

Bioaccumulation of Heavy Metals in Vegetables: A Threat to Human Health

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ABSTRACT

Rapid growth in urbanization and industrialization has increased the levels of heavy metals in the environment and consequently in the food chain. Consumption of contaminated food by human beings and other animals may pose a serious threat to their health. Vegetables are a major portion of the human diet, providing micro- and macronutrients, fibers, antioxidants, vitamins, etc. Vegetables are often grown in suburban areas commonly contaminated with heavy metals. Depending on the nature of vegetables, some of them have a great potential to accumulate higher concentrations of heavy metals than others. The present review describes the uptake and accumulation of heavy metals in vegetables, their role in remediation of heavy metals from contaminated areas and the negative impact of heavy metals on vegetables and human health through their consumption.

Keywords: antioxidants, health hazard, heavy metal uptake, phytochelatin, remediation, toxicity

CONTENTS

INTRODUCTION.....	13
SOURCES OF HEAVY METALS IN VEGETABLES.....	14
ROUTE OF HEAVY METAL UPTAKE THROUGH VEGETABLES	14
ACCUMULATION OF HEAVY METALS IN VEGETABLES	14
TOXICITY OF HEAVY METALS IN VEGETABLES	19
EFFECTS OF SOIL AND PLANT FACTORS ON ACCUMULATION OF HEAVY METALS	20
HEALTH HAZARDS FROM HEAVY METAL EXPOSURE	20
CONCLUSION	21
REFERENCES.....	21

INTRODUCTION

Human health is closely linked with a healthy and clean environment. Maintenance of a clean environment and attenuation of pollution have been points of world-wide concern. Vegetables are known to have positive effects on human health as they play a crucial role in preventing a number of chronic diseases. These protective effects have been attributed to a wide range of compounds present in the vegetables. These are antioxidants such as ascorbic acid, carotenoids, tocopherols, glutathione, phenolic acids and flavanoids (Ames *et al.* 1993; Rice-Evans and Miller 1995; Sara *et al.* 2005). The contents of antioxidants in vegetables vary with factors such as genotype, environmental growing conditions, growth stage, post-harvest techniques and storage conditions (Howard *et al.* 2002). Antioxidants also act as buffering agents for acidic substances produced during the digestion process. Studies have been conducted in many parts of the world to assess the levels of heavy metal contamination in vegetables, which are important components of the human diet. Tripathi *et al.* (1997) observed the concentrations of heavy metals such as Pb, Cd, Cu and Zn in air particulates, water and food samples collected from different areas in Bombay city during 1991-1994. The concentrations of Pb and Cu were higher in *Vigna radiata* (green gram) and Cd in *Amaranthus tricolor* (amaranthus). The total intake of Zn, Cu, Pb and Cd through air, water and food were 10500.0, 1500.0, 30.0, and 43.0 $\mu\text{g day}^{-1}$, res-

pectively. The major contribution of daily intake was the ingestion route rather than inhalation. Through food substances only, daily intake for Pb, Cd, Cu and Zn was 25.1, 4.30, 1464.0 and 10492.0 $\mu\text{g day}^{-1}$, respectively. There may be an adverse impact on human health by consuming these contaminated food substances. Singh *et al.* (2004) assessed the impact of wastewater/sludge disposal from sewage treatment plants (STPs) in Jajmau, Kanpur (5 million L day⁻¹) and Dinapur, Varanasi (80 million L day⁻¹) on health, agriculture and environmental quality in the receiving/application areas around Kanpur and Varanasi in Uttar Pradesh, India. The result showed elevated level of metals in all the environmental media. In the soil a critical level of heavy metals was found to be higher than the area receiving no effluents. Total daily intake (TDI) was computed for each metal by calculating the mean concentration of individual toxicant in the respective media and the mean daily intake of the same media by a single person. The TDI (mg day⁻¹) for Cd, Cr, Cu and Pb was 0.42, 30.0, 48.0 and 3.0, respectively. Due to consumption of these heavy metals through vegetables, they were found in the human blood and urine of the population living in wastewater-irrigated areas.

Leafy vegetables like *Spinacia oleracea* (spinach), *Brassica oleracea* var. *capitata* (cabbage) and *Brassica caulorapa* (knol knol) can be used as accumulator plants for the remediation of heavy metals from contaminated soils, depending upon their absorption capacities (Sinha *et al.* 2005). Use of leafy vegetables for the purpose of remedia-

tion of contaminated soil is one of the easiest and cheapest techniques, but it may be harmful for both the plants and human beings as heavy metals interfere with their metabolic activities. The consumption of *Lactuca sativa* (lettuce), spinach, cabbage loaded with heavy metals grown on contaminated soil has been found to pose a health risk to consumers (Kachenko and Singh 2006). Heavy metals such as Pb, As, Hg, Cd and Cr used for commercial purpose are toxic and their indiscriminate use resulted into upsurge of such metals in soil and various crops, which ultimately resulted in clinical problem in human beings like kidney, liver and nervous system damage (Bunce 1990). For crop protection use of waste has resulted in the accumulation of heavy metal in soil and water, which is a health hazard to human beings (Smith *et al.* 1996).

The present review is mainly concerned with recent reports on the uptake and accumulation of heavy metals in different vegetables, particularly leafy vegetables, and variations in their accumulating tendency. The review also deals with the role of vegetables in the remediation of heavy metals from contaminated areas and their impact on vegetables. Consumption of contaminated vegetables may lead to health hazards, which are negative aspects of these remediation techniques and this aspect is also dealt with in the review.

SOURCES OF HEAVY METALS IN VEGETABLES

Heavy metal contamination of an ecosystem is one of the major and most widely discussed ecotoxicological problems. Some heavy metals (Cu, Fe, Ni, Zn, Mn, etc.) are essential for the growth and development of plants when present in trace amounts, but at excessive concentrations these become toxic. Both natural and anthropogenic sources are responsible for increasing the levels of heavy metals in the environment. Natural sources include parent geologic rock material, volcanic outcropping, spontaneous contributions or forest fires, whereas anthropogenic sources include sewage sludge, pesticides, organic matter, composts, fertilizer supplements (Lopez-Alonso *et al.* 2000; Singh and Agrawal 2007), industrial waste, mining, smelting and metallurgical industries (Singh 2001) and use of treated or untreated industrial and municipal effluents for irrigation purposes (Barman *et al.* 2000; Singh *et al.* 2004; Mapanda *et al.* 2005; Singh and Kumar 2006; Sharma *et al.* 2006, 2007). In Mexico, mining activities have caused considerable increase in concentrations of As, Ni, Co and Cu in the soil (Razo *et al.* 2004). Mining and smelting processes have also contaminated wide areas of Japan, Indonesia and China with Cd, Cu and Zn (Herawati *et al.* 2000). Agricultural practices like the use of pesticides, fungicides and organic and inorganic fertilizers have increased the concentrations of heavy metals (Cd, Ni, Mn, Co and Cu) in the top layer of the soil and consequently in crops via their uptake (McBride 2003).

Aerosols also cause heavy metal contamination of Cd, Pb, Zn, Cr and Ni in soil through atmospheric deposition, which are consequently absorbed and accumulated by plants or get adsorbed on aerial surfaces of the plants (Temmerman and Hoenig 2004). Energy supplying power stations such as coal burning power plants, petroleum combustion, nuclear power stations and high-tension electric lines also contribute heavy metals (Se, B, Cd, Cu, Zn, Cs and Ni) to the environment (Verkleij 1993). Electricity supply like power lines/cables contributed to 31% of the total antimony, 42% of the total cadmium, 38% of the total cobalt and 43% of the total Hg in ambient air in Australia. Metal ore mining also contributed substantially to the reported emission of metallic ions such as beryllium (93%), chromium VI (26%), copper (60%), manganese (~100%), and nickel (74%). Sewage and drainage services in Australian states and territories contributed about 32% and hospitals about 36% of the total heavy metal contamination. Petroleum refining was a major contributor of chromium III compound emission (about 85%; NPI 2001). Vegetable-growing areas, mostly situated

in or near the smelters such as Boolaroo and Port Kembla, have an elevated risk of potential contamination. These smelters are an important source of Pb pollution which can affect human health (Kachenko and Singh 2006).

ROUTE OF HEAVY METAL UPTAKE THROUGH VEGETABLES

All sources contribute heavy metals to the soil from where these are translocated into different plant parts via root uptake. Accumulation of heavy metals and their uptake by different plant parts depend on the concentrations of available heavy metals in the soil and form of metals. Positive metal ions are attracted to negative charges like hydroxyl groups and electron pairs of oxygen in the structure of clay minerals and to the carboxyl and phenolic groups of organic substances (Mengel and Kirkby 1982), whereas negative metal ions are attracted to positively charged hydrous oxides of Fe and Al. The rate of solubilisation of metals and differences in plant species also affect the availability of metals due to differences in their genotype and transport properties (Phalsson 1989; Kafka and Kurus 1997). Accumulation of heavy metals in soil has the potential to alter the physico-chemical properties of soil, cause toxicity to plants and contaminate the food chain. Heavy metals enter the human body either through inhalation or the intake of contaminated foods, including vegetables, or by drinking water. The intake of heavy metals via ingestion mainly depends on the food habit. Green vegetable like *B. vulgaris* grown on heavy metal-contaminated soil accumulated more heavy metals than those grown in uncontaminated areas (Singh and Agrawal 2007). *Capsicum annuum* (green pepper), *Solanum melongena* L. (aubergine), *Cucurbita pepo* (vegetable marrow), *Cucumis sativus* (cucumber), and *Phaseolus vulgaris* (green bean) were collected from 17 greenhouse borders in Almeria, Spain. There was a significant difference in the levels of metallic concentration among different vegetables. Except for Cu other metals (Pb, Cd, Zn, Mn) were found to be higher in green bean than in other vegetables (Zurera-Cosano *et al.* 1989). The difference in heavy metal uptake of vegetables may be due to the difference in root uptake of heavy metals that affect the cuticular formation by forming epicuticular lipids which are shorter; these, by having a higher polarity result in higher permeability and increased uptake by the leaves of plants (Greger *et al.* 1993) and due to more translocation to above-ground parts a higher level of heavy metals were found in the leafy portions of amaranthus, *Brassica oleracea* L. (cauliflower), and spinach (Sinha *et al.* 2006).

ACCUMULATION OF HEAVY METALS IN VEGETABLES

Information on contamination and subsequent accumulation of heavy metals in leafy and non-leafy vegetables from different sources has been widely reported in the literature (Tables 1, 2). Concentrations of heavy metals in vegetables varied from below the detection limit to above the safe limits depending upon the sources of heavy metal contamination. Singh and Kumar (2006) assessed heavy metal concentrations in vegetables spinach and *Abelmoschus esculentus* L. (lady's finger) grown in peri urban areas of Delhi (India), contaminated with heavy metals through industrial effluents, sewage sludge and vehicular emission. Results showed that the concentrations of heavy metals (mg kg^{-1}) varied from 7 to 50 for Cu, 51 to 282 for Zn, 1.4 to 9.0 for Cd and 1.7 to 9.2 for Pb in spinach and in lady's finger it varied from 12 to 29 for Cu, 39 to 156 for Zn, 0.4 to 6.0 for Cd and 0.8 to 7.3 for Pb. It was further observed that the accumulation of all the heavy metals was higher in *S. oleracea* compared to *A. esculentus*. This difference is ascribed to the physiology and morphology of plants like variation in root interception of metal ions, variation in entry of the metal ions through mass flow and diffusion and translocation of metal ions from the root to shoot, their accumulation

Table 1 Heavy metal concentrations (mg kg⁻¹) in edible portion of leafy vegetables.

Vegetables	Sources of Heavy metals	Cu	Zn	Cd	Pb	Ni	Cr	Mn	As	Hg	References
<i>Amaranthus blitum</i> (Amaranthus)	Agricultural activities	42.82	-	0.16	1.91	-	1.85	-	0.67	0.27	Liu <i>et al.</i> 2006
	Atmospheric deposition	-	-	-	0.19	-	-	-	-	-	Tripathi <i>et al.</i> 1997
	Wastewater irrigation	21.94	80.26	-	-	-	30.92	176.90	-	-	Sinha <i>et al.</i> 2006
<i>Beta vulgaris</i> var. All Green (Palak)	Waste water Irrigation	28.58	41.51	4.36	15.74	7.57	27.83	117.94	-	-	Sharma <i>et al.</i> 2007
	Do	8.10	87.45	5.90	28.00	15.0	51.15	-	-	-	Sharma <i>et al.</i> 2006
	Sewage sludge	25.30	79.0	23.70	1.90	5.65	2.90	56.0	-	-	Singh and Agrawal 2007
	Atmospheric deposition	0.07	-	0.01	0.27	0.81	0.23	-	-	-	Agrawal <i>et al.</i> 2004
<i>Apiumng graveolens</i> (Celery)	Sewage sludge	0.91	-	0.020	0.42	-	-	-	-	-	Dogheim <i>et al.</i> 2004
	Agricultural activities	109.89	-	0.10	1.76	-	0.08	-	0.49	0.31	Liu <i>et al.</i> 2006
<i>Coriandrum sativum</i> (Coriander)	Atmospheric deposition	8.21	49.70	0.23	2.98	8.50	1.21	75.82	-	-	Stalikas <i>et al.</i> 1997
	Sewage sludge	1.62	-	0.020	0.35	-	-	-	-	-	Dogheim <i>et al.</i> 2004
	Atmospheric deposition	25.42	41.05	0.495	0.143	-	-	-	-	-	Jassir <i>et al.</i> 2005
<i>Lectuca sativa</i> (Lettuce)	Wastewater irrigation	22.24	186.40	-	-	-	83.06	65.64	-	-	Sinha <i>et al.</i> 2006
	Industrial effluents, vehicular pollution	59.93	39.50	0.34	9.70	6.30	-	-	-	-	Demirezen and Aksoy 2006
	Urban and industrial activities	0.92	-	0.01	0.07	-	-	-	-	-	Dogheim <i>et al.</i> 2004
	Atmospheric deposition	-	-	0.213	2.49	-	-	-	-	-	Kachenko and Singh 2006
	Urban and industrial activities	0.90	42.0	1.04	3.70	0.70	-	20.37	-	-	Mohamed <i>et al.</i> 2003
	Compost amendment	13.5	1171.0	-	4.90	-	-	1246.6	-	-	Intawongse and Dean 2006
	Atmospheric deposition	-	-	0.07	0.58	-	-	-	-	-	Radwan and Salama 2006
	Atmospheric deposition	25.07	42.10	0.280	0.155	-	-	-	-	-	Jassir <i>et al.</i> 2005
	Sewage sludge	16.3 - 23.0	182 - 571	2.0 - 47.3	9.2 - 20.6	4.0 - 78.9	3.0 - 13.4	-	-	-	Smilde 1992
	<i>Mentha piperita</i> (Mint)	do	2.15	-	0.010	0.59	-	-	-	-	-
Atmospheric deposition		-	-	1.89	43.00	-	-	-	-	-	Kachenko and Singh 2006
Wastewater irrigation		17.34	192.00	-	-	-	-	-	-	-	Sinha <i>et al.</i> 2005
<i>Nasturtium officinales</i> (Watercress)	Atmospheric deposition	17.19	46.45	0.495	0.106	-	-	-	-	-	Jassir <i>et al.</i> 2005
	Urban and industrial activities	1.96	105.20	1.22	14.37	42.62	-	18.77	-	-	Mohamed <i>et al.</i> 2003
	Sewage sludge	1.11	-	0.080	0.29	-	-	-	-	-	Dogheim <i>et al.</i> 2004
<i>Petroselinum crispum</i> (Parsley)	Atmospheric deposition	24.89	43.54	0.062	0.099	-	-	-	-	-	Jassir <i>et al.</i> 2005
	Sewage sludge	1.82	-	0.010	0.43	-	-	-	-	-	Dogheim <i>et al.</i> 2004
	Industrial effluents, vehicular pollution	53.12	259.20	0.84	9.90	3.47	-	-	-	-	Demirezen and Aksoy 2006
	Urban and industrial activities	3.34	21.00	-	3.29	0.60	-	13.09	-	-	Mohamed <i>et al.</i> 2003
	Atmospheric deposition	-	-	0.067	0.34	-	-	-	-	-	Kachenko and Singh 2006
	Municipal, domestic, industrial discharge	72.0	194.0	0.60	2.0	64.0	24.40	272.0	-	-	Stalikas <i>et al.</i> 1997
<i>Spinacia oleracea</i> (Spinach)	Atmospheric deposition	-	-	-	3.29	-	-	-	-	-	Kachenko and Singh 2006
	Industrial effluents, vehicular pollution	50.0	282	9.2	9.00	-	-	-	-	-	Singh and Kumar 2006
	Atmospheric deposition	4.48	20.9	0.11	0.34	-	-	-	-	-	Radwan and Salama 2006
	Compost amendment	32.3	632	-	5.20	-	-	6631	-	-	Intawongse and Dean 2006
	Atmospheric deposition	-	-	-	0.07	-	-	-	-	-	Tripathi <i>et al.</i> 1997
	Urban and industrial activities	2.71	9.6	0.77	9.44	17.14	-	9.90	-	-	Mohamed <i>et al.</i> 2003
	Atmospheric deposition	-	-	0.36	4.31	-	-	-	-	-	Kachenko and Singh 2006
	Urban and industrial activities	1.18	-	0.03	0.56	-	-	-	-	-	Dogheim <i>et al.</i> 2004
	Sewage sludge	21 - 59.3	316 - 513	1.9- 44.4	0.24 - 0.68	0.51 - 54.8	0.05 - 0.28	-	-	-	Smilde 1992
	Wastewater irrigation	23.0	85.08	-	-	-	8.55	155.6	-	-	Sinha <i>et al.</i> 2005
	Urban and industrial activities	0.24	-	0.004	-	-	-	-	-	-	Dogheim <i>et al.</i> 2004
	Agricultural activities	37.62	-	0.076	1.0	-	0.66	-	0.81	0.21	Liu <i>et al.</i> 2006
	do	35.06	-	0.20	2.05	-	0.44	-	0.45	0.15	Liu <i>et al.</i> 2006
	do	28.39	-	0.12	1.55	-	0.28	-	1.12	0.15	Liu <i>et al.</i> 2006
	do	9.52	-	0.05	0.34	-	0.64	-	0.59	0.12	Liu <i>et al.</i> 2006
	Atmospheric deposition	-	-	0.24	0.041	-	-	-	-	-	Kachenko and Singh 2006
	Urban and industrial activities	0.43	14.9	0.56	-	0.29	-	21.71	-	-	Mohamed <i>et al.</i> 2003
Wastewater irrigation	8.19	66.49	-	-	-	11.21	57.48	-	-	Sinha <i>et al.</i> 2005	

Table 2 Heavy metal concentrations (mg kg⁻¹) in edible portion of non leafy vegetables.

Vegetables	Sources of Heavy metals	Cu	Zn	Cd	Pb	Ni	Cr	Mn	As	Hg	References
<i>Abelmoschus esculentus</i> L. (Lady's Finger)	Wastewater irrigation	11.30	116.36	-	-	-	6.00	29.22	-	-	Sinha <i>et al.</i> 2005
	Industrial effluents, vehicular pollution	32.0	182.0	7.30	6.00	-	-	-	-	-	Singh and Kumar 2006
	do	37.54	15.56	0.58	10.70	2.70	-	-	-	-	Demirezen and Aksoy 2006
<i>Allium cepa</i> (Onion)	Wastewater irrigation	5.10	132.70	6.60	28.0	10.60	12.80	-	-	-	Sharma <i>et al.</i> 2006
	Industrial effluents, vehicular pollution	53.83	21.34	0.97	8.70	4.60	-	-	-	-	Demirezen and Aksoy 2006
	Urban and industrial activities	2.81	17.60	0.76	10.29	18.37	-	3.62	-	-	Mohamed <i>et al.</i> 2003
<i>Brassica oleracea</i> (Cauliflower)	Atmospheric deposition	1.49	11.40	0.02	0.14	-	-	-	-	-	Radwan and Salama 2006
	Industrial effluents, vehicular pollution	1.70	21.5	-	-	-	-	-	-	-	Singh and Kumar 2006
	Wastewater irrigation	12.08	173.21	-	-	-	40.30	28.40	-	-	Sinha <i>et al.</i> 2006
<i>Daucus carota</i> (Carrot)	Municipal, domestic, industrial discharge	0.94	36.03	0.113	1.20	7.73	0.94	23.64	-	-	Stalikas <i>et al.</i> 1997
	Atmospheric deposition	1.51	8.03	0.18	0.01	-	-	-	-	-	Radwan and Salama 2006
	Compost amendment	37.60	149.50	27.40	8.50	-	-	758.90	-	-	Intawongse and Dean 2006
<i>Lycopersicon esculentum</i> (Tomato)	Agricultural activities	27.12	-	0.085	0.92	-	0.38	-	0.15	0.24	Liu <i>et al.</i> 2006
	Urban and industrial activities	0.98	9.60	0.81	7.94	17.54	-	6.14	-	-	Mohamed <i>et al.</i> 2003
	Wastewater irrigation	-	59.58	6.32	-	-	-	-	-	-	Sharma and Agrawal 2006
<i>Raphanus sativus</i> (Radish)	Municipal, domestic, industrial discharge	7.38	11.12	0.102	1.31	2.60	1.50	21.40	-	-	Stalikas <i>et al.</i> 1997
	Agricultural activities	201.75	-	0.11	5.23	-	0.34	-	0.46	0.13	Liu <i>et al.</i> 2006
	Atmospheric deposition	1.83	7.69	0.26	0.01	-	-	-	-	-	Radwan and Salama 2006
<i>Solanum melongena</i> (Brinjal)	Wastewater irrigation	8.70	42.45	7.20	29.00	-	-	-	-	-	Sharma <i>et al.</i> 2006
	Industrial effluents, vehicular pollution	32.60	3.56	0.41	9.70	3.10	-	-	-	-	Demirezen and Aksoy 2006
	Urban and industrial activities	4.47	14.40	0.77	2.59	14.64	-	7.39	-	-	Mohamed <i>et al.</i> 2003
<i>Solanum tuberosum</i> (Potato)	Wastewater irrigation	16.38	106.95	-	-	-	-	30.95	-	-	Sinha <i>et al.</i> 2005
	Agricultural activities	8.65	-	0.083	0.47	-	0.38	-	0.22	0.21	Liu <i>et al.</i> 2006
	Compost amendment	26.90	500.30	68.20	11.80	-	-	271.0	-	-	Intawongse and Dean 2006
<i>Solanum melongena</i> (Brinjal)	Wastewater irrigation	14.0	80.75	-	-	-	-	-	-	-	Sinha <i>et al.</i> 2005
	do	7.76	49.56	-	-	-	7.26	18.25	-	-	Sinha <i>et al.</i> 2005
	Urban and industrial activities	2.93	50.70	0.69	4.57	11.87	-	21.66	-	-	Mohamed <i>et al.</i> 2003
<i>Solanum tuberosum</i> (Potato)	Wastewater irrigation	4.80	55.20	9.20	24.00	-	-	-	-	-	Sharma <i>et al.</i> 2006
	Industrial effluents, vehicular pollution	37.38	9.35	0.43	7.20	4.6	-	-	-	-	Demirezen and Aksoy 2006
	Atmospheric deposition	1.41	11.50	0.02	0.21	-	-	-	-	-	Radwan and Salama 2006
<i>Solanum tuberosum</i> (Potato)	Agricultural activities	41.37	-	0.16	1.30	-	1.15	-	0.98	0.26	Liu <i>et al.</i> 2006
	Wastewater irrigation	23.40	91.46	-	-	-	-	-	-	-	Sinha <i>et al.</i> 2005
	Wastewater irrigation	11.80	46.53	-	-	-	-	8.85	-	-	Sinha <i>et al.</i> 2005
<i>Solanum tuberosum</i> (Potato)	Atmospheric deposition	0.83	7.16	0.02	0.01	-	-	-	-	-	Radwan and Salama 2006
	Urban and industrial activities	0.88	4.50	0.84	2.81	10.74	-	5.67	-	-	Mohamed <i>et al.</i> 2003

tendency and retention capacity (Carlton-Smith and Davis 1983).

The study conducted by Sharma *et al.* (2006) in suburban areas of Varanasi, India, where the use of treated and untreated wastewater is one of the most common agronomic practices, showed that the concentration of heavy metals (mg kg⁻¹) in the edible portion of vegetables including *Spinacia oleracea* (palak), lady's finger, *Solanum melongena* (brinjal), amaranthus, *Lycopersicon esculentum* (tomato) and cabbage collected in late autumn ranged between 0.55 and 10.30 for Cu, 29.35 and 469.45 for Zn, 1.55 and 6.90 for Cd, 9.00 and 28.0 for Pb, 4.05 and 15.0 for Ni, and 2.75 and 51.15 for Cr. Palak accumulated more Cu, Cr, Pb, Ni and Cd than amaranthus and cabbage. Among different metals Cu and Cr concentrations were found to be higher in leafy vegetables (palak, amaranthus and cabbage) than in non-leafy vegetables (brinjal, lady's finger and tomato). In the edible portion of palak, the concentrations of heavy metals (mg kg⁻¹) varied from 10.95 to 28.58 for Cu, 2.22 to 41.51 for Zn, 0.5 to 4.36 for Cd, 3.09 to 15.74 for Pb, 1.81 to 7.57

for Ni and 5.37 to 27.83 for Cr. The study showed that Zn, Cr and Mn concentration in plants are influenced by seasonal variations. At the Dinapur site of Varanasi the concentration of Cd (4.2 mg kg⁻¹), Zn (29 mg kg⁻¹) Cr (18 mg kg⁻¹) and Mn (125 mg kg⁻¹) were found to be higher during summer and Cu (16.5 mg kg⁻¹), Pb (16.0 mg kg⁻¹), and Ni (7.5 mg kg⁻¹) during winter (Sharma *et al.* 2007). Due to high decomposition rate of organic matter during the summer season there is more release of heavy metals in soil solution for uptake by plants (McGrath *et al.* 1994).

Vegetable samples were collected from two different agricultural lands of Greece irrigated by municipal, domestic and some industrial discharges (Stalikas *et al.* 1997). Among all the metals (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V and Zn), higher concentrations of Cd, Cu, and Pb (0.043, 2.45, and 0.134 mg kg⁻¹, respectively) were found in spinach plants than in other leafy and non-leafy vegetables. Intawongse and Dean (2006) analyzed heavy metal concentrations in lettuce, spinach, *Raphanus sativus* (radish) and *Daucus carota* (carrot) grown in compost-containing soil

through batch culture. In the soil heavy metals like Cd ($10 \mu\text{g g}^{-1}$), Cu ($150 \mu\text{g g}^{-1}$), Mn ($300 \mu\text{g g}^{-1}$), Pb ($10 \mu\text{g g}^{-1}$), Zn ($100 \mu\text{g g}^{-1}$) were added in two doses, high (50 times than control) and low (10 times than control). The study showed that the accumulation of Cd, Zn, Mn was higher in the leafy portion than in the root portion of the plants. The concentrations of heavy metals (mg kg^{-1}) ranged, respectively for Cu, Pb and Zn from 12.8 to 274.9, 1.2 to 4.9 and 73.9 to 2611, respectively in lettuce and from 25.8 to 182.4, 0.9 to 16.3 and 137.4 to 1351, respectively in spinach (Intawongse and Dean 2006).

Liu *et al.* (2006) analyzed the concentrations of metals in 23 vegetable species from agricultural soil of four sampling sites located in the suburb of Zhengzhou city, Henan Province, China. Maximum concentration of Cd (0.20 mg kg^{-1}) was recorded in radish leaves and in *Brassica campestris* L. spp. Pekinensis (Lour) Olsson (Chinese cabbage) (0.2 mg kg^{-1}) followed by radish leaves (0.18 mg kg^{-1}). The concentration of Pb exceeded the tolerance limit of China by approximately 38 and 25 times in *Vigna unguiculata* w. ssp. *sesquipedalis* (L.) verd. (asparagus bean) and tomato, respectively. Among different vegetables, 87% of the vegetable species exceeded the tolerance limit of the Food Sanitary Regulation of China for Cu and Cd, 96% for Pb, 65% for As and Cr and about 100% for Hg. Mohamed *et al.* (2003) collected 15 different species of vegetables including cucumber, *Cucurbita pepo* (vegetable marrow), tomato, *Solanum tuberosum* (potato), green pepper, *Solanum melongena* (eggplant), carrot, *Petroselinum crispum* (parsley), lettuce, spinach, *Allium cepa* (onion), *Allium porrum* (leek), *Nasturtium officinale* (watercress) and cabbage from Al-Taif district of Saudi Arabia. Results showed that concentrations (ppm) of Cd (1.22), Ni (42.62) and Zn (105.2) were highest in the watercress and of Cu and Pb were highest in vegetable marrow (5.71 ppm) respectively. Among different vegetables watercress showed higher element concentrations than other vegetables. The variations in concentrations of heavy metals between test vegetables were ascribed to the differences in the metal selectivity and their accumulation tendency in vegetables from soil solution (Mohamed *et al.* 2003).

Demirezen and Aksoy (2006) found that the levels of heavy metals such as Cd, Pb, Cu and Ni in vegetables like cucumber, tomato, green pepper, lettuce, parsley, onion, *Phaseolus esculentus* (bean), eggplant, *Mentha piperita* (peppermint), *Cucurbita pepo* (pumpkin) and *Abelmoschus esculentus* (okra) obtained from urban areas affected from municipal, domestic, traffic and some industrial discharges were higher than those of the rural areas affected by traffic and industrial activities except Zn having higher concentration in rural areas of Turkey. Concentrations of heavy metals (mg kg^{-1}) in vegetables like cucumber, tomato, green pepper, lettuce, parsley, onion, bean, eggplant, peppermint, pumpkin and okra collected from urban areas of Kayseri, Turkey ranged from 0.34 to 0.97 for Cd, 5.3 to 10.7 for Pb, 32.6 to 76.5 for Cu, 1.8 to 13.45 for Ni and 3.56 to 39.5 for Zn, whereas in rural areas the concentrations ranged from 0.24 to 0.63 for Cd, 3.00 to 8.00 for Pb, 22.19 to 60.40 for Cu, 0.44 to 4.10 for Ni and 47.13 to 259.20 for Zn (Demirezen and Aksoy 2006). The results showed that peppermint had the ability to accumulate more concentration of Cd, Cu, Pb, and Ni than other vegetables. Enhanced levels of heavy metals observed in vegetables showed a direct correlation with the concentrations of metals in the soil (Demirezen and Aksoy 2006).

Atmospheric deposition also contributes to elevating the levels of heavy metals in vegetables. The deposition of heavy metals on a vegetable's surface depends upon several factors. These factors are the levels of air pollutant, especially dust in the air, the nature of the roads, traffic loads and the period of exposure or duration to which the vegetables are exposed to urban atmosphere at the time of marketing (Agrawal 2003; Dogheim *et al.* 2004; Radwan and Salama 2006). Many studies have shown that washing can reduce the levels of heavy metal contamination in vegetables signi-

ficantly (Agrawal 2004; Jassir *et al.* 2005; Singh and Kumar 2006; Nabulo *et al.* 2006). In a study done by Jassir *et al.* (2005) the vegetable samples were randomly divided into two fractions. The first fraction was soaked in tap water for 15 minutes to remove the soil impurities, and then washed twice. The second fraction was subjected to digestion without washing and hence labeled as unwashed samples then analyzed the heavy metal concentrations in the edible portions of commonly consumed green leafy vegetables *Coriandrum sativum* (coriander), watercress, parsley, *Portulaca oleracea* (purslane) and lettuce collected from different selling points at Riyadh city in Saudi Arabia before and after washing with tap water. Collectively in all the leafy vegetables the reductions due to washing of the samples were about 41% for Pb, 26% for Cd, 42% for Cu and 24% for Zn. The order of levels for Pb concentration in washed samples from highest to lowest was coriander > lettuce > purslane > watercress > parsley > garden rocket. The concentrations of Cu (20.18 mg kg^{-1}) and Zn (41.93 mg kg^{-1}) were highest in purslane and Cd (0.384 mg kg^{-1}) in garden rocket. Cd accumulation was more in leafy vegetables than in other vegetables.

A market-based study was conducted by Radwan and Salama (2006) to assess the atmospheric deposition of heavy metals in fruits and vegetables sold in Egyptian markets. The average concentrations of metals ranged from 0.01 to 0.87, 0.01 to 0.15, 0.83 to 18.3 and 1.36 to 20.9 mg kg^{-1} for Pb, Cd, Cu and Zn, respectively. The higher range of Pb and Cd concentrations were higher than the permissible limits of heavy metals in food given by FAO/WHO (Table 3). Among all the fruits and vegetables, leafy vegetables, lettuce and spinach accumulated highest concentrations of Pb and Cd. Dogheim *et al.* (2004) assessed the heavy metal concentrations in leafy vegetables and some aromatic medicinal plants from local markets of Egypt. Leafy vegetables were found to be contaminated by heavy metals more frequently than other vegetables. Among the total samples about 97% of the leafy vegetables were contaminated with heavy metals and 39% of leafy vegetables exceeded the maximum limits established for Cd, Cu and Pb. Cu was accumulated more frequently in leafy vegetables, being recorded in 97% of the samples. A greater accumulation of heavy metals in the leaves of leafy vegetables may be ascribed to their higher biomass accumulation as compared to other parts such as stem, root and fruits. The higher uptake of heavy metals in leafy vegetables is due to higher transpiration rate of plant to maintain the growth and moisture content of plant (Tani and Barrington 2005).

Industrial effluents from electroplating industry contain heavy metals like Cd, Cr, Cu, Ni and Zn, their effect on growth, development and tissue concentrations of these heavy metals in radish and spinach were studied by Pandey (2006). Accumulations of Cr (374%), Ni (207.9%) Zn (23.5%), Cu (27.3%) and Cd (5.23%) were higher in spinach than radish after 45 days of treatment with 50% of industrial effluents (Pandey 2006). The tendency of plants to accumulate heavy metals not only depends upon the environmental contamination, but also on the plant species (Steinborn and Breen 1999). Concentrations of Cd and Pb in vegetables (*Vernonia amygdalina* (bitter leaf), *Talinum triangulare* (Ceylon spinach), *Amaranthus hybridus* (amaranth) and *Telfaria occidentalis* (fluted pumpkin)) commonly consumed by the communities of the Niger-Delta, Nigeria contaminated by oil refineries, petrochemicals, natural gas and steel processing industrial waste varied from 0.002 to 0.35 and 0.016 to 4.91 mg kg^{-1} , respectively (Eriyamremu *et al.* 2005). *A. hybridus* and *T. occidentalis* showed a higher tendency to accumulate Cd and Pb, respectively more than other vegetables. In Chinese cabbage, *B. campestris* L. spp. *chinensis* (pakchoi), *Ipomoea aquatica* (water spinach), *Luffa cylindrica* Roem (towel gourd), brinjal, *Vigna unguiculata* (cow pea) mean concentrations of Cd were 0.021 mg kg^{-1} , 0.022 mg kg^{-1} , 0.029 mg kg^{-1} , 0.008 mg kg^{-1} , 0.024 mg kg^{-1} , 0.007 mg kg^{-1} , whereas for Pb it was 0.052 mg kg^{-1} , 0.061 mg kg^{-1} , 0.097 mg kg^{-1} ,

Table 3 Guidelines on heavy metal concentrations (mg kg⁻¹) for food safety set by different countries.

Country standard	Element	Cd	Cu	Pb	Zn
Indian Standards – mg kg ⁻¹		1.5	30	2.5	50
UK – Lead in Food (Amendment) Regulations (1985/912)		-	-	1.0	-
UK - Food Standards Committee Guidelines (1950)		-	20	-	50
Committee Regulation (EC) 466/2001		0.2	-	0.3 (brassica, leafy vegetables and all cultivated fungi)	-
Codex Alimentarius Maximum Levels (2001) – mg kg ⁻¹		0.1	-	0.3 (brassica and leafy vegetables excluding spinach)	-
Australia and New Zealand – ML of metal contaminants in food – Standard 1.4.1 (2002)		0.1 (leafy vegetables, root and tuber vegetables)	-	0.1 (vegetables excluding brassica)	-
Permissible limit set by Ministry of Public Health, Thailand (MPHT, 1986)		-	133	6.67	667
International Council for the Exploration of the Sea (ICES, 1988) for status		1.80	-	3.00	-
Food and Drug Administration of the United States (USFDA, 1990)		25	-	11.5	-
China standards 1995		0.30	100	-	250
FAO/WHO, 2001		0.2	30	0.3	60

0.028 mg kg⁻¹, 0.029 mg kg⁻¹, 0.052 mg kg⁻¹, respectively. Result showed that accumulation of Cd and Pb was higher in leafy vegetables (chinese cabbage, pakchoi, water spinach) as compared to the non leafy vegetables (towel gourd, brinjal, cow pea) (Wang *et al.* 2006).

Kachenko and Singh (2006) recorded the highest accumulation of Cd in mint (2.22 mg kg⁻¹) followed by spinach (0.743 mg kg⁻¹), lettuce (0.424 mg kg⁻¹), leek (0.200 mg kg⁻¹) and then cabbage (0.062 mg kg⁻¹) collected from urban and metal smelter contaminated sites (Boolaroo, Port Kembla, Cowra and Sydney Basin) across New South Wales, Australia. Cd concentration for mint, spinach and lettuce was higher than the limits given by Codex alimentarius commission (**Table 3**). The high accumulation of Cd in vegetables at Boolaroo was attributed to more availability of Cd due to the acidic nature of the soil. More adsorption of aerial deposits of Cd by leafy vegetables was also observed at Boolaroo. Temmerman and Hoenig (2004) successfully used leafy vegetables such as spinach, lettuce, *Chichorium endivia* (endive) and *Valerianell locusta* (lamb's lettuce) as bioaccumulators of Cd and Pb in the garden around a nonferrous metal smelter area during 1998-2002 by growing vegetables in containers filled with peat soil and supplied with a semi-automatic watering system. Spinach showed a maximum concentration of Cd (0.022 mg kg⁻¹), whereas Pb was maximum (0.020 mg kg⁻¹) in lamb lettuce among all the vegetables grown under ambient conditions.

Concentrations of Cd, Ni and Zn in the edible portion of palak plants grown at 20 and 40% sewage sludge amended soil were above the permissible limits of Indian standards (Singh and Agrawal 2007). Tandi *et al.* (2004) also compared the uptake capability of Zn and Cu in lettuce and *Brassica juncea* (mustard rape) by performing an experiment at Pension farm, near Harare, Zimbabwe having a long term application of sewage sludge and effluents. Lettuces showed 7 and 3 times whereas mustard rape showed 14 and 2 times higher concentrations of Zn and Cu, respectively compared to the control. Fytianos *et al.* (2001) analyzed the heavy metal (Pb, Ni, Cd, Cu, Mn and Zn) concentrations in vegetables collected from an industrial area in the northeast part of Northern Greece. The value for the concentration factor (ratio of heavy metal concentration in plants to heavy metal concentration in soil) of Cd was more than the unit for leafy vegetables (1.67 and 1.75, respectively for spinach and lettuce). High concentrations of Cd in leafy vegetables were reported when the concentration of Zn increased in soil (Smilde *et al.* 1992). On the other hand,

McKenna *et al.* (1993) observed a strong antagonistic effect of Zn on the accumulation of Cd in leafy vegetables at a low concentration of Cd in the soil. Leafy vegetables can be used as accumulator plants, but the selection of plants should be done after getting information on the distribution and translocation of heavy metals in the plant system from the contaminated area (Barman *et al.* 2000).

Active monitoring using accumulator plants is suggested to be an alternative to study the impact of heavy metals on plants, when the local soil borne proportion of the heavy metals is expected to be important (Temmerman and Hoenig 2004). Singh and Agrawal (2007) showed that a higher uptake of Cd, Ni, Cu, Cr, Pb and Zn in palak plants grown on sewage sludge amended soil more than those grown on unamended soil. As leafy vegetables generally have a higher tendency for uptake and accumulation of heavy metals, these can be conveniently used for the removal of toxic heavy metals from polluted agricultural field. In order to survive in contaminated area plants develop some resistant mechanism. Resistance of plants against heavy metal ions can be achieved by mobilization of metal in root and cell walls (Prasad 2004). Due to accumulation of heavy metals and to survive safely these vegetables have developed a detoxification mechanism consisting mostly of chelation and sequestration of toxic metals by small metal binding peptides and proteins. Metallothioneins (MTS) or phytochelatin (PCS) are proteins found in plants which are capable of binding metal ions (Robinson *et al.* 1993; Prasad 2004). These proteins contain high percentage of cysteine sulphhydryl groups which bind and convert heavy metals in to very stable complexes. Cloning and characterization of MT-genes families in plants has already been done in last few years (Prasad 2006). Kramer (2000) showed that hyperaccumulator species *Thlaspi caerulescens* and nonaccumulator species *T. arvense* differ in their transcriptional regulation of ZNT 1 (Zn-Plant increases synthesis of heavy metal transporter 1) controlling the uptake of Cd⁺² and Zn⁺². Infect little is known about the molecular basis of heavy metal detoxification and hyperaccumulation in plants. Polypeptides (PCs) are a very good example in plant stress biology showing an adaptive stress response. Its induction and accumulation takes place in a range in plants (Shaw *et al.* 2006). Effective transportation of metals to cell vacuoles for storage is another aspect of PC-mediated tolerance of plants to heavy metals. Vogeli-Lange and Wanger (1990) showed that vacuoles of isolated mesophyll protoplast from tobacco contained 110 ± 8% of protoplast Cd and 104 ± 8% protoplast PCs, suggesting the synthesis of PCs in cytosol and

then transfer of heavy metal (Cd) and PCs (as complex) in to vacuoles. In case of *Arabidopsis* sp. Grotz *et al.* (1998) isolated three ZIP genes encoding putative Zn transporters. By increasing the expression of these ion transporters, the heavy metal uptake can be enhanced. Various ligands for heavy metals (Cd, Cu, Ni and Zn) are produced by plants like carboxylic acid and amino acid such as citric, malic and histidine, they play a role in tolerance and detoxification by scavenging heavy metals (Hall 2002). Citric and oxalic acid are organic acids that function as chelators of heavy metals inside the cell and converting the metals into nontoxic forms by forming metal-organic acid complexes. These complexes may remain in the cytoplasm or in the vacuole. Tolerance of heavy metals is also linked with the ability of plants to fight against reactive oxygen species produced due to heavy metal stress. Shaw and Rout (1998) found enhanced synthesis of ascorbate peroxidase in response of Hg, protecting the plant against oxidative stress produced by metal. Ascorbate peroxidase induced more in *Alssum maritimum* (Ni-sensitive plant) than in *A. argentums* (metal tolerant, hyperaccumulator) (Schicker and Caspi 1999). Superoxide dismutase (SOD) is also found in plants exposed to various heavy metals and play important role in heavy metal tolerance (Cakmak and Horst 1991; Przymusinski *et al.* 1995). The mechanism of detoxification adapted by plants varies from metal to metal, from species to species and it is difficult to predict the reason of tolerance by of any single mechanism (Shaw *et al.* 2006). Although consumption of such contaminated vegetables may pose a health risk to human beings. Lokeshwari and Chandrappa (2006) observed translocation factor (TF) that is obtained by dividing the plant metal content originating from soil and total metal content in the soil (Chamberlain 1983). The highest values were found for Cd (2.5) and Zn (1.1). These heavy metals are more mobile in nature so more accumulation takes place in plants. Spinach showed a high accumulation of Fe, Ni and Cd due to an increase in contamination at a South African bituminous coal mine dump soil (Chunilall *et al.* 2006). Metal bioavailability varied widely between heavy metals and the type of plant. Bioavailability of heavy metals was calculated as 63.7% for Mn, 45.2% for Zn in lettuce and 62.5% for Cu, 54.9% for Cd and 45.8% for Mn in radish (Intawongse and Dean 2006).

TOXICITY OF HEAVY METALS IN VEGETABLES

Heavy metals available to plants are present in air, water as well as in soil and sediments. Plants are able to take up heavy metals from all of these media, depending on their concentrations. Heavy metals are first absorbed by the apoplast of roots and transported further into other parts of the cells. Heavy metals are translocated to different plant parts through various pathways and result into reductions in growth by altering the physiological, biochemical and metabolic activities of the plants. Cadmium toxicity induced changes in plant water relations and oxidative metabolism of *Brassica juncea* L. grown in soil pot culture in a glasshouse. At 500 ppm concentration of Cd treatment significant reduction was observed for plant height, and fresh and dry matter (Singh and Tiwari 2003). The concentration of chlorophyll decreased significantly due to involvement of Cd in inhibition of heme biosynthesis a chlorophyll formation by interacting with the functional -SH group of sulphhydryl requiring enzyme (Stobart *et al.* 1985). Accumulation of heavy metals in excessive concentrations was found to be toxic for the plants. Effects of industrial waste water irrigation on growth of *P. radiatus* and *R. sativus* were studied (Dengyi and Youbao 2003). Reductions in above and below ground dry weight, and length of shoots respectively were 41.79 and 24.76%, and 24% in *P. radiatus* and 62.50 and 64.70%, and 19% in *R. sativus* as compared to their respective controls. Cd proved to be more toxic than Cr, Cu, Ni, Pb and Zn, as the lowest dose (100 mg kg⁻¹ substrate significantly suppressed dry weight of several sensitive crops including spinach and lettuce (Smilde 1981).

Singh and Agrawal (2007) showed that increases in heavy metal concentrations in foliage of palak grown at 20 and 40% sewage sludge amended soil led to adverse effects on physiological, biochemical and morphological characteristics. Root and shoot length decreased significantly in palak grown at 40% sewage sludge amendment. Leaf area also decreased by about 32.5% at 40% sewage sludge amendment. Photosynthetic rate reduced by 23.6 and 28.8% in palak at 20 and 40% sewage sludge amendment, respectively. As compared to the unamended soil, foliar thiol content decreased by 41.6% and 53.8% at 20 and 40% sewage sludge amendment, respectively. Lipid peroxidation increased significantly in palak at both the sewage sludge amendment ratios. Heavy metals Cd, Ni and Pb induced the formation of free radicals and reactive oxygen species, which enhanced the lipid peroxidation due to disorganization of membrane structure of cells. The chlorophyll content, fluorescence ratio (Fv/Fm) and protein content also decreased, but peroxidase activity increased with increasing uptake of heavy metals at increasing amendment ratio of sewage sludge. Heavy metals have been shown to replace lipids from plasma and chloroplast membranes of *Pisum sativum* (Hernandez and Cooke 1997) and *Lycopersicon esculentum* (Mazhoudi *et al.* 1997).

Reductions in photosynthetic activity may result both from the disturbance of photochemical and biochemical photosynthetic reductions and damage of ultrastructure of chloroplast. Sinha *et al.* (2006) have studied the effects of tannery sludge contaminated soil on lipid peroxidation, morpho-anatomical changes and antioxidant levels of *S. oleracea*. Garden soil was amended with different amendment (10%, 20%, 35%, 50% and 100%) of tannery sludge. Tannery sludge contaminated soil showed significant increments in shoot length and leaf area at all the exposure periods compared to garden soil. Increments of 79.71, 165.4 and 232.70% in shoot length, leaf area and numbers of leaves, respectively were observed in plants grown on 35% tannery sludge after 90 days of growth as compared to the plants grown in the garden soil. Root length decreased significantly in plants grown at 50 and 100% tannery sludge at 75 and 90 days of exposure, respectively. SEM studies made on epidermal features showed an increase of 29.31% in the stomatal length of *S. oleracea*. The significant increase in stomatal length was observed on 25% tannery sludge amended soil, whereas at 50% and 100% it had decreased. After 60 days of treatment of tannery sludge, cytosine, non-protein thiol, ascorbic acid and protein contents in the leaves increased by 233.31, 336.80, 71.48 and 396.16%, respectively in the plants grown at 100% of tannery sludge (Sinha *et al.* 2006). Increments in foliar ascorbic acid and protein contents of *S. oleracea* at an initial phase of treatment were suggested to be a defense strategy to combat heavy metal stress in the plants grown on tannery waste contaminated soil (Singh *et al.* 2004; Singh and Sinha 2005). Studies conducted under greenhouse and natural field conditions have shown that heavy metal stress influenced the antioxidant capacities in plants such as *Brassica juncea* (Singh and Tewari 2003) and *Beta vulgaris* (Singh and Agrawal 2007). In the case of *B. juncea* different treatment (100 ppm, 250 ppm, 500 ppm) of Cd concentration showed deleterious effects on oxidative metabolism by enhancing generation of reactive oxygen species and that can be reduced by scavenging these radicals through the activity of antioxidants like catalase and peroxidase (Gratao *et al.* 2005). There was about 19%, 18%, and 27% increase in catalase activity and 163%, 200%, and 248% increase in peroxidase activity at 100, 250 and 500 ppm concentration of Cd treatment, respectively compared to the control (Singh and Tewari 2003). In *S. oleracea* also antioxidants like peroxidase activity and proline concentration increased in plants grown in sewage sludge-amended soils (Singh and Agrawal 2007).

EFFECTS OF SOIL AND PLANT FACTORS ON ACCUMULATION OF HEAVY METALS

Plants are used for monitoring heavy metal contamination in the terrestrial environment and it depends upon the cognizance of the complicated and integrated effects of different sources of pollutants and interaction between soil and plant variables. Soil has a tendency to accumulate heavy metals, but the concentrations do not reach high levels due to continuous removal of heavy metals by plants (Sharma *et al.* 2007). The availability of heavy metals to plants from soil is governed by the solubility and the thermodynamic activity of the uncomplexed ions (Jenne and Luoma 1977). Soluble species of heavy metals remained longer in soil solution. Solubility of heavy metals strongly influences the longevity in soil, uptake by plants, mobility in plant parts and cells and also toxicity to the plants (Tiffin 1977). The solubilization rates of heavy metals are governed by the physico-chemical properties of the deposited material, soil processes and properties of soil. The most important soil physico-chemical parameters influencing the solubility of heavy metals are Eh (Redox potential), pH (Hydrogen potential), density, any type of changes on soil colloids and surface area available for the reaction (Keeney and Wildung 1972). The geographical parameters like topography, type of parent materials, climate, and biological processes are responsible for controlling the soil characteristics of any region. For monitoring of heavy metals contamination using plants, it is necessary to evaluate the type of soil, characteristics and geographical locations because availability of heavy metals depends upon these characteristics (Barshad 1964).

Plant factors also influence the uptake of heavy metals. The processes in plants such as root intrusion, water and ion fluxes, kinetics of membrane transport, ion interactions, metabolic fate of absorbed ions and ultimate ability of plants to adapt them against the environmental stress are important in governing the plant response under heavy metal stress conditions. Complexation of ions is the physiological mechanism responsible for the mobility of ions in the plants (Tiffin 1977). Leaves of plants have capacity to retain the heavy metals. The retention degree is influenced by weather conditions, pollutant properties, plant surface characteristics, plant and leaf morphology and particle size (Harrison and Chirgawi 1989).

Uptake mechanisms of individual ions are quite specific and there are competitions among the heavy metals for the absorption. Cd, Ti and Ni showed competitive interactions with nutrients like Zn⁺², Cu⁺², Fe⁺², Mn⁺² and Co⁺² (Cataldo and Wildung 1978). There are specific interactions in the absorption of nutrient (Mo, Mn, Cu and Zn) and non-nutrient anions (Pb, Ni, Cd, Ti, As and Sn). Thus the use of municipal sludge in agricultural soils led to higher concentrations of heavy metals in plants with a passivity of reduction in the uptake of required nutrients due to competition for the absorption between the heavy metals and nutrients (Greger and Lindberg 1987). Sharma and Agrawal (2006) evaluated the effects of different concentrations of Cd and Zn, singly and in combination, on the uptake and accumulation of these metals in *Daucus carota*. The results showed that uptake and total accumulation rate of Cd and Zn were concentration dependent phenomena. Zn interacts synergistically with Cd at low Zn+Cd application rates and antagonistically at higher concentration of Zn+Cd.

HEALTH HAZARDS FROM HEAVY METAL EXPOSURE

Food, water and air are the main sources through which human beings are constantly exposed to heavy metals. Investigations on possible health and environmental hazards due to heavy metal intake in the body have led many countries to restrict the use of chemicals containing heavy metals and enforce tolerance levels for residues in food and feed (Table 3). Heavy metal intake through the food chain by

human populations has been widely reported throughout the world. The exposure of human beings to heavy metals increased with an increase in the use of heavy metals in industrial processes and the consumption of the products that has been contaminated by the toxic heavy metals directly or indirectly. Due to the non-biodegradable and persistent nature, these toxic heavy metals are accumulated in the tissues of human beings such as the kidney, bone and liver and result in various problems to human health. The chemical nature of heavy metals, age and nutritional status of human beings are responsible for the amount of heavy metals absorbed by the digestive tract. The degree of toxicity depends upon the rate of daily intake of the toxic heavy metals. Dietary intake of heavy metals and their accumulation in the human body have resulted in various health problems like retardation in the development of the body, a decrease in blood pH, cancers of many organs, and sometimes even death (Varathon 1997).

Tripathi *et al.* (1997) showed that leafy vegetables contributed higher concentrations of Pb and Cd to daily intake by the population living in suburbs of Bombay city in India having a higher load of particulate matter in the air. A study was conducted near Harare, Zimbabwe to determine the effect of long term (>30 years) application of sewage sludge and effluents on Zn and Cu contamination of lettuce and mustard rape and their toxicological implication for poor urban households (Tandi *et al.* 2004). Maximum daily intake of Cu and Zn, respectively were calculated as 1.0 and 23.8 mg person⁻¹ day⁻¹ through lettuce and 0.6 and 49 mg person⁻¹ day⁻¹ through mustard rape. Cu constituted only 40% of the maximum daily intake through the consumption of both leafy vegetables. The toxicity of Zn was more severe exceeding the maximum daily intake by 77% through lettuce consumption and by 251% through mustard rape consumption. The study concluded that there was a risk of Zn toxicity to poor communities that reside around the study sites due to consumption of leafy vegetables. Muchuweti *et al.* (2006) also reported that the health of urban populations consuming vegetables cultivated on agricultural fields irrigated with sewage water is under risk due to contamination by heavy metals. Intawongse and Dean (2006) assessed the bioavailability of metals (Cd, Cu, Zn, Mn) in the human gastrointestinal tract by extracting the edible part of plants using an *in vitro* gastrointestinal (GI) extraction technique. This technique measures the fraction of solubilized metal from a contaminated sample under simulated gastrointestinal conditions available for absorption. Results showed that bioavailability of heavy metals depended upon their solubility rate. For the gastric (acidic) extraction phase, the greatest extent of metal-releasing capacity has been observed in lettuce (for Mn, 63.7% and Zn, 45.2%), and radish (for Cd, 54.9% for Mn, 45.8% for Cu, 62.5%). The minimum concentrations of metals were found in the intestinal extraction having neutral pH.

Pb is a very toxic heavy metal because of its global distribution, accumulation tendency in the body and toxicity even at very low concentration. It causes convulsions, coma, renal failure and even death when the metabolic function of the body is disturbed (ATSDR 2000). If diets are deficient in Ca, Fe and Zn, individuals absorb more Pb from their food (Mahaffey 1990). The magnitude of heavy metal contamination in soil and vegetable samples at 46 sites across four vegetable-growing regions in South Wales, Australia was studied to identify the risk to human health due to Cd, Pb, Zn and Cu (Kachenko and Singh 2006). All the samples collected in the vicinity of the smelter at Boolaroo exceeded the Australian food standard maximum level (0.01 mg kg⁻¹ fresh wt.) of Cd and Pb. International food standard guidelines set by the commission of the European communities and the Codex Alimentarius commission was exceeded by 63% of samples collected from different vegetable growing regions. The study highlighted that cultivation of leafy vegetables should be avoided near smelters due to their high potential of heavy metal accumulation.

Eriyamremu *et al.* (2005) evaluated the Pb and Cd

levels in consumed vegetables in the Niger Delta Oil area of Nigeria, which were slightly higher than the limits of heavy metals in the United Kingdom and resulted in a health risk to people who were dependent on these contaminated vegetables for their daily meals. To quantify the health risk values, a target hazard quotient (THQ) was calculated. This quotient has been developed by the United States Environmental Protection Agency to provide an indication of the risk due to pollutant exposure for both carcinogens and non-carcinogens. It depends upon exposure frequency (the number of days the food is consumed per year), exposure duration (the life expectancy of the person), the quantity of food consumed per day, the concentration of metals in the food with respect to reference dose), average weight of body and an exposure time for non-carcinogens. If $THQ > 1.0$, then it indicates a potential concern for health. The values of THQ (calculated by using the average monthly values of heavy metal concentrations taken via food and the relative amount of food consumed) ranged between 1.4 to 3.8 for the wet season and 2.6 to 4.2 for the dry season. The variations in these values indicated a risk to human health (Holden and Malamud 2006). Cadmium damages the proximal tubules of each nephron of the kidney causing the leakage of low molecular weight proteins and essential ions like Ca into urine, which ultimately leads to kidney failure (Satarug *et al.* 2000).

It has been shown that even the concentrations of heavy metals in soil were within the safety limit but the vegetable crops grown on this soil contained higher concentrations of heavy metals even higher than the safety limits prescribed for the human consumption (Pasquini 2006; Sharma *et al.* 2006, 2007). As toxicity is dependent upon its chemical nature, inorganic arsenic and trivalent arsenite are found to be more toxic. Even a lower concentration of As results in hyper-pigmentation, peripheral nerve damage, weakness in the hands and feet, blood vessel damage resulting into gangrenous condition affecting the extremities (Col *et al.* 1999). Cd is also one of the non-essentials and mobile toxic heavy metals which can be easily translocated to plants through the root system and contaminate food crops grown in heavy metal contaminated areas. Tripathi *et al.* (1997) reported higher concentrations of Cd in leafy vegetables (amaranth) than in other vegetables. Long term exposure to Cd resulted in severe respiratory irritation, lung disease, testicular degradation and prostrate cancer (Ye *et al.* 2000). Contaminated sites with heavy metals are suggested to be used for growing ornamental and timber plants rather than growing vegetables to minimize transfer of heavy metals to human beings through various food chains.

A risk assessment of Cd, Cu, Ni and Zn exposure to population subgroups living on and growing foods on contaminated urban sites was conducted using a model to a geochemical data base of urban conurbation in the west midlands in the UK, a premier industrial region since the 19th century (Hough *et al.* 2004). Values of the Hazard index (HI) were mapped for three population subgroups: average persons, highly exposed persons, and highly exposed infants (assumed to be a 2 year-old child) thus showing where the greatest potential for risk was located. The result showed that food grown on 92% of the urban area has minimal risk to the average person subgroup, however, for the highly exposed person population subgroups, 44% of the urban area provided a hazard index (HI) between 1 and 2. For the highly exposed infant's population subgroups 52% of the urban area provides an HI of between 2 and 3. The largest contribution was found by Pb (above 40% of HI) and Cd (about 30% of HI). Ni and Cu contributed 10 and 14%, respectively to HI. Most HI was attributable to dietary exposure. The contribution from dust inhalation exposure was 8% of the hazard index in highly exposed persons. The HI value of more than 1.0 showed potential risk of heavy metal exposure from consumption of contaminated vegetable (Hough *et al.* 2004).

CONCLUSION

Heavy metals are one of the major globally distributed toxic pollutants and their removal from contaminated areas are urgently required to reduce their impacts on various food chains and to maintain the concentrations of heavy metals within safe limits. Vegetables are one of the main components of common food habit because they provide essential micro and macronutrients, proteins, antioxidants and vitamins to the human body. All vegetables are often grown in suburban areas experiencing high concentrations of heavy metals both through aerial deposition and contamination through soil and irrigation water. Leafy vegetables are good accumulators of toxic heavy metals due to their higher capacity of absorption both from contaminated soil and aerial deposits. The advantage of high biomass production and easy disposal also makes vegetables useful to remediate heavy metals from a contaminated environment, but the excessive intake and consequent accumulation in human beings through long-term consumption of contaminated food may result in negative effects on human health. They have more potential to accumulate heavy metals from a contaminated environment. Remediation and safe consumption of vegetables are two opposite concerns of heavy metal impact on the environment. Stringent enforcement of standards should be followed for maximum allowable intake of heavy metals to avoid risk to human health. Heavy metals not only contaminate food but also reduce the nutritional value of vegetables. In case of use of vegetables for remediation of heavy metals from contaminated sites, consumption by animals and human beings should be avoided.

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