Factors Controlling the Deposition of Airborne Metals on Plant Leaves in a Subtropical Industrial Environment

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ABSTRACT

This study was conducted in an industrial city (Bilaspur) representative of subtropical area in central India. In order to assess the metal deposition on plant, concentrations of six target metals (i.e., Fe, Mn, Pb, Cu, Cd, and Cr) in both plant leaf and dust (deposited on its surface) samples were measured from six different sites. Metal concentrations in dust samples were found on the order of Fe>Mn> Cr>Pb>Cu>Cd. In contrast, the concentration of metals in plant leaves were seen on the order of Fe>Mn>Cr>Cd>Cu>Pb. As such, Cd showed significantly high concentration in leaves relative to their corresponding dust samples. A high accumulation potential for Fe and Cd was seen from Butea monosperma, while Mn and Pb were accumulated noticeably in Pongamia pinnata and Butea monosperma. Likewise, Cr and Cu were enriched in Calotropis procera, Alstonia scholaris, and Butea monosperma. The overall results of our study suggest that the foliar uptake pattern should vary considerably by an interactive role between plant and metal types.

Key words: Industrial pollution, Dust deposition, Biomonitoring, Metal pollution, Foliar transfer

1. INTRODUCTION

The term "heavy metal" refers to any metallic element that has a relatively high atomic density and is toxic or poisonous even at low concentration (Nagajyoti *et al.*, 2010). Heavy metal pollution is one of the serious environmental problems around the world. The heavy metal pollution results from both natural and anthropogenic activities such as industrial, mining, and transportation (Sawidis *et al.*, 2011). As heavy metals are readily bound to dust particles, they are responsible for the contamination in vast surface areas on the earth via deposition (Yongming *et al.*, 2006; Charlesworth *et al.*, 2003). These dust particles can directly interact with human beings, animals, and plants (Yongming *et al.*, 2006; Banerjee, 2003).

The use of plant as a potential biomonitor, especially for heavy meals has gained a good deal of attention (Przybysz et al., 2014). Both bark and leaves of trees have been used for this purpose (Gueguen et al., 2012; Gratani et al., 2008). The dust containing these metals is deposited on surfaces such as foliage of plants, especially for evergreen plants (Przybysz et al., 2014). Plants are easy for long term monitoring without the cost of expensive equipment (Przybysz et al., 2014; Snezana et al., 2012; Sawidis et al., 2011; Markert, 1993). Therefore, these metals can be transferred/ accumulated in plant leaves through various pathways (Saarela et al., 2005). Taking this into account, plants growing in dust-prone areas can be explored for their interactive relationship. In this study, the concentrations of metals in dust deposited on the leaves of selected subtropical plants were monitored in a heavily industrialized area of Bilaspur region, Chhattisgarh, India. In order to assess the transfer/accumulation of metals in those selected plant samples, their contents in leaf samples were also investigated.

2. MATERIALS AND METHODS

Bilaspur city is located in central India in Chhattisgarh state. Its population is estimated as 452,000 and area is 145.76 km². This region is a subtropical zone. The study area is approximately 7 to 30 km distant from Bilaspur city center (21°55 N; 82°01 E). Plant leaf samples were collected from six different industrial locations in February, 2014 (These sites were named as Site 1 to 6) (Fig. 1). These sites represent highly polluted areas due to strong man-made activities (including stone crusher, cement, iron, and oil factory). Site 1 is located 10 m away from the oil industry where pits are used to store disposal oil and is also affected by trans-



Fig. 1. Geographical location of study sites (Bilaspur, C.G., India).

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port activities of heavy trucks. The sampling site 2 is located 15 m away from sponge iron industry. Site 3 is located 20 m away from a stone crusher while site 4 was located 12 m away from a cement industry. Sites 5 and 6 are located approximately 20 m away from respective sponge iron industries (Table 1).

Plant leaf/dust samples were collected from all the study sites from a height of approximately 2 m (ambient height) within one day to minimize temporal changes (14 February, 2014 corresponding to post-monsoon in the area). These plants were selected because they were commonly growing in the study area. Leaf samples were collected in the zip lock plastic bags and carried into the laboratory. The dust from leaves was removed in a closed glass chamber to avoid loss of fine dust particles due to this separation procedure. Dust was removed from both surfaces of leaves with the help of fine brush. For each site, a new/clean brush was used for dust removal to avoid the carryover of dust from the previous samples. After the removal of dust, leaves were washed individually through tap and micro-distilled water. Washed leaves were placed in 50 mL of chloroform and rinsed off for 5 min in ceramic container to remove dust trapped on epicuticular wax surface on leaf (e.g., Sgrigna et al., 2015). The leaves were oven dried for 24 hours at 30°C and crushed into fine powder. The weight of samples (both dust and leaf powder) was 0.5 gram. Considering the differences in shape and sizes of leaves among different plants, a

Table 1. Description of sampling sites for dust and plant samples.

1		
Site	Name of the plants species	Descriptions of site
1	Pongamia pinnata	Avinash oils industry, Raipur road, Bilaspur
2	Calotropis procera	Nova steel iron pvt. Ltd. Dagori, Bilaspur
3	Butea monosperma	Goyal stone crusher, Raipur road, Bilaspur
4	Alstonia scholaris	Cement industry, Rambod, Bilaspur
5	Butea monosperma	Mangal sponge Iron pvt. Ltd. Bilha, Bilaspur
6	Butea monosperma	Radha madhav power plant, Rambod, Bilaspur

uniform weight of leaves (0.5 gram) were considered for extracting and calculating the concentration of metals.

Both dust and leaf powders were digested separately into 10 mL of aqua-regia solution (HNO₃: HCl v/v 3:1). Digested solution was incubated at room temperature for 24 hours. After heating to reflux for 15 min, it was cooled down. Then, distilled H₂O was added to make up the volume up to 50 mL. Samples were filtered through Whatman No. 1 and collected into test tube for the analysis of heavy metal (EPA method 3050) by fol-

(a) In dus	t deposited on plant leaves.						
Sites	Plants	Fe	Mn	Cr	Pb	Cd	Cu
1	Pongamia pinnata	3632	1147	60.0	26.9	0.86	10.5
2	Calotropis procera	3589	968	24.6	44.7	0.77	8.08
3	Butea monosperma	3526	520	16.2	37.9	0.86	6.99
4	Alstonia scholaris	3531	756	36.0	8.57	0.06	2.31
5	Butea monosperma	3637	957	37.8	15.9	1.31	11.7
6	Butea monosperma	3625	412	33.6	14.1	0.27	2.38
(b) In leat	f						
Sites	Plants	Fe	Mn	Cr	Pb	Cd	Cu
1	Pongamia pinnata	1967	340	0.82	1.22	1.22	8.48
2	Calotropis procera	2761	412	2.40	7.96	6.70	14.9
3	Butea monosperma	1549	158	8.40	0.84	6.83	1.56
4	Alstonia scholaris	1705	108	16.8	0.84	8.55	0.54
5	Butea monosperma	2459	196	3.10	0.84	7.56	1.43
6	Butea monosperma	1075	177	32.4	11.6	9.05	3.05

Table 2. Metal concentration at different study sites ($\mu g g^{-1}$).

Table 3. Results of correlation analysis between metals in each of dust and leaf samples.

(a) Dust on leaf					(b) Leaf								
	Fe	Mn	Cr	Pb	Cd	Cu		Fe	Mn	Cr	Pb	Cd	Cu
Fe	1						Fe	1					
Mn	0.40	1					Mn	0.66	1				
Cr	0.61	0.62	1				Cr	-0.82*	-0.54	1			
Pd	-0.15	0.21	-0.39	1			Pd	-0.21	0.26	0.61	1		
Cd	0.42	0.49	0.06	0.41	1		Cd	-0.26	-0.60	0.61	0.36	1	
Cu	0.48	0.73*	0.31	0.40	0.95**	1	Cu	0.60	0.97**	-0.41	0.38	-0.45	1

*Correlation is significant at 0.05 level (1 Tailed)

**Correlation is significant at 0.01 level (1-Tailed)

lowing the procedures of Serbula *et al.* (2012). These samples were analysed by Atomic Absorption Spectrophotometer (AAS 7000, Model Shimadzu, Japan). The detection limit (DL: $\mu g g^{-1}$) of target metals were 0.04 (Fe), 0.01 (Mn), 0.08 (Cr), 0.08 (Pb), 0.006 (Cd) and 0.009 (Cu). The precision was below 5% for all the metals in terms of the relative standard deviation (RSD). The statistical analysis of data was made using Microsoft excel.

3. RESULTS AND DISCUSSION

The concentrations of metals determined from dust/ leaf samples are presented in Table 2. As shown in Table 2, dust samples collected from sites 1 to 6 correspond to the surface deposition on six different plants, i.e., *Pongamia pinnata*, *Calotropis procera*, *Butea monosperma*, *Alstonia scholaris*, *Butea monosperma*, and Butea monosperma, respectively. Fe showed the dominance over all the metals at all the sites. However, it was distributed in a relatively narrow range with 3% variations (3526 (site 3) to 3637 μ g g⁻¹ (site 5)). Mn in dust was found in a relatively broad range (412 (site 6) to 1147 μ g g⁻¹ (site 1)). High Mn concentration at site 1 should reflect the effect of smoke released from oil factory. In dust samples, Cr ranged from 16.2 (site 3) to 60 μ g g⁻¹ at (site 1). Site 1 is affected with heavy traffic load and Cr in dust can be derived from the Chrome plating of motor vehicle parts (Alshayep and Seaward, 2001). The concentration of Pb in dust ranged from 8.57 (site 4) to 44.7 μ g g⁻¹ (site 2). Site 2 was impacted by heavy vehicular transport (raw material transport to the sponge iron industry). Pb in dust samples was commonly reported to come from traffic activities (Christoforidis and Stamatis, 2009). On the other hand, Cd ranged from 0.06 (site 4) to $1.31 \,\mu g \, g^{-1}$ (site 5). The maximum concentration of Cu in dust sample (11.7 μ g g⁻¹) was observed at site 5. Cu was reported to be released and combined with dust due to the metallic corrosion of engine wears of running vehicles (Al-khashman and Shawabkeh, 2006; Divrikli *et al.*, 2003).

In the case of leaf samples, Calotropis procera showed the highest concentrations ($\mu g g^{-1}$) for both Fe (2761 $\mu g g^{-1}$) and Mn (412 $\mu g g^{-1}$), probably due to its larger surface area. The leaves of Pongamia pinnata showed the lowest concentration of Cr (site 1), whereas Butea *monosperma* showed the maximum value $(32.4 \ \mu g \ g^{-1})$. The highest concentration of Pb was recorded in leaves of *Butea monosperma* at site 6 (11.6 μ g g⁻¹). It showed relatively low concentration in the same plant species at other sites (Butea monosperma at sites 3 and 5). Spatial factors in their distribution are thus also likely to be important but need further investigation. In the case of Cu, Calotropis procera showed maximum concentration (14.9 $\mu g g^{-1}$) with the high potential for its accumulation. In contrast to other metals, Cd showed relatively high concentrations from all leaf samples, indicating its fast transfer in the leaves of all the plant species.

A correlation analysis between different metals indicates the existence of significant correlations between

Table 4. Correlation of metals between leaf and dust for selected plants of all sites.

Metals	Correlations (r)	p Value
Fe	0.996*	0.028
Mn	0.914	0.133
Cr	0.996*	0.028
Pb	0.914	0.133
Cd	0.999*	0.014
Cu	0.988*	0.049

*Correlation is significant at 0.05 level (1-Tailed)

(a) Dust deposited on leaf

pairs of Cu and Mn (r=0.73, p < 0.05) and Cu and Cd (r=0.95, p < 0.01) (Table 3). As such, dust contamination of metals is likely to originate from common manmade sources. In order to see the probable accumulation of these metals, a correlation analysis was performed between pairs of a particular metal in dust and leaves of respective plant species (Table 4). Alstonia scholaris and Butea monosperma showed good correlation values for Fe (r=0.996, p=0.028) and Cr (r=0.996, p=0.028). For Pb, Pongamia pinnata and Butea monosperma were found as good accumulator (r=0.914, p=0.133). Likewise, Calotropis procera and Butea monosperma showed a good correlation for Cd (r=0.999, p=0.014)

In order to evaluate the contamination level of these metals, the results of our study were also compared with those of previous studies (Table 5). In dust, our mean concentration of Fe (3590 μ g g⁻¹) was about one order of magnitude lower than that of Calcutta (2.18% $(21800 \ \mu g \ g^{-1}))$. Similarly in leaf, its mean concentration (1920 μ g g⁻¹) was nearly half the value of Calcutta counterpart (0.38% (3800 $\mu g g^{-1}$)) which was measured near a lead factory. In leaf samples, Mn (232 μ g g⁻¹) values were one order of magnitude higher than those of Huelva city (35.45 μ g g⁻¹) and Waste bank city (71.8 μg^{-1}). In Huelva city, Pine leaves were used for the assessment of airborne heavy metal pollution. In this study, Cr in dust (34.7 μ g g⁻¹) was one order of magnitude lower than that of Huizhou city (364.7 μ g g⁻¹). The Huizhou city is home to many industrial activities such as production of petrochemicals, computers, and consumer electronics. The mean concentration of Pb $(24.5 \ \mu g \ g^{-1})$ in dust is lower by two and one order(s) of magnitude than the reported values for Calcutta $(1030 \ \mu g \ g^{-1})$ and Hangzhou/Huizhou (150.9 to 410.4 $\mu g g^{-1}$), respectively. In leaf, our Cd value (6.65 $\mu g g^{-1}$) was about one order of magnitude higher than those of

Table 5. Comparison with previous study or standard (All concentration are in $\mu g g^{-1}$).

*							
City	Fe	Mn	Cr	Pb	Cd	Cu	Reference
Calcutta	21800 (2.18%)	820	97	1030	1.78	269	Chatterjee and Banerjee, 1999
Hangzhou	45.6	526.7	73.3	150.9	2.62	63.7	Lu et al., 2008
Huizhou	-	_	364.7	410.4	8.6	603.3	Qiu et al., 2009
Bilaspur	3590	793	34.7	24.5	0.69	7.00	Present Study
(b) Metal accumulated	in leaf						
City	Fe	Mn	Cr	Pb	Cd	Cu	Reference
Calcutta	3800 (0.38%)	141	16.6	214	0.47	40	Chatterjee and Banerjee, 1999
Waste bank	349	71.8	2.63	1.4	0.14	14.5	Swaileh et al., 2004
Huelva city (Median)	233.1	35.45	0.43	2.85	_	24.15	Oliva and Mingorance, 2006
Bilaspur	1919	232	10.7	3.87	6.65	4.99	Present Study

both Calcutta (0.47 μ g g⁻¹) and Waste Bank city (0.14 μ g g⁻¹). The mean value of Cu (7 μ g g⁻¹) in dust is two orders of magnitude lower than Calcutta (269 μ g g⁻¹) and Huizhou (603.3 μ g g⁻¹). In leaf (4.99 μ g g⁻¹), it was one order of magnitude lower than all respective cites.

4. CONCLUSION

This study was conducted to assess the deposition/ accumulation of metals (i.e., Fe, Mn, Pb, Cu, Cd, and Cr) on different plant species naturally growing at industrial locations. The overall results of this study indicate that Cd recorded the maximum accumulation in plants leaves from dust relative to other metals. Especially, Butea monosperma exhibited the highest accumulation of Cd. It was generally observed that in all metal cases, Butea monosperma showed the maximum accumulation of all tested plants species. Moreover, Alstonia scholaris also had good accumulation potential for all metals. The results of our study suggest that Butea monosperma and Alstonia scholaris should be a suitable plant species for the control of metal pollution to be planted on road side or nearby areas of industrial areas. However, it needs a thorough investigation to assure such effect in relation to metal distribution over diverse locations, plant types, and seasonality. Moreover, as these metals can also be absorbed/accumulated through soil, consideration of their distribution in the root zone soils of the target plant species should also be made.

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REFERENCES

Al-Khashman, O., Shawabkeh, R. (2006) Metal distribution in soils around the cement factory in southern Jordan. Environmental Pollution 140, 387-394.

- Alshayep, S.M., Seaward, M.R.D. (2001). Heavy metal content of roadside soils along ring road in Riyadh (Saudi Arabia). Asian Journal of Chemistry 13, 407-423.
- Banerjee, A.D.K. (2003) Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environmental Pollution 123, 95-105.
- Charlesworth, S., Everett, M., McCarthy, R., Ordonez, A., Miguel, E. (2003) A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. Environment International 29, 563-573.
- Chatterjee, A., Banerjee, R.N. (1999) Determination of lead and other metals in a residential area of greater Calcutta. The Science of the Total Environment 227, 175-185.
- Christoforidis, A., Stamatis, N. (2009). Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. Geoderma 151, 257-263.
- Divrikli, U., Soylak, M., Elci, L., Dogan, M. (2003). Trace heavy metal levels in street dust samples from Yozgat City Center, Turkey. Journal of Trace and Microprobe Techniques 21, 351-361.
- Gratani, L., Crescente, M.F., Varone, L. (2008) Long-term monitoring of metal pollution by urban trees. Atmospheric Environment 42, 8273-8277.
- Gueguen, F., Stille, P., Geagea, M.L., Boutin, R. (2012) Atmospheric pollution in an urban environment by tree bark biomonitoring-part I: trace element analysis. Chemosphere 86, 1013-1019.
- Lu, S.G., Zheng, Y.W., Bai, S.Q. (2008) A HRTEM/EDX approach to identification of the source of dust particles on urban tree leaves. Atmospheric Environment 42, 6431-6441.
- Markert, B. (1993) Plants as biomonitors/indicators for Heavy metals in the terrestrial Environment. VCH Press, Weinheim.
- Nagajyoti, P.C., Lee, K.D., Sreekant, T.V.M. (2010) Heavy Meatals, occurrence and toxicity for plants: a review. Environmental Chemistry Letters 8, 199-216.
- Oliva, S.R., Mingorance, M.D. (2006) Assessment of airborne heavy metal pollution by aboveground plant parts. Chemosphere 65, 177-182.
- Przybysz, A., Sæbø, A., Hanslin, H.M., Gawroński, S.W. (2014) Accumulation of particulate matter and trace elements on vegetation as affected by pollution level, rainfall and the passage of time. Science of the Total Environment 481, 360-369.
- Qiu, Y., Guan, D., Song, W., Huang, K. (2009) Capture of heavy metals and sulfur by foliar dust in urban Huizhou, Guangdong Province, China. Chemosphere 75, 447-452.
- Saarela, K.E., Harju, L., Rajander, J., Lill, J.O., Heselius, S.J., Lindroos, A., Mattsson, K. (2005) Elemental analyses of pine bark and wood in an environmental study. Science of the Total Environment 343, 231-241.

- Sawidis, T., Breuste, J., Mitrovic, M., Pavlovic, P., Tsigaridas, K. (2011) Trees as bioindicator of heavy metal pollution in three European cities. Environmental Pollution 159, 3560-3570.
- Serbula, S.M., Miljkovic, D.D., Kovacevic, R.M., Ilic, A.A. (2012). Assessment of airborne heavy metal pollution using plant parts and topsoil. Ecotoxicology and Environmental safety-76, 209-214.
- Sgrigna, G., Sæbø, A., Gawronski, S., Popek, R., Calfapietra, C., 2015. Particulate Matter deposition on Quercus ilex leaves in an industrial city of central Italy. Environmental Pollution 197, 187-194.
- Snezana, M., Dusanka, D.J., Renata, M., Ana, A. (2012) Assessment of airborne heavy metal pollution using

plant parts and topsoil. Ecotoxicology and Environmental Safety 76, 209-214.

- Swaileh, K.M., Hussein, R.M., Abu-Elhai, S. (2004) Assessment of Heavy Metal Contamination in Road Side Surface Soil and Vegetation from the west bank. Archives of Environmental Contamination and Toxicology 47, 23-30.
- Yongming, H., Peixuan, D., Junji, C., Posmentier, E. (2006) Multivariate analysis of heavy metal contamination in urban dusts in Xian, Central China. The Science of the Total Environment 355, 176-186.

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