SYNERGISTIC EFFECTS OF ATMOSPHERIC DEPOSITION AND ORGANIC AMENDMENT ON METAL ACCUMULATION IN *SPINACIA OLERACIA* L.

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Abstract: Pot–culture experiments were conducted to study the accumulation of heavy metals as influenced by atmospheric deposition in organic farming system, in which spinach (*Spinacia oleracea L.*) was grown in earthen pots containing soil and farm yard manure (4:1) at three sites in Varanasi. Heavy metal accumulation in spinach showed synchrony with atmospheric deposition, the values being maximum at Bypass and minimum at BHU site. Concentration of metals in spinach ranged from 0.095 to 5.860 µg g^{-1} for Cd; 0.189 to 13.96 µg g^{-1} for Cr; 0.160 to 23.49 µg g^{-1} for Cu; 0.059 to 6.42 µg g^{-1} for Ni and 0.57 to 18.81 µg g^{-1} for Pb. About 75%, 75% and 33% of vegetable samples contained Cd, Ni and Zn above their safe limits respectively. Our study suggests that atmospheric deposition at Varanasi have reached to the level to substantially elevate heavy metal accumulation in vegetables with a sizable increase in the dietary intake of toxic metals to local residence.

Keywords*:* Agricultural sustainability, Atmospheric deposition, Metal accumulation, Organic farming, Pot–culture

INTRODUCTION

Global scientific efforts during last few decades have added to our basic knowledge in the field of environmental research ranging from regional transport and deposition of pollutant aerosols to global issues including global warming, stratospheric ozone depletion and sustainability of environmental domains. Atmospheric aerosols play a significant role in regulating various atmospheric processes including the cooling effects of stratospheric aerosols and warming effects of tropospheric soot particles. Aerosols in the stratosphere (mainly injected through volcanic eruptions) induce global cooling and in troposphere especially soot particles, contribute to the warming effect by absorbing sun's radiation. Fine particulates in upper atmosphere also participate in photochemical reactions and / or undergo the process of condensation and coagulation and finally deposit to the earth surface. Such depositions depending upon their chemical nature may induce a variety of effects on life and life support systems. Increased anthropogenic activities have dramatically raised the atmospheric deposition of essential and non–essential elements in many parts of the world including India. Atmospheric pollutants coupled with wind actions are adding air pollutants even in areas far away from source oriented sites (Thornton and Dise, 1998; Pandey, 2005). Several studies have pointed out the importance of atmospheric input in the biogeochemical cycling of heavy metals (Fitzgerald *et al*., 1991; Lindberg *et al*., 1991; Kelly *et al*., 1996; Jackells, 1998; Bargagli, 1998). Deposition of nutrients and trace elements is a natural process by which gases and particulates are removed from atmosphere and slowly get deposited on the earth's surface. Wind is the major factor for the dispersal of pollutants even to remote areas. Amendments and addition of synthetic fertilizers are the main source of large–scale contamination of cultivated soils (Azimi *et al*., 2004). Agricultural land adjacent to urban areas are exposed to increasing loads of air pollutants which are urban origins. This is associated mainly to rapidly increasing urban populations, frequency of motor vehicles, use of fuels with poor environment performance, badly maintained roads and ineffective environmental regulations (Agrawal *et al*., 2003; Singh and Agrawal, 2005). Agricultural run–off also degrades the quality of water and alters the trophic status. Continuous addition of chemical fertilizers and pesticides although increased the global food production of agricultural lands, have lowered the quality and taste of agricultural produce and have increased the health and environmental risk to human beings (Tilman *et al.,* 2001; Pandey and Pandey, 2009b) . These ill–effects of modern agriculture forced people, especially in countries with high–income economics (European countries, USA, Canada, Australia, etc) to demand food grown without fertilizers and pesticides. This paved the way for organic farming globally (Prasad, 2005).

The growing consciousness about sustainable agriculture and health risks associated with agrochemicals has brought a major shift in people's preference towards safe and quality food. Prevention of heavy metal accumulation in soil has become one of the pre–requisites for sustainable agriculture (Witter, 1996). The aim of sustainable heavy metal management in agro – systems, in fact, is to ensure long term protection of soil fertility along with the quality of agricultural produce (Moolennaar *et al*., 1997). Organic farming has emerged as one of the fastest growing sectors of environmental friendly sustainable agriculture. Organic farming which rely on 'biologically driven nutrients' instead of synthetic fertilizer, adopts management of soil organic matter to enhance physical, chemical and biological properties of soil (Pandey and Pandey, 2009b).

Varanasi, in spite of being an ancient living city and a cultural heritage of Hindus, is one of the important centers for commerce and trade in north India and continue to witness increase loading and deposition of air pollutants. However, literatures available till date provide only fragmentary data on atmospheric deposition of pollutant aerosols for Varanasi city. The present study aimed to evaluate the atmospheric deposition of six heavy metals in urban and sub–urban area of Varanasi and its environmental impact on organic farming system.

METHODOLOGY

The study area ($25^0 18^/$ N lat and 83^0 $1^/$ 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 sometimes exceeds 44^0C. 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 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 2009a). Immediately after collection, the samples were acidified with HNO_3 (special purity, Merck), filtered and stored in dark at ambient temperature before analysis. 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 used in this study, spinach (*Spinacia oleracea* L.) is an important vegetable crop of Indian tropics. Seeds of this vegetable were sown uniformly in earthen pots of 40 cm diameter and 30 cm height filled with well manured garden soil (4 : 1 ratio for soil and compost) and exposed to variable amount of atmospheric deposition (BHU, Cantt and Bypass) from the date of sowing. To maintain constant soil moisture, pots were uniformly watered thrice a week during dry seasons.

For the measurement of leaf area of plant leaf area meter was used. Root shoot length was measured by meter scale. For heavy metal analysis in spinach, leaves were separated from the finally harvested plant material and properly washed to remove surface dust. Dead and yellow leaves were discarded. Cleaned plant samples were chopped into small pieces, oven dried at 80^0C, 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.

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 (µg 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. Blank and drift standards (Sisco Research Laboratory Pvt. Ltd., India) were run after five reading to calibrate the instrument. Heavy metal pollution index (HPI) was calculated by the formula given by Usero *et al*. (1997) and metal enrichment in soil was calculated by the formula given by 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 1.69 to 21.89 g ha^{-1} y^{-1}; Cu from 9.67 to 118.57 g ha^{-1} y^{-1}; Cr from 4.95 to 60.87 g ha^{-1} y^{-1}; Ni from 6.45 to 68.21 g ha^{-1} y^{-1} and Pb from 21.22 to 142.00 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 continue 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 the world including India, receiving similar air emissions (Moseholm *et al.*, 1992; Jain *et al.*, 2000; Azimi *et al*., 2004; Singh and Agrawal, 2005; Pandey *et al*., 2009a). 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. 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 in compost amended soil (Table 2), where concentrations of Cd, Cr, Cu, Ni and Pb in cultivated soil were 11.53, 56.32, 24.88, 108.56, 125.36 µg g^{-1} respectively. Concentration of Cd, Cr, Cu, Ni and Pb were lower when control soil was compared to the amended soil at each site. Compost amendment provides binding sites to heavy metals through which metals become insoluble in soil and are least transferred to plants. Organic matter converts metals to non available form to plants (Waker *et al*., 2004). Metal enrichment in soil appeared highest for Cd (2.44 to 33.91) and lowest for Cu (1.29 to 10.15) (Table 2).

Variation in heavy metal concentrations in cultivated soil appeared to be source dependent. Concentration of Pb in both control and amended soil was found to be highest followed by Ni, Cr, Cu and Cd. Difference between control and amended soil was highly significant. Soil metal levels recorded in this study appeared comparable to those recorded in soils of other areas (Krezyztof *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. Increase in soil metal levels indicates the role of atmospheric deposition which could in turn, increase vegetable accumulation of toxic metal ions. Organic matter amendment may be a beneficial treatment to prohibit the metal accumulation in vegetables and food chain. 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.

Leaf area per plant was recorded highest BHU site followed by Cantt and minimum at Bypass site (Fig. 1). At all site, spinach shown in compost amended soil showed significant increase over spinach shown in control soil. Atmospheric deposition was maximum at Bypass site and reduced the growth significantly in terms of leaf area when it was compared with other sites. Leaf area of spinach at different study sites ranged from 106.44 cm^2 to 255.64 cm^2 (Fig. 1). The literature available on plant performance in urban areas shows that air pollution reduces plant growth and the extent of growth reduction depends on the plant species, concentration and distribution of pollutants and number of environmental factors (Mansfield and Freer-Smith, 1981; Pandey and Agrawal, 1994).

Root: shoot ratio (in terms of length) was observed maximum at Bypass site and minimum at BHU site (Fig. 2). Lower root shoot ratio indicates the availability of nutrients and organic matter in soil and because of the availability of nutrients, roots show normal growth. In case of control where organic matter is not amended, roots grow more than compost amended soil in length to accumulate sufficient nutrient for their growth thus root shoot ratio increases. In spinach root shoot ratio was recorded lowest for compost in comparison to control showing easy availability of organic matter to plants (Agren and Ingestad, 1987; Agren and Franklin, 2003).

Vegetal heavy metal levels varied with site, amendment and atmospheric deposition. Concentration of metals was significantly lower in compost amended soil in comparison to control soil. Concentration of metals ranged from 0.095 to 5.860 $\mu g\ g^{-1}$ for Cd; 0.189 to 13.96 $\mu g\ g^{-1}$ for Cr; 0.160 to 23.49 $\mu g\ g^{-1}$ for Cu; 0.059 to 6.42 $\mu g\ g^{-1}$ for Ni and 0.57 to 18.81 $\mu g\ g^{-1}$ for Pb (Fig.3). Concentration of Cu was found maximum followed by Pb, Cr, Ni and Cd. With respect to site, concentrations of heavy metals were found to be maximum at Bypass followed by Cantt and minimum at BHU site.

Heavy metal determination in spinach indicated that the concentration of Cd, Ni and Pb frequently exceeded the safe limits of both Indian and WHO standards. At two of the sampling locations (Cantt and Bypass), in both cases 89 % of the leaf sample contained Cd, Ni and Pb above their respective safe limits of Indian standards safe limits {Cd (1.5); Cr (23); Cu (30); Ni (1.5); Pb (2.5) $\mu g\ g^{-1}$ respectively } (Awasthi 2000).Variations in heavy metal concentration in vegetables could be due probably to variable capabilities of plants to absorb and accumulate heavy metals (Pandey *et al*., 2009b), 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 (Sharma *et al.* 2007; Pandey *et al*., 2009b). 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 significantly small. Thus, for the observed differences in heavy metal levels at different sites, atmospheric deposition appeared to be the main determinant. This was clearly evidenced through vegetal metal synchrony with sites coupled with HPI of deposition and foliar metal level. Large surface area of leaves directly exposed to urban atmosphere could accelerate metal absorption. 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.

CONCLUSION

The study indicates that leafy vegetables are maximally contaminated with heavy metals when it was compared with other studies conducted in the same laboratory. Leafy vegetables will increase the dietary intake of toxic heavy metals and pose health hazards to the users. Thus, the practices of avoiding wastewater for irrigation in vegetable cultivation alone is not sufficient to obtain safe agricultural produce, since airborne heavy metals coupled with wind pattern could contaminate agricultural lands even to those situated away from direct emitting sources. This has merit attention especially for developing countries like ours where newly establishing industries and extensive urbanization is continue to raise heavy metals in the air shed. This study shows that organic amendments and atmospheric depositions both are significantly influencing the growth and heavy metal accumulation in plants. This is concluded from the present study that organic farming is beneficial for good quality produce even in areas of high atmospheric input.

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

Site	Cd	Cr	Cu	Ni	Pb	HPI
BHU	1.69 ±0.18	4.95 ±0.54	9.67 ±0.94	6.45 ±0.57	21.22 ±2.43	6.68
Cantt	20.41 ±2.11	56.83 ±4.41	107.40 ±10.36	61.62 ±5.51	109.36 ±9.20	60.59
Bypass	21.89 ±1.93	60.87 ±5.58	118.57 ±10.45	68.21 ±6.14	142.0 ±13.79	67.71

Values are mean (n = 72) ± 1SE

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

Site		Cd	Cr	Cu	Ni	Pb
BHU						
	Control	0.83±0.088 (2.44)	3.61±0.29 (1.30)	2.45±0.25 (1.29)	7.04±0.60 (2.24)	10.35±0.91 (1.95)
	Compost	1.28±0.082 (3.76)	4.35±0.36 (1.57)	3.10±0.27 (1.63)	7.69±0.64 (2.45)	12.32±1.13 (2.33)
Cantt						
	Control	7.78±0.82 (22.88)	38.44±2.74 (13.93)	18.6±1.76 (9.79)	61.93±5.44 (19.72)	95.12±9.93 (17.98)
	Compost	9.30±0.91 (27.35)	40.56±3.62 (14.69)	21.39±1.89 (11.26)	66.73±5.56 (21.25)	103.42±8.7 (19.55)
Bypass						
	Control	9.63±1.18 (28.32)	51.77±3.44 (18.76)	19.24±1.96 (10.13)	96.44±8.56 (30.71)	119.2±12.74 (22.53)
	Compost	11.53±1.29 (33.91)	56.32± 5.02 (20.41)	24.88±2.39 (10.15)	108.56±9.60 (34.57)	125.36±10 (23.69)
Safe limit		3–6	23	135–270	75–150	250–500
ANOVA						
Site (s)		*	*	*	*	*
Metal (m)		*	*	*	*	*
s x m		*	*	*	*	*

Values are mean (n = 54) ± 1SE. Values in parentheses represent soil enrichment factor of metal ions.
* Level of significance: $p < 0.001$

Fig. 1 Leaf area per plant measured for spinach under different amendments at selected sites at Varanasi. Values are mean (n = 54) ± 1SE. Level of significance: **$p < 0.05$; ***$p < 0.001$

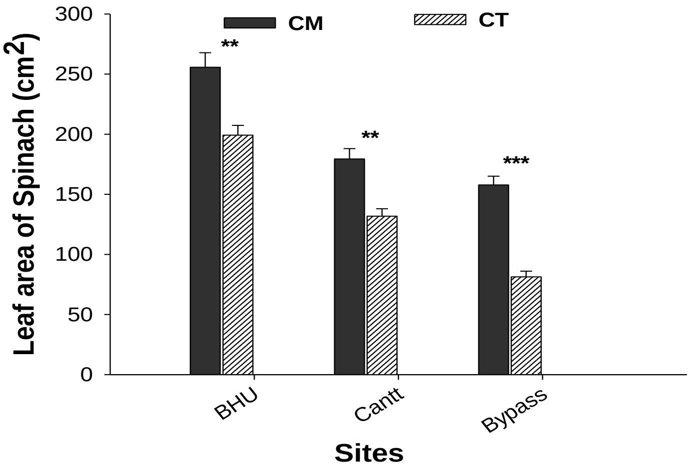


Fig.2 Root: shoot ratio of selected vegetables under different amendments as influenced by atmospheric deposition.

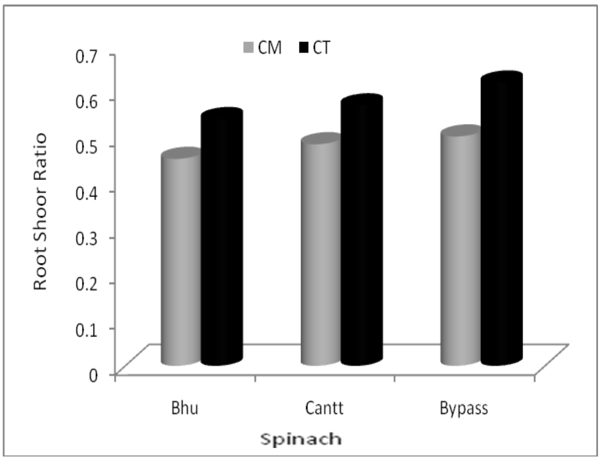
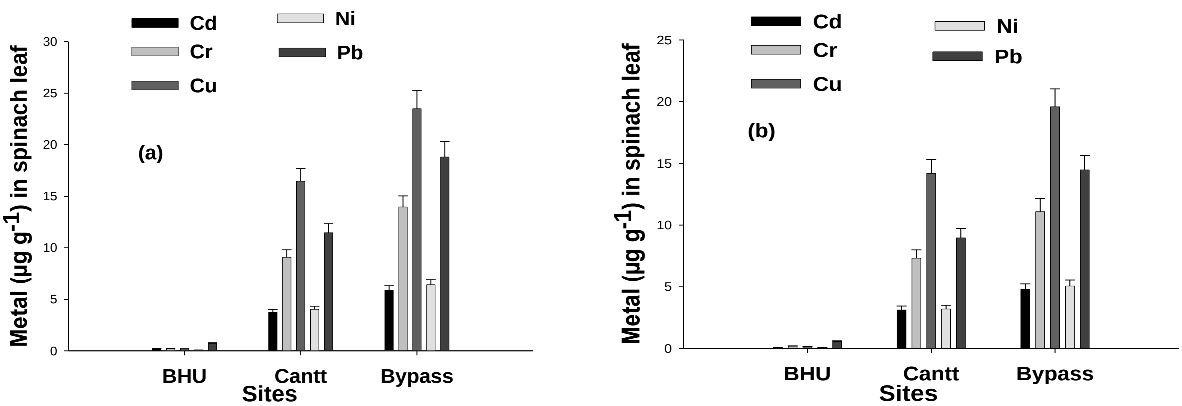


Fig.3 Heavy metal concentrations (µg g^{1}) in spinach leaf grown at three experimental sites (a: control and b: compost amendment) under the influence of atmospheric deposition. Values are mean (n = 54) ±1SE. Differences significant at $p < 0.01$.



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