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Monitoring the Atmospheric Deposition of Heavy Metals at Source and Non-Source Oriented Sites of Varanasi, India

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Abstract: We measured the atmospheric depositions of total particulates and seven heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) at twentytwo urban and sub-urban locations of Varanasi, a holy city of India. Heavy metals in bulk deposits were measured using atomic absorption spectrophotometry. Atmospheric depositions of Zn remained highest (31.65 to 636.15 g $ha^{-1}y^{-1}$) followed by Mn (8.1 to 379.5 g $ha^{-1}y^{-1}$), Pb (5.0 to 140 g $ha^{-1}y^{-1}$), Cu (4.5 to 122.7 g $ha^{-1}y^{-1}$), Ni (2.0 to 58.1 g $ha^{-1}y^{-1}$), Cr (5 to 55 g $ha^{-1}y^{-1}$) and Cd remained the lowest (0.45 to 17.7 g $ha^{-1}y^{-1}$). The deposition of heavy metals remained highest during winter and lowest during rainy season. Atmospheric emissions coupled with wind actions appeared to have raised atmospheric loadings of heavy metals even in areas far away from source oriented sites. Since the city of Varanasi is flanked by a vast stretch of holy river Ganga at one side and agricultural lands at other sides, our data have relevance establishing air-soil-water-vegetable continuum of heavy metals from a human health perspective.

Key words: Atmospheric deposition, heavy metal, tropical city, Ganges, Varanasi.

Introduction

Increased anthropogenic activities have dramatically raised the atmospheric deposition of pollutant aerosols in many parts of the world including India. Atmospheric emissions coupled with wind actions are adding air pollutants even in areas far away from source oriented sites (Thornton and Dise, 1998; Pandey, 2005). Several authors have shown a relationship between atmospheric deposition and elevated elemental levels in crops and vegetables (Azimi et al., 2004; Sharma et al., 2007; Pandey and Pandey, 2009). Urban and peri-urban areas are worst affected by heavy metal contamination (Polkowska et al., 2001; Khillare et al., 2002). These heavy metals are non-biodegradable and cause health hazards including carcinogenesis-induced tumor promotion (Dolk and Vrijheid, 2003).

The developed countries such as the USA have achieved some control on atmospheric emissions through control devices and high efficiency process technologies. Depositions of heavy metals even in some European countries are declining (Azimi et al., 2005). Developing countries, including India, however, continue to witness increasing atmospheric loading and deposition of pollutant aerosols due to high rate of urban and industrial growth (Pandey and Agrawal, 1994; Pandey, 2005). Depositions of pollutant elements in many parts of our country have reached the level known to be detrimental to plant growth and contaminate soil, water and vegetables (Pandey and Pandey, 2009).

During a couple of years, the city of Varanasi has witnessed massive expansion and industrial resurgence. Haphazard and unplanned urban-industrial growth coupled with unprecedented population increase continue

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to add massive amount of air pollutants in this region (Pandey and Agrawal, 1994; Pandey and Shubhashish, 2006). Literature so far available indicated fragmentary data on atmospheric deposition of heavy metals for this region. However, more systematic data are required for assessing direct health effects and/or through soil-water-vegetable contaminations of toxic metals. The present study aimed at evaluating the atmospheric deposition of toxic heavy metals in urban and peri-urban areas of Varanasi and along the banks of Ganges. Our data will enable establishing air-water-plant-human continuum of heavy metals and designing appropriate site specific airshed management plans.

Materials and Methods

The data presented here are the results of two consecutive years of the study (March 2006 to February 2008) conducted at selected urban and sub-urban sites of Varanasi (25° 18′ N latitude and 83° 1′ E longitude and at 76.19 metre above msl). The climate of the region is tropical monsoonal. The temperature remain lowest in December (9.9 to 26.1°C) and highest usually in June (27.8 to 40.9°C). The rainy months normally remain warm and wet with humidity reaching close to saturation. Wind direction shifts predominantly westerly and south-westerly in October through April and easterly and north-westerly in remaining months.

For the purpose of the present study, the urban, peri-urban and river sides of Varanasi were divided into 22 sampling stations and three sites were selected at each station. Of the 22 sampling stations, Godowlia (Gdl), Lahurabeer (Lhb), Lanka (Lnk), Mahmoorgang (Mhg), Maidagin (Mdn), Orderly Bazar (Odb), Rathyatra (Rty), Sigra (Sgr) and Cantt (Cnt) constitute urban-commercial areas. Kurukchhetra (Kct) and Shankuldhara (Skd) include urban-residential areas. Pandeypur (Pdp), Ramnagar (Rng), Umrahan (Urh), Sarnath (Snt) and Shivpur (Svp) are suburbs. Bhaidaini (Bdn) and Samneghat (Sng) are river side sampling stations. DLW (Dlw) and Lahartara (Lhr) stations are characterized by commercial and industrial activities. Banaras Hindu University campus (Bhu) and Bypass (Bps) sampling stations are characterized by sub-urban plantation sites and sub-urban high traffic highways respectively.

Bulk depositions were collected using bulk samplers which combine the precipitation and dry fallout in the same container. These collection systems were maintained at a height of 2 m to avoid collection of re-suspended soil particulates and were devised to avoid bird nesting as described in Pandey and Pandey (2009). As soon as the samples were brought to the laboratory, the samples were acidified with HNO_3 (Merck), filtered and stored in dark at ambient temperature before analysis.

Ternary acid digestion procedure was followed for extraction of heavy metals in atmospheric particulates (Allen et al., 1986). The concentrations of heavy metals in digested filtrates were determined with an Atomic Absorption Spectrophotometer (Perkin Elmer model 2130, USA), fitted with a specific lamp of particular metal using appropriate drift blank. The chemicals used were Merck analytical grade (AR). Quality control measures were taken to assess contamination and reliability of data. Blank and drifts standards (Sisco Research Laboratory Pvt. Ltd., India) were run after five readings to calibrate the instrument.

Significant spatial and temporal variations were assessed by using analysis of variance (ANOVA) following appropriate transformations whenever required. Standard error of mean (SEM) and coefficient of variation (CV) across time were computed for expressing data variability. The statistical analysis were done using SPSS Programme for micro-computers.

Results and Discussion

The average annual deposition of particulates at Varanasi ranged from 4.95 to 18.2 t ha^{-1} y^{-1} during summer, 4.00 to 16.5 t ha^{-1} y^{-1} during monsoon and 5.39 to 18.6 t ha^{-1} y^{-1} during winter season (Table 1). The values, in general, remained maximum at Bypass and minimum at BHU sites. Atmospheric particulate deposition at Ramnagar, Lahartara, Rathyatra and Cantt sites remained in higher ranges and at Pandeypur, Shankuldhara, Umrahan and Samneghat sites remained in lower ranges. Particulate deposition was recorded maximum during winter followed by summer and rainy season. The variations with respect to site, season and their interactions were significant (Table 2). High deposition during winter could be attributed to low mixing height coupled with temperature inversion and increased frequency of vehicles. Winter season witnessed increased tourist flux and regional mobility and hence high vehicular frequency. Particulate depositions recorded in the present study, although comparable to those recorded at some rural and urban sites of Europe (Lawlor and Tipping, 2003; Azimi et al., 2004) and Asia (Singh and Agrawal, 2005), were higher than those observed at some urban sites of USA (Conko et al., 2004; Reinfelder et al., 2005).

Atmospheric deposition of Cd ranged from 0.45 to 17.7 g ha^{-1} y^{-1} (Figure 1), the values being highest at Sarnath and lowest at Shankuldhara. The Cantt, Lahartara, Pandeypur and Sigra sites received almost similar input of Cd as those observed for Sarnath. Variations due to site, season and their interaction were significant (Table 2). Although the season appeared to be an important source of variation, the effect of the former on percent contribution of heavy metals to total atmospheric deposition was not well marked (Table 3).

Table 1: Atmospheric deposition of total particulates (t ha^{-1} y^{-1}) at selected urban and sub-urban locations. Values are mean (n = 24) ± 1 SE

Site	*Summer*	*Rainy*	*Winter*
Bdn	8.89 ± 0.45	8.00 ± 0.23	9.47 ± 0.95
Bhu	4.95 ± 0.33	4.25 ± 0.28	6.35 ± 0.254
Bps	18.2 ± 0.61	16.5 ± 1.03	18.6 ± 1.86
Cnt	11.30 ± 0.51	10.87 ± 0.54	11.65 ± 0.65
Dlw	7.12 ± 0.36	6.99 ± 0.44	7.200 ± 0.36
Gdl	10.81 ± 0.37	10.82 ± 0.57	11.5 ± 0.52
Kct	7.11 ± 0.23	7.00 ± 0.32	7.20 ± 0.36
Lhr	11.00 ± 1	9.50 ± 0.48	11.9 ± 0.30
Lhb	11.00 ± 1	10.50 ± 0.88	11.3 ± 0.66
Lnk	9.56 ± 0.40	8.00 ± 0.23	10.0 ± 0.50
Mhg	5.40 ± 0.2	5.60 ± 0.2	5.51 ± 0.12
Mdn	8.00 ± 0.23	8.00 ± 0.23	8,56 ± 0.143
Odb	9.55 ± 0.36	9.01 ± 0.41	10.0 ± 0.50
Pdp	5.30 ± 0.28	4.00 ± 0.15	5.39 ± 0.36
Rng	17.0 ± 1.55	16.04 ± 0.53	17.4 ± 0.916
Rty	14.81 ± 0.53	14.00 ± 0.88	15.8 ± 1.05
Sng	5.02 ± 0.36	5.00 ± 0.21	5.4 ± 0.45
Snt	8.40 ± 0.6	8.40 ± 0.56	8.60 ± 0.57
Skd	7.00 ± 0.32	6.66 ± 0.30	7.2 ± 0.36
Svp	5.50 ± 0.25	5.00 ± 0.21	5.51 ± 0.12
Sgr	8.00 ± 0.28	7.51 ± 0.54	8.01 ± 0.267
Urh	5.90 ± 0.28	5.00 ± 0.21	6.09 ± 0.28

Table 2: F-ratios obtained from two-way analysis of variance (ANOVA) for atmospheric depositions of particulates and heavy metals

Heavy metal	*Source of variation*		
	Season	*Site*	*Season × site*
Particulates	148.73^{**}	269.50^{**}	67.80^{**}
Cd	116.00^{**}	86.30^{**}	17.00^{**}
Cr	14.50^{**}	32.10^{**}	0.72^{NS}
Cu	66.30^{**}	102.51^{**}	18.24^{**}
Mn	52.00^{**}	154.46^{**}	31.79^{**}
Ni	132.74^{**}	47.00^{**}	26.00^{**}
Pb	86.00^{**}	46.95^{**}	24.86^{**}
Zn	119.05^{**}	22.15^{**}	3.50^{*}

Level of significance: $^{*}p < 0.01$; $^{**}p < 0.001$; NS: not significant.

Table 3: Percent contributions of different heavy metals to total atmospheric deposition at Varanasi

Heavy metal	*% contribution (× 10^{-4})*		
	Summer	*Rainy*	*Winter*
Cd	0.61	0.62	0.79
Cr	2.49	2.50	2.60
Cu	5.20	5.30	5.30
Mn	15.5	17.5	16.0
Ni	2.30	2.10	2.80
Pd	6.20	6.10	6.20
Zn	26.0	29.0	29.0

Seasonal trends for deposition of Cr were similar to that of Cd, although spatial patterns appeared altogether different (Figure 1). Deposition of Cr was recorded maximum at Ramnagar site (50.1 to 55.5 g ha^{-1} y^{-1}) and minimum at Samneghat site (5.0 to 8.1 g ha^{-1} y^{-1}). Lahartara, Cantt., Lahurabeer, Pandeypur and Bypass sites also witnessed high input of Cr (Figure 1).

Similar to Cd and Cr, the depositions of Mn, Ni, Pb, Cu and Zn were observed maximum during winter followed by summer and rainy season, although spatial trends appeared invariably different (Figures 2-4). Variations in atmospheric deposition of these heavy metals were significant with respect to site, season and their interactions (Table 2). Data variability remained within the limit of 30%. Atmospheric deposition of Mn varied between 8.1 (DLW) and 379.5 g ha^{-1} y^{-1} (Cantt) and Ni between 2.0 (Shankuldhara) and 58.1 g ha^{-1} y^{-1} (Lahartara). Depositions of Cu and Zn remained highest at Bypass and lowest at DLW site. For Pb, deposition remained maximum at Bypass (140.3 g ha^{-1} y^{-1}) and minimum at Godowliya sites (5.0 g ha^{-1} y^{-1}). Highest depositions of Pb, Cu and Zn were 140.3, 122.7 and 636.15 g ha^{-1} y^{-1}, respectively, during winter season.

Atmospheric deposition of heavy metals recorded in this study was comparable to the values recorded in other parts of our country receiving similar atmospheric loadings (Jain et al., 2000; Singh and Agrawal, 2005). Except for Mn, deposition of Zn appeared about 3 to 10 fold higher than other elements which could be ranked as Mn > Pb > Cu > Ni > Cr > Cd. Such patterns have also been observed at other urban sites (Azimi et al., 2004), although long-term studies have indicated a rapidly declining trend in the atmospheric deposition of Pb (Pandey and Pandey, 2009). Since the air mass flow of the region is mainly from west and south-west, the urban-industrial emissions could sizably contribute to the bulk deposition of the area. The street topography, traffic volume, average speed of vehicles and frequency of

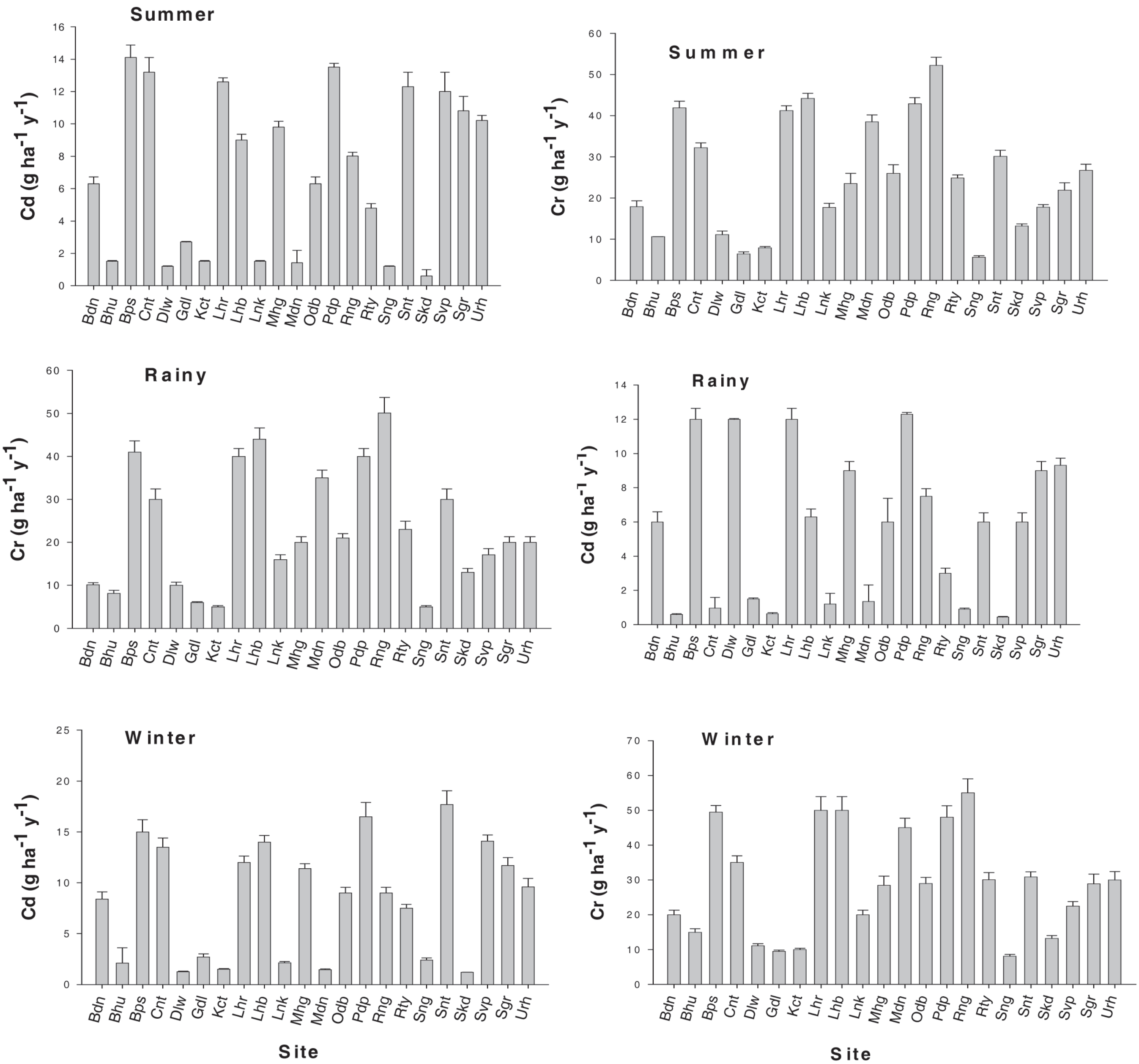

Figure 1: Atmospheric deposition of cadmium and chromium at selected urban and sub-urban locations of Varanasi. Values are mean (*n* = 24) ± 1 SE.

traffic congestion appeared to be the other major determinants. High depositions of heavy metals at Lahartara and Cantt sites were probably due to the contributions from railway emissions and city plumes in addition to vehicular exhaust. Bypass sites showed superiority over most of the sites with respect to the deposition of heavy metals. This site is characterized by very high frequency of heavily loaded high duty vehicles. Studies conducted earlier have indicated that vehicle exhaust accounts for about 50% of total pollution load in metropolitan areas (Pandey et al., 1992). Sites such as Bypass, Lahartara, Cantt, Lahurabeer and Rathyatra encompassing heavy traffic densities and frequent traffic congestions showed higher atmospheric deposition. The traffic densities at Shankuldhara and DLW sites were considerably low. Substantially high deposition of Zn could be due to industries manufacturing zinc containing fungicide, viscose, rayon fibres, zinc galvanization and dezincification units in addition to other general sources. Deposition of trace metals recorded in the present study although higher to those measured in northern England (Lawlor and Tipping, 2003), at Chesapeake and Delware

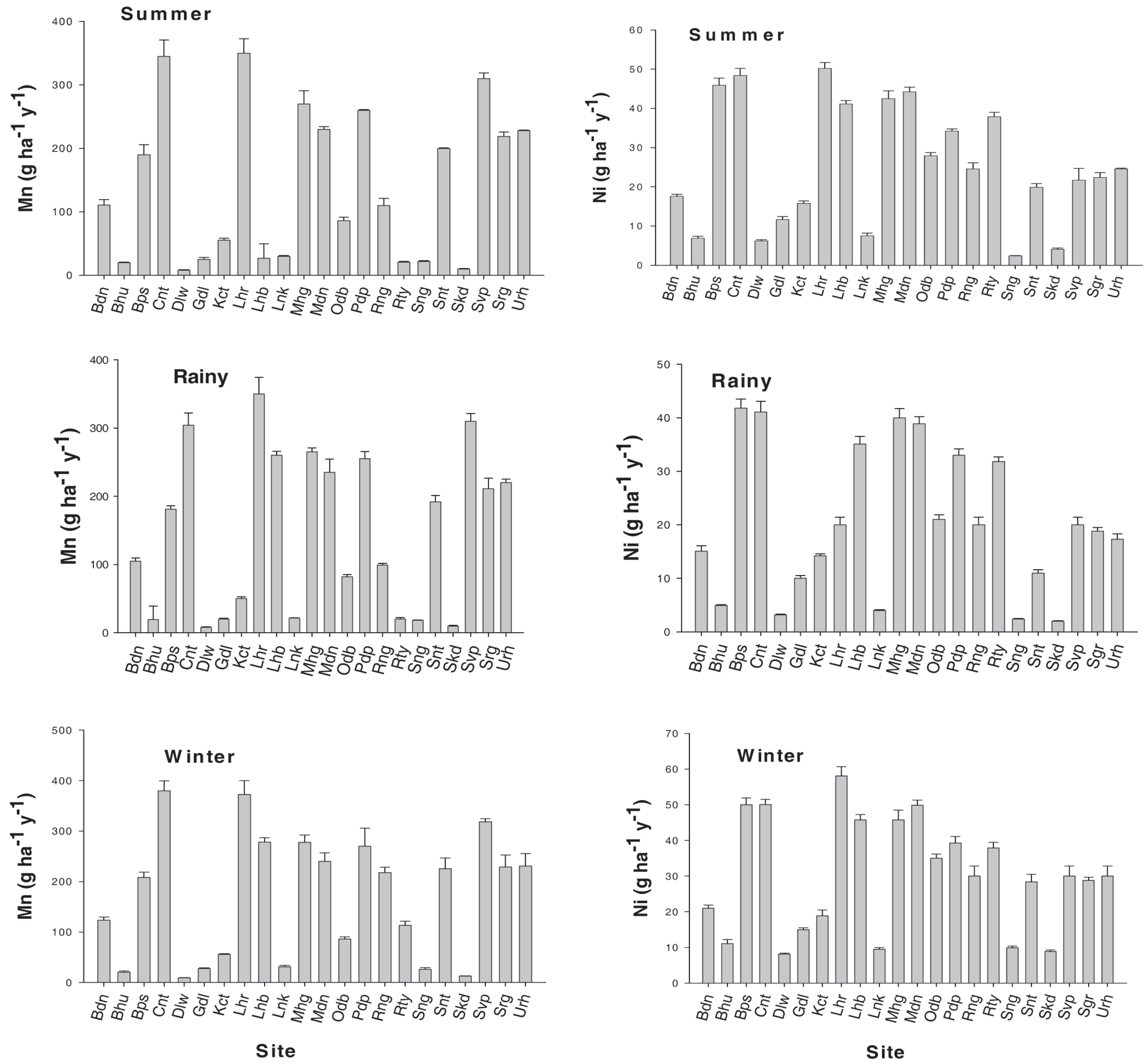

Figure 2: Atmospheric deposition of manganese and nickel at selected urban and sub-urban locations of Varanasi. Values are mean (*n* = 24) ± 1 SE.

Bay site (Kim et al., 2000) and Great Lake sites (Sweet et al., 1998), were comparatively lower than those observed at some other urban and sub-urban locations of the world (Moseholm et al., 1992; Azimi et al., 2004; Pandey and Pandey, 2009).

With respect to season, atmospheric depositions of heavy metal were high during winter. Low temperature, weak wind and concurrent formation of inversion layer during winter reduce long-range transport and accelerate atmospheric deposition (Pandey and Agrawal, 1994; Polkowska et al., 2001). Furthermore, use of fossil fuel increases during winter for producing the same amount of energy (Stern et al., 1984). Depositions were maximum in down-wind of urban agglomeration. Some of the remote sites of this study were also under the strong influence of urban-industrial emissions due to the air mass flow. In particular, high deposition of most heavy metals at Sarnath in spite of its being away from direct emission sources could be due to frequent flushing of south-westerly winds enriched in urban emission. This has merit attention, since Sarnath is an internationally known place for tourists. Atmospheric depositions recorded at this site

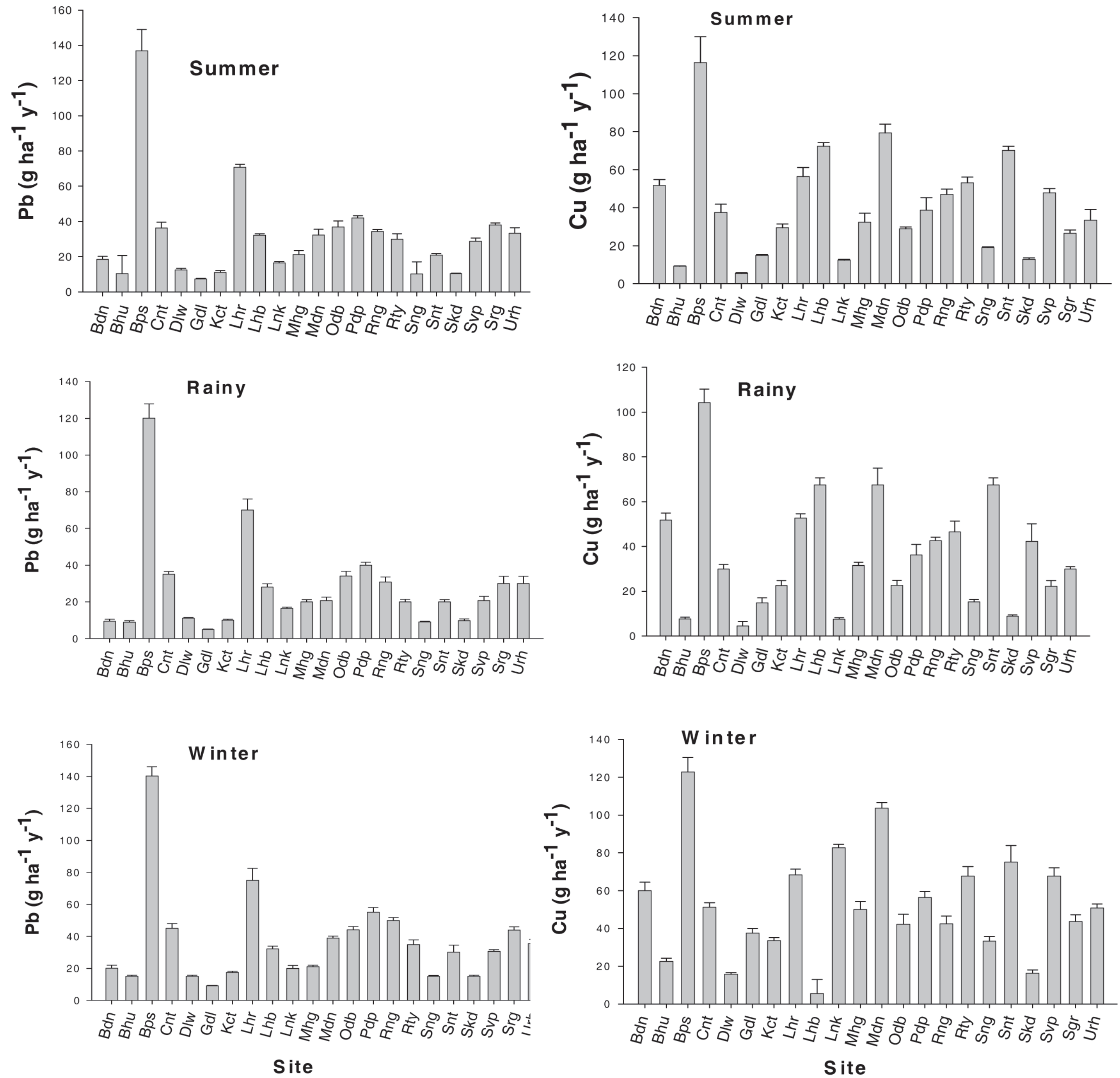

Figure 3: **Atmospheric deposition of lead and copper at selected urban and sub-urban locations of Varanasi. Values are mean (*n* = 24) ± 1 SE.**

were more than 3-4 times higher than that recorded for most of the non-source oriented sites. This suggests that the sub-urban sites even situated away from direct anthropogenic emissions, could be under strong influence of atmospheric loading through airshed.

The deposition of pollutant aerosols in the city is also affected by the buildings along the streets. Building geometry determines the flow and hence the dispersion and deposition of pollutant aerosols. The building ratio H/W (H = height of building, W = distance between buildings) are often considered as an important parameter for characterizing air pollutant dispersion (Pandey et al., 1992). This parameter seemed important in the present study as the deposition of the pollutant aerosols were relatively higher at sites with narrower street width and greater building heights. Atmospheric deposition at Godowlia, Lahurabeer, Maidagin and Rathyatra could have the influence of these determinants in a major way.

The present study clearly indicates that urban and peri-urban areas of Varanasi are invariably receiving high

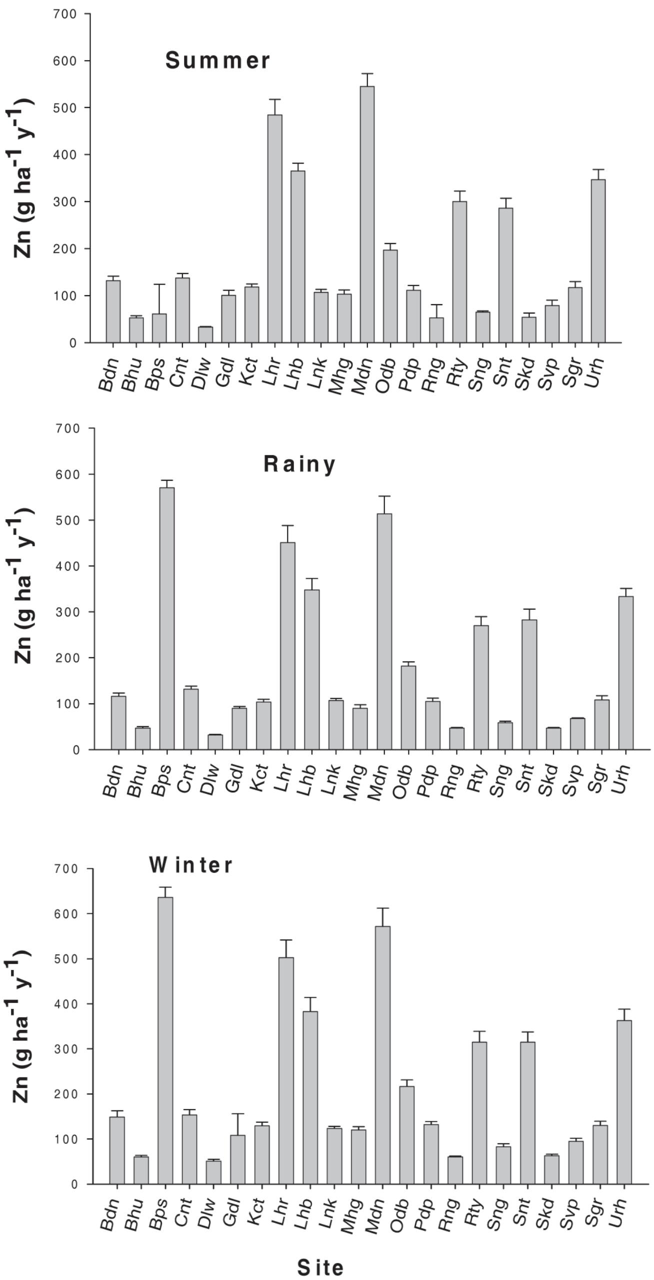

Figure 4: Atmospheric deposition of zinc at selected urban and sub-urban locations of Varanasi. Values are mean (*n* = 24) ± 1 SE.

concentrations of heavy metals. The study also indicates that the atmospheric depositions of heavy metals at Varanasi were dependent on anthropogenic emissions, traffic congestions and meteorological conditions. Building geometry, low speed of vehicles and high frequency traffic congestion has significantly raised the deposition of pollutant aerosols in this urban agglomeration. Except for Mn, Zn appeared 3 to 10 fold higher than other elements in atmospheric deposition which could be ranked in order as Mn > Pb > Cu > Ni > Cr > Cd. Dry seasons witnessed higher depositions of heavy metals due to additional contributions from surface deposits. Increasing deposition of toxic metals in this holy city of Varanasi is a matter of serious concern from human health perspectives. This seasonally dry tropical city of India is flanked by a long tract of holy river Ganga, which is the main source of drinking and irrigational water use of the region. The river is situated down wind of Varanasi urban agglomeration. High metal input through atmospheric deposition into the river will substantially increase the level of chronic metal exposure to the inhabitants through drinking water use and dietary intake along with the raised respiratory influx through inhalation.

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References

Allen, S.E., Grimshaw, H.M. and A.P. Rowland (1986). Chemical analysis. *In:* Methods in Plant Ecology. 2nd ed. P.D. Moore and S.B. Chapman (eds). Blackwell Scientific Publication, Oxford, London, 285-344.

Azimi, S., Cambier, P., Lecuyer, I. and D. Thevenot (2004). Heavy metal determination in atmospheric deposition and other fluxes in northern France agroecosystems. *Water, Air, and Soil Pollution,* **157:** 295-313.

Azimi, S., Rocher, V., Gamaud, S., Varreult, G. and D.R. Thevenot (2005). Decrease of atmospheric deposition of heavy metals in urban areas from 1994 to 2002, Paris, France. *Chemosphere,* **61:** 645-651.

Conko, K.M., Rice, K.C. and M.M. Kennedy (2004). Atmospheric wet deposition of trace elements to a suburban environment, Reston, Virginia, USA. *Atmospheric Environment*, **38:** 4025-4033.

Dolk, H.M. and M. Vrijheid (2003). The impact of environmental pollution on congenital anomalies. *British Medical Bulletin*, **68**: 25-45.

Jain, M., Kulshrestha, U.C., Sarkar, A.K. and D.C. Parashar (2000). Influence of crustal aerosols on wet deposition at urban and rural sites in India. *Atmospheric Environment*, **34:** 5129-5137.

Khillare, P.S., Balachandran, S. and B.R. Meena (2002). Spatial and temporal variation of heavy metals in atmospheric aerosol of Delhi. *Environmental Monitoring and Assessment*, **90:** 1-21.

Kim, G., Scudlark, J.R. and T.M. Church (2000). Atmospheric wet deposition of trace elements to Chesapeake and Delaware Bays. *Atmospheric Environment*, **34:** 3437-3444.

Lawlor, A.J. and E. Tipping (2003). Metals in bulk deposition and surface waters at two upland locations in Northern England. *Environmental Pollution*, **121**: 153-167.

Moseholm, L., Larsen, E.H., Andersen, B. and M.M. Nielsen (1992). Atmospheric deposition of trace elements around point sources and human health risk assessment. I: Impact zones near a source of lead emissions. *The Science of the Total Environment*, **126:** 243-262.

Pandey, J., Agrawal, M., Khanam, N., Narayan, D. and D. Rao (1992). Air pollutant concentrations in Varanasi, India. *Atmospheric Environment*, **26B:** 91-98.

Pandey, J. and M. Agrawal (1994). Evaluation of air pollution phytotoxicity in a seasonally dry tropical urban environment using three woody perennials. *The New Phytologist*, **126:** 53-61.

Pandey, J. (2005). Evaluation of air pollution phytotoxicity downwind of a phosphate fertilizer factory in India. *Environmental Monitoring and Assessment*, **100:** 249-266.

Pandey, J. and K. Shubhashish (2006). Atmospheric deposition of nutrient elements at selected urban sites of Varanasi, India. *In:* Proceedings of Environmental Degradation and Conservation, 16-17 December, 2006. Jaspal Prakashan, Patna, India.

Pandey, J. and U. Pandey (2009). Accumulation of heavy metals in dietary vegetables and cultivated soil horizon in organic farming system in relation to atmospheric deposition in a seasonally dry tropical region of India. *Environmental Monitoring and Assessment*, **148:** 61-74.

Polkowska, Z., Grynkiewicz, M., Górecki, T. and J. Namieœnik (2001). Level of lead in atmospheric deposition in a large urban agglomeration in Poland. *Journal of Environmental Monitoring,* **3:** 146-149.

Reinfelder, J.R., Totten, L.A. and S.J. Eisenreich Michael Aucott (2005). Research Project Summary. New Jersey Atmospheric Deposition Network (April, 2005).

Sharma, R.K., Agrawal, M. and M. Marshall (2007). Heavy metal contamination of soil and vegetables in suburban area of Varanasi, India. *Ecotoxicology and Environmental Safety*, **66:** 258-266.

Singh, R.K. and M. Agrawal (2005). Atmospheric depositions around a heavily industrialized area in a seasonally dry tropical environment of India. *Environmental Pollution*, **138:** 142-152.

Stern, A.C., Boubel, R.W., Turner, D.B. and D.L. Pox (1984). Sources of air pollution. *In:* Fundamentals of Air Pollution, 2nd edn. Academic Press, New York. 76-100.

Sweet, C.W., Weiss, A. and S.J. Vermette (1998). Heavy metal balances of agro-ecosystems in the Netherlands. *Netherlands Journal of Agricultural Science*, **46:** 171-192.

Thornton, G.J.P. and N.B. Dise (1998). The influence of catchment characteristics, agricultural activities and atmospheric deposition on the chemistry of small streams in the English Lake District. The *Science of the Total Environment*, **216:** 63-75.