

Accumulation of Metals in Soils, Groundwater and Edible Parts of Crops Grown Under Long-Term Irrigation with Sewage Mixed Industrial Effluents

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Abstract Farmers in developing countries irrigate crops using raw urban and industrial effluents with consequent risks from metal contamination. Therefore, soils, crops and groundwater from an effluent irrigation use site were assessed for Cd, Cr, Ni and Pb. Total and available contents of metals in soil followed the order Pb > Ni > Cr > Cd. Crops accumulated more Pb, followed by Cd, Ni and Cr. Pb exceeded the permissible limit with wastewater irrigation only, but Cd exceeded the limit even with combined irrigations of wastewater and groundwater. Among crops, sugar beet assimilated highest Cd ($3.14 \mu\text{g g}^{-1}$) and Pb ($6.42 \mu\text{g g}^{-1}$) concentrations. Legumes accumulated more metals than cereals. Long-term use of wastewater and its conjunctive use with groundwater led to toxic accumulations of Cd, Pb, Ni and Cr. Cd with higher availability and mobility indices and lower toxicity limit, posed the maximum risk of food-chain contamination.

Keywords Metals availability · Toxicity indices · Food chain contamination

Wastewater (WW) produced from urban agglomerations and industries contains a variety of pollutants. Its usage has certain negative environmental impacts in the form of pathogens causing diseases, metals accumulation and soil salinization (Qadir et al. 2009; Drechsel and Evans 2010). Resource poor nations, due to prohibitive costs of conventional treatment, dispose larger portions of WW, either raw or after partial treatment, in surface streams or on land, generally for irrigation in peri-urban vegetables and food grains (Gupta and Deshpande 2004). The bioavailability and mobility of metals-added WW irrigation govern their uptake by plants and potential food chain contamination (Yadav et al. 2003; Sharma et al. 2007). In contrast to organic pollutants, metals are non-biodegradable and accumulate in soils, typically with an initial fast retention, subsequent slow reactions, and ultimate quasi-steady state between available and residual forms (Han et al. 2003; Lokeshwari and Chandrappa 2006). Soil characteristics, climatic conditions, and WW composition regulate the mobility of metals in soil and groundwater (GW) and their bioavailability to crops grown. Dietary intake of metals assimilated in edible parts of crops and GW poses a major threat to food safety and public health (Minhas et al. 2006; Lal et al. 2008). Assimilation and translocation of specific metals to different plant parts depends on the physiology of individual crops (Ebbs et al. 1997; Landonin 2002). The information generated on behavior of specific metals accumulation in edible parts of different crops under WW irrigation would help in discarding the crop/crop part tending to accumulate more than permissible levels of metals. With this consideration, the present investigation was carried out to assess metal (Cd, Cr, Ni and Pb) distribution in long-term WW irrigated soils of a semi-arid region and their accumulation in edible parts of different crops grown and GW.

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Materials and Methods

The study site covers an area 2.5 km on either side of a 6.0 km long disposal channel receiving effluents (~50 MLD, 30 industrial + 20 domestic) from a sewage treatment plant (STP) in Samaipur (28.24–29.04°N and 77.18–78.31°E), Faridabad (Haryana), India. Farmers have been irrigating their crops either with raw or partially treated WW carried through this channel for the past 25 years, while some of them are either combining the WW and GW pumped from 20 to 22 m deep bore tube-wells (CW) or using GW only. Soils of the research site are deep, moderately drained, hyperthermic Typic Ustochrepts dominated by illite and mixed layer minerals. The climate of the site is semi-arid monsoonal with two cropping seasons [winter (*rabi*)-November to April and summer (*kharif*)-July to October]. Mean monthly highest and lowest temperatures, and morning/evening relative humidity of 39.2 ± 0.6 and $18.2 \pm 0.8^\circ\text{C}$, and $63 \pm 1.4/38 \pm 2.0\%$ and $96 \pm 1.7/10.3 \pm 0.3\%$ are observed during June and January, respectively. The study area receives 620 mm average annual rainfall, of which ~80% occurs during monsoon (July–September). Evaporation exceeds rainfall, except during monsoon.

Soil samples were collected during *rabi* and *kharif* down to 0.9 m depth from 54 [24, 18 and 12 irrigated with WW, CW and GW (also designated as control), respectively] sites existing at 50, 100, 500, 750, 1000, 1500 and 2000 m along and 50, 100, 500, 750, 1000, 1500, 2000 and 2500 m across the disposal channel. Physicochemical properties of surface (0.3 m) soils of 13 (3, 4 and 6 irrigated with GW, CW and WW, respectively) sites were measured using standard procedures described in Page et al. (1982). Total (HF/HClO₄ digested) and available (DTPA extractable) contents of Cd, Cr, Ni and Pb in GW, CW and WW soils were measured by Analytik Jena Double beam ZENit 700P atomic absorption spectrophotometer (AAS) with detection limit of $25 \mu\text{g kg}^{-1}$ for different metals in soils and plants. Residual fraction of metals was calculated by subtracting the available contents from total contents. The threshold base limits for bioavailability and the maximum allowable additions of four metals causing their accumulation beyond the permissible limits were established using linear regression functions between total and available contents of respective metals. Fractional distribution index (DI), a measure of relative distribution of a metal between its available and residual fractions, was computed with the equation, $DI = Ca/Cc$, as described by Han et al. (2003). Where, C_a is the ratio of available/residual fraction to the total contents of a metal in WW or CW soils and C_c is the ratio of the same fraction to the total contents of that metal in GW soil. Redistribution index (RDI), a function of

relative availability of a metal in contaminated soil, was calculated by summation of the products of the ratio of available/residual fraction to the total contents of a metal and their respective DI values, using the equation,

$$RDI = \sum_{i=a/r}^i (C_i * DI_i).$$

where, C_i is the ratio of available (a)/residual (r) fraction to the total concentration of a metal in WW soil and DI_i is the DI of a particular component.

Wastewater was collected in duplicate, from the point of mixing of domestic and industrial effluents in the disposal channel, inlet and outlet of STP, during April, July and October. Simultaneously, GW was also collected from the four tube wells existing at 750/2000, 1500/1000, 2000/600 and 2500/850 m across/along the channel. Irrigation parameters were determined using standard procedures (USSL 1954), whereas metals were estimated after wet acid digestion (HNO₃:HClO₄ in 3:1) using AAS.

Wheat (*Triticum aestivum*), spinach (*Spinacea oleracia*), fenugreek (*Trigonella foenumgraecum*), radish (*Raphanus sativus*) and Egyptian clover (*Trifolium alexandrinum*) in *rabi*, and sorghum (*Sorghum bicolor*) and cluster bean (*Cyamopsis tetragonoloba*) in *kharif* irrigated separately with WW, CW and GW were sampled. The vegetable crops [cauliflower (*Brassica oleracia* L.), sugar beet (*Beta vulgaris*) and faba bean (*Vicia faba*) during *rabi* and brinjal (*Solanum melogena*), okra (*Abelmoschus esculentus*) and bottle gourd (*Lagenaria siceraria*) in *kharif*] irrigated with WW were also sampled. Three whole plants (including edible parts) of every crop were randomly collected from six fields of each of WW, CW and GW. These were washed, air-dried, partitioned in root, shoot and fruits/pods/grains; oven-dried at 70°C and ground, digested in 4:1 mixture of HNO₃ and HClO₄, and contents of Cd, Cr, Ni and Pb determined using AAS. Transfer factor (TF) of different metals from soil to edible parts of crops was calculated as:

$$TF = Ps (\mu\text{g g}^{-1} \text{ dry weight}) / St (\text{mg kg}^{-1} \text{ dry weight})$$

where, P_s is metal content in edible plant parts and S_t is the total content of that metal in soil. The TF for any metal in WW, CW and GW soils was calculated by dividing the sum of TF values of individual crops with number of species grown in a particular category of soil. Similarly, mean TF values of WW crops used for root, green leaves/stalk, fruit/reproductive parts, grain and straw were calculated by dividing the sum of TF of the individual crops by their number in each category.

Arithmetic means and standard deviations of contents of metals in soils and edible parts of crops were calculated for WW, CW and GW. The significance of differences be-

tween means of metals in different crops irrigated with WW alone was judged by least significant difference at 5 % level of Tukey's adjustment after analysis of variance test in complete randomized design using the MStat-C program.

Results and Discussion

Average composition of raw industrial and sewage mixed effluents from STP inlet, primarily treated mixed effluents from STP outlet, and GW is presented in Table 1.

The values of studied parameters in raw sewage and industrial effluents were higher than WHO (2000) limits for irrigation. Partial treatment decreased only BOD and COD from 230 and 319 to 106 and 178 mg L⁻¹, respectively. Decrease in BOD and COD of WW during partial treatment was mainly because of settling of suspended organic matter and enhanced oxygen supply during lagooning. Unregulated discharge of such WW is likely to cause eutrophication of surface water, contamination of GW and potentially the food chain. Values for GW were within the normal limits of irrigation for a monsoonal climate; however, continuous use may lead to temporal development of salinity and sodicity (Yadav et al. 2003). Cd, Cr and Pb concentrations were within safe limits for irrigation, but beyond the permissible levels for drinking.

Study site soils were sandy loam (sand:silt:clay ratio of 55 ± 1.6:28 ± 1.3:16 ± 0.7 %) in texture with mean pH, electrical conductivity (EC), organic carbon (OC), bulk density (BD) and cation exchange capacity values of 8.2 ± 0.3, 3.5 ± 0.3 dS m⁻¹, 0.24 ± 0.04 %, 1.44 ± 0.04 g cm⁻³ and 11.0 ± 0.3 c mol p kg⁻¹, respectively. Available contents of Cd, Cr, Ni and Pb in GW surface soils were 0.36 ± 0.09, 2.49 ± 0.54, 2.86 ± 0.23 and 10.32 ± 1.48 mg kg⁻¹,

respectively. These increased to 0.92 ± 0.11, 6.87 ± 0.83, 7.37 ± 0.51, and 17.52 ± 2.92 mg kg⁻¹, respectively, in CW and 1.18 ± 0.11, 7.99 ± 0.68, 8.26 ± 0.59 and 17.36 ± 2.54 mg kg⁻¹, respectively, in WW soils. The order of accumulation of both total and available forms of metals in soils was Pb > Ni > Cr > Cd. The highest accumulation occurred with WW followed by CW and the least was in GW. Greater differences in total and available contents of metals among WW, CW and GW irrigated soils were observed only in surface 0–0.3 m soils, which decreased with depth (Fig. 1).

However, presence of 0.43, 0.42, 0.38 and 0.49 times the surface layer total contents of Cd, Cr, Ni and Pb, respectively in 0.6–0.9 m WW soil indicated the mobility of metals and possibilities of shallow GW contamination. The residual fraction of Cd, Cr, Ni and Pb in surface 0.3 m of GW irrigated soils was 0.74, 0.84, 0.85 and 0.60, respectively while the values were 0.67, 0.81, 0.82 and 0.57, respectively, in CW and 0.64, 0.80, 0.80 and 0.58, respectively, with WW (Table 2).

WW and CW increased available Cd by 0.38 and 0.27 times, respectively over GW. Respective increases in fractional availability of Cr, Ni and Pb were 0.19, 0.29 and 0.07 with CW and 0.25, 0.23 and 0.05 with WW. Progressive increase in the content and DI of available fraction of metals with increasing WW use indicated higher affinity of the soil exchange complex to metals and their slower conversion in residual forms as also observed by Han et al. (2003) and in long-term WW irrigated Ethiopian soils by Fitamo et al. (2007). Mineralization of organic matter added with WW, and the acids produced during its decomposition, favor release and availability of metals that substantiate the findings of McBride et al. (2000). The RDI of 1.01–1.06 for above metals in sandy loam Ustochrepts after 25 years of irrigation with WW or CW further

Table 1 Composition of wastewater and groundwater used for irrigation (n = 6)

Parameters	Wastewater			Groundwater (distance, m from channel)			
	Industrial effluent (IE)	Sewage + IE	Tr sewage with IE	750/2000	1500/1000	2000/600	2500/850
EC (dS m ⁻¹)	10.0 ± 2.3	5.1 ± 0.36	5.2 ± 0.28	4.2 ± 0.32	3.2 ± 0.41	3.2 ± 0.29	2.8 ± 0.17
pH	7.3 ± 0.38	8.1 ± 0.56	8.1 ± 0.88	8.4 ± 0.45	8.2 ± 0.37	7.9 ± 0.62	8.4 ± 0.54
SAR	36 ± 5.2	9.3 ± 1.2	10.2 ± 1.3	15.7 ± 1.6	14.6 ± 0.8	13.3 ± 1.1	13.8 ± 1.4
RSC (meq L ⁻¹)	4.5 ± 0.3	4.5 ± 0.4	4.4 ± 0.4	3.0 ± 0.2	2.8 ± 0.3	1.6 ± 0.1	1.9 ± 0.3
BOD (mg L ⁻¹)	295 ± 39	230 ± 41	106 ± 24	NT	NT	NT	NT
COD (mg L ⁻¹)	763 ± 84	319 ± 29	178 ± 14	NT	NT	NT	NT
Cd (mg L ⁻¹)	37 ± 4	24 ± 4	20 ± 3	1.8 ± 0.3	1.6 ± 0.4	1.0 ± 0.2	1.4 ± 0.3
Cr (mg L ⁻¹)	139 ± 16	94 ± 18	98 ± 14	0.6 ± 0.1	0.6 ± 0.2	0.5 ± 0.1	0.3 ± 0.1
Ni (mg L ⁻¹)	140 ± 23	88 ± 9	76 ± 11	4.3 ± 0.3	3.1 ± 0.2	5.5 ± 0.4	5.8 ± 0.6
Pb (mg L ⁻¹)	166 ± 31	101 ± 12	86 ± 17	7.0 ± 1.3	6.2 ± 1.4	5.7 ± 0.9	4.6 ± 0.7

EC electrical conductivity, pH reaction, SAR sodium adsorption ratio, RSC residual sodium carbonate, BOD biological oxygen demand, COD chemical oxygen demand, Tr treated, NT not traceable

Fig. 1 Depth wise distribution of total and available contents of metals in GW, CW and WW soils [horizontal bars represent standard errors (\pm) of means]

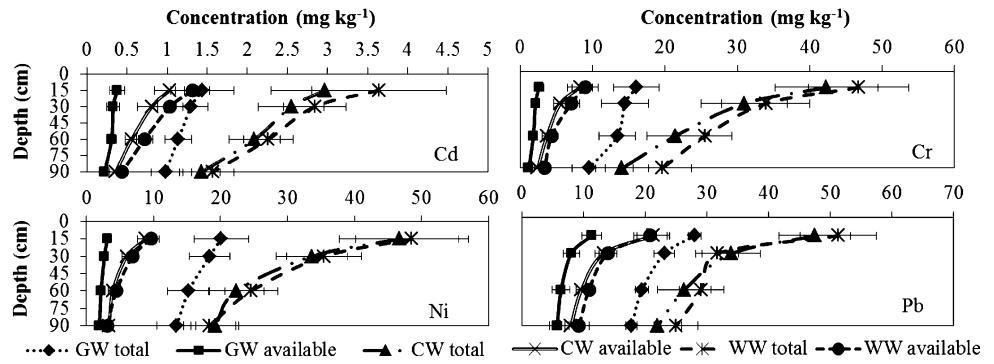


Table 2 Metals distribution indices in surface (0.3 m) soils and their transfer factors to crops

Indices	Cd	Cr	Ni	Pb
<i>Groundwater (GW)</i>				
Total (mg kg^{-1})	1.38 ± 0.32	15.24 ± 4.85	19.21 ± 5.02	25.57 ± 4.67
Available (mg kg^{-1})	0.36 ± 0.09	2.49 ± 0.54	2.86 ± 0.23	10.32 ± 1.48
Residual (mg kg^{-1})	1.02 ± 0.23	12.75 ± 2.71	16.35 ± 2.67	15.25 ± 3.02
FD	0.26/0.74	0.16/0.84	0.15/0.85	0.40/0.60
TF	0.383	0.019	0.011	0.091
<i>Combined use of ground and wastewater (CW)</i>				
Total (mg kg^{-1})	2.76 ± 0.45	36.92 ± 8.41	40.15 ± 7.10	40.73 ± 7.58
Available (mg kg^{-1})	0.92 ± 0.11	6.87 ± 0.83	7.37 ± 0.51	17.52 ± 2.92
Residual (mg kg^{-1})	1.84 ± 0.29	30.05 ± 4.64	32.77 ± 3.84	23.22 ± 4.38
FD	0.33/0.67	0.19/0.81	0.18/0.82	0.43/0.57
DI	$1.27 + 0.91$	$1.19 + 0.96$	$1.20 + 0.96$	$1.07 + 0.95$
RDI	$0.42 + 0.61$	$0.23 + 0.78$	$0.22 + 0.79$	$0.46 + 0.54$
TF	0.478	0.026	0.028	0.087
<i>Wastewater (WW)</i>				
Total (mg kg^{-1})	3.24 ± 0.71	40.29 ± 7.38	42.03 ± 6.32	41.50 ± 7.03
Available (mg kg^{-1})	1.18 ± 0.12	7.99 ± 0.68	8.26 ± 0.59	17.36 ± 2.54
Residual (mg kg^{-1})	2.06 ± 0.42	32.30 ± 4.05	33.78 ± 3.48	24.15 ± 4.79
FD	0.36/0.64	0.20/0.80	0.20/0.80	0.42/0.58
DI	$1.38 + 0.86$	$1.25 + 0.95$	$1.38 + 0.94$	$1.05 + 0.97$
RDI	$0.50 + 0.54$	$0.26 + 0.76$	$0.27 + 0.75$	$0.44 + 0.56$
TF	0.616	0.028	0.031	0.107

FD ratio of available/residual, DI distribution index, RDI redistribution index, TF transfer factor

suggested that the distribution of metals had tended to approach nearly quasi-equilibrium between the two forms (Olajire et al. 2003). Linear functions between total (X) and available (Y) contents of Cd, Cr, Ni and Pb, best explained the metal threshold base limits and their maximum allowable additions (Fig. 2).

The availability of Cd, Cr, Ni and Pb in soils started when total contents reached threshold base limits of 0.24, 0.80, 1.53 and 1.73 mg kg^{-1} , respectively, of soil. The available contents of Cd, Cr, Ni and Pb crossed their permissible limits of 0.5, 2.0, 2.0 and 5.0 mg kg^{-1} of soil, respectively, when their total contents exceeded 1.72,

13.12, 15.59 and 14.42 mg kg^{-1} , respectively. Prolonged irrigation either with WW or CW caused accumulation of metals beyond safe limits in active root zone soil and plant uptake. Quasi-equilibrium observed between available and residual fractions of different metals suggests that further additions would be prone to leaching, runoff and toxicity to crops and perhaps contaminate the food chain.

Cadmium contents in edible parts of crops were below permissible limits when irrigated with GW, but surpassed the limits with CW or WW (Fig. 3). When averaged for edible parts of all crops, higher Cd was recorded with WW

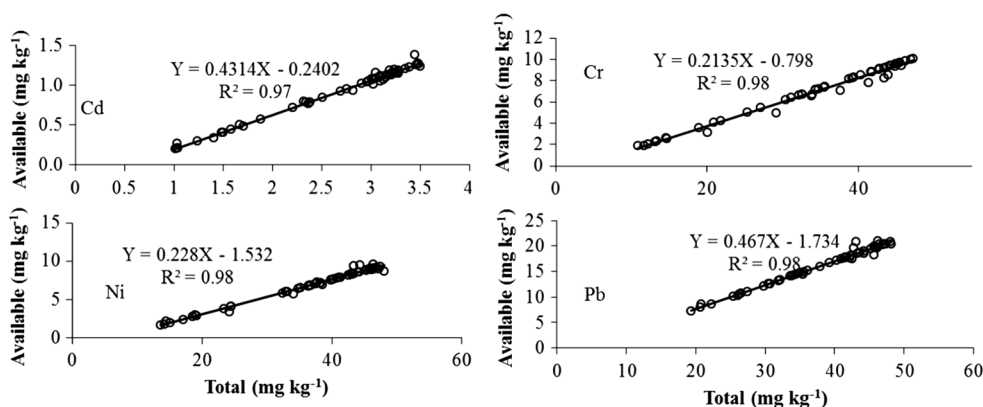


Fig. 2 Linear functions between total (X) and available (Y) contents of Cd, Cr, Ni and Pb

(2.05 $\mu\text{g g}^{-1}$) and CW (1.33 $\mu\text{g g}^{-1}$) than GW (0.53 $\mu\text{g g}^{-1}$). TF of Cd was 0.38, 0.48 and 0.62 for GW, CW and WW, respectively.

Among different crops, green spinach accumulated more Cd (1.46 $\mu\text{g g}^{-1}$) followed by green fenugreek (1.36 $\mu\text{g g}^{-1}$), wheat grain (1.20 $\mu\text{g g}^{-1}$), radish root (1.02 $\mu\text{g g}^{-1}$) and cluster bean green pods (0.98 $\mu\text{g g}^{-1}$). Even the wheat straw accumulated more Cd (1.90 $\mu\text{g g}^{-1}$) than sorghum fodder (1.50 $\mu\text{g g}^{-1}$). Under WW, Cd accumulation was beyond the permissible limit in faba-bean, okra, brinjal, bottle gourd and beet root with contents ranging from 0.92 (cauliflower curd) to 3.14 $\mu\text{g g}^{-1}$ (beetroot; Fig. 4). However, mean TF values of Cd for root, leaves/green stalk, fruit, grain and straw crops were 0.70, 0.67, 0.45, 0.57 and 0.74, respectively.

Second degree polynomials best explained the relation ($R^2 = 0.94\text{--}0.97$) between Cd accumulation in edible parts of crops and its available contents in soil. The critical available contents of Cd beyond which its accumulation

crossed safe limits in wheat (straw), cluster bean (straw), sorghum fodder, green fenugreek, green spinach, wheat (grain), radish, Egyptian clover and cluster bean (pod) were 0.37, 0.60, 0.63, 0.77, 0.78, 0.79, 0.84, 0.89 and 0.92 mg kg^{-1} of soil, respectively; while the threshold values of total Cd contents in soil for respective crops were 0.6, 1.2, 1.2, 1.6, 1.6, 1.6, 1.7, 1.8 and 1.9 mg kg^{-1} of soil. Excessive Cd accumulation (3.64 mg kg^{-1}) in the rhizosphere and uptake in all crops beyond safe limits poses health risks.

Chromium accumulation (0.95 $\mu\text{g g}^{-1}$) in edible crop parts (Fig. 3) with CW was higher than GW (0.29 $\mu\text{g g}^{-1}$) but comparable with WW (1.29 $\mu\text{g g}^{-1}$). Cr contents in crops remained within permissible limit of 2.0 $\mu\text{g g}^{-1}$ with GW, but surpassed the safe level in Egyptian clover (2.23 and 2.90 $\mu\text{g g}^{-1}$) and fenugreek (2.03 and 2.93 $\mu\text{g g}^{-1}$) with CW and WW, respectively. Cr contents were within the safe limits in all WW alone irrigated crops and no significant differences were observed in uptake of Cr among different crops (Fig. 4). The average TF values for

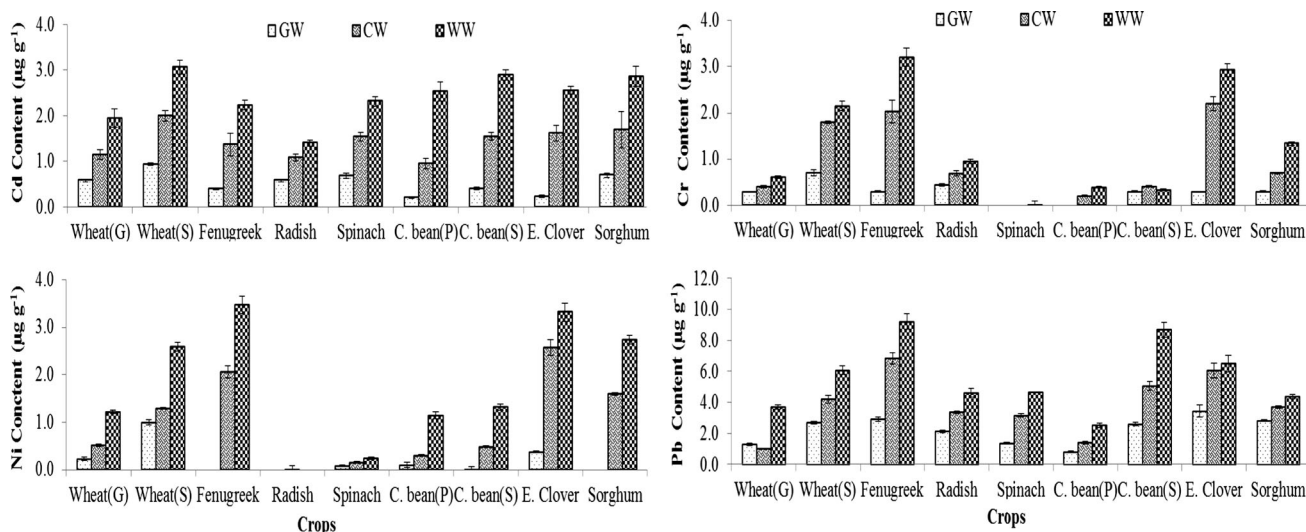
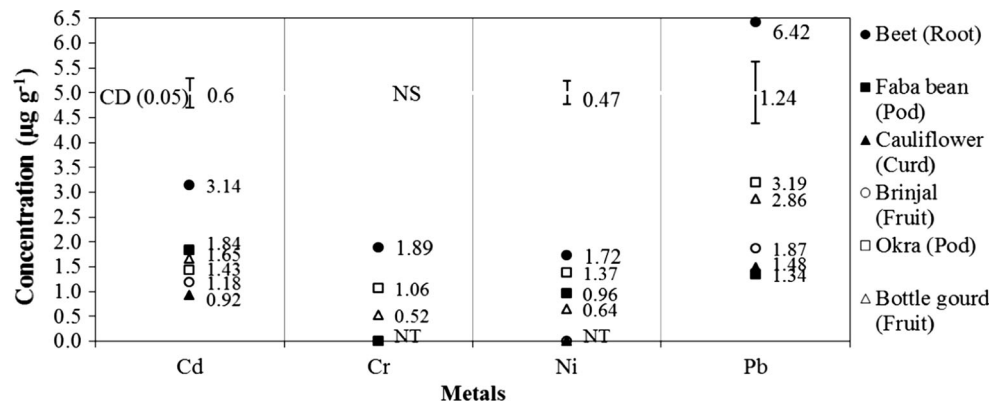


Fig. 3 Partitioning of metals (Cd, Cr, Ni and Pb) in different parts of differently irrigated crops (bars on histograms indicate standard errors)

Fig. 4 Concentration ($\mu\text{g g}^{-1}$) of metals in wastewater irrigated vegetables. Vertical bars are CD (0.05 %) in respective treatments



WW irrigated fruits, grain, straw, roots and leafy/green stalk crops were 0.01, 0.02, 0.03, 0.03, and 0.05, respectively. Second degree polynomials described the relationship very well ($R^2 = 0.90\text{--}0.97$ except for spinach) between crop uptake of Cr and its availability in soil. Uptake of Cr in Egyptian clover and fenugreek reached the safe limit when available Cr in soil was 6.39 and 7.98 mg kg^{-1} of soil, respectively. For sorghum, radish, wheat straw, cluster-bean pods, wheat grain and spinach, the respective available Cr values in soil were 9.44, 11.74, 14.9, 15.01, 17.8 and 24.96 mg kg^{-1} .

Threshold limits for Cr loading which caused its accumulation beyond safe limit in Egyptian clover, fenugreek, sorghum, radish, wheat straw, cluster-bean pods, wheat grain and spinach were 29.1, 36.6, 43.4, 54.2, 69.0, 69.5, 82.6 and 116.1 mg kg^{-1} , respectively.

Similar to Cr, Ni accumulation was within the safe limit of 2.0 $\mu\text{g g}^{-1}$ with GW and CW, except for Egyptian clover (2.58 $\mu\text{g g}^{-1}$) and fenugreek (2.07 $\mu\text{g g}^{-1}$). Continuous WW use resulted in higher Ni accumulation, with values being 26, 25, 8 and 2.1 times in sorghum, fenugreek, Egyptian clover and wheat straw, respectively compared to GW (Fig. 3). Average TF for Ni in WW irrigated root, leafy, fruit, grain and straw crops were 0.02, 0.05, 0.02, 0.03 and 0.04, respectively. Though Ni content in WW alone irrigated crops were within safe limits, beet root and okra fruits accumulated significantly higher Ni than other crops (Fig. 4). Uptake of Ni in edible parts of crops followed second degree polynomial order. Critical available contents of Ni in soil beyond which Egyptian clover, fenugreek, sorghum, wheat straw, cluster bean straw, cluster bean pod, wheat grain and spinach accumulated more than the safe limits of Ni were 6.1, 7.5, 7.6, 8.1, 9.7, 10.3, 11.3 and 16.7 mg kg^{-1} , respectively. The total additions of Ni > 25.3, 31.4, 31.8, 33.9, 40.8, 43.5, 47.8 and 71.8 mg kg^{-1} of soil resulted in its uptake beyond the safe limit in Egyptian clover, green fenugreek, sorghum fodder, wheat straw, cluster bean straw, cluster bean pod, wheat grain and green spinach, respectively.

Though Pb contents in crops were highest among the four metals, its average accumulation (4.78 $\mu\text{g g}^{-1}$) did not cross the safe limit of 5.0 $\mu\text{g g}^{-1}$ even under WW (Fig. 3). Crops with GW or CW did not accumulate Pb beyond the safe limit except Egyptian clover, fenugreek, cluster bean, wheat straw and sugar beet under CW or WW. The TF was 0.13, 0.13, 0.05, 0.08 and 0.11, respectively in root, leafy and green stalk, fruits, grain and straw crops. Among WW alone irrigated crops, Pb accumulation in beet root (6.42 $\mu\text{g g}^{-1}$) was beyond safe limits and significantly higher than other crops (Fig. 4). Critical concentrations of available Pb in soil beyond which its uptake crossed the safe limit in Egyptian clover, fenugreek, cluster bean straw, wheat straw and sorghum were 13.8, 15.2, 16.0, 18.0 and 19.2 mg kg^{-1} of soil, respectively. Total contents of Pb > 27.6, 30.8, 32.5, 36.8 and 39.5 mg kg^{-1} of soil resulted in its accumulation beyond safe limit in Egyptian clover, fenugreek, cluster bean straw, wheat straw and sorghum, respectively. Critical contents of Pb in soil for radish, spinach, cluster-bean pod and wheat grain were not established as Pb accumulation in these did not exceed the safe limit, even with WW.

The contents of metals in plants and their edible parts increased with increasing concentrations of metals in soil as a consequence of long-term irrigation with WW and CW. It was mainly because of long-term irrigated WW and CW soils have approached quasi-equilibrium among total, available and residual fractions of metals; thereby the increase in total contents of metals resulted in a corresponding proportional increase in their available contents and ultimately accumulation in plants. Earlier McGrath et al. (1994) also recorded accumulation of metals in surface soil matrix with WW irrigation and ascribed it to release from decomposition of added organic load, low solubility and limited uptake by plants. Accumulation of Cd, Cr, Ni and Pb in food and fodder crops was mainly concentration dependent but their quantum differed among metals and crop species. Elevated levels of metals have been observed in WW irrigated vegetables and cereals

(Karanja et al. 2010). Contrary to our observations, Rattan et al. (2005) recorded proportionately lower transfer of metals to vegetables than their elevated concentration in soil under long-term WW irrigation. Similarly, Amerasinghe et al. (2013) suggested that, due to lower daily intake, WW irrigated vegetables even with higher contents of metals posed lesser health risks than rice and wheat with lower contents of metals but higher contribution in daily diet. Cd accumulation crossed the safe limit under CW and WW and would potentially pose health risks due to higher bioavailability and the lower provisional tolerable daily intake of $60.0 \mu\text{g person}^{-1}$ (JECFA 2003). In conformity to our observations, Wang et al. (2012) also recorded that among the six studied metals, only Cd with the highest TF exceeded the maximum acceptable limit in Beijing and Tianjin city cluster. They observed the order of TFs of six metals as $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb} > \text{As} > \text{Cr}$, which were dependent on the vegetable species. Crops harvested for leaves were found to have the weakest barrier to metal uptake. Metals such as Cr, Ni and Pb had strong soil–plant barrier in roots, and even if they accumulate, their translocation to reproductive parts is generally low (Lokeshwari and Chandrappa 2006). Phyto-accumulation and translocation of Cr and Ni to reproductive parts was less than Cd, thus these would pose lesser risk except in fenugreek and fodder crops (Egyptian clover and sorghum). Accumulation of Pb crossed the permissible limit only with WW irrigation in dicots, and the major part was retained in roots; therefore, health risks can be reduced by avoiding the cultivation of root and dicot crops.

Sandy loam Ustochrepts of semi-arid regions progressively approach quasi-steady state between available and total contents of Cd, Cr, Ni and Pb added through prolonged use of irrigation WW and its combined use with GW. Though the major proportion of metals was retained in surface (0.6 m) soil, long-term (25 years) WW irrigation resulted in contamination of 20–22 m deep GW beyond safe limits for drinking. Sugar beet, fenugreek, Egyptian clover and cluster bean with metal contaminated WW irrigation, tend to accumulate metals beyond safe limits. Thus, they should not be grown with metal laden WW irrigation. Among the studied metals, Cd poses the highest risk to potential food chain contamination because of the maximum increase in its availability and the lowest toxicity limits.

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