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Heavy Metals in Soils and Vegetation from Wastewater Irrigated Croplands Near Ahmedabad, Gujarat: Risk to Human Health

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ABSTRACT

Heavy metal accumulation in soils, and subsequently, in vegetation by long-term wastewater irrigation has a potentially detrimental effect on humans via their transfer along the food chain. In this reconnaissance study the effects of wastewater irrigation on the accumulation of heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) in soils and vegetables from croplands along some ~60 km stretches of Sabarmati River, near Ahmedabad city were assessed. Geochemical factors associated with metals in the soil-water environment seem to regulate more the metal transfer (soil-to-vegetable) than the physiological factors associated with the vegetable's types.

The risk associated with the dietary intake of metal contaminated vegetables was quantified by Hazard Quotient (HQ). HQ was found to be very less sensitive on to the dietary intake pattern (e.g., leafy versus non-leafy vegetables) of the consumers. In contrast to low risk associated with Co, Cu, Ni and Zn with very low HQ values, high risk was found for Pb (HQ of ~6.1±0.6) followed by both Mn and Cr (HQ of ~1.0 ± 0.1). Based on the results on wastewater irrigation in the studied region, we suggest more efficient treatment of wastewater facilities and semi-decadal monitoring of heavy metal in vegetables grown under wastewater irrigated soils.

INTRODUCTION

Discharge of untreated or inefficiently treated municipal and industrial wastewater to waterways/soils resulting in degradation of water/soil quality is a major environmental concern in many (semi) urban areas of several countries. A decline in the availability of clean surface water or groundwater has led farmers to look for easily available alternate sources of irrigation waters in the form of domestic/municipal/ industrial wastewaters. In addition, higher crop productivity has tempted farmers to the use of wastewaters for irrigation as these waters are enriched with essential NPK-nutrients.

It is now well recognized that long-term wastewater irrigation by and large leads to increasing levels of metals (e.g., Cr, Cu, Pb, Ni, Zn, Hg, Co, Mn, etc.) in irrigated soils and vegetations, and has a potentially detrimental effect on humans via heavy metal transfer via the food chain (Chopra 2015, Milacic & Kralj 2003 Singh et al. 2004, Jassir et al. 2005, Sharma et al. 2006, Singh & Jaswant 2006, Akpor et al. 2014). A few of these heavy metals (e.g., Zn, Mn, Ni, Cu and Cr) though are required by humans in trace levels, but uptake of heavy metals beyond their respective permissible limits into the human body leads to cardiovascular, nervous, kidney and bone diseases (WHO 1998, Jarup 2003). For example, Cd, As and Cr are carcinogenic, whereas, Hg and Pb are known to cause abnormal growth of children and reduction in haemoglobin synthesis (Ahmad 2016, Chopra 2015). As vegetables are important sources of carbohydrates, proteins, minerals and fibres and are one of the major components of the human diet, accumulation of higher levels of heavy metals in vegetables is a cause of concern to human health (Tripathi et al. 1997, Khillare et al. 2004, Wang et al. 2005, Demirezen & Aksoy 2006, Chary et al. 2008, Tiwari et al. 2011). In the above context, it is thus important to assess heavy metals in vegetable crops grown in wastewater irrigated croplands.

Previously, investigations have been carried out in this domain in several countries (Mapanda et al. 2005, Gebrekidan et al. 2013, Hu et al. 2014, Ahmad et al. 2016, Qureshi et al. 2016). For example, extensive studies have been carried out in Ethiopia wherein it was concluded that risk to human health associated with the heavy elements in vegetables was low but the long-term effect needs to be assessed further

(Woldetsadik et al. 2017, Gebreyohennes et al. 2018). In contrast, Mapanda et al. (2005) reported significantly high Cr, Cu, Cd, Zn, Pb and Ni in wastewater irrigated croplands in Zimbabwe. In China, Hu et al. (2014) on their study on greenhouse vegetation and its soils concluded that the leafy vegetables had relatively higher concentrations of heavy metals and higher transfer factor than root-type and fruit-type vegetables. In Dubai, prohibition exists for wastewater use in agriculture and it was found from experiments conducted using treated wastewater that heavy metals posed little threat to human health (Qureshi et al. 2016).

In India, urbanization has resulted in a high population density in the medium-to-large scale cities. This has led to increasing processing-demands on the municipal wastewater treatment plants and has resulted in the spreading of the wastewater irrigated lands surrounding the cities (Chary et al. 2008). The potential impact of wastewater irrigation in accumulation of heavy metals in the soils and subsequently in vegetables has resulted in a few studies from Indian cities (Gupta et al. 2010, Ghosh et al. 2012, Chopra et al. 2015, Saha et al. 2015). For example, the sewage water irrigated vegetables in Kolkata (3rd most populated Indian city) were found to have higher concentrations of Pb and Cd than their respective limits prescribed by FAO/WHO (Saha et al. 2015). One of the recent studies (Chopra et al. 2015) analysed the trend of trace metal accumulation in different parts of plants; e.g., Pb accumulated in the flower part, Cu and Zn in the leafy part whereas Ni, Cd and Cr in the root part. Gupta et al. (2010) linked a stress-like condition in two plant species (*Colocasia esculentum* and *Raphanus sativas*) to trace metal accumulation in their tissues which increased the sugar content and decrease in their chlorophyll and soluble protein contents. Higher accumulation levels of heavy elements were found in vegetation grown in wastewater irrigated soils compared to tube-well irrigated soils highlighting the risk in their consumption (Rattan et al. 2005, Tiwari et al. 2011). Sharma et al. (2009) pointed out that post-harvest processes of transport and storage can lead to higher heavy metals concentration in vegetables collected at the production site, i.e. irrigated field, compared to those from the market areas.

The case studies above are skewed to the northern and eastern regions of the country (Agrawal 2003, Sharma et al. 2006, 2008, 2009, Tiwari et al. 2011), and except for a few (Tiwari et al. 2011, Tripathi et al. 1997), case studies focusing on the western regions of India are sparse. The present study is focused on wastewater irrigation from Ahmedabad, a city which has a history of wastewater irrigation since the last few decades (Palrecha et al. 2012). There has not been, to the best of our knowledge, any article published from the region on wastewater irrigation. Therefore, this reconnaissance study is an attempt to bridge the existing gap and was undertaken to assessing heavy metals in vegetable crops grown in wastewater irrigated croplands along some ~60 km stretch of Sabarmati River and their effects on a large population, from an important yet unexplored region in western India.

The specific goals of the present study are: (i) to get baseline data of the selected heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) above in a group of largely consumed vegetables such as brinjal, tomato, cabbage, cauliflower and spinach, collected from different locations where wastewater irrigation has the predominant role, (ii) quantitative assessment of the transfer of metals by using the index transfer factor from soils to the vegetables, and the factors controlling it, and (iii) finally a quantitative assessment of the health risk by using the index hazard quotient posed by the ingestion of metals via consumption of vegetables to the greater population of the Ahmedabad city.

MATERIALS AND METHODS

Study area: The study area is located around the disposal point of Vasna Sewage Treatment Plant (STP) of Ahmedabad city, which is located along the bank of the River Sabarmati. Ahmedabad city has a population of greater than six million and an urban area of 464 km^2. According to Ahmedabad Municipal Corporation (2011), the city has an existing wastewater treatment capacity of 1075 Million Litre per Day (MLD) compared to the actual requirement of 1186 MLD. According to an estimate by International Water Management Institute, New Delhi (2012), about 9450 hectares in and around the Ahmedabad region is irrigated by wastewater. This comprises nearly 45% of the net irrigated area of 21086 hectares.

Vasna STP (capacity 240 MLD) is located along the bank of Sabarmati River and processes domestic wastewater emanating from household and small business activities within the limits of Ahmedabad Municipal Corporation (AMC). The catchment area of the Sabarmati River is surrounded by two semi-industrial units, Narol and Vatva, which host many small to medium-sized industries (e.g., plastics, small-scale chemical factories, metal and alloy processing, electrochemical processing, dyes and paints, wood and paper mills, etc.). Mixing of industrial effluents into the environs of the area studied occurs by two pathways. Firstly, wastewaters from these industrial units are carried directly or indirectly through small channels or sub-channels into the Sabarmati River. Regulations by the state government's pollution control authority, Gujarat Pollution Control Board, require efficient treatment of all industrial effluents before they are discharged to the environs; however, the industrial units are not well known for adopting the best practices and inefficiently treated industrial effluents are released often into the environs. Secondly, through drainage channels, the semi-treated/untreated industrial effluents from the industrial sites are carried into the sewer channels and finally into the Vasna STP. The latter of the two above processes is expected to have a lower impact on the environment due to wastewater treatment at the STP before their release to the Sabarmati River. Therefore, the croplands in the study area which are irrigated by wastewater from Sabarmati River channels derive their heavy metals from the domestic activities and a significant yet uncertain contribution from the industrial activities. Therefore, this process underscores the potential risk of pollutant transfer to the vegetation grown in croplands of the study area.

Sampling and Sample Processing

Samples used for this study included five types of different vegetables (n = 38), wastewater irrigated soils in which vegetation are grown (n = 8) and wastewater samples (n = 3). For the collection of soils and vegetation, eight different sampling locations were selected: Gyaspur, Visalpur, Kasindra, Saroda, Chandisar, Kaloli, Asmalli and Khada (Fig. 1). At two locations, two of the vegetable samples were not available for collection. Gyaspur is the point from where the wastes from Vasna STP are disposed to Sabarmati River; three samples were collected from this site. The sampling sites are located along the Sabarmati River up to a maximum distance of 60 km from the point of disposal (i.e., Vasna).

Samples were collected during October and November of the year 2015. In the study area, July, August and September generally account for most of the rains during the year and very scanty rainfall occurs during the sampling months. In fact, during the two sampling-months, the total number of rainy days was zero. The impact of low rainfall during October and November leads to the very low flow of the Sabarmati River and hence underscores the contamination effect of river water by the wastewater.

Five different types of vegetation samples such as brinjal (*Solanum melongena*), tomato (*Solanum lycopersicum*), cabbage (*Brassica oleracea* var. capitata), cauliflower (*Brassica oleracea* var. botrytis) and spinach (*Spinacia oleracea*) were collected. These largely constitute the staple diet of the population in the study area and consumed mainly amongst the vegetables. The samples were washed with tap water profusely, followed by de-ionized water and uneatable portions were removed and then samples oven-dried at 80°C. Dried samples were crushed by using an agate mortar and pestle, homogenized and stored in plastic containers to avoid heavy metal contamination. For extraction of heavy elements, 0.3 g of samples was digested with 6 mL of HNO_3 at 175°C for 10 min at 30 bar pressure and 50°C at 30 bar pressure. After digestion, samples were diluted up to 30 mL with 2% HNO_3. The digested samples were stored for analysis of Co, Cr, Cu, Mn, Ni, Pb and Zn.

Eight soil samples were collected from the croplands where municipal wastewater drawn from the Sabarmati River is used for irrigation. Samples were collected by using a plastic scoop from a depth of 15 cm and were sieved with 1-mm sieve (100 mesh) to remove unwanted particles, and dried at 105°C for 24 hours. The samples were stored in airtight zip-lock pouches at room temperature. For heavy element analysis in soil samples, 0.3 g of sample was taken, mixed

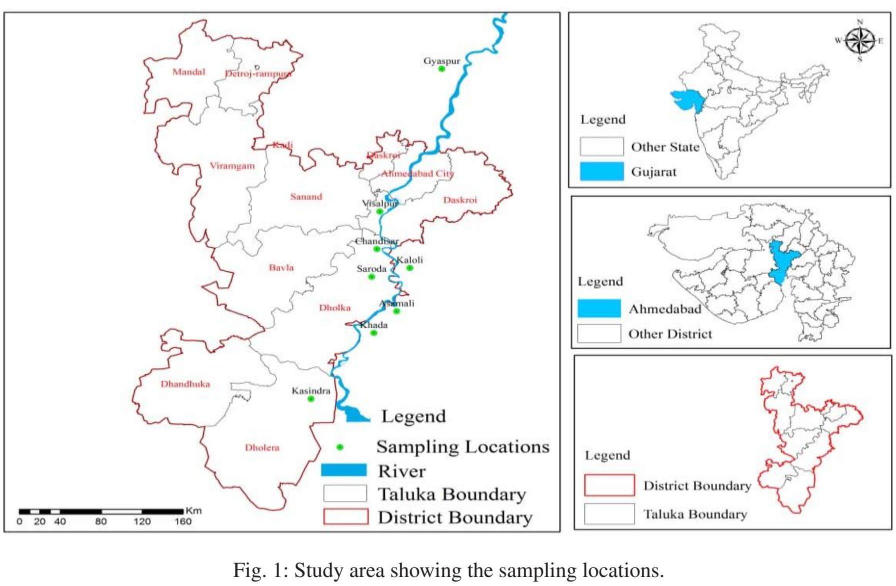

Fig. 1: Study area showing the sampling locations.

with 6 mL of HNO_3 and 1 mL of HF. The samples were then digested in Titan MPS Direct Temperature Control™ digester of Perkin Elmer.

Three wastewater samples (~500 mL) were collected in HDPE bottle from three different points of disposal. To avoid deterioration due to microbial activity, 2 mL of concentrated HNO_3 was added after filtration of the samples. Measurement of pH, electrical conductivity, total dissolved solids, and the temperature was carried out on site. For heavy metal analysis, the sample was diluted up to 300 µS of conductivity. Samples were acidified and stored at 4ºC till further analysis.

During sampling and its processing care was taken to avoid contact of the samples with metals surfaces, to avoid any heavy metal contamination from any processes/sources in and around the working environment.

Analysis of Samples

The heavy metal concentration in digested samples was measured by inductively coupled plasma mass spectrometry (ICP-MS; PerkinElmer, Thermo-X series2) at Physical Research Laboratory, Ahmedabad. The digested samples were analysed for various heavy elements like Co, Cr, Cu, Mn, Ni, Pb, Zn by aspirating the sample in ICPMS, which was calibrated using Merck multi-elemental standards. The instrument reproducibility was determined by carrying out replicate the analysis for the elements analysed while the accuracy was observed using certified reference standards such as NOVA (Amin et al. 1972) and MAG (Govindaraju 1994). Analytical precisions of measurement for heavy elements were better than ±5% and accuracy within ±6% (Banerji et al. 2017).

The pH, electrical conductivity, total dissolved solids, and temperature of the sewage samples were measured by a multiple parameter kit. Soil pH was measured by a hand-held pH meter in the samples by mixing a known weight of soil with de-ionized water in the weight ratio of 1:2 and keeping it undisturbed for 10 minutes.

Statistical and Uncertainty Analyses

Student's *t*-test was used to compare averages with their corresponding *p*-values to bring out the statistical significance (or otherwise) of such comparisons. The statistical and mathematical tools of Microsoft Excel Software were used for such calculations. Principal Component Analysis (PCA) was performed by using Statistical Package for Social Services (SPSS) software, statistics version 23. Additionally, overall uncertainty in parameters such as transfer factors and hazard quotients was carried out by using error propagation technique assuming a certain % error on the individual parameters in their respective equations.

RESULTS AND DISCUSSION

Heavy Metals in Wastewater

The pH, TDS, temperature and heavy metal concentration in the three wastewater samples are reported in Table 1. These parameters provide information about the quality of one of the important point sources (i.e., sewage) that contaminate the water of the river. pH in the samples ranged from nearly neutral to moderately alkaline (7.1 to 8.4) while the temperature varied from 32.0°C to 32.7°C. A large variation, a factor of 6, was observed in the electrical conductivity (2117 to 12750 $µS.cm^{-1}$) and the total dissolved solids (1061 to 6360 ppm).

Concentrations of heavy metals ($µg.mL^{-1}$) in the disposed sewage water samples were found to vary in the following ranges (Table 2): Co (2.1-2.2), Cr (1.4-1.9), Cu (0.1-0.9), Mn (0.2-3), Ni (1-1.9), Pb (0.4-1.6) and Zn (5.1-19). These values are higher than their respective prescribed safe limits of heavy metals used for irrigation provided by Indian Standard, World Health Organization (WHO) and European Union Standards. For example, when compared to the Indian Standard values, the average Cr is found be higher by a factor of ~3, whereas these factors are ~12 for Pb, ~2 for Cu, ~13 for Mn and ~2.5 for Zn. For Ni the Indian standard value is not reported; however, when compared

Table 1: Physico-chemical characteristics and heavy metal concentration ($µg.mL^{-1}$) in sewage samples.

Outlet No	pH	EC (µS/cm)	TDS (ppm)	Temp (°C)	Co	Cr	Cu	Mn	Ni	Pb	Zn
1	7.09	2117	1061	32.0	2.1	1.5	0.9	1	1.7	1.5	17.4
2	7.50	12750	6360	32.6	2.2	1.9	0.1	3	1.9	1.6	19
3	8.45	5950	2980	32.7	2.1	1.4	0.1	0.2	1	0.4	5.1
Guideline for safe limits of heavy metals in irrigated water ($µg.mL^{-1}$)											
Indian Standard (2000)					-	0.05	0.05	0.10	-	0.10	5.0
WHO/FAO (2007)					-	0.10	0.20	0.20	0.20	5.0	2.0
European Standard (2006)					-	-	-	-	-	-	-

to the EU value, the average Ni was found to higher by a factor of ~6. Such comparison could not be made for Co as the permissible limits by the Indian, WHO and EU were not reported.

A comparison of the wastewater concentration data in the present study was made with those collected from a nearby city, Vadodara (Tiwari et al. 2011), though industrial wastewater was used for irrigation. It was observed that the average Cr, Pb and Ni in industrially treated wastewater are higher by factors of about 3.5-4 than in the sewage treated water, whereas for Mn it is ~7 and for Cu it is ~16. Such a higher concentration of heavy metals in industrially treated water is not unexpected considering the difference in nature of the samples in the two studies. In our study, the collected wastewater is treated wastewater from the STP which is linked to domestic activities and a few small scale industrial activities operating near the treatment plant, and by and largely unaffected by large scale industrial activities. In the case study of Tiwari et al. (2011), industrial wastewater in their study area was primarily derived from chemical, petrochemical, dyes and paints, and agrochemical industries. Tiwari et al. (2011) also found 1-2 orders of magnitude lower levels of heavy metals in groundwater compared to the industrial wastewater. From the discussion above, from a qualitative standpoint, the metal concentrations generally followed the trend: $[\text{Metal}]_{\text{Industrial Water}} > [\text{Metal}]_{\text{Sewage Water}} >> [\text{Metal}]_{\text{Ground Water}}$

Heavy Metals in Wastewater Irrigated Soils

For the collected soil samples, the pH varied from 6.5 to 7.8 (Table 2). The soil samples closest to and farthest from the point-of-discharge, i.e. Gyaspur and Khada respectively, have alkaline pH of 7.8 and 7.4, respectively, while sample at Saroda (~20 km downstream) was acidic (pH=6.5). Rest of the samples have close to neutral pH, in the range of 7.0 ± 0.2. The mobility of metals in soil zones is regulated by processes such as adsorption, precipitation and complexation, and soil pH is one of the parameters which affects these processes. Processes/factors regulating soil pH though complicated depends on the exchangeable cations in soils, the chemistry of the water that passes through the soil zones, presence of ligands and the soil carbonates.

Average concentrations ($\mu g.g^{1}$) of metals in the eight soil samples follow the trend: Zn (421 ± 62) > Mn (336 ± 49) > Cu (201 ± 30)> Cr (71 ± 20)> Ni (51 ± 8) > Pb (42 ± 6) > Co (9 ± 1); the observed variability between the lowest and highest concentrations in all metals are within a factor of 2. Successive-pair *t*-tests show that the averages are statistically different with confidence limits of > 99% ($p < 0.01$).

A closer analysis of the soil data highlights a few important observations. All the metals exceed the range/upper limit of WHO/EU standard values. Good inter-correlations (r^2 ranges from 0.73-0.99) between almost all of the metal concentrations were observed which is suggestive of common processes/sources that contribute to these metals in the soils. Among the eight soil sample collection sites, the sample collected from Gyaspur had the maximum concentration of all analysed metals compared to other sites. Gyaspur is the area where the effluents from Vasna treatment plant get disposed off which leads to the maximum accumulation of these metals in the agricultural field compared to all other sites.

Table 2: pH and heavy metal concentration ($\mu g.g^{-1}$) in irrigated soil samples.

Location	pH	Co	Cr	Cu	Mn	Ni	Pb	Zn
Kasindra (S1)	6.82	9.5	55.7	216	367	55.9	43.6	465
Saroda (S2)	6.53	9.3	92.0	212.1	363	53.4	46.3	447
Chandisar (S3)	6.83	8.8	64.7	210.2	338	52.8	45.8	428
Kaloli (S4)	6.95	7.9	64.4	171.4	281	41.9	37.9	367
Asamali (S5)	7.20	7.8	52.2	161.1	280	42.4	34.6	341
Khada (S6)	7.40	8.3	62.3	185.3	311	46.3	35.1	385
Gyaspur (S7)	7.80	11.2	109.3	255.6	425	64.6	50.2	535
Visalpur (S8)	7.28	8.9	66.2	197.7	323	49.3	44.7	400
Guideline for safe limits of heavy metals in irrigated soil ($\mu g.g^{-1}$)								
Indian Standard (2000)[a]		-	-	135-270	-	75-150	250-500	300-600
WHO/FAO (2007)[a]		-	-	-	-	-	-	-
European Standard (2006)[a]		-	150	140	-	75	300	300
MACs for trace elements in agricultural soils[b]		20-50	50-200	60-150	-	20-60	20-300	1-300

[a] Singh et al. (2010); [b] Kabata-Pendias & Mukherjee (2007)

There was a decrease in metal concentration as a function of distance from the Gyaspur site. When concentrations of individual metals were plotted as a function of distance, all other metals (except for Cr) show reasonably good correlation ($r^2 > 0.56$) with negative slopes and positive intercepts. The intercept of each plot provides an assessment of the concentration at the Gyaspur-site (0 km), and it is interesting to note that these values matched reasonably well with their respective measured values. The decrease of metal concentration in soils at the downstream sites can be attributed to natural variation or a linear decrease, or a combination of both. Natural variability as a cause for the downstream decrease may still be likely for metals Pb, Cr and Co where the decrease is reasonably low; however, for the other metals, it is unlikely as the decrease in concentrations is large considering the distance from the origin-site. The most likely cause for a decrease of Ni, Cu, Mn and Zn is their particle reactivity when they are carried along the course of the river, which in turn, is reflected in the soils at respective sites.

Heavy Metals in Vegetables

Concentrations (dry wt. basis) of Co, Cr, Cu, Mn, Ni, Pb and Zn (Table 3) in edible parts of the vegetables varied

Table 3: Heavy metal concentrations ($\mu g.g^{-1}$; dry weight basis) in vegetable samples.

Plant species	Co	Cr	Cu	Mn	Ni	Pb	Zn
Brinjal: Visalpur	0.34	5.60	5.90	106.7	3.10	1.00	12.44
Saroda	0.12	5.80	8.80	15.10	2.80	0.70	12.74
Khada	0.12	5.80	8.50	15.62	2.80	0.70	13.40
Asmalli	0.13	6.40	9.10	15.81	3.00	0.60	14.57
Gyaspur	4.20	7.00	0.04	47.00	0.70	6.90	44.10
Kasindra	0.09	7.20	7.60	12.78	3.50	0.50	11.44
Chandisar	0.10	7.50	9.30	12.35	3.80	0.50	12.53
Kaloli	0.20	8.80	8.10	17.37	4.10	1.30	15.86
Tomato: Chandisar	0.35	6.70	6.20	13.57	3.50	3.70	10.05
Kaloli	0.121	9.00	9.90	15.00	4.20	0.80	19.13
Asmalli	0.23	5.90	7.10	16.27	2.90	1.70	12.27
Saroda	0.33	5.80	5.10	21.14	3.10	4.00	9.00
Visalpur	0.20	5.40	7.20	20.77	2.70	0.90	12.81
Kasindra	0.46	7.60	7.50	17.79	3.80	5.00	12.19
Khada	0.51	5.80	7.20	19.96	2.90	5.60	12.06
Gyaspur	2.20	6.70	0.04	25.00	1.20	4.20	21.50
Cabbage: Chandisar	0.323	7.8	3	60.14	4.2	1.6	10.6
Saroda	0.124	5.4	2.2	15.31	2.8	0.4	13.99
Visalpur	0.481	6	3.3	24.71	3.1	4.5	8.93
Kasindra	0.317	7.6	2.3	31.73	4	2.4	10.5
Khada	0.322	5.6	2.1	39.12	3.1	1.4	10.49
Gyaspur	2.2	5.3	2.0	18.0	2.8	0.4	4.4
Chandisar	0.323	7.8	3	60.14	4.2	1.6	10.6
Saroda	0.124	5.4	2.2	15.31	2.8	0.4	13.99
Cauliflower: Chandisar	0.227	7.1	3.4	19.06	3.8	1.3	16.4
Kaloli	0.146	6.2	3.7	13.08	3.3	1.3	14.64
Asmalli	0.165	5.6	2.3	18.12	2.9	1.1	16.04
Saroda	0.212	5.3	2.2	20.43	2.7	0.8	14.76
Visalpur	0.193	5.6	2.5	18.98	3.0	1.7	18.78
Kasindra	0.213	7.8	2.4	19.14	3.9	0.8	14.09
Khada	0.142	5.2	2.1	14.97	2.7	0.8	14.34

Plant species	Co	Cr	Cu	Mn	Ni	Pb	Zn
Gyaspur	2.2	6.2	0.07	13.0	0.8	0.4	9.5
Spinach: Chandisar	0.412	8.9	9.8	40.13	3.9	2.4	31.22
Kaloli	0.302	5.6	6.8	109.8	3.1	0.7	16.19
Asmalli	0.316	5.3	5.7	104	2.7	0.7	11.86
Saroda	0.126	5.8	8.7	15.59	2.8	0.6	13.93
Visalpur	0.246	5.4	6.5	86.4	2.3	1.1	16.71
Kasindra	0.381	9.5	8.9	41.51	4.1	2.4	32.57
Khada	0.276	5.6	7	88.12	2.5	1.1	19.5
Gyaspur	11.3	11.8	0.067	15.0	2.9	8.4	11.3
Guideline for safe limits of heavy metals in agricultural products ($\mu g.g^{-1}$)							
Indian Standard (2000)[a]	-	30.0	-	1.5	2.5	50.0	
WHO/FAO (2007)[a]	-	40.0	-	-	5.0	60.0	
European Standard (2006)[a]	-	-	-	-	5.0		
Mean TE concentrations in food crop and Vegetables grown in various countries[b]	0.005-0.27	3-8	-	0.06-1.3	0.2-2.4	1.2-2.7	

[a] Singh et al. (2010); [b] Kabata-Pendias and Mukherjee (2007)

substantially among the different vegetables and different metals, indicating that the metal assimilation process is both plant and element-specific. Tiwari et al. (2011) pointed out that metal accumulation and its translocation into different parts of the plant is metal-specific and did not follow any particular pattern. In the following discussion, concentrations of elements in different vegetables, and a comparison with values reported from other studies are made.

Cobalt (Co): Co is required by *Rhizobium* that fixes the nitrogen. The range of Co reported for vegetation worldwide is 0.005-0.27 $\mu g.g^{-1}$ and the range obtained from this study falls within 0.1-4.2 $\mu g.g^{-1}$, excluding one sample with a value of 11.3 $\mu g.g^{-1}$. It is interesting to note that the highest Co values observed in all vegetable categories belong to the Gyaspur site; the average Co value at the Gyaspur site is 4.4 $\mu g.g^{-1}$ compared to values of 0.2-0.3 $\mu g.g^{-1}$ for the remaining sites ($p<0.01$). The maximum average concentration was observed for the (leafy) spinach (1.7 $\mu g.g^{-1}$) which is ~2.5 times of the average obtained for brinjal, tomato, cabbage, and ~4 times that of the average value of cauliflower (spinach > brinjal > tomato ≈cabbage > cauliflower) (p = 0.025). Kabata-Pendias & Mukherjee (2007) reported that the leafy plants like lettuce, cabbage and spinach had a high Co concentration compared to grasses and cereals.

Chromium (Cr): Cr in all vegetables ranged from 5.2 to 11.8 $\mu g.g^{-1}$ with an average of 6.6 ± 1.5 $\mu g.g^{1}$. All values in the present study are higher than the range (0.01-0.41 $\mu g.g^{-1}$) found in vegetation all over the world (Kabata-Pendias & Mukherjee 2007). The average (plant) values are also higher than tolerable level (2 $\mu g.g^{-1}$) and to the toxic levels (5 $\mu g.g^{-1}$) for plants reported by Kabata-Pendias & Mukherjee (2007). The spinach sample collected at Gyaspur have the highest Cr (11.8 $\mu g.g^{-1}$) and cauliflower from Khada area have the lowest Cr (5.2 μg/g). Based on the average concentration in vegetable samples the following trend was obtained: spinach > brinjal > tomato > cabbage > cauliflower (p = 0.001); however, all average values are similar within their (1σ) variation.

Copper (Cu): Cu is one of the essential nutrients to plants due to its physiological effect on the growth of the plant; however, excess of it is detrimental to plants as it causes membrane damage and suppresses enzymatic activities (Alaoui-Sosse et al. 2004). Critical limit of Cu toxicity in plants is reported to be 20-30 $\mu g.g^{-1}$. Compared to these values the WHO/FAO values are much lower, in the range of 0.2-5.0 $\mu g.g^{-1}$, while the range that has been reported for various countries fall in 3-8 $\mu g.g^{-1}$ (Kabata-Pendias & Mukherjee 2007).

In the analysed samples, Cu ranges from 0.04-9.9 $\mu g.g^{-1}$ and amongst the vegetables the average values follows the order: brinjal > spinach > tomato > cabbage > cauliflower (p = 0.009). None of the samples exceeds the toxic limit; however, ~60% of the samples exceed the upper limit of the WHO/FAO range. Interestingly, Chary et al. (2008) reported much lower values of Cu (0.1-1.7 $\mu g.g^{-1}$) in vegetation grown in sewage irrigated soils from Hyderabad. Due to the strong absorption of Cu^{2+} into an inorganic fraction and/or its complexation with organic matter, Cu is less mobile in soils. Cu bioavailability is reduced when the pH value exceeds 7.0 (Avci & Deveci 2013) and at higher pH hydrolysed species of Cu becomes important for its uptake by plants. Intriguingly, very low levels of Cu (0.04-2 $\mu g.g^{-1}$) in vegetables were observed at the Gyaspur site which has relatively high soil pH of 7.8. The average Cu at the eight sites (considering all vegetables) ranges from 0.4-7.1 $\mu g.g^{-1}$ and shows a moderate negative correlation (r^2=0.51) with pH, and corroborates with the above proposition of Avci & Deveci (2013).

Manganese (Mn): Mn is essential nutrient for the growth of plants that helps in the formation of the chloroplasts, nitrogen metabolism and synthesis of some enzymes. In the measured vegetable samples, Mn varies from ~12 (brinjal) to ~110 $\mu g.g^{-1}$ (spinach), and amongst the vegetables the average values follow the order: spinach > cabbage > brinjal > tomato > cauliflower (p = 0.017). The average Mn in spinach is 2-3 times higher compared the other vegetables suggesting leafy structure accumulate more of Mn compared to non-leafy ones.

Nickel (Ni): Ni is an important component of plant enzyme involved in N-fixation from urea/inorganic nitrogen and regulates normal growth of the plant tissues. Due to its role, Ni gets absorbed by many plant species in their tissues naturally and is found at relatively higher levels (Yusuf et al. 2011). Ni is also found in irrigation waters where sewage sludge and animal waste are mixed.

The Ni concentration in the samples varies from 0.7-4.2 $\mu g.g^{-1}$ and it compares to the range of 0.05-5.0 $\mu g.g^{-1}$ (Adriano 2001) and 0.06-1.3 $\mu g.g^{-1}$ for various countries reported by Kabata-Pendias & Mukherjee (2007). The average concentration in all but one vegetable samples centred on the value of ~3 $\mu g.g^{-1}$, and a slightly higher average value is observed for the cabbage samples (~3.3 $\mu g.g^{-1}$). These average values are very similar to those (2.0-4.7 $\mu g.g^{-1}$) reported in Turkish vegetation (Avci & Deveci 2013). About 90% of the samples exceed the Indian MAC limit of Ni (1.5 $\mu g.g^{-1}$); however, these average values are all higher by a factor of ~15 compared to the WHO/EU and WHO/FAO safe limits of 0.2 $\mu g.g^{-1}$.

It is also interesting to note that the average value at Gyaspur (1.7 $\mu g.g^{-1}$) is significantly lower than a somewhat similar value (3.8 ± 0.1 $\mu g.g^{-1}$) observed at Kasindra, Chandisar and Kaloli. In the Indian context, similar observations and range of values were reported for leafy vegetables such as spinach, cabbage and amaranthus having more absorption affinity towards Ni (Singh et al. 2010, Sharma et al. 2006). For instance, Chary et al. (2008) reported average values of 3.1 $\mu g.g^{-1}$ for spinach and brinjal samples from wastewater irrigated areas near Hyderabad.

The mobility of Ni in soil plays an important role for bioavailability, due to moderate alkali condition the mobility of Ni increase in the soil. An increasing trend (with a weak correlation; r^2= 0.54) is observed between soil pH and average Ni in plants which possibly is an indication that soil pH influences the mobility of Ni from the soil-water system to the plants amidst other parameters that also can regulate Ni in plants. The trend observed for Ni was cabbage > spinach > tomato > brinjal > cauliflower (p = 0.001).

Lead (Pb): Pb is a persistent toxicant to plants and is derived through atmospheric depositions and from soil uptake. Pb gets accumulated in the soil through various sources like industrial emission and discharges, burning of gasoline, and wastewater irrigation. Pb is not required in plants as a nutrient (similar to Cd), and possibly is reflected by generally low levels in uncontaminated soils (Kabata-Pendia & Mukherjee 2007), with less temporal and spatial variability (Rai & Triapthi 2008).

Pb in the samples varies from 0.4-8.4 $\mu g.g^{-1}$ with an average of ~2 $\mu g.g^{-1}$. These values compare with the range of Pb in plants in several countries (0.2-2.4 $\mu g.g^{-1}$; Kabata-Pendias & Mukherjee 2007) and ~30% of samples have Pb greater than or equal to the upper limit and all samples are in excess of the lower limit of the range. The average Pb values of all the plant types in this study (1.0-3.2 $\mu g.g^{-1}$) are higher than the FAO/WHO guidelines (0.5-1.0 $\mu g.g^{-1}$) and to the WHO/EU range of 0.1-0.3 $\mu g.g^{-1}$. On the basis of average values, the decreasing trend follows the order: tomato > spinach > cabbage > brinjal > cauliflower (p = 0.006). The samples from the Gyaspur site in particular exhibit high Pb levels with an average of 4.1 $\mu g.g^{-1}$ and the highest Pb (8.4 $\mu g.g^{-1}$) was measured in the spinach sample-facts that underscore the risks of growing vegetation near to the wastewater disposal point, and the retention of Pb by leafy vegetables as pointed out by Adriano (2001). The soil pH/alkaline nature of the soil is one of the major factors for limited bioavailability of Pb (Avci & Deveci 2013), a fact supported by a linear decrease of average Pb in all vegetables and the soil pH with a moderate correlation between them (r^2 = 0.43).

Zinc (Zn): Involvement in metabolic activities makes Zn an essential plant nutrient. Zn in the vegetables varies from 4 $\mu g.g^{-1}$ in cabbage to a maximum of 44 $\mu g.g^{-1}$ in brinjal, incidentally from the same site. The range observed in the study compares to the range of 1-27 $\mu g.g^{-1}$ observed for plants world-wide (Kabata-Pendias & Mukherjee 2007); 1.1-11.2 $\mu g.g^{-1}$ (Chary et al. 2008); 8-148 $\mu g.g^{-1}$ (Avci & Deveci 2013); 22-47 $\mu g.g^{-1}$ (Arora et al. 2008). Chary et al. (2008) have observed that ~40% of the Zn was associated in soluble and/or exchangeable phase(s) and was the most bio-available among other metals such as Cr, Cu, Ni, Co and Pb; however, that did not result in higher Zn in the vegetation compared to values reported in other studies. Chary et al. (2008) attributed high percentages of exchangeable/soluble Zn might be due to low soil pH (5.9-7.3). A somewhat contrasting observation was reported by Avci & Deveci (2013) who measured higher Zn in vegetables grown in soils whose pH varied from 7.5 to 8.3. The concentration of metal in vegetable samples followed the trend of spinach > brinjal > cauliflower > tomato > cabbage ($p = 0.001$).

Principal Component Analysis (PCA) is applied to the vegetable samples to group heavy metals for source identification based on the % of the variance in the dataset. While performing PCA, varimax rotation method was used with Kaiser Normalization. Based on the Eigenvalues > 1, three components suggest 76.34% of the total variation. Principal Component-1 (PC1) accounts for 32.70% of variance, whereas PC2 for 25.9% and PC3 for 17.73%. Values greater than 0.7 in each component were considered. Factor 1 has higher positive loading for Cr, Pb, Co; Factor 2 has higher positive loading for Ni and Cu, and Factor 3 has for Mn and Zn. It is understood that heavy metals in vegetables are ultimately derived from the soil (soil-water system) hence it is important to identify the sources that contribute to the metals in the wastewaters. Effluents from small-scale metal and alloy processing, electrochemical processing, and dye and paint units hosted even (in domestic areas) within the limits of AMC and close to Vasna STP also act as a source of metals such as Fe, Pb, Cd, Cu, Zn and Cr found in the wastewaters of municipal wastewater treatment plant. Zn is contributed from different household items such as laundry detergents and cosmetics and can be derived from fertilizers. Cr and Ni mainly mix into the sewage through the usage of stainless steel cookware and through the process of cleaning them and to a large extent from metal and metal processing industries. Similarly, the sewer hook-ups and old pipelines act as the source of Pb and Cu. Different food grains, nuts, vegetables, and faeces are known to contribute a significant amount of Mn in the wastewater (Drozdova 2019).

Transfer of Heavy Metals From Soil to Vegetables

Enrichment of heavy elements in plants is defined in terms of soil to plant transfer factor (TF; equation-1). It is defined as the ratio of concentrations (dry weight basis) of any metal in the plant (C^M_{plant}) to that in the irrigated soil (C^M_{soil}). In equation-2, all 'e-terms' refer to the error involved in their respective parameters.

$$TF^M_{plant} = \frac{C^M_{plant}}{C^M_{soil}} \quad \ldots(1)$$

$$e_{TF^M_{plant}} = TF^M_{plant} \times \left[\left(\frac{e_{C^M_{plant}}}{C^M_{plant}}\right)^2 + \left(\frac{e_{C^M_{soil}}}{C^M_{soil}}\right)^2 \right]^{1/2} \quad \ldots(2)$$

Where, the sub-/super-script *M*, *plant* and *soil* refer to metal, plant and soil, respectively.

Transfer factor is important to be studied as it provides the first step in metal transfer to plants before it enters human via plants. According to (Mirecki et al. 2015) a TF value of >1 would indicate that elements are accumulated by the plants, ratio ~1 indicates less uptake, and ratio < 1 would indicate that plants would exclude metal from uptake. In the above equation-1, it is assumed that C^M_{plant} is derived exclusively from the soil (i.e. by root uptake); however, this assumption is not valid if there is any other source (e.g., atmospheric deposition) of a metal, or other post-harvest processes (e.g. transport, storage) increase the metal concentration. This latter apprehension assumes importance from the study of (Sharma et al. 2009) in which they reported higher concentrations in vegetables at the market sites compared to those at production sites. The ramification of the above finding, if true, though requires validation from other studies, is that urban consumers are even at higher risk than rural consumers provided the source of the vegetable remains the same.

In this study, the calculated values of TFs (Table 4) of heavy elements vary from <0.00 to 0.40, with an exceptionally higher value of 1.01 for a spinach sample collected from the Gyaspur site. Error propagation analyses showed that 5% measurement-uncertainty in each of concentration values translate to an overall uncertainty of 7.1% in calculated value of transfer factor. For the cases of metals, the following ranges, average and standard deviation in their TF values were observed: TF^{Cr} (0.05-0.14; 0.10 ± 0.02), TF^{Ni} (0.01-0.10; 0.06 ± 0.02), TF^{Cu} (< 0.00-0.06; 0.03 ± 0.02), TF^{Pb} (0.01-0.17; 0.04 ± 0.04), TF^{Mn} (0.03-0.39; 0.10 ± 0.10), TF^{Zn} (0.01-0.08; 0.04 ± 0.02) and TF^{Co} (0.01-1.01; 0.08 ± 0.17). Amongst the vegetables, the following ranges, average and standard deviation were observed: $TF_{brinjal}$ (<0.00-0.38; 0.06 ± 0.07), TF_{tomato} (< 0.00-0.38; 0.07 ± 0.03), $TF_{cabbage}$ (0.01-0.20; 0.05 ± 0.04), $TF_{cauliflower}$ (<0.00-0.20; 0.04±0.03) and $TF_{spinach}$ (< 0.00-1.01; 0.09 ± 0.15).

TF values in this study are low compared to those reported in other Indian studies. For instance, for spinach reported values ranged from 0.5-0.91 (Tiwari et al. 2012 from Vadodara); 0.20-0.82 (Sharma et al. 2008 from Varanasi); 0.10-0.25 (Lokeshwari et al. 2006 from Bangalore) and to a very high set of values (9-32) reported by Rattan et al. (2005) in and around the capital city, Delhi. Our sets of values (<0.00-1.01) are somewhat similar to those observed by Chary et al. (2008) who reported in the range of 0.00-0.58. For cabbage, the reported values ranged from 0.50-0.65 (Tiwari et al. 2012); 0.26-1.36 (Sharma et al. 2008) and these compare to the values of 0.01-0.20 obtained in this study. For another commonly consumed vegetable, brinjal, the values (0.00-0.38) obtained in this study are higher than values 0.0-0.06 (Chary et al. 2008); however, are lower than

Table 4: Transfer factor of heavy metals in vegetable grown in wastewater irrigated soils.

Plant	TF	Co	Cr	Cu	Mn	Ni	Pb	Zn
Brinjal	Range	0.01-0.30	0.07-0.10	0.01-0.05	0.03-0.30	0.01-0.10	0.01-0.10	0.02- 0.80
	Mean	0.06	0.09	0.03	0.09	0.06	0.03	0.03
	SD	0.10	0.02	0.01	0.10	0.02	0.04	0.01
Tomato	Range	0.01-0.10	0.06-0.10	0.01-0.05	0.04-0.06	0.01-0.10	0.02-0.10	0.01-0.05
	Mean	0.05	0.09	0.03	0.05	0.06	0.07	0.03
	SD	0.02	0.02	0.01	0.01	0.02	0.04	0.01
Cabbage	Range	0.01-0.10	0.04-0.10	0.01-0.10	0.04-0.20	0.04-0.07	0.01-0.10	0.008-0.03
	Mean	0.06	0.07	0.01	0.08	0.05	0.04	0.02
	SD	0.02	0.03	0.003	0.05	0.01	0.03	0.008
Cauliflower	Range	0.01-0.10	0.05-0.10	0.001-0.01	0.03-0.06	0.01-0.07	0.01-0.03	0.01-0.05
	Mean	0.04	0.08	0.01	0.05	0.05 0.02	0.008	0.03
	SD	0.06	0.01	0.006	0.01		0.02	0.01
Spinach	Range	0.01-1.00	0.08-0.10	0.001-0.04	0.03-0.30	0.04-0.07	0.01-0.10	0.02-0.07
	Mean	0.15	0.10	0.03	0.20	0.06	0.04	0.04
	SD	0.30	0.01	0.01	0.10	0.01	0.05	0.01

the ranges of 0.60-0.79 (Tiwari et al. 2012) and 0.26-1.36 (Sharma et al. 2008).

An attempt was made to understand the high variability in the TF values. Variations in TFs are expected for both the cases, fixed plant-different metals and fixed metal-different plants. In the case of fixed plant-different metals, physiological aspects of metal uptake from soil by the plant remain somewhat similar and the variations are largely due to the differential (bio-) geochemical aspects related to the different metals in/around the prevailing soil-water system. Most important factors are pH of the soil-water system, organic ligands in the soils, abundances of organic/inorganic carbon in soils, bioavailable fraction of any metal, abundance of Fe-Mn oxides or (oxy-) hydroxides. In the case of fixed metal-different plants, variations in TFs are due to their physiological aspects of metal uptake. Since the factors controlling TF values for a fixed plant (& different metals case) are more than the case with fixed metal (& different plants) we anticipate more variations in the former case which has been found to hold good for our case study.

For the two cases, variability in TFs is assessed by the maximum to the minimum values. For fixed plant-different metals case, the following order was observed in the maximum-to-minimum values: spinach (3849) > brinjal (2282) > tomato (1255) > cauliflower (717) > cabbage (25). In contrast, when the metal is fixed and vegetables remain the variant the corresponding lowest value (maximum to minimum) was found for Cr (3) and the highest for Cu (369); and amongst metals, it follows the order: Cu (369) > Co (97) > Pb (21) > Mn (13) > Zn (10) ≈Ni (9) > Cr (3).

One of the studies (Tiwari et al. 2011) which reported TF values in vegetables irrigated using tube-well water, as well as wastewater, provides important insights into the factors controlling heavy element transfer to the edible portion of the plants. Transfer factor values were found to be higher for tube-well water irrigated ones compared to wastewater ones for metals (Cd, Cu, Fe, Mn, Ni and Zn). Exceptions were observed for Cr and Pb, as these two metals were found to be below the detection limit in the vegetable samples irrigated using tube-well water, resulting in a zero TF value. Despite lower metal concentration in tube-well water irrigated vegetables compared to wastewater ones, the reason for the higher values of TFs in the former is a disproportionately lower metal concentration in the tube-well irrigated soils compared to wastewater irrigated soils. Therefore, the sensitivity of the term C_{soil}^{M} is more than that of C_{plant}^{M} in determining the magnitude of TF. The important implication of the above analysis, if it can be extended to other field sites, is that the use of TF in any kind of *prima-facie* risk-assessment associated with consumption of vegetable can be misleading without knowing its origin, i.e. the soil in which it is grown.

Risk Assessment

In this study hazard quotient (HQ; equation 3) is used as the index for risk-assessment (Chien et al. 2002). An HQ_M value of >1 (for any metal) means that there is a potential risk associated with the metal due to its dietary intake-the higher is the value of HQ, the greater is the risk associated with it (Khaled & Muhammad 2016). Hazard quotient is preferred for risk assessment for the facts that it incorporates the reference dose (which is the prescribed upper limit of dose for any metal) in the calculation and, interpretation of HQ value for risk assessment becomes simpler. HQ values calculated in this study and many earlier ones will provide lower bound estimates of the overall risk associated with any metal as other components (other than vegetables) of human consumption are not considered, and other routes of metal intake/ingestion to the body (inhalation and skin exposure) are not taken into account in the calculation.

$$HQ_M = \frac{C_M \times (1 - f_{Moisture}) \times CR}{BW \times RFD_M} \times 10^{-3} \quad \ldots(3)$$

$$e_{HQ_M} = H_{Q_M} \times \left[(\frac{e_{C_M}}{C_M})^2 + (\frac{e_{f_{moisture}}}{f_{moisture}})^2 + (\frac{e_{CR}}{CR})^2 + (\frac{e_{BW}}{BW})^2 + (\frac{e_{RFD_M}}{RFD_M})^2 \right]^{1/2} \quad \ldots(4)$$

Where, C_M is the (consumption weighted) average metal concentration on a dry weight basis (in μg.g^{-1}); $f_{moisture}$ = fraction of moisture content in vegetables (a reported value of 0.915 was used, also verified from our laboratory experiments); CR = consumption rate of (uncooked) vegetable (in g day^{-1}; value of 300 g was used); BW= average (kilogram) body weight (kg bw; 58 kg was used based on Indian standard value for an adult); RFD_M = reference dose for the metal in mg (kgbw)$^{-1}$ day^{-1} (taken from values reported in Qu et al. 2012 and references therein). In equation-4, all 'e-terms' refer to the error of the parameters explained above.

In the equation above assigning a representative value of the metal concentration in vegetables (μg.g^{-1}) is a sensitive parameter to the calculated value of HQ, and hence, a sensitivity analysis was made by choosing three different approaches: (i) nature of vegetables (n = 38) were not segregated by consumption pattern and daily vegetable consumption of 300 g (fresh) vegetable was used in the calculation, (ii) vegetables were segregated into leafy (spinach; n = 8) and non-leafy (others; n = 30), and consumption amounts of 100 and 200 g, respectively, were used, and (iii) furthermore, non-leafy was segregated into the four vegetables and therefore, the consumption amounts in the third approach used are 50 g each for the four vegetables (cabbage, cauliflower, tomato and brinjal) and 100 g for the spinach. Therefore, it follows from the above discussion that the latter two approaches are by and large consumption weighted average metal concentrations.

Based on the three approaches, the following ranges were found for the HQ values (Table 5): Cr (0.970-0.984); Ni (0.067); Cu (0.056-0.059); Pb (6.149-6.239); Mn (1.007-1.166); Zn (0.022-0.023) and Co (0.018-0.021). HQ values calculated from these approaches show very consistent results indicating lesser sensitivity on how the average concentration is calculated, and would, therefore, be representative values. Error propagation analyses showed that 5% uncertainty in each of parameters (in equation-3) translates to an overall uncertainty of ~11% in the calculated value of HQ values. Results indicate that there is little risk associated with Zn, Co, Cu and Ni, even if other components (e.g., other food/drink components) would have been considered in the calculation. For instance, an increase in consumption amount by a factor of ~5 would increase HQ by the same factor (say, the maximum HQ value of Ni would increase from ~0.07 to a value ~ 0.35), yet well beyond the HQ limit of 1 for any risk to human health.

HQ_{Cr} values of ~0.97 ± 0.10 are very close to the threshold value underscoring the risk associated with Cr from vegetables. Error propagation analysis leads to the upper limits of these values greater than 1. If other food components are included in the calculation there is the likelihood that HQ_{Cr} values would be greater than critical risk value of 1. Along with similar arguments, there is a risk associated with Mn with higher than one HQ_{Mn} values (1.01 ± 0.10). The most notable risk associated is with the case of Pb with the highest HQ values (6.15 ± 0.61) and the population of the Ahmedabad city are exposed severely to the risk of Pb due to ingestion via vegetable consumption. The continuous use of sewage for irrigation may increase the exposure dose to the human being, which may cause various health-related

Table 5: Hazardous quotient values.

Heavy Metals	R_fD Values (mg.kg^{-1}day^{-1})	Source	Approach-1	Approach-2	Approach-3
Co	0.02	Kamunda et al.[c]	0.018	0.021	0.021
Cr	0.003	IRIS [a]	0.970	0.984	0.984
Cu	0.04	Qu et al.[b]	0.056	0.059	0.059
Mn	0.014	Harmanescu et al.[d]	1.007	1.156	1.156
Ni	0.02	IRIS [a]	0.067	0.067	0.067
Pb	1.4×10^{-4}	Qu et al.[b]	6.149	6.255	6.239
Zn	0.3	IRIS [a]	0.022	0.023	0.023

[a] Integrated Risk Information System, U.S. EPA; [b] Qu et al. (2012); [c] Kamunda et al. (2016); [d] Harmanescu et al. (2011)

threats and it should seriously be considered at the least for Pb, and Mn, and likely also for Cr.

CONCLUSIONS

Concentrations of heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) in wastewaters, in soils and, in vegetations grown in wastewater irrigated croplands near Ahmedabad city, India, were measured by high-precision ICP-MS. The basic objective is to assess the potential risk to human health to a significant fraction of ~six million population of the city. The study, perhaps the first reports, brings out the following observations and the conclusions:

1. Concentrations of heavy metals [e.g., Co (2.1-2.2), Cr (1.4-1.9), Cu (0.1-0.9), Mn (0.2-3), Ni (1-1.9), Pb (0.4-1.6) and Zn (5.1-19); all in $\mu g\ ml^{-1}$] in wastewaters exceed their respective MACs values for irrigation purpose set by Indian/WHO/European agencies.
2. Average concentrations ($\mu g.g^{1}$) of metals in the eight soil samples follow the trend: Zn (421 ± 62)> Mn (336 ± 49)> Cu (201 ± 30)> Cr (71 ± 20)> Ni (51 ± 8) >Pb (42 ± 6) > Co (9 ± 1). The average are distinctly different with confidence limit >90% ($p < 0.01$). Good inter-correlations between the analysed metals are observed which is suggestive of common sources/ process contributing to them, predominantly enriched by the wastewater irrigation. Except for Cr, all metals show a downstream decrease of concentrations.
3. Concentrations of metals in vegetables vary in the range [Co (0.10-11.3), Cr (5.2-11.8), Cu (0.04-9.9), Mn (12.3-110), Ni (0.7-4.2), Pb (0.4-8.4) and Zn (4.4-44); all in $\mu g.g^{1}$; dry weight basis]. Variation of concentration though is plant-specific; bio-availability of metals is an important factor for metal assimilation in plants. The pH of the soil-water system seems to regulate bio-availability of (at least) Cu, Pb, Ni and Zn.
4. High variability was observed in the transfer factor values. Geochemical factors related to different metals in the soil-water system seem to regulate more the transfer factor than the physiological differences between various plant species.
5. Hazard quotient was calculated for assessing the risk associated with heavy metals via consumption of the vegetables. HQ values suggest that there is no risk associated with Co, Cu, Ni and Zn; however, there is a high risk associated with Pb and Mn, and likely also from Cr. Finally, more efficient treatment of wastewater treatment facilities and, frequent monitoring of heavy metals in soils and in vegetation from the area are suggested.

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