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Air-Borne Heavy Metal Contamination to Dietary Vegetables: A Case Study from India

J. Pandey · Richa Pandey · K. Shubhashish

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Abstract Contamination of edible parts of three dietary vegetables, Spinach (*Spinacia oleracea* L.), Radish (*Raphanus sativus* L.), and Tomato (*Lycopersicon esculentum* Mill.) by air-borne cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb) was determined using pot culture experiments at three sites in the city of Varanasi, India. The data revealed that although Cr and Cu in vegetables remained below their safe limits, about 68% of the total samples contained Cd, Ni, and Pb above their respective safe limits of 1.5, 1.5, and 2.5 μg g^{-1}. Site wise synchrony and air accumulation factor (AAF) indicated that atmospheric deposition was the main contributor of metal contamination to vegetables. The study suggests that if the present trends of atmospheric deposition are continued, air-borne heavy metals will contaminate the agricultural produce with long-term health implications.

Keywords Atmospheric deposition · Heavy metal · Sustainable agriculture · Vegetables

Continuously increasing demand for food by burgeoning human population and food chain associated health hazards due to environmental release of toxic chemicals have become the subject of global concern. Heavy metal contamination of vegetables through soil, water, and air-borne sources may pose a serious threat to human health in long-run. Except for occupational exposures, dietary intake through contaminated food has become the main route of human intake of heavy metals (Sharma et al. 2007; Pandey and Pandey 2009). In addition to serious health hazards including carcinogenesis-induced tumor promotion, heavy metal affects soil microbial interaction, and reduces soil fertility leading agroecosystems to remain unsustainable in long-run. For this reason, protection of soil fertility along with the quality of agricultural produce has become the major concern for sustainable agriculture (Moolennaar et al. 1997).

Accumulation of heavy metals in vegetables has been well linked with soil heavy metal and irrigation water from long back. Atmospheric deposition has now been identified as the principal source of heavy metals entering into plants and soil especially around urban-industrial areas. The metal aerosols deposited onto the soil can be absorbed through root or deposited on leaves and fruits and absorbed directly. Leafy vegetables have been reported to accumulate sizable amount of air-borne Pb, Cr, and Cd (Voutsa et al. 1996; Pandey and Pandey 2009). A number of investigators have shown significant relationships between atmospheric depositions and elevated element levels in crops and soils (Sanchez-Camazano et al. 1994; Demirezen and Aksoy 2006). Thus, despite all efforts to raise safe and hazard-free agricultural produce, addition of atmospherically driven toxic metals will continue to contaminate agroecosystems even to those situated far away from the sources of emission. At a time, when food production and the quality of agricultural produce have become a major concern globally, a better understanding of heavy metal dynamics in air–soil–edible produce continuum seems to have particular significance.

In situ experiment is one of the important methods for such studies, however, because of the heterogeneity of the plant materials growing together and variation in irrigation water use, it may be difficult to determine unequivocally which source is the major determinant of heavy metal

J. Pandey (✉) · R. Pandey · K. Shubhashish
Centre of Advanced Study in Botany, Banaras Hindu University, Varanasi 221005, India
e-mail: jiten_pandey@rediffmail.com

accumulation in plant parts. Transplant studies, in which plants from common sources are grown in pots, enabling some control over the root environment, and to some extent the biotic interference, provides a better basis for quantifying accumulation and validity of comparison between sites (Pandey and Agrawal 1994). The present study was an effort to investigate atmospheric deposition of heavy metals and their accumulation in edible parts of three vegetable crops common to Indian tropics. Attempts were made to elucidate relative contribution from atmospheric deposition and soil-borne heavy metals to vegetable contamination.

Materials and Methods

The study area (25°18′ N lat and 83°1′ E long; 76.19 m above msl) is characterized by tropical monsoonal climate with three distinct seasons, summer (March–June), rainy (July–October), and winter (November–February). The summer temperature some times exceeds 44°C. The rainy months normally remains warm with humidity reaching close to saturation. Wind direction shifts predominantly westerly and south-westerly in October to April and easterly and north-westerly in remaining months. For the purpose of the present study, the city was divided into three zones with three sub-stations in each zone. Zone I which includes Banaras Hindu University campus is characterized by sub-urban institutional and residential areas with tree plantation. Zones II and III representing cantonment and Bypass areas, respectively, are characterized by major highways receiving pollutants from heavy duty vehicles, small-scale industries and railway emission.

Bulk atmospheric depositions were continuously collected using bulk samplers maintained in pairs at a height of 2 m to avoid contamination of re-suspended soil particulates and were devised to avoid bird nesting (Pandey and Pandey 2009). Immediately after collection, the samples were acidified with HNO_3 (special purity, Merck), filtered and stored in dark at ambient temperature before analysis. The effect of fortnightly exposition of deposition collectors at ambient temperature on the stability of samples was examined in preliminary studies before the beginning of these experiments. Only 0.2%–0.4% changes in the concentrations of standard solutions were observed indicating that fortnightly exposure of the collectors had no significant effect on the amount of heavy metals collected during this period. Tri-acid mixture (70% high purity HNO_3, 65% $HClO_4$, and 70% H_2SO_4; 5:1:1) was used for digestion of particulates and soil samples (Allen et al. 1986).

The plant species considered for this study, spinach (*Spinacia oleracea* L.), tomato (*Lycopersicon esculentum* Mill.), and radish (*Raphanus sativus* L.) are important vegetable crops of Indian tropics. Seeds of these vegetables were sown uniformly in earthen pots of 40 cm diameter and 30 cm height filled with well manured garden soil and placed at each site. As per the established agricultural practices, uniformly sized seedlings of tomato were transplanted in similar earthen pots exposed to atmospheric deposition from the date of sowing. To maintain constant soil moisture, pots were uniformly watered thrice a week during dry seasons with distilled water.

For the heavy metal analysis in vegetables, edible portions were separated from the finally harvested plant materials and properly washed to remove surface dust. Dead and yellow leaves of spinach and radish were discarded. Cleaned plant samples were chopped into small pieces, oven dried at 80°C, ground in a stainless steel blender and then passed through a 2 mm sieve and were kept at room temperature for further analysis. Powdered samples were digested using tri-acid mixture (Allen et al. 1986) and filtered using Whatman No. 42 filter paper. The final solution was kept for heavy metal analysis at room temperature.

Acid digested filtrates of atmospheric particulates, soil, and vegetable samples were analyzed for Cd, Cr, Cu, Ni, and Pb using an Atomic Absorption Spectrophotometer (Perkin-Elmer, model-2130, USA) fitted with a specific lamp of particular metal using appropriate drift blanks. A quality control has been performed using acidified water blanks for checking the contamination during field collection and sample treatments. The detection limits of heavy metals ($\mu g\ ml^{-1}$) were: 0.0005 (Cd); 0.002 (Cr); 0.001(Cu); 0.004 (Ni); and 0.01 (Pb). The chemicals used for analysis were Merck analytical grade. Quality control measures were taken to assess contamination and reliability of data. Blank and drift standards (Sisco Research Laboratory Pvt. Ltd., India) were run after five reading to calibrate the instrument. Analytical variances of the data obtained remained below 10% for all metals. Precision and accuracy of analysis were also ensured through replicate analysis of samples. Vegetal analysis was performed separately for leaf (spinach and radish), root (radish), and fruit (tomato). The efficiency of heavy metal accumulation through atmospheric deposition and soil were computed in terms of air accumulation factor (AAF) and concentration factor (CF), respectively (Harrison and Chirgawi 1989). Heavy metal pollution index (HPI) was calculated as per the formula given below (Usero et al. 1997):

$$\mathrm{HPI} : (\mathrm{Cf}_1 \times \mathrm{Cf}_2 \times \mathrm{Cf}_3 \cdots \mathrm{Cf}_n)^{1/n}$$

where Cf_i is the concentration for the metal *i* in the sample.

Enrichment of metal was calculated in terms of the ratio of concentration of metal in surface soil (0–10 cm) to the concentration of metal in subsurface soil (below 10 cm) (Galloway and Likens 1979)

Significant effects of site and plant species were assessed using analysis of variance (ANOVA) following appropriate transformations whenever required. Standard error of means (SEM) was computed for expressing data variability. The statistical analyses were done using SPSS Programme.

Results and Discussion

Atmospheric depositions of heavy metal (g ha^{-1} y^{-1}) at different study sites are presented in Table 1. Deposition of Cd ranged from 1.77 to 20.99 g ha^{-1} y^{-1}; Cu from 9.56 to 116.57 g ha^{-1} y^{-1}; Cr from 4.86 to 60.57 g ha^{-1} y^{-1}; Ni from 5.45 to 67.11 g ha^{-1} y^{-1}; and Pb from 20.35 to 140.00 g ha^{-1} y^{-1}. Atmospheric depositions of all the metals were found to be maximum at Bypass site and minimum at BHU site (Table 1). Peri-urban and urban areas of developing countries are continued to receive rising levels of heavy metals through atmospheric deposits. Atmospheric deposition of heavy metals recorded in this study was, in general, comparable to the values recorded in other parts of our country receiving similar air emissions (Jain et al. 2000; Singh and Agrawal 2005). Deposition of Pb appeared higher than other elements which ranked in the order Pb > Cu > Ni > Cr > Cd. Azimi et al. (2004) have also reported similar pattern at other urban sites. The depositions recorded in the present study although comparable to those measured at some urban and peri-urban locations of the world (Moseholm et al. 1992; Azimi et al. 2004), were higher than those observed in northern England (Lawlor and Tipping 2003), at Chesapeake and Delaware Bay sites (Kim et al. 2000) and at the Great Lake sites (Sweet et al. 1998). Our data revealed that the anthropogenic activities in Varanasi have elevated the levels of heavy metals in urban atmospheric deposits.

Heavy metal levels in cultivated soil varied with site and were found to be maximum at Bypass site (Table 2), where concentrations of Cd, Cr, Cu, Ni, and Pb in cultivated soil were 9.60, 51.67, 19.20, 96.24, 118.2 μg g^{-1}, respectively. Metal enrichment in soil appeared highest for Pb (2.66–99.05) and lowest for Cu (1.05–9.40) (Table 2). Variation in heavy metal concentrations in cultivated soil appeared to be the source dependent. Concentration of Pb in soil was found to be highest followed by Ni, Cr, Cu, and Cd. Soil metal levels recorded in this study appeared comparable to those recorded in soils of other areas (Sanchez-Camazano et al. 1994; Kezyztof et al. 2004; Sharma et al. 2007). Concentrations of Cu, Ni, and Pb although remained below their safe limits, about 68% of the samples contained Cd and Cr above the safe limits of Indian standards (Awasthi 2000). Increase in soil metal levels indicates the role of atmospheric deposition which could in turn, increase vegetable accumulation of toxic metal ions. It appears that the agricultural lands around highways and city agglomerations are increasingly being contaminated by heavy metal through atmospheric deposition. High frequency of metal emitting sources in and around Varanasi city coupled with prevailing wind may contaminate vast stretch of highly fertile lands of peri-urban areas with long-term effects on health and agricultural sustainability.

Vegetal heavy metal levels varied with species as well as with plant parts considered for analysis. Concentrations of heavy metals were maximum in leaves (spinach and radish) followed by fruit (tomato) and minimum in root (radish). Concentration in edible parts ranged from 0.078 to 4.80 μg g^{-1} for Cd; 0.099 to 11.08 μg g^{-1} for Cr; 0.23 to 19.58 μg g^{-1} for Cu; 0.049 to 5.06 μg g^{-1} for Ni; and 0.12 to 14.47 μg g^{-1} for Pb (Fig. 1). In spinach leaf, concentration of Cu was found maximum followed by Pb, Cr, Ni, and Cd. Similar trend was observed in radish leaf. Concentration of Cu in all the plant parts remained highest and that of Cd remained lowest (Fig. 1). With respect to site, concentrations of heavy metals in all the edible parts of vegetable were found to be maximum at Bypass followed by Cantt and minimum at BHU site.

Heavy metal determination in different dietary vegetables indicated that the concentration of Cd, Ni, and Pb frequently exceeded the safe limits of both Indian and WHO standards. Exceedence of safe limits was highest in leaves (spinach and radish), followed by fruits (tomato), and then in roots (raddish). At two of the sampling locations (Cantt and Bypass), 89% of the total leaf samples contained Cd, Ni, and Pb above their respective safe limits of Indian standards (Awasthi 2000). For these sites, heavy metal pollution index (HPI) was also found to be maximum

Table 1 Atmospheric deposition (g ha^{-1} y^{-1}) of heavy metals at different study sites

Site	Cd	Cr	Cu	Ni	Pb	HPI
BHU	1.77 ± 0.18	4.86 ± 0.54	9.56 ± 0.94	5.45 ± 0.57	20.35 ± 2.43	6.54
Cantt	20.11 ± 2.11	56.53 ± 4.41	106.40 ± 10.36	60.62 ± 5.51	107.76 ± 9.20	60.19
Bypass	20.99 ± 1.93	60.57 ± 5.58	116.57 ± 10.45	67.11 ± 6.14	140.0 ± 13.79	67.41

Values are mean (n = 9) ±1 SE

Table 2 Heavy metal concentrations (μg g^{-1}) in cultivated soil at different study sites

Site	Cd	Cr	Cu	Ni	Pb	HPI
BHU	0.8 ± 0.088 (4.08)	3.51 ± 0.29 (2.39)	2.25 ± 0.25 (1.05)	6.94 ± 0.60 (4.08)	10.15 ± 0.91 (2.66)	3.39
Cantt	7.68 ± 0.82 (6.56)	38.34 ± 2.74 (9.36)	18.36 ± 1.76 (8.10)	61.73 ± 5.44 (19.12)	94.92 ± 9.93 (37.45)	31.22
Bypass	9.6 ± 1.18 (13.52)	51.67 ± 3.44 (9.95)	19.20 ± 1.96 (9.40)	96.24 ± 8.56 (29.28)	118.2 ± 12.74 (99.05)	42.30
Safe limit	3–6	23	135–270	75–150	250–500	
ANOVA						
Site (s)	*	*	*	*	*	
Metal (m)	*	*	*	*	*	
s × m	*	*	*	*	*	

Values are mean (n = 27) ±1 SE. Values in parentheses represent soil enrichment factor of metal ions

Significant * $p < 0.001$

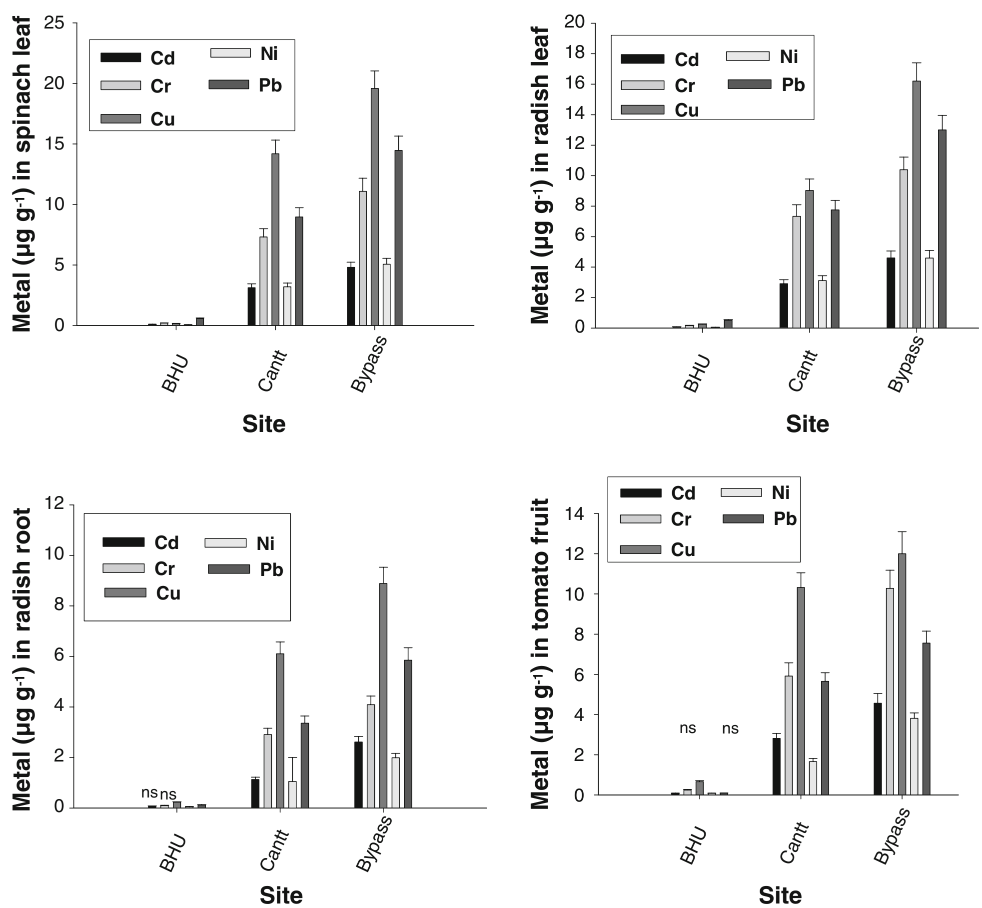

Fig. 1 Heavy metal concentrations (μg g^{-1}) in edible parts of vegetables grown at three experimental sites. Vartical bars: 1 SE (n = 9). Differences significant at $p < 0.01$ unless otherwise marked as ns. Safe limits (μg g^{-1}): Cd (1.5); Cr (23); Cu (30); Ni (1.5); Pb (2.5) (Awasthi 2000)

for leaves (6.22 and 9.47 for spinach and 5.41 and 8.57 for radish leaf, respectively). Variations in heavy metal concentration in vegetables could be due probably to variable capabilities of plants to absorb and accumulate heavy metals (Pandey and Pandey 2009), variations in growth period and growth rates (Moseholm et al. 1992) as well as to variable concentrations of heavy metals in air, atmospheric deposits and in soil (Verloo and Eeckhout 1990; Sharma et al. 2007). Plants generally take nutrients and trace elements available in the air and in the root environment. In pot culture experiments, contributions from other sources to vegetal metal concentrations remain insignificantly small. Thus, for the observed differences in vegetal heavy metal levels, atmospheric deposition

Table 3 The efficiency of heavy metal accumulation in vegetables through air measured in terms of air accumulation factor (AAF) and through soil as measured in terms of concentration factor (CF)

Metal	AAF (m^3 g^{-1})			CF		
	Spinach	Radish	Tomato	Spinach	Radish	Tomato
Cd	286	106	227	0.198	0.167	0.174
Cr	46.4	9.2	24.8	0.066	0.045	0.080
Cu	68.6	18.2	32.6	0.209	0.102	0.135
Ni	42.1	7.5	24.3	0.065	0.042	0.075
Pb	36.8	16.6	22.7	0.040	0.030	0.035

appeared to be the main determinant. This was clearly evidenced through air accumulation factor (Table 3) and vegetal metal synchrony with sites coupled with HPI of deposition and foliar metal levels. Large surface area of leaves directly exposed to urban atmosphere could accelerate metal absorption. For metal levels in root, soil-linked accumulation appeared equally important. Moseholm et al. (1992) have observed a linear relationship between airborne Pb and its foliar concentrations in Kale and Italian rye grass and showed that the magnitude of uptake was dependent upon atmospheric concentration. Hovmand et al. (1983) observed that 12%–60% of total metal in the foliage of certain agricultural crops were due to atmospheric deposition. However, in non polluted areas, soil Cd has been shown to contribute upto 63% of total Cd in roots (Hovmand et al. 1983). In the present study, metal concentration in roots varied significantly depending upon metal species.

The results of this study clearly indicate that atmospheric deposition can substantially elevate the levels of heavy metals in edible parts of vegetables especially in fruits and leaves. The study further indicates that vegetable leaves (spinach and radish) are maximally contaminated with heavy metals followed by fruits (tomato) and roots (radish). Such vegetables will increase the dietary intake of toxic heavy metals and pose health hazards to the users. Thus, the practice of avoiding waste water for irrigation in vegetable cultivation alone is not sufficient to obtain safe agricultural produce, since air-borne heavy metals coupled with wind could contaminate agricultural lands to even those situated away from direct emitting sources. This has merit attention especially for developing countries like ours where newly establishing industries and extensive urban growth are continue to raise heavy metals in the air shed.

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