	4.5	22.2	0.006	65.9
	LSD (0.05)	0.001	0.1	1.2	0.02	2.5

associated Mn was  $4.5 \text{ mg kg}^{-1}$ , organically bound Mn was  $0.006 \text{ mg kg}^{-1}$  and the exchangeable form of Mn was found in negligible quantities.

### Copper (Cu)

Copper concentrations were substantially higher in WW contaminated fields and profoundly lower in the non-contaminated (rainfed) fields (Table 6). The Cu fractions differed among sampling sites after long-term WW irrigation in the order: residual Cu ( $262\text{--}354 \text{ mg kg}^{-1}$ ) > oxide bound Cu ( $126\text{--}182 \text{ mg kg}^{-1}$ ) > carbonate bound Cu ( $62\text{--}112 \text{ mg kg}^{-1}$ ) > organically bound Cu ( $22\text{--}54 \text{ mg kg}^{-1}$ ) > exchangeable Cu ( $3.6\text{--}11.5 \text{ mg kg}^{-1}$ ). The contents of Cu in rainfed soils were observed in smaller quantities, regardless of the type of Cu fraction. Ma & Rao (1997) and Hickey & Kittrick

(1984) reported that the majority of Cu contents in the soils and sediments were associated with the residual fraction. Vegetables cultivated in wastewater-irrigated soils take up HM in large enough quantities to cause potential health risks to the consumers (Ghosh *et al.* 2012). The consumption of HM-contaminated food can seriously deplete some essential nutrients in the body that are further responsible for decreasing immunological defenses, intrauterine growth retardation, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer rates (Türkdoğan *et al.* 2003).

### Cadmium (Cd)

The ranges of Cd concentration in soils irrigated with industrial WW were apparently wide (Table 7). Among the

**Table 6** | Fractionation of Cu ( $\text{mg kg}^{-1}$ ) in soil of wastewater irrigated fields

Wastewater (WW) irrigation	Sampling field	Exch. Cu	Carbonate Cu	Oxide Cu	Organic Cu	Residual Cu
WW-irrigated	Field 1	11.5	111	182	36.8	348
	Field 2	3.6	82.6	132	22.4	276
	Field 3	7.4	62.8	126	42.1	354
	Field 4	9.6	96.5	174	54.6	262
	Mean	8.0	88.2	153.5	38.9	310
Rainfed	Field 1	0.008	0.01	6.8	0.005	11
	Field 2	0.001	0.08	4.2	0.006	16
	Field 3	0.001	0.06	9.6	0.001	32
	Field 4	0.001	0.09	2.1	0.008	21
	Mean	0.002	0.06	5.6	0.005	20
	LSD (0.05)	0.001	0.1	1.5	1.3	2.3

**Table 7** | Fractionation of Cd ( $\text{mg kg}^{-1}$ ) in soil of wastewater irrigated fields

Wastewater (WW) irrigation	Sampling field	Exch. Cd	Carbonate Cd	Oxide Cd	Organic Cd	Residual Cd
WW- irrigated	Field 1	4.3	36.4	86.2	16.4	164.8
	Field 2	0.5	23.4	76.4	14.6	182.5
	Field 3	1.8	25.6	92.6	11.4	191.6
	Field 4	0.16	38.2	71.4	19.8	174.3
	Mean	1.6	30.9	81.6	15.5	178.3
Rainfed	Field 1	0.001	1.6	16.5	0.005	22.6
	Field 2	0.002	0.01	5.5	0.007	11.2
	Field 3	0.001	0.64	11.2	0.008	36.5
	Field 4	0.042	0.12	6.2	0.001	48.1
	Mean	0.01	0.6	9.8	0.005	29.6
	LSD (0.05)	0.001	0.1	1.6	1.2	3.7

sampling fields applied with wastewater, the average concentration of residual Cd was  $178 \text{ mg kg}^{-1}$ , oxide bound Cd was  $81.6 \text{ mg kg}^{-1}$ , carbonate associated Cd was  $31 \text{ mg kg}^{-1}$ , organically bound Cd was  $15.5 \text{ mg kg}^{-1}$  and the exchangeable form of Cd was  $1.6 \text{ mg kg}^{-1}$ . Among the rainfed fields (non-irrigated), the average concentration of residual Cd was  $29.6 \text{ mg kg}^{-1}$  and oxide bound Cd was  $10 \text{ mg kg}^{-1}$ . The other fractions of Cd, namely carbonate, organically bound and exchangeable forms, were found in smaller quantities. Usman & Ghallab (2006) reported that irrigation of soil with WW resulted in the transformation of metals from the carbonate fraction towards the exchangeable, Fe–Mn oxide, and organic fraction for Zn, towards the exchangeable, organic, and residual fraction for Cu, and towards the exchangeable fraction for Cd. Higher levels of HM in soil and plants in the study area is quite alarming. Noreen *et al.* (2015) reported the concentrations of Cd as  $20.9 \text{ mg kg}^{-1}$  in coriander,  $16.3 \text{ mg kg}^{-1}$  in brassica,  $15.5 \text{ mg kg}^{-1}$  in spinach and  $12.4 \text{ mg kg}^{-1}$  in radish. This indicated that the consumers were at higher risk after the consumption of these vegetables, which may lead to adverse health effects. Metals can cause serious health risks to the consumers through intake of the contaminated food crops if these metals exceed the permissible limits (Zhao *et al.* 2014).

### Iron (Fe)

The Fe concentrations were surprisingly found to be higher in the rainfed fields as compared to the water contaminated fields (Table 8). Among the WW contaminated fields, the

residual form of Fe was highest in field 3 ( $264 \text{ mg kg}^{-1}$ ) and lowest in field 1 ( $154.6 \text{ mg kg}^{-1}$ ). Residual Fe ranged from 132 to  $392 \text{ mg kg}^{-1}$  in the rainfed fields. Oxide bound Fe ranged from 64 to  $92.5 \text{ mg kg}^{-1}$  in the WW-irrigated fields and from 86 to  $174 \text{ mg kg}^{-1}$  in the rainfed fields. Carbonate bound Fe ranged from 22.5 to  $92.5 \text{ mg kg}^{-1}$  in the WW applied fields and in the rainfed fields the carbonate form of Fe ranged from 32 to  $96 \text{ mg kg}^{-1}$ . Organically bound Fe and exchangeable Fe ranged from 12.8 to  $18.7 \text{ mg kg}^{-1}$  and from 0.9 to  $4.2 \text{ mg kg}^{-1}$  in the WW-irrigated fields, respectively. In the rainfed sites, the Fe fractions differed as residual > oxide bound > carbonate associated > organically bound > exchangeable. The average concentration of residual Fe was  $237 \text{ mg kg}^{-1}$ , oxide bound Fe was  $120 \text{ mg kg}^{-1}$ , carbonate associated Fe was  $59 \text{ mg kg}^{-1}$ , organically bound Fe was  $15 \text{ mg kg}^{-1}$  and exchangeable Fe was  $0.2 \text{ mg kg}^{-1}$ .

### Zinc (Zn)

Extractability of Zn was the function of sampling sites and the extraction reagents used (Table 9). The average Zn concentrations among WW-irrigated fields were 206, 93.5, 50.9, 17.4 and  $2.2 \text{ mg kg}^{-1}$  in residual, oxide bound, carbonate associated, organically bound and exchangeable form, respectively. The average Zn concentrations among non-irrigated fields were lower than wastewater contaminated fields. The concentrations found were 143.6, 66.6, 21, 11 and  $0.13 \text{ mg kg}^{-1}$  in residual, oxide bound, carbonate associated, organically bound and exchangeable form,

**Table 8** | Fractionation of Fe ( $\text{mg kg}^{-1}$ ) in soil of wastewater irrigated fields

Wastewater (WW) irrigation	Sampling field	Exch. Fe	Carbonate Fe	Oxide Fe	Organic Fe	Residual Fe
WW-irrigated	Field 1	4.2	22.5	64.8	16.98	154.6
	Field 2	1.2	92.5	86.2	12.83	184.6
	Field 3	0.9	42.6	92.5	14.65	264.1
	Field 4	1.8	31.2	76.5	18.75	182.6
	Mean	2.0	47.2	80	15.8	196.47
Rainfed	Field 1	0.40	54	123	11.5	282.4
	Field 2	0.16	32	86	16.4	143.1
	Field 3	0.54	96	174	15.8	392.5
	Field 4	0.05	54	98	16.4	132.5
	Mean	0.20	59	120.2	15.0	237.6
	LSD (0.05)	0.1	1.4	2.2	1.8	3.7

**Table 9** | Fractionation of Zn (mg kg<sup>-1</sup>) in soil of wastewater irrigated fields

Wastewater (WW) irrigation	Sampling field	Exch. Zn	Carbonate Zn	Oxide Zn	Organic Zn	Residual Zn
WW-irrigated	Field 1	4.8	22.5	64.5	16.4	264.1
	Field 2	1.2	38.6	84.8	12.1	151.8
	Field 3	2.6	96.5	132.1	18.4	286.5
	Field 4	0.5	46.2	92.7	22.7	122.4
	Mean	2.2	50.9	93.5	17.4	206.2
Rainfed	Field 1	0.06	31.5	92.6	19.8	185.4
	Field 2	0.15	19.5	74.5	1.8	132.6
	Field 3	0.21	16.2	45.1	5.2	92.6
	Field 4	0.10	18.6	54.3	16.7	164.1
	Mean	0.13	21.4	66.6	10.8	143.6
LSD (0.05)		0.1	1.6	2.7	1.2	3.8

**Table 10** | Heavy metal concentrations in soil irrigated with contaminated water (mg kg<sup>-1</sup>) and the maximum admissible concentrations of toxic metals in soils from the USA, UK and EU

HM	Previous studies (Pakistan) (Jamali <i>et al.</i> 2009)	Previous studies (India) (Chandra <i>et al.</i> 2009)	USA	UK	EU
Cd	2.4 ± 0.18	10 ± 0.76	20	3	1–3
Cu	39.2 ± 2.1	40.83 ± 2.3	750	135	50–140
Ni	36.0 ± 1.2	42.24 ± 3.3	210	75	30–75
Pb	75.5 ± 4.3	30.81 ± 2.2	150	300	50–300
Zn	235 ± 7.2	143 ± 4.2	1,400	300	150–300
Mn	–	1,352 ± 10	–	–	–
Fe	–	13,925 ± 12	–	–	–

respectively. HM contamination in soil is also dependent on properties of soils. Several soil properties, such as CEC, OM and clay minerals, the content of the oxides of iron (Fe), aluminum (Al), and manganese (Mn), and the redox potential regulate the retention and immobilization of HM in soils. These factors regulate the bioavailability of HM and result in the appearance of plant toxicity. Long-term application of sewage WW led to substantial accumulation of Zn in the oxidizable fraction (Fitamo *et al.* 2007) or exchangeable, reducible, and oxidizable forms (Usman & Ghallab 2006). The availability of HM is influenced by pH, OM, CEC, calcium carbonate, Fe and Mn oxides (Vamerali *et al.* 2010). Higher levels of HMs in agricultural fields marginalizes soil quality and impairs food security (Kelepertzis 2014). The long-term WW irrigation leads to accumulation of MnO/FeO- and OM-complexes, which are less bioavailable and less mobile (Salbu *et al.* 1998). Incubation studies using HM-spiked soils indicated that the HM pools were transformed into more stable fractions over time (Jalali &

Khanlari 2008). Mapanda *et al.* (2005) reported higher concentrations of HM (Cu, Zn, Cd, Ni, Cr and Pb) in soils irrigated with WW for ten years. Kabala *et al.* (2011) reported that the largest fraction of Cu, Pb, and Zn in WW-irrigated soils was strongly bound in a residual form, while exchangeable and the other labile fractions were negligible. Municipal WW applied soil showed considerable amounts of OM, macro- and micronutrients, which were partially taken up by plants, and partly accumulated in soil (Wang *et al.* 2003; Singh *et al.* 2009). Heavy metal concentrations in soil irrigated with contaminated water and the maximum admissible concentrations of toxic metals in soils from the USA, UK and EU are given in Table 10.

## CONCLUSIONS

This study investigated the HM fractions in agricultural soils irrigated long-term with wastewater (WW). The



fractionation of HM indicated that the HM in WW-irrigated soils significantly increased in the residual form, followed by oxides bound and carbonate associated HM fractions as compared to non-irrigated soils. Transformation of HM in WW irrigated soils were varied as residual metal > oxide associated metal > carbonate associated metal > organically bound metal > exchangeable metal. Due to the increasing demands for food safety and the risk associated with consumption of food products contaminated with HM, we suggest a restricted use of WW for the prevention of potential health hazards in arable land. Interval monitoring of HM in soil and crops irrigated WW is required to control their excessive accumulation in the food chain.

## ACKNOWLEDGEMENT

Funding for this research through the national research program for universities (project No. NRPU-4831) by the Higher Education Commission of Pakistan is gratefully acknowledged.

## REFERENCES

- Amacher, M. C. 1996 Nickel, cadmium, and lead. In: *Methods of Soil Analysis, Part 3: Chemical Methods* (D. L. Sparks, ed.). SSSA Book Series No. 5, SSSA and ASA, Madison, WI, pp. 739–768.
- Aziz, M. A. 2007 *Agricultural use of Sewage Water: Metal Contamination of Soils and Crops and Management Through Amendments*. PhD Thesis, Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan.
- Chand, S., Pandeyand, A. & Patra, D. D. 2012 Influence of nickel and lead applied in combination with vermicompost on growth and accumulation of heavy metals by *Mentha arvensis* Linn cv Kosi. *Indian J. Nat. Products Resour. (IJNPR)* **3**, 256–261.
- Chandra, R., Bharagava, R. N., Yadav, S. & Mohan, D. 2009 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**, 1514–1521.
- Chiroma, T. M., Hymore, F. K. & Ebawele, R. O. 2003 Heavy metals contamination of vegetables and soils irrigated with sewage water in Yola. *Nigerian J. Eng. Res. Dev.* **2** (3), 20–106.
- Datta, S. P., Biswas, D. R., Saharan, N., Ghosh, S. K. & Rattan, R. K. 2000 Effect of long-term application of sewage effluents on organic carbon, bioavailable phosphorus, potassium and heavy metals status of soils and uptake of heavy metals by crops. *J. Indian Soc. Soil Sci.* **48**, 836–839.
- Dougherty, T. C. & Hall, A. W. 1995 *Environmental Impact Assessment of Irrigation and Drainage Projects*. FAO Irrigation and Drainage Paper 53 [Online]. Available from: [www.fao.org/docrep/v8350e/v8350e00.htm](http://www.fao.org/docrep/v8350e/v8350e00.htm).
- Ensink, J. H. J., Simmons, R. W. & Hoek, W. V. 2004 Wastewater use in Pakistan: the cases of Harronabad and Faisalabad. In: *Wastewater Use in Irrigate Agriculture: Confronting the Livelihood and Environmental Realities* (C. A. Scott, N. I. Faruqi & L. Raschid-Sally, eds). CAB International, Wallingford, pp. 91–99.
- Fitamo, D., Itana, F. & Olsson, M. 2007 Total contents and sequential extraction of heavy metals in soils irrigated with wastewater, Akaki, Ethiopia. *Environ. Manage.* **39**, 178–193.
- Gee, G. W. & Bauder, J. W. 1986 Particle-Size Analysis. In: *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods, Agronomy Monograph No. 9*, 2nd Edition (A. Klute, ed.). American Society of Agronomy/Soil Science Society of America, Madison, WI, pp. 383–411.
- Ghosh, A. K., Bhatt, M. A. & Agrawal, H. P. 2012 Effect of long term application of treated sewage water on heavy metal accumulation in vegetables grown in northern India. *Environ. Monitor. Assess.* **184**, 1025–1036.
- Gray, C. W., Dunhan, S. J., Dennis, P. G., Zhao, F. J. & McGrath, S. P. 2006 Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud. *Environ. Pollut.* **142**, 530–539.
- Han, F. X. 2007 Biogeochemistry of trace elements in arid environments. In: *Environmental Pollution 13*. Springer, Dordrecht, The Netherlands, pp. 710–714.
- Hickey, M. G. & Kittrick, J. A. 1984 Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediment containing high levels of heavy metals. *J. Environ. Qual.* **13**, 372–376.
- Hussain, A. 2000 *Irrigation of Crops with Sewage Effluent: Implications and Movement of Pb and Cr as Affected by Soil Texture, Lime, Gypsum and Organic Matter*. PhD thesis, Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan.
- Hussain, A. 2010 *Accumulation and Partitioning of Cadmium, Zinc and Copper in Cereal and Legume Crops Under City Effluent Irrigation and Phosphorus Application*. PhD thesis, Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan.
- Ihenyem, A. 1991 A comparative study of Pb, Cu and Zn in roadsides sediments in Metropolitan Lagos and Benin. *Nig. Environ. Int.* **18** (1), 103–105.
- Jalali, M. & Khanlari, Z. V. 2008 Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran. *Geoderma* **143**, 26–40.
- Jamali, M. K., Kazi, T. G., Arain, M. B., Afridi, H. I., Jalbani, N., Kandhro, G. A., Shah, A. Q. & Baig, J. A. 2009 Heavy metal

- accumulation in different varieties of wheat (*Triticum aestivum* L.) grown in soil amended with domestic sewage sludge. *J. Hazard. Mater.* **164**, 1386–1391.
- Jeanne, C. C. & Sidle, R. C. 1991 Fate of heavy metals in an abandoned zinc tailing pond. *J. Environ. Qual.* **20**, 745–751.
- Kabala, C., Karczewska, A., Szopka, K. & Wilk, J. 2011 Copper, zinc, and lead fractions in soils long-term irrigated with municipal wastewater. *Commun. Soil Sci. Plant Anal.* **42**, 905–919.
- Kelepertzis, E. 2014 Accumulation of heavy metals in agricultural soils of Mediterranean: insights from Argoloda basin, Peloponnese, Greece. *Geoderma* **221–222**, 82–90.
- Lone, M. I., Aslam, R. & Khan, K. S. 2000 Water quality and soil contamination in some industrial areas of Pakistan. *Pak. J. Soil Sci.* **18**, 1–6.
- Ma, L. Q. & Rao, G. N. 1997 Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *J. Environ. Qual.* **26**, 259–264.
- Mapanda, F., Mangwayana, E. N., Nyamangara, J. & Giller, K. E. 2005 The effects of long-term irrigation using wastewater on heavy metal contents of the soil under vegetables in Harare, Zimbabwe. *Agric. Ecosyst. Environ.* **107**, 151–165.
- Masona, C., Mapfai, L., Mapurazi, S. & Makanda, R. 2011 Assessment of heavy metal accumulation in wastewater irrigated soil and uptake by maize plants (*Zea mays* L.) at Firl farm in Harare. *J. Sustain. Dev.* **4** (6), 132–137.
- Narwal, R. P. & Singh, B. R. 1998 Effect of organic materials on partitioning, extractability, and plant uptake of metals in an alum shale soil. *Water Air Soil Pollut.* **103**, 405–421.
- Nelson, D. W. & Sommers, L. E. 1982 Total carbon, organic carbon and organic matter. In: *Methods of Soil Analysis. Part 2. Agronomy Monographs 9* (A. L. Page, ed.). ASA and SSSA, Madison, WI, pp. 539–579.
- Noureen, R., Irshad, M. & Faridullah, 2015 Assessing selected heavy metals in vegetables and soils irrigated with wastewater at Haripur, Pakistan. *Minerva Biotechnol.* **27**, 99–105.
- Nyles, C. B. & Ray, R. N. 1999 *The Nature and Properties of Soils*, 12th edn. Macmillan, New York, pp. 743–784.
- Okoronkwo, N. E., Ano, A. O. & Onwuchekwa, E. C. 2005 Environment, health and risk assessment: a case study of the use of an abandoned municipal waste dump site for agricultural purposes. *Afr. J. Biotechnol.* **4** (11), 1217–1221.
- Radojevic, M. & Bashkin, V. N. 2010 *Practical Environmental Analysis*, 2nd edn. RSC Publishing, UK.
- Salbu, B., Krekling, T. & Oughton, D. H. 1998 Characterization on radioactive particles in the environment. *Analyst* **123**, 843–849.
- Schmidt, J. P. 1997 Understanding phytotoxicity threshold for trace elements in land-applied sewage sludge. *J. Environ. Qual.* **26**, 4–10.
- Sial, R. A., Chaudhary, M. F., Abbas, S. T., Niaz, A., Haq, M. A. & Chaudhary, E. H. 2005 Effect of various effluents from Hattar Industrial area on some characteristics of two soil series. Caerno de Pesquisa. *Bio. Santa Cruz Sul.* **17** (2), 107–116.
- Sial, R. A., Chaudhary, M. F., Abbas, S. T., Latif, M. I. & Khan, A. G. 2006 Quality of effluents from Hattar Industrial Estate. *J. Zhejiang Univ. Sci. B* **7** (12), 974–980.
- Singh, J. & Kalamdhad, A. S. 2013 Bioavailability and leachability of heavy metals during composting – a review. *Int. Res. J. Environ. Sci.* **2**, 59–64.
- Singh, A., Sharma, R. K., Agrawal, M. & Marshall, F. 2009 Effects of wastewater irrigation on physicochemical properties of soils and availability of heavy metals in soil and vegetables. *Commun. Soil Sci. Plant Anal.* **40**, 3469–3490.
- Smith, C. J., Hopmans, P. & Cook, F. J. 1996 Accumulation of Cr, Pb, Cu, Ni, Zn and Cd in soil following irrigation with untreated urban effluents in Australia. *Environ. Pollut.* **94** (3), 317–323.
- Türkdogan, M. K., Fevzi, K., Kazim, K., Ilyas, T. & Ismail, U. 2003 Heavy metals in soil, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey. *Environ. Toxicol. Pharmacol.* **13**, 175–179.
- Usman, A. R. A. & Ghallab, A. 2006 Heavy-metal fractionation and distribution in soil profiles short-term-irrigated with sewage wastewater. *Chem. Ecol.* **22**, 267–278.
- Vamerali, T., Bandiea, M. & Mosca, G. 2010 Field crops for phytoremediation of metal-contaminated land. A review. *Environ. Chem. Lett.* **8**, 1–17.
- Wang, Z., Chang, C., Wu, L. & Crowley, D. 2003 Assessing the soil quality of long-term reclaimed wastewater-irrigated cropland. *Geoderma* **114**, 261–278.
- WHO 1992 *Cadmium Environmental Health Criteria*, Vol. 134. World Health Organization, Geneva.
- Yadav, R. K., Goyal, B., Sharma, R. K., Dubey, S. K. & Minhas, P. S. 2002 Post-irrigation impact of domestic sewage effluent on composition of soils, crops and ground water – a case study. *Environ. Int.* **28**, 481–486.
- Zhao, Q., Wang, Y., Cao, Y., Chen, A., Ren, M., Ge, Y., Yu, Z., Wan, S., Hu, A., Bo, Q., Ruan, L., Chen, H., Qin, S., Chen, W., Hu, C., Tao, F., Xu, D., Xu, J., Wen, L. & Li, L. 2014 Potential health risks of heavy metals in cultivated topsoil and grain, including correlations with human primary liver, lung and gastric cancer, in Anhui province, Eastern China. *Sci. Total Environ.* **470–471**, 340–347.

First received 20 February 2018; accepted in revised form 12 July 2018. Available online 10 September 2018