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Heavy Metal Contamination in Vegetables Grown in Wastewater Irrigated Areas of Varanasi, India

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The contamination of agricultural products with heavy metals has become an important concern throughout the world due to the potential adverse effects of heavy metals on human health. Growth media (soil, air and water) is the main route of heavy metal transport to plants. The concentrations of heavy metals in agricultural soils have been found to be elevated due to continuous use of pesticides, fertilizers, sewage sludge and municipal and industrial effluents. Many studies have shown that wastewater irrigation has elevated the levels of heavy metals in receiving soils (Singh et al. 2004; Mapanda et al. 2005; Sharma et al. 2006). The accumulation of heavy metals in edible portions of vegetables has serious adverse effects on human health and plants (Wenzel and Jockwer 1999). Several heavy metals such as Cd, Cr, Ni and Pb are reported carcinogenic in nature (Trichopoulos 1997).

In many parts of the world, including India, wastewater application to agricultural land is a common practice (Feigin et al. 1999; Singh et al. 2004; Sinha et al. 2006). Urban and industrial effluents, deterioration of sewerage pipes and treatment works and wear of household plumbing fixture cause contamination of irrigation water at suburban region of many cities. The relationship between the concentration of heavy metals in plants and soil is rarely observed, but elevated levels of heavy metals in soil may lead to increase uptake by plants. The absorption of heavy metals by plants depends on a wide range of soil factors such as pH, organic matter, soil metals availability and cation exchange capacity. The uptake of heavy metals also depends on season and presence of other heavy metals in soil (Sharma et al. 2006; Sharma and Agrawal 2006). The interaction between different heavy metals occurs at root surface and also within the plant, which ultimately affects the uptake and translocation of heavy metals (Sharma and Agrawal 2006). The present study was conducted to investigate the level of heavy metals in irrigation water, soil and vegetables grown in the area having long term uses of treated and untreated wastewater. The levels of contamination were also compared with established safe limits to assess the potential health hazard due to heavy metals.

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MATERIALS AND METHODS

The Varanasi city having more than 2 million inhabitants and 112.3 Sq. km area is located in Eastern Gangetic plain of northern India. The three major suburban agricultural areas, irrigated by treated and/ or untreated wastewater were selected for this study. The common industries discharging effluents are fabric printing, batteries, paints, dyeing, electric cables and tire manufacturing. The common vegetables and other crops grown in suburban areas are rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), cauliflower (*Brassica oleracea* var. *botrytis*), cabbage (*Brassica oleracea* var. *capitata*), tomato (*Lycopersicon esculentum* Miller), radish (*Raphanus sativus* L.), palak (*Beta vulgaris* var. *all green H1*)), egg plant (*Solanum melongena* L.), mustard (*Brassica nigra* L.), okra (*Abelmoschus esculentus* L.), corn (*Zea mays* L.), amaranthus (*Amaranthus triclour* L.) etc.

Samples of vegetables (palak, cabbage, amaranthus, okra, tomato and egg plant) top – soil (0 – 15 cm depth) and irrigation water were collected in triplicate from the sites during the late autumn. The samples were brought back to laboratory, stored and processed further as soon as possible. Vegetable samples were washed with tap water and non-edible portions were removed as per the normal household practices. Then the vegetables were chopped into small pieces, oven dried at 80 ^{0}C till the constant weight was achieved. The dried materials were ground in a stainless steel blender and then passed through a 2 mm size sieve. Soil samples were air dried, crushed and ground to pass through a 2 mm size sieve. All samples were stored at ambient temperature before analysis.

The chemicals used were Merck, analytical grade (AR). Reagents used for wet acid digestion were concentrated nitric acid (AR), perchloric acid (AR) and concentrated sulphuric acid (AR). Standard stock solutions of known concentrations of different heavy metals were of Sisco Research Laboratories Pvt. Ltd., India.

Monoacid method (concentrate HNO_3; 10 ml) was used to digest 50 ml irrigation water samples (APHA 1985). However, 1g of soil and vegetable samples were digested with 15 ml of concentrated HNO_3, H_2SO_4 and $HClO_4$ in 5:1:1 ratio at 80 ^{O}C until a transparent solution was obtained (Allen et al. 1986). The digested samples of irrigation water, soil and vegetables were filtered through Whatman no. 42 filter paper and diluted to 50 ml with distilled water. A Perkin–Elmer, model 2130 Flame Atomic Absorption Spectrophotometer was used to determine the concentration of heavy metals (Cd, Cu, Zn, Pb, Ni and Cr) in the filtrate of irrigation water, soil and vegetable samples. The limits of detection of different heavy metals are given in Table 1. The precision of metal analysis was controlled by repeated analysis of samples against NIST – SRM, 1570 for all heavy metals. The results were found within ± 2% of the certified value. Quality control measures were taken to assess contamination and reliability of data. Blank and

Table 1. Detection limit (μg /ml) for each element measured from flame atomic absorption spectrophotometer.

Elements	Detection Limit
Cd	0.0005
Cu	0.001
Cr	0.002
Ni	0.004
Pb	0.01
Zn	0.0008

drift standards (Sisco Research Laboratories Pvt. Ltd, India) were run after five determinations to calibrate the instrument. The coefficient of variation of replicate analysis was determined for different determinations. The mean, median, minimum and maximum and standard deviation were done in irrigation water, soil and vegetable samples using SPSS/PC$^+$ (version 11) for microcomputer.

RESULTS AND DISCUSSION

The mean concentrations of heavy metals Cd, Cu, Zn, Pb, Ni and Cr in soils, (n = 27) and irrigation water (n = 33) are shown respectively in Table 2 and 3. The mean concentrations of heavy metals (μg/g dry wt) in soil were below the safe limit of Indian Standard (Table 2). The comparison of mean concentrations of heavy metals in studied soil with that of typical uncontaminated soil reported by Bowen (1966) showed that wastewater application to agricultural soil has increased the levels of Zn, Cr, Cd and Pb (Table 2). The upper limits of heavy metals in the present soils were also higher than the values reported by Temmerman et al. (1984) for non polluted soil (Table 2). Singh et al. (2004) and Mapanda et al. (2005) also found increased levels of heavy metals in soil irrigated by wastewater. The higher standard deviation suggests higher variations in heavy metal concentrations between the sites. This variation may be due to variation in heavy metals concentrations in irrigation water and other agronomic practices of the respective area. Among the studied heavy metals, Cr concentration was the highest followed by Zn, Ni, Cu, Cd and Pb (Table 2). The low concentrations of heavy metals in the soil may be ascribed to its continuous removal by vegetables grown in these areas.

The concentration of heavy metals in wastewater (μg/ml) at suburban areas of Varanasi ranged between 0.02 to 0.13 for Cu, 0.02 to 1.25 for Zn, 0.02 to 0.04 for Cd, 0.04 to 0.37 for Pb, 0.05 to 0.10 for Ni and 0.03 to 0.30 for Cr (Table 3). The higher standard deviation observed for heavy metals Cu, Zn and Cr in wastewater suggests that these metals were not uniformly present at all sites. This may be ascribed to variety of industries discharging their treated and/ or untreated wastewater into the drains used for the irrigation purposes. The concentrations of heavy metals in industrial effluents also depend on the process of product manufacture and raw materials used in the industries. The comparison of mean concentrations of heavy metals in irrigation water with recommended value of

WHO showed that the concentrations of Cd was three fold higher, whereas Cr was only approaching the recommended value (Table 3). The levels of heavy metals in wastewater were higher than the clean (ground water; metals were not detected) water. This result suggests that heavy metals based industries such as fabric printing, battery, paints, and cables and tire manufacturing are using heavy metals such as Cd, Cu, Zn, Pb, Ni and Cr in colours, pigments, electroplating and metal surface treatments are the main source of elevated heavy metal concentrations in wastewater.

The range and mean concentrations of heavy metals (μg/g dry wt) in leafy and other vegetables are presented in Table 4. In leafy vegetables (palak, amaranthus and cabbage), the concentrations of heavy metals (μg/g dry wt) ranged between 0.55 to 10.30 for Cu, 29.35 to 469.45 for Zn, 1.55 to 6.90 for Cd, 9.00 to 28.00 for Pb, 4.05 to 15.00 for Ni and 2.75 to 51.15 for Cr (Table 4). The mean concentration of Zn (116.41 μg/g dry wt) in amaranthus was higher than cabbage (98.54 μg/g dry wt) and palak (54.52 μg/g dry wt) (Table 4). Tripathi et al. (1997) and Gopalan et al. (1991) also reported more concentration of Zn in amaranthus than palak. The concentrations of other metals Cu, Cr, Pb, Ni and Cd were highest in palak, followed by amaranthus and cabbage (Table 4). Tripathi et al. (1997) however, reported higher concentrations of Cd, Cu and Pb in amaranthus than palak plants. The concentrations of heavy metals (μg/g dry wt) in fruit vegetables varied between 1.75 to 8.70 for Cu, 18.85 to 132.70 for Zn, 1.10 to 9.20 for Cd, 6.50 to 29.00 for Pb, 3.45 to 12.00 for Ni and 2.95 to 12.85 for Cr (Table 4). Among the fruit vegetables (okra, tomato and egg plant), the maximum concentrations of heavy metals were observed in okra followed by tomato and then egg plant (Table 4). Tripathi et al. (1997) found similar trend for Cd, Cu, Zn and Pb in okra and other fruit vegetable samples collected from suburbs of Bombay city (India). Sinha et al. (2005) have reported higher value of Zn concentrations in palak, egg plant and tomato (91.42 μg/g dry wt; 46.53 μg/g dry wt and 106.95 μg/g dry wt) then the present study (Table 4). Higher levels of Cu in cabbage, palak, okra, egg plant and tomato (8.19 μg/g dry wt; 23.42 μg/g dry wt; 11.3 μg/g dry wt; 11.80 μg/g dry wt and 16.38 μg/g dry wt) than the present study were also reported (Sinha et al. 2005). Cr concentrations in cabbage (5.40 μg/g dry wt) and okra (11.73 μg/g dry wt) observed in the present study were respectively higher and lower than the values reported by Sinha et al. (2005) for cabbage (11.21 μg/g dry wt) and okra (6.00 μg/g dry wt). The levels of heavy metals (Cd, Pb, Cr and Cu) in vegetables were many folds higher in the present study than values reported by Liu et al. (2006) in Republic of China. The comparisons of the mean concentrations of heavy metals Cd, Cu, Pb, Zn, Ni and Cr with the established safe limit of Prevention of Food Adulteration Act 1954 (Awashthi 2000) showed that the concentrations of heavy metals such as Cd, Pb and Ni were above the safe limit in all the examined vegetables (Table 4). The concentration of Zn was above the safe limit in cabbage, egg plant, palak and amaranthus. Copper and Cr concentrations were below the safe limits of Prevention of Food Adulteration Act 1954 (Awashthi 2000) in all the vegetables (Table 4). Sharma et al. (2006) have also reported that the concentrations of Cd,

Table 2. Mean, median, minimum and maximum and standard deviation of heavy metal concentrations in soils (n = 27): µg/g dry soil.

Metals	Safe limit[a]	Uncontaminated Soil		Contaminated Soil (Present study)				
		Soil[b]	Soil[c]	Mean	Med.	Min.	Max.	S.D.
Cu	135 – 270	25	20	10.46	8.80	2.55	29.85	6.51
Zn	300 – 600	150	50	68.71	59.40	21.7	207.85	44.26
Cd	3 – 6	1	0.06	3.03	3.05	0.90	5.65	1.38
Pb	250 – 500	50	100	16.83	16.50	8.50	24.50	3.87
Ni	75 – 150	1	40	18.10	18.85	6.90	33.35	5.59
Cr	n/a	30	100	115.16	25.85	13.4	468.05	167.40

[a]Range of safe limit of heavy metal concentrations in soil given by Prevention of Food Adulteration Act 1954 (Awashthi 2000)

[b]Elemental composition of typical uncontaminated soils (Bowen 1966)

[c]Upper limit of heavy metal concentrations in non – polluted soil (Temmerman et al. 1984)

Table 3. Mean, median, minimum and maximum and standard deviation of heavy metal concentrations in irrigation water (n = 33): µg/ml.

Metals	Safe Limit	Present Study				
		Mean	Median	Minimum	Maximum	S.D.
Cu	0.2	0.04	0.03	0.02	0.13	0.03
Zn	2.0	0.30	0.06	0.02	1.25	0.33
Cd	0.01	0.03	0.03	0.02	0.04	0.01
Pb	0.5	0.26	0.28	0.04	0.37	0.08
Ni	0.2	0.07	0.07	0.05	0.10	0.01
Cr	0.1	0.09	0.05	0.03	0.30	0.07

[a]Safe limit of toxic heavy metals in irrigation water for agricultural purpose

Pb and Ni were above the safe limits of Prevention of Food Adulteration Act 1954 (Awashthi 2000) in edible portion of palak plants during summer season, whereas Cd was also higher in winter season. The variations in heavy metals concentrations in vegetables were due to variations in their absorption and accumulation tendency. Soil properties such as pH, organic matter, cation exchange capacity (CEC), redox potential, soil texture and clay content may also affect the heavy metal uptake (Verloo and Eeckhout 1990). Change et al. (1987) found that soil temperature also plays an important role in governing the heavy metals uptake by crops. The accumulation of heavy metals also depends on plant age and on plant parts. The mean concentrations of heavy metals in soil and irrigation water were within the safe limits. However, Cd and Cr concentrations in irrigation water were respectively, above and equal to the safe limit set for the agricultural purpose. The mean concentrations of heavy metals Cd, Ni and Pb in examined vegetables were above the safe limits but Cu and Cr were found below the safe limits. The results suggest that vegetables produced under wastewater

Table 4. Heavy metal concentrations (μg/g dry wt) in vegetables grown in wastewater receiving areas of Varanasi: Mean and (range).

Vegetables	n	Cu	Zn	Cd	Pb	Ni	Cr
Safe limit[a]		30	50	1.5	2.5	1.5	20
Amaranthus	15	5.30 (1.95 – 10.30)	116.41 (31.35 – 469.45)	5.28 (4.25 – 6.15)	20.60 (12.50 – 27.00)	8.74 (5.15 – 13.95)	14.42 (6.00 – 23.20)
Cabbage	6	2.25 (0.55 – 3.95)	98.54 (68.25 – 122.30)	4.25 (1.55 – 6.90)	16.83 (9.00 – 24.00)	6.28 (4.05 – 9.70)	5.40 (2.75 – 8.75)
Palak	9	5.42 (2.95 – 8.10)	54.52 (29.35 – 87.45)	5.54 (4.70 – 5.90)	24.28 (20.50 – 28.00)	9.86 (5.55 – 15.00)	21.11 (6.20 – 51.15)
Egg plant	12	3.10 (1.75 – 4.80)	29.42 (16.85 – 55.20)	4.70 (1.10 – 9.20)	17.54 (6.50 – 24.00)	7.25 (3.45 – 9.75)	5.48 (2.95 – 9.25)
Okra	3	5.03 (4.95 – 5.10)	130.14 (127.82 – 132.70)	6.48 (6.35 – 6.60)	25.00 (22.50 – 28.00)	10.20 (9.95 – 10.60)	11.73 (10.40 – 12.80)
Tomato	12	4.38 (2.05 – 8.70)	31.44 (22.95 – 42.45)	5.35 (4.10 – 7.20)	21.96 (13.00 – 29.00)	8.62 (5.50 – 12.00)	6.80 (4.00 – 9.80)

n: number of samples

[a]Safe limit of heavy metals in food given by Prevention of Food Adulteration Act 1954 (Awashthi 2000).

irrigation practices may pose health hazards in human being residing at urban fringes and regularly using these products.

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