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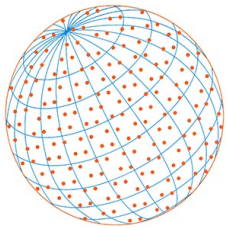

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Foliar Uptake of Toxic Metals Bound to Airborne Particulate Matter in an Urban Environment

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ABSTRACT

In this research, the foliar uptake patterns of three toxic metals (Pb, Cd, and Cu) bound to airborne particulate matter (PM) were investigated using two evergreen tree species (*Senna siamea* and *Alstonia scholaris*) at six different locations (two residential, traffic, commercial, and industrial) plus one control site in a subtropical urban environment. The concentrations of Pb, Cd, and Cu were measured from foliar dust, leaf, road dust, and soil samples collected from the target sites over two consecutive years. Their temporal variations in leaves were examined at monthly, seasonal, and annual scales. The data were evaluated statistically by One-way Analysis of variance ANOVA and correlation analysis along with enrichment factor (*EF*). There were significant variations on the monthly as well as the seasonal basis. Accordingly, PM-bound toxic metals in leaves come from an airborne route. In addition, leaves of *S. siamea* showed a moderately improved accumulation pattern relative to *A. scholaris*. This study suggests that these plants can be used efficiently as basic tools to assess the pollution and associated behavior of PM-bound toxic metals in an urban environment.

Keywords: Air pollution, Anthropogenic activity, Leaf accumulation, Toxic metals, biomonitoring

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1 INTRODUCTION

Metals are released from anthropogenic as well as natural sources. Anthropogenic activities such as traffic, industrialisation, and urbanisation significantly contribute to toxic metal pollution in the environment. Most of the toxic metals that occur in urban soil and air tend to originate from diverse man-made activities such as industrial and urban development and road traffic (Li *et al.*, 2013; Zheng *et al.*, 2010; Przybysz *et al.*, 2014). Plants perform remediation of soil pollution as they can accumulate toxic metals through their roots and leaves (Cho-Ruk *et al.*, 2006). In the last decade, some researchers have studied accumulation of PM-bound toxic metals in aerial plant parts (leaf and bark) (Sawidis *et al.*, 2011; Ayo, 2013; Gajbhiye *et al.*, 2016a, 2016b, 2016c), and plants with a large canopy cover and leaves have shown the ability to absorb PM-bound toxic metals effectively (Mori *et al.*, 2015). Hence, plants may also be used as biological filters for airborne PM and PM-bound metals (Simon *et al.*, 2014).

A great deal of effort has been made to explore the role of bioaccumulation/phytoremediation of toxic metals through soil. Most of the studies have been conducted for short periods (days or fortnight intervals) for phytomonitoring purposes (e.g., Simon *et al.*, 2016; Gajbhiye *et al.*, 2019). However, the concentration levels of these toxic metals can vary across different matrices (soil, road dust, foliar dust, and leaf) under the control of dynamic source processes and varying environmental conditions. Moreover, there is a scarcity of research work to help address the toxicity of airborne metals and their accumulation in plants. Thus, a long-term study is required to evaluate the foliar uptake pattern of these airborne toxic metals in relation to fluctuating environmental variables. Recently, it was reported that the trees *Senna siamea* and *Alstonia scholaris* have a higher

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accumulation potential for airborne toxic metals when compared to other dominant plants growing in similar areas such as *Mangifera indica*, *Pongamia pinnata*, *Kigelia pinnata*, *Butea monosperma*, *Ficus religiosa*, and *Azadirachta indica* (*Ref*). Taking the above fact into consideration, the present study encompasses a systematic long-term (2-year: March 2014 to February 2016) study at six sites of diverse source characteristics in the representative subtropical city of Bilaspur, India. *S. siamea* and *A. scholaris* were selected to study the accumulation pattern of toxic metals in leaves. To date, relatively little is known about the spatiotemporal variations in foliar transfer patterns of PM-bound metals on a real long-term basis. Hence, the present study was conducted to offer a deeper insight into the processes governing metal accumulation in plants. This in turn will help determine appropriate plants for the removal/management of the toxic species across the plant-air interface.

2 MATERIALS AND METHODS

2.1 Study Area

The study area (Bilaspur, C.G., India) is located between N 22°9–22°06 to E 82°15–82°04 and represents a tropical savanna climate zone (Köppen climate classification: Aw) (Gajbhiye *et al.*, 2016c). During the study period, the summers were very hot and dry and the maximum temperature rose to 47.5°C with an average temperature of 30.7°C. In the monsoon (rainy) season, the highest rainfall was recorded in July (352 mm) with an average of 218 mm. The temperature in winter varied between 9°C and 21.8°C (Source: TBC, IGKV, Bilaspur).

Bilaspur has seen substantial urbanization in the last few years, with many plans related to eco-tourism and industrialization. Due to this, use of vehicles in the city has also increased. The city is affected by a considerable number of strong source activities of toxic metals such as traffic, industry, and commercial business. The roads have been in a development stage for the last 10 years due to the operation of a mega-sewage project, and the problem of dust/PM is significant as a result. Due to these anthropogenic activities, the general public is prone to face health-related problems.

2.2 Description of Study Sites

Six study sites were selected to cover different directions in and around Bilaspur. The distance from Site 1 to Site 6 was 13.0 km. Sites were selected based on the characteristics of pollution sources, location, micro-meteorological parameters, availability of both target plants, and feasibility of sampling (Table 1).

The control site, Guru Ghasidas University, is 5 km north of Bilaspur's city center. This site was selected to assess the normal background level of target toxic metals in comparison to other sites that are affected considerably by anthropogenic activities. Site 2, Nature City, is a residential area located 5 km west of the city center (Fig. 1). This site is a road-side location with low traffic activity. Site 3, Rajiv Vihar residential area, is 6 km east of the city center and is in the vicinity of a busy

Table 1. Description of study sites.

S. No.	Site	Selected plants	GPS location	Site description
1	Site 1	1. *Senna siamea* 2. *Alstonia scholaris*	N = 22°07'34.9" E = 82°08'20.2"	Control, Guru Ghasidas University campus, Bilaspur. Clean and green environment.
2	Site 2	1. *Senna siamea* 2. *Alstonia scholaris*	N = 22°05'50.5" E = 82°06'09.6"	Nature city residential area, Uslapur, Bilaspur. Low traffic area.
3	Site 3	1. *Senna siamea* 2. *Alstonia scholaris*	N = 22°05'20.7" E = 82°10'59.6"	Rajiv Vihar residential area, Rajkishor nagar, Bilaspur, moderate traffic residential area.
4	Site 4	1. *Senna siamea* 2. *Alstonia scholaris*	N = 22°05'22.6" E = 82°08'35.5"	Nehru Chowk, Bilaspur. Heavy traffic load, dusty environment, heavy PM deposition on leaf surfaces.
5	Site 5	1. *Senna siamea* 2. *Alstonia scholaris*	N = 22°03'56.8" E = 82°08'47.7"	Vyapar Vihar, Bilaspur. Commercial area with considerable traffic.
6	Site 6	1. *Senna siamea* 2. *Alstonia scholaris*	N = 22°02'43.9" E = 82°07'55.2"	Sirgitti industrial area, Parsada, Bilaspur. Heavy PM deposition on leaves.

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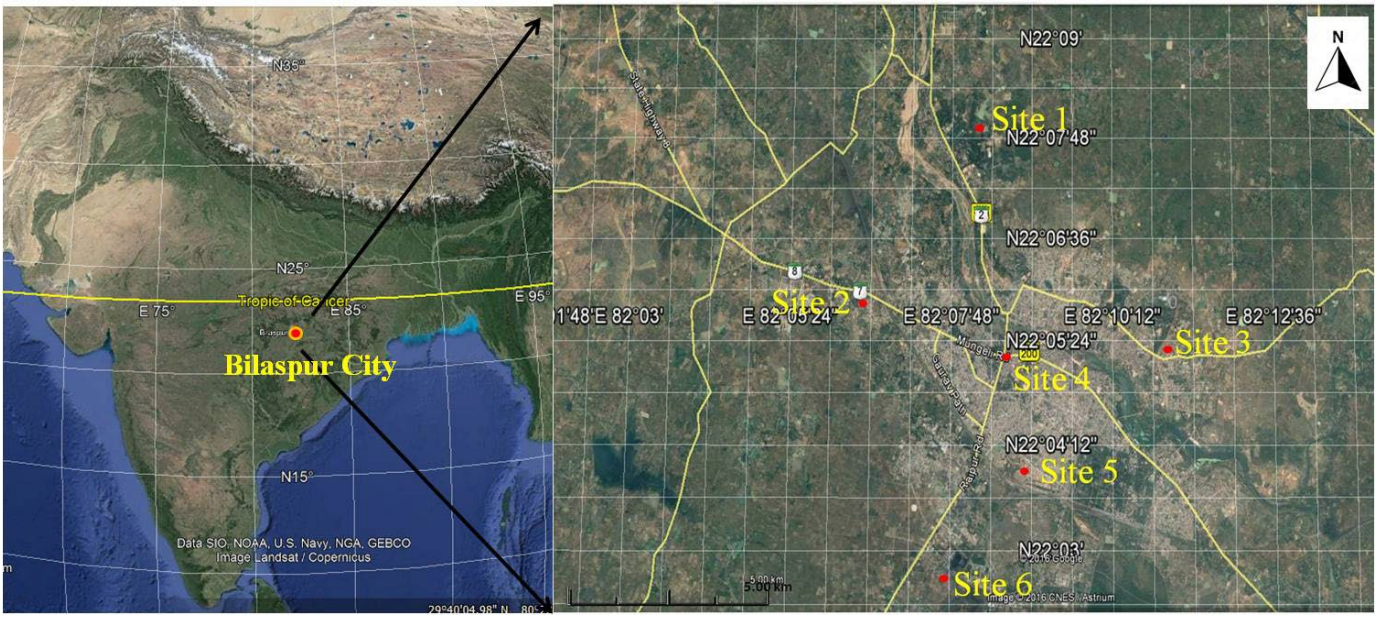

Fig. 1. Geographic locations of study sites in Bilaspur, Chhattisgarh, India: (1) Site 1- Control site: Guru Ghasidas University, Koni. (2) Site 2- Nature City residential area. (3) Site 3- Rajiv Vihar residential area. (4) Site 4- Nehru Chowk traffic square. (5) Site 5- Vyapar Vihar commercial area. (6) Site 6- Sirgitti industrial area. (Image source = Google earth).

road with moderate traffic. Site 4, Nehru Chowk, is the main traffic square of Bilaspur in the center of the city. This square is located at a national highway (NH 130) and is also the origin point of two highways, NH 130 A: Bilaspur (C.G.) to Pondi (C.G.) and NH 49: Bilaspur (C.G.) to Kharagpur (West Bengal). Nehru Chowk appears to be one of the most polluted and busiest squares of Bilaspur with high traffic/vehicular load. Site 5, Vyapar Vihar, is a commercial area 4 km south of the city center where most of the city's business activities take place. This area is also considered a polluted area of Bilaspur as it is affected by commercial vehicular pollution with a high load of PM. Site 6, Sirgitti, Parsada, is about 8 km south of the city center in an industrial zone. This area is developed by Chhattisgarh State Industrial Development Corporation Limited and is situated in Parsada at a national highway (NH 200). The industrial area is spread over 338 hectares, and 324 industries are established here (CSIDC, 2019). To meet the power supply, many big industries operate power plants. A large amount of air pollutants are released into the ambient air due to these industrial activities as well as through heavy vehicular exhaust. This site was selected to represent an industrial area.

2.3 Description of Target Plants for Detailed Study

Two predominant tree species were selected for the present study. *Senna siamea* (Lam.) H.S. Irwin & Barneby and *A.* scholaris (L.) R. Br. belong to the Fabaceae and Apocynaceae families, respectively. Detailed descriptions of these plants are given in SM.

2.4 Collection of Samples

Leaf, foliar dust (dust deposited on leaf surfaces), road dust, and soil samples were collected from each site. All samples were collected three times per month for two consecutive years (March 2014 to February 2016, n = 72).

2.4.1 Leaf samples

Leaves of *S. siamea* and *A. scholaris* were collected from each study site. Leaf samples were collected at a height of nearly 2.5 m above ground level at all sites to match the ambient height and minimize road dust re-suspension during sample collection**,** from the side of the edge facing the road. Special care was taken to collect only healthy leaves. The samples were collected in triplicate at each site.

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2.4.2 Foliar dust

For recovery of foliar dust, leaves were washed in deionized water (100 mL for 5 minutes) in a ceramic container. The container was then shaken gently. The suspension was heated at 100°C on a hot plate to evaporate the water. The PM was recovered after complete evaporation of water (Simon *et al.*, 2014).

2.4.3 Road dust

Road dust samples (10 g) were collected from four different places at each site near the plant locations using a steel tray. These four subsamples from each site were pooled and mixed properly to obtain a common sample. They were then sealed in airtight Ziploc bags and transported to the laboratory for further analyses (Gajbhiye *et al.*, 2019).

2.4.4 Soil samples

Soil samples were also collected from the topsoil (lower A-Horizon) ~35 cm depth and around the roots near the *S. siamea* and *A. scholaris* tree trunks by scraper plate method (Gajbhiye *et al.*, 2019). Four samples of topsoil were randomly collected from each study site. All collected samples were mixed to form a single uniform composite sample (10 g) from each site (Škrbić *et al.*, 2012).

2.5 Sample Preparation and Analysis of Metals

Foliar dust, washed leaves, road dust, and soil samples were dried up in an oven and crushed separately with a mortar and pestle to extract 0.5 g of sample for each sample type (Gajbhiye *et al.*, 2019). The mortar and pestle was washed and sterilized after each grinding of the sample. These samples were digested in a separate test tube in 10 mL of aqua-regia solution (HNO_3: HCl v/v 3:1). Samples were heated at 95 ± 5°C for 15 min without boiling to make the final volume up to 5 mL. Digested solutions were filtered through Whatman No. 1 filter paper and volumes were increased to 50 mL by adding distilled water for metal analysis (U.S. EPA, 1996).

The samples were analysed by a flame atomic absorption spectrophotometer (AA 7000, Shimadzu, Japan). Standard solutions for atomic absorption calibration were obtained from Inorganic Ventures, 300 technology drives, Christiansburg, VA 24073, USA. The standard solutions were primarily obtained at higher concentrations, i.e., for Fe (AAFe-1, 1000 ± 10 μg mL^{-1}, 2% (v/v) HNO_3 + de-ionized water, traceable to NIST-SRM 31269, for Pb (AAPb-1, 1000 ± 10 μg mL^{-1}, 0.5% HNO_3 + de-ionized water, traceable to NIST-SRM 3128), for Cd (AACd-1, 1000 ± 10 μg mL^{-1}, 3% (v/v) HNO_3 + de-ionized water, traceable to NIST-SRM 3108), and for Cu (AACu-1, 1000 ± 10 μg mL^{-1}, 3% (v/v) HNO_3 + de-ionized water, traceable to NIST-SRM 3114. These standard solutions were diluted to create a five-point calibration curve (ranging from 10 μg mL^{-1} to 200 μg mL^{-1}). Concentrations of target metals were measured based on the calibration curve and expressed in μg g^{-1}. Standard absorbance values were deducted according to the mean blank value for making calibration curves. Absorbance of unknown sample was also deducted according to the mean blank value. The US EPA method was used to determine the method detection limit (MDL) (U.S. EPA, 2016). The values of the MDL of four target metals were 0.046 μg g^{-1}, 0.007 μg g^{-1}, 0.011 μg g^{-1}, and 0.036 μg g^{-1} for Pb, Cd, Cu, and Fe, respectively. The limit of quantification (LOQ) values were 0.145 μg g^{-1}, 0.021 μg g^{-1}, 0.035 μg g^{-1}, and 0.114 μg g^{-1} for Pb, Cd, Cu, and Fe, respectively (Table S1). The precision was assessed in terms of % relative standard deviation (% RSD) by running three replicates of standard solutions and it fell below 5% for all metals (Table S1).

2.6 Enrichment Factor (EF)

EF was calculated as given by Lorenzini *et al.* (2006) and Ho *et al.* (2010).

$$EF = \frac{\left(S_{(E)}/S_{(R)}\right)_{sample}}{\left(C_{(E)}/C_{(R)}\right)_{crust}} \quad (1)$$

where $S_{(E)}$ is the concentration of a target metal (E) in the examined environmental sample, $S_{(R)}$ is the concentration of the reference metal in the examined environmental sample, $C_{(E)}$ is the concentration of a target metal (E) in the crust and $C_{(R)}$ is the concentration of the reference metal

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in crust. The $C_{(E)}$ value for Pb, Cd, and Cu were 20, 0.098, and 25 ppm (w/w), respectively. In this study, Fe was taken as a reference element ($C_{(R)}$ = 35,000 ppm) for derivation of EF (Taylor and McLennan, 1995). Accordingly, five categories of contamination were arbitrarily established as follows (Sutherland and Tolosa, 2000): EF < 2 = deficiently to minimal enrichment, 2 ≤ EF < 5 = moderate enrichment, 5 ≤ EF < 20 = significant enrichment, 20 ≤ EF < 40 = very high enrichment, EF ≥ 40 = extremely high enrichment. The concentration of Fe in different samples is given in Table S2.

3 RESULTS AND DISCUSSION

3.1 Spatio-temporal Variation in the Concentration of Metals

The concentrations of metals in the four different sample types (soil, road dust, foliar dust, and leaf of both plants) were determined on various spatio-temporal scales, i.e., annual (two years average), seasonal, and monthly.

3.1.1 Long-term (annual) variation in concentration of Pb, Cd, and Cu

As shown in Table S3(a), in soil samples, average Pb concentration varied from 11.6 ± 1.87 μg g^{-1} (control site: Site 1) to 23.3 ± 4.70 μg g^{-1} (Site 4). Likewise, in the case of road dust samples, Pb concentration was lowest at the control site (Site 1: 15.1 ± 1.35 μg g^{-1}) and highest at Site 4 (173 ± 41.5 μg g^{-1}). The foliar dust and leaf samples followed a similar trend and showed minimum concentration at the control site and maximum at Site 4 in both plants. However, there were moderate variations in the value of foliar dust and leaf samples between the two plants. For instance, in *S. siamea*, the concentration of Pb in foliar dust ranged from 8.34 ± 0.67 μg g^{-1} (Site 1) to 187 ± 45.9 μg g^{-1} (Site 4). In *A. scholaris*, the concentration of Pb in foliar dust ranged from 11.0 ± 1.39 μg g^{-1} (Site 1) to 172 ± 42.0 μg g^{-1} (Site 4). Likewise, in *S. siamea*, the concentration of Pb in leaf samples varied from 0.33 ± 0.13 μg g^{-1} (Site 1) to 52.7 ± 16.3 μg g^{-1} (Site 4). However, in *A. scholaris*, Pb in leaf samples ranged from 0.32 ± 0.05 μg g^{-1} (Site 1) to 35.5 ± 12.9 μg g^{-1} (Site 4).

Cd and Cu also showed a similar pattern as found in Pb. For instance, Cd and Cu showed the lowest concentration at the control site and the highest at Site 4 for all samples (soil, road dust, foliar dust and leaf) of *S. siamea* and *A. scholaris* (Tables S3(b) and S3(c)).

Analysis of variance (ANOVA) was conducted between average annual concentrations of Pb, Cd, and Cu across different study sites for different samples (Figs. 2(a–c)). Based on ANOVA, the variation in concentration of metals in soil samples across different sites was not statistically significant ($p > 0.05$). However, it was significant in the case of road dust, foliar dust, and leaves of both plants ($p < 0.001$).

When the magnitude of concentrations of Pb, Cd, and Cu at different sites were compared, the control site (Site 1) showed the lowest concentrations of Pb, Cd and Cu in all samples. The maximum concentrations of Pb, Cd and Cu were found at Site 4. Extending the comparison between metals, Cu showed the highest concentration followed by Pb and Cd, respectively. For instance, in soil samples, the maximum concentration of Cu (30.2 ± 9.02 μg g^{-1}) was more than 100 times higher than the Cd concentration (0.29 ± 0.20 μg g^{-1}). However, Pb (23.3 ± 4.70 μg g^{-1}) showed somewhat moderate and comparable values with Cu concentration in the soil samples. Similarly in the case of road dust, the maximum concentration of Cu was 196 ± 49.2 μg g^{-1} (Site 4), which was comparable with Pb concentration at Site 4 (173 ± 41.5 μg g^{-1}) but 50 times higher than Cd concentration (3.52 ± 1.70 μg g^{-1}) at the same site.

In the case of *S. siamea* foliar dust, Cu showed the highest concentration (305 ± 113 μg g^{-1}) at Site 4. At the same site, the concentrations of Pb (187 ± 45.9 μg g^{-1}) and Cd (4.70 ± 2.06 μg g^{-1}) were highest in foliar dust of *S. siamea*. A similar trend was observed in foliar dust samples of *A. scholaris*: Cu showed maximum concentration (292 ± 101 μg g^{-1}) followed by Pb (172 ± 42.0 μg g^{-1}) and Cd (3.67 ± 1.87 μg g^{-1}) at Site 4. In *S. siamea* leaf samples, the highest concentration of Pb (52.7 ± 16.3 μg g^{-1}) was comparably higher than the highest concentration of Cu (35.7 ± 15.3 μg g^{-1}) and nearly 20 times higher than the Cd concentration (2.28 ± 1.10 μg g^{-1}) at Site 4. In *A. scholaris* leaf samples, the highest Cd concentration (1.63 ± 0.96 μg g^{-1}) was nearly 20 times lower than the highest concentrations of Pb (35.5 ± 12.9 μg g^{-1}) and Cu (31.3 ± 15.0 μg g^{-1}) at Site 4 (Table S3).

As the different environmental samples were analysed for two consecutive years, the year-wise

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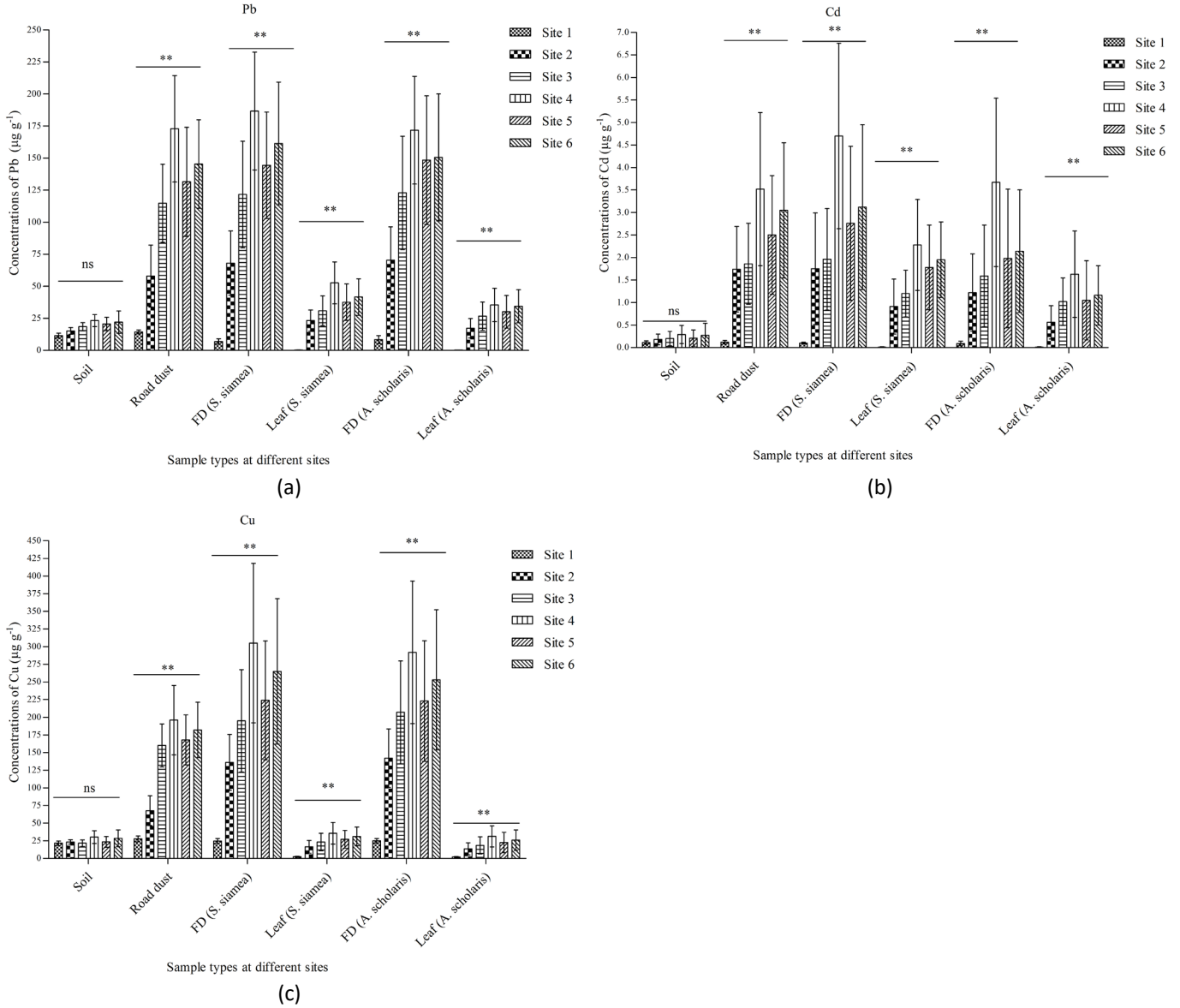

Fig. 2. Average concentrations (μg g^{-1}) of Pb, Cd, and Cu at six different study sites measured across the entire study period (2014–2016). The concentration values are expressed as mean ± SD (n = 72), The different numbers of asterisks on the bars shows ANOVA conducted across various sample types at different sites *$p < 0.05$, **$p < 0.001$, and ns = $p > 0.05$ (non-significant).

differences in the concentration of metals for all the samples were also evaluated. The results showed that there were slight variations in mean concentration of target metals between two years. When these differences were assessed for statistical significance based on a t-test, there were significant differences ($p < 0.05$) for only two cases (at Site 2 and Site 5 for Pb) (Fig. S1). However, there were insignificant differences in the mean concentrations of Pb between two years at other sites (Site 3, 4, and 6). On the other hand, no significant differences were found for the mean concentrations of other target metals (Cu and Cd) between two years.

3.1.2 Seasonal variation in toxic metal concentrations at different study sites

In order to study the impact of seasonality on Pb, Cd, and Cu concentrations, the data sets were grouped and averaged on a seasonal basis (i.e., summer, rainy, and winter).

At the control site (Site 1), the variations for all the sample types across seasons were insignificant based on ANOVA (Table S4(a), Fig. 3(a)). Moreover, there were insignificant variations (ANOVA, $p > 0.05$) in soil samples across three seasons at all the sites (Site 1 to Site 6). These results suggest

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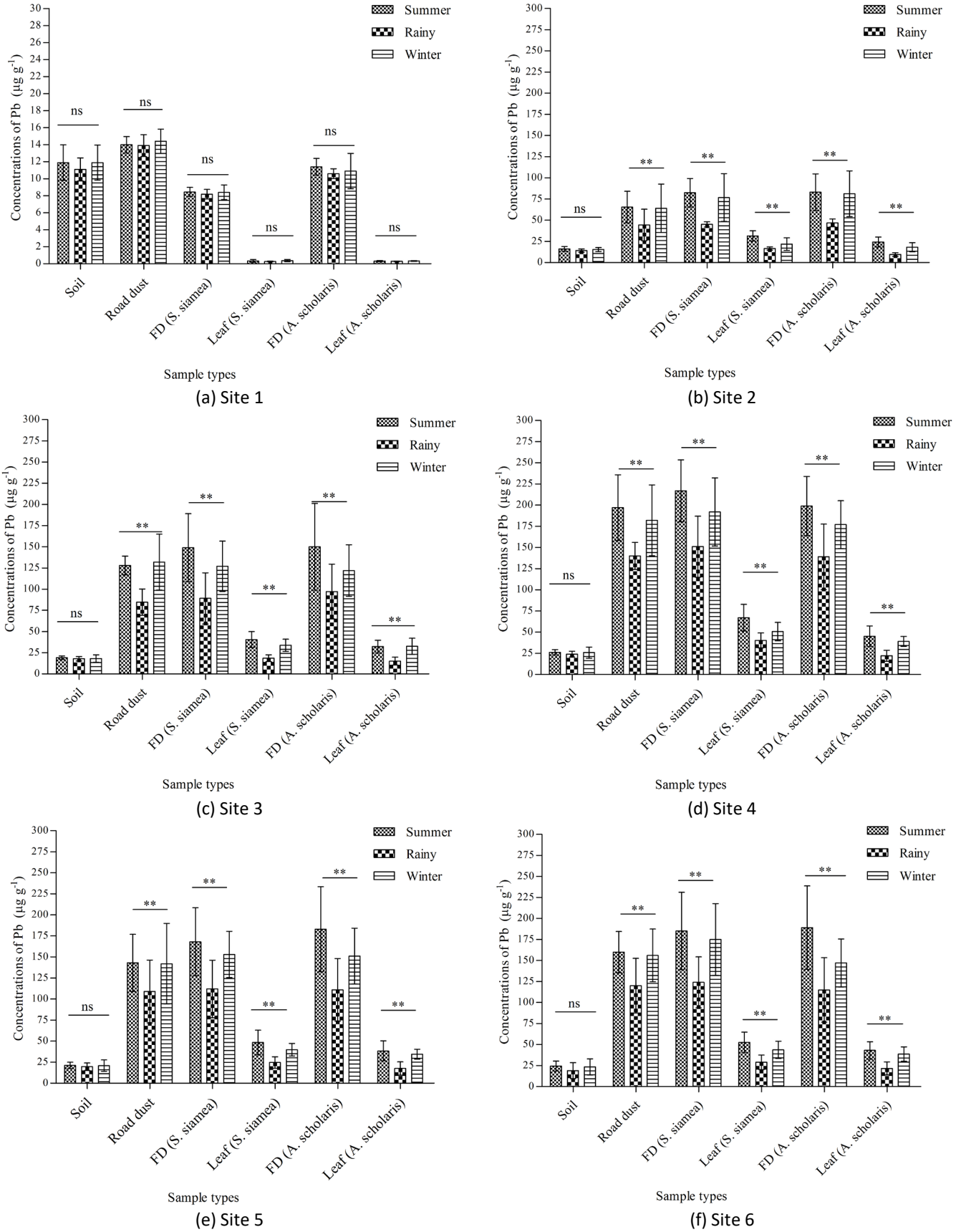

Fig. 3. Seasonal variations in concentration of Pb in different samples (soil, road dust, foliar dust, and leaf) during the entire study period (2014–2016). The concentration values are expressed as mean ± SD (n = 72), The different numbers of asterisks on the bars shows ANOVA conducted across various sample types at different sites *$p < 0.05$, **$p < 0.001$, and ns = $p > 0.05$ (non-significant).

that the control site was not affected by significant source activities. On the other hand, in other samples (road dust, foliar dust and leaf samples of both plants), the highest concentrations were found in summer, followed by winter and the rainy season (Figs. 3(b–f)). Moreover, seasonal Pb concentration showed significant variation (ANOVA, $p < 0.001$) in road dust, foliar dust, and leaf at Site 2 to Site 6. The results suggest that there are seasonal influences on partitioning of target toxic metals. Cd and Cu followed a similar trend as Pb (Tables S5, S6 and Figs. 4, 5).

3.1.3 Monthly variation in toxic metal concentrations at different study sites

As shown in Figs. S2(a), S3(a), S4(a), the control site (Site 1) did not show significant variations in concentrations of Pb, Cd, and Cu in different sample types (soil, road dust, foliar dust, and leaf). Moreover, the variations were not significant for soil samples from other sites (Site 2 to Site 6) across monthly concentrations of Pb, Cd, and Cu (ANOVA, $p > 0.05$). However, monthly concentrations of Pb, Cd and Cu at Site 2 to Site 6 showed highly significant variations in road dust, foliar dust, and leaf samples ($p > 0.05$ and $p > 0.001$) (Figs. S2(b–f), S3(b–f), and S4(b–f)).

3.2 Distribution Behavior of Target Metals in Different Matrices across Different Study Sites

The concentrations of metals in all samples followed the same order, i.e., the highest at Site 4 followed by Site 6, Site 5, Site 3, Site 2, and Site 1 (control site). High concentrations of metals in all samples at Site 2 to Site 6 revealed that they came from anthropogenic activities like traffic emissions, industrialisation, and power plant emissions (e.g., Al-khashman and Shawabkeh, 2006; Christoforidis and Stamatis, 2009). Site 4 represents the highest traffic density of both heavy and light vehicles compared to other sites. On the basis of concentration of toxic metals (Pb, Cd, and Cu) in samples, Site 6 can be ranked as the second most polluted site in the present study. Site 6 is an industrial site that includes coal and fly ash-based power plants and sponge iron industries along with traffic emissions from transportation. Site 5, with light and commercial vehicular activity, showed moderate levels of toxic metal emission in all samples. Site 2 and Site 3 were residential areas with moderate traffic. The least concentration of toxic metals in all samples was found at Site 1 with minimal/negligible anthropogenic source signatures.

Other than soil, if we compare the magnitude of concentration between different sample types, the highest concentration was found in foliar dust followed by road dust and leaf, respectively. Moreover, variations in metal concentrations between all sites were significant at $p < 0.001$ level for road dust, foliar dust, and leaf samples of both plants. Hence, non-significant variation ($p > 0.05$) in soil samples from all sites revealed that Pb, Cd, and Cu were not significantly enriched by anthropogenic influence in soil samples. However, the significant concentrations of toxic metals in other samples (road dust, foliar dust, and leaf) at Site 2 to Site 6 showed low to significant anthropogenic impact, especially from airborne sources.

On a seasonal basis, the highest concentrations of Pb, Cd, and Cu were found in all the sample types in summer, followed by winter and the rainy season. If we extend this comparison more specifically between seasons, the results of rainy season distinguished more prominently. However, when we consider site-wise seasonal variation for the entire study period, all sites showed significant variations for all samples except Site 1 and soil samples. This is probably due to negligible pollution sources on Site 1 and soil samples. The seasonal concentrations of Pb, Cd, and Cu showed a similar pattern with the maximum in summer followed by winter and rainy seasons, respectively in almost all samples from Site 2 to Site 6. The control site (Site 1) showed a mixed pattern in metal concentrations in samples as it seems to be affected by minimal anthropogenic activity. The other sites showed significant variations in seasonal concentration in all sample types except soil. The maximum concentrations of all metals were at Site 4 (heavy traffic square site) and minimum at Site 1 (control site). It was also noticed that the soil samples of all sites did not show significant variations in their seasonal concentration for all three metals. On the other hand, other samples showed significant seasonal variation in their concentrations. This reveals that the distribution in metal concentration is influenced by meteorological factors (Voutsa *et al.*, 2002; Pacyna *et al.*, 2007). Thomaidis *et al.* (2003) reported that concentrations of airborne toxic metals in PMs were notably affected by meteorological conditions (wind direction, air temperature, and relative humidity) in Athens, Greece, at different study sites.

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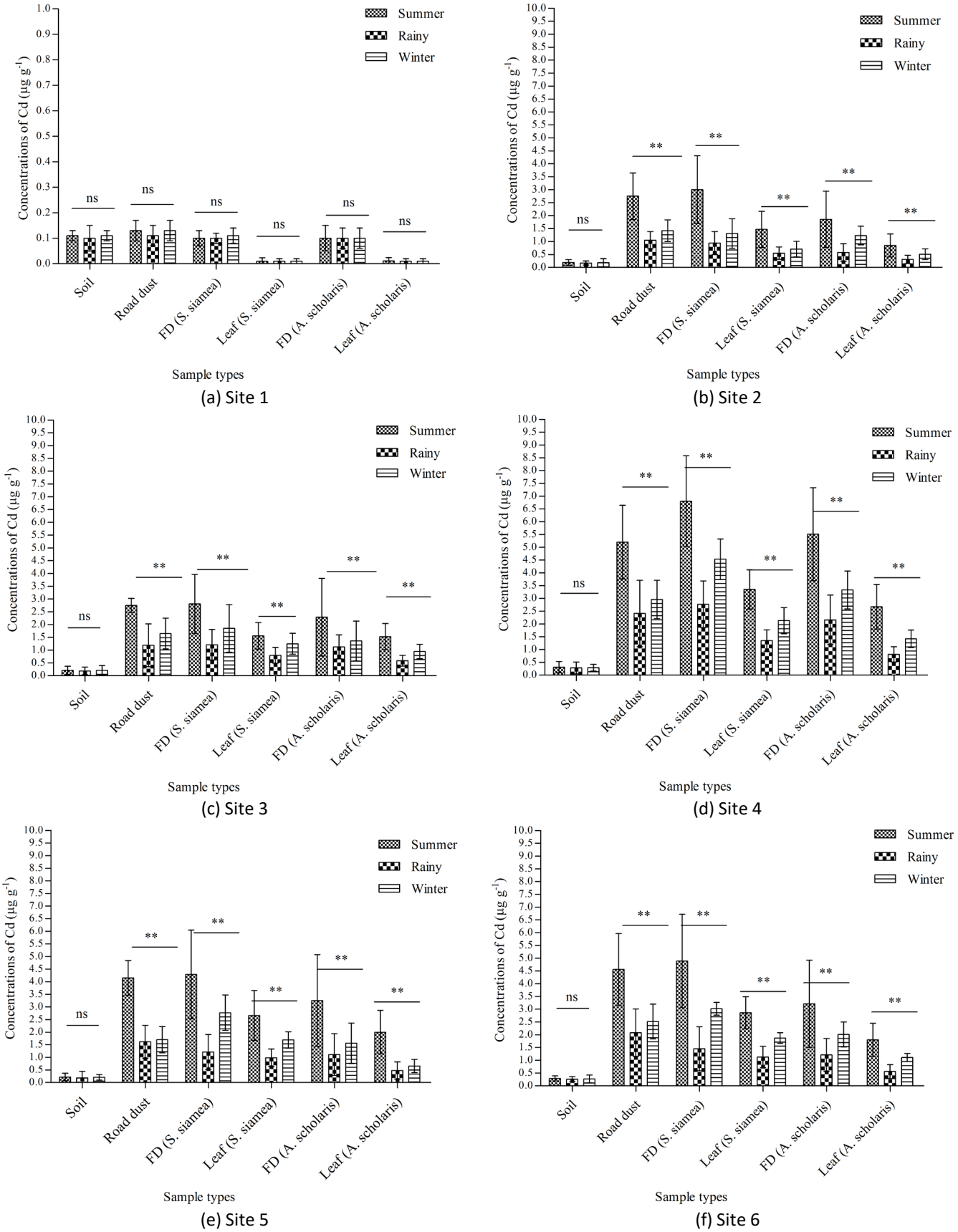

Fig. 4. Seasonal variations in concentrations of Cd in different samples (soil, road dust, foliar dust, and leaf) during the entire study period (2014–2016). The concentration values are expressed as mean ± SD (n = 72), The different numbers of asterisks on the bars shows ANOVA conducted across various sample types at different sites *$p < 0.05$, **$p < 0.001$, and ns = $p > 0.05$ (non-significant).

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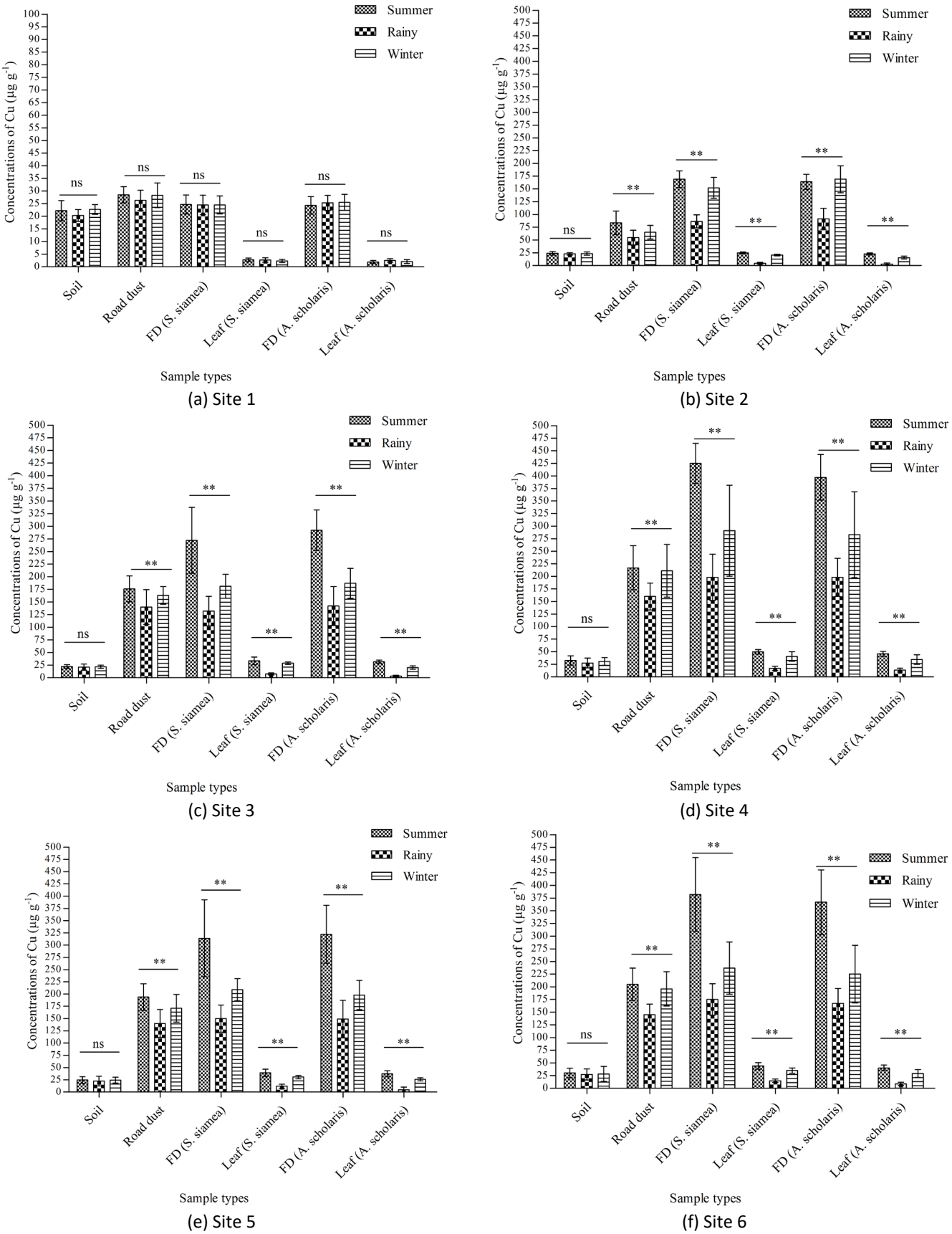

Fig. 5. Seasonal variations in concentrations of Cu in different samples (soil, road dust, foliar dust, and leaf) during the entire study period (2014–2016). The concentration values are expressed as mean ± SD (n = 72), The different numbers of asterisks on the bars shows ANOVA conducted across various sample types at different sites *$p < 0.05$, **$p < 0.001$, and ns = $p > 0.05$ (non-significant).

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In contrast to the present study, concentrations of metals in PM_{10} were highest during the winter in Thessaloniki, Greece, and showed temporal changes in metal concentration due to traffic activity and meteorological conditions (Voutsa *et al.*, 2002). Moreover, there were significant spatio-temporal variations in metal concentrations in leaf samples of *Betula verrucose*, *Salix fragilis*, *Acer plantanoides*, and *Tilia platyphyllos* (Piczak *et al.*, 2003). Similarly, the leaves of *Aesculus hippocastanum* showed a seasonal influence on Pb and Cd concentration (Kim and Fergusson, 1994). Hence, seasonal variations in metal concentration represent the meteorological effect in their distribution and contamination levels. The results of the present seasonal study are in agreement with those from Istanbul, Turkey (Baycu *et al.*, 2006). They reported that the maximum concentration of metals in different deciduous plants leaves was found in the spring and the minimum in the autumn. Temporal changes in metal concentration depended on atmospheric deposition (Baycu *et al.*, 2006; Mijic *et al.*, 2010; Gajbhiye *et al.*, 2016c). As such, atmospheric depositions may contain airborne toxic metals, which may be partitioned from traffic activity and resuspension of road dust (Mijic *et al.*, 2010; Aničić *et al.*, 2011).

Based on the aforementioned discussion, it is apparent that leaves of *S. siamea* and *A. scholaris* have potential to accumulate the target toxic metals from airborne sources. Except at the control site (Site 1) and in soil samples from all sites, foliar dust, road dust, and leaf showed significant variations in metal concentrations (ANOVA). This indicates that metal concentration is highly influenced by varying levels of source activities (e.g., traffic, industrial, power plant emission, and long-range transport).

3.3 EFs of Target Metals in Different Matrices

In order to assess the pollution level of target metals and ascertain their probable anthropogenic origin, EF was determined, considering Fe as a reference element in the earth's crust (e.g., Lorenzini *et al.*, 2006).

EFs of Pb at different study sites derived across the entire study period (March 2014–February 2016) are summarized in Table 2. In soil samples, EF ranged from 0.44 (control site, Site 1) to 0.75 (Site 4), which corresponds to deficiency to minimal enrichment. On the other hand, the value of EF at the control site for all samples (soil, road dust, foliar dust and leaf) was also below 2 with negligible anthropogenic influence. In the case of road dust, EF ranged from 2.36 (Site 2) to 6.50 (Site 4). Sites 4, 5, and 6 showed EF values in the significant enrichment category ($5 \leq EF < 20$). In the case of *S. siamea* foliar dust, EF ranged from 7.87 (Site 2: significant enrichment) to 21.2 (Site 4: very high enrichment). In *A. scholaris* foliar dust, EF ranged from 6.04 (Site 2) to 12.0 (Site 4).

Table 2. EFs of target metals in different matrices.

	Plant	Sample	S1	S2	S3	S4	S5	S6
Pb		Soil	0.44	0.47	0.57	0.75	0.68	0.71
		Road dust	1.01	2.36	4.47	6.5	5.34	5.51
	Senna siamea	Foliar dust	0.47	7.87	14.5	21.2	15.5	18.9
		Leaf	0.23	13.6	20	33.4	23.1	25.6
	Alstonia scholaris	Foliar dust	0.59	6.04	8.92	12	10.6	11.2
		Leaf	0.22	11.7	18	25.7	20.6	25
Cd		Soil	0.84	1.14	1.27	1.91	1.41	1.76
		Road dust	1.63	14.4	14.7	27	20.7	23.6
	Senna siamea	Foliar dust	1.15	41.3	47.4	109	60.4	74.8
		Leaf	1.42	109	158	295	223	244
	Alstonia scholaris	Foliar dust	1.1	21.4	23.5	52.2	29	32.5
		Leaf	1.39	77.5	140	241	147	175
Cu		Soil	0.65	0.58	0.54	0.78	0.62	0.73
		Road dust	1.48	2.2	4.97	5.9	5.44	5.53
	Senna siamea	Foliar dust	1.11	12.6	18.5	27.7	19.2	24.9
		Leaf	1.43	7.77	12	18.1	13.3	15.3
	Alstonia scholaris	Foliar dust	1.08	9.7	12	16.3	12.8	15
		Leaf	1.17	7.38	10	17.9	12.4	15.4

Hence, for foliar dust, all sites had a value between $5 \leq EF < 20$, suggesting significant enrichment. In *S. siamea* leaf samples, EF ranged from 13.6 (Site 2) to 33.4 (Site 4). Except Site 2, other sites (Site 3, Site 4, Site 5, and Site 6) had EF values between $20 \leq EF < 40$ (very high enrichment). In *A. scholaris* leaf samples, EF ranged from 11.7 (Site 2) to 25.7 (Site 4). Sites 2 and 3 showed significant enrichment ($5 \leq EF < 20$). Moreover, Sites 4, 5, and 6 showed very high EF (between $20 \leq EF < 40$: very high enrichment).

Cd and Cu showed a similar EF pattern to Pb. For instance, in soil samples, EF was below 2 (Table 2). In addition, all samples from the control site showed EF in the deficiency to minimal enrichment ($EF < 2$) categories. However, other samples showed different patterns of EF. In the case of Cd, in foliar dust of *S. siamea*, all sites showed an $EF \geq 40$, corresponding to extremely high enrichment. In foliar dust of *A. scholaris*, Sites 2, 3, 5, and 6 showed EF at $20 \leq EF < 40$, or very high enrichment. Moreover, Site 4 had EF (52.2) at $EF \geq 40$, in the extremely high enrichment category. In *S. siamea* and *A. scholaris* leaves, both plants showed a similar trend ($EF \geq 40$: extremely high enrichment of Cd). For Cu, in foliar dust of both plants, all sites showed an $EF < 20$ as significant enrichment. Moreover, foliar dust of *S. siamea* at Site 4 (EF = 27.7) and Site 6 (EF = 24.9) showed very high enrichment. EF in leaf samples of both plants ranged from 7.38 (Site 2: leaf of *S. siamea*) to 17.9 (Site 4: *A. scholaris*), suggesting significant enrichment ($5 \leq EF < 20$).

EFs were also derived on a seasonal basis for all three metals. Results revealed that at the control site (Site 1) all samples showed an EF value below 2 (Table S7, S8, and S9). In general, soil samples showed deficiency to minimal enrichment ($EF < 2$) at all sites (Site 1 through Site 6).

If the magnitude of EF were compared across sample types, in the case of Pb and Cd, maximum EF was found in leaf followed by foliar dust and road dust. In Cu, it was highest in foliar dust followed by leaf and road dust. Moreover, maximum EF was found at Site 4, which revealed extreme influence of anthropogenic activity in metal concentration. Moreover, sites other than the control site showed maximum EF in summer, followed by winter and the rainy season.

In the case of Pb and Cd, leaf samples of both plants showed higher EF in comparison to the other samples (foliar dust, road dust). EFs were higher in foliar dust in most cases except a few, where it was highest in leaves. On the seasonal basis, EF followed the order summer > winter > rainy (in road dust, foliar dust, and leaf samples of both plants) for all three target metals. This agrees with previous studies in Belgrade (Serbia) and Europe that anthropogenic emissions of metals prevail in the summer (Pacyna *et al.*, 2007; Aničić *et al.*, 2011). In leaves, both plants showed a regular seasonal accumulation trend for the selected metals (Pb, Cd, and Cu: summer > winter > rainy). In contrast, the leaves of *Aesculus hippocastanum* and *Tilia* spp. did not show regular seasonal accumulation patterns for Cu (Aničić *et al.*, 2011). Moreover, the highest EF was found in Cd followed by Pb, and Cu.

3.4 Inter-relationships of Target Metal Concentrations between Different Matrices

In the present study, a Pearson correlation was conducted between leaves of both plants vs. soil, road dust, and foliar dust to identify the major route of metal contamination.

For Pb, Cd, and Cu, the correlation between leaf vs. soil and road dust was not significant at the control site (Site 1). At the other sites (Site 2 to Site 6), the correlations between leaf vs. soil samples were not significant (Table S10, S11, and S12). In the present study, concentrations of Pb, Cd, and Cu in soil did not show significant correlations with leaf samples, suggesting that the plants had less chance of accumulation of metals from the soil. This is in agreement with recent studies conducted in Bilaspur (Gajbhiye *et al.*, 2016c, 2019). On the other hand, a significant correlation ($p < 0.05$ to $p < 0.001$) was found between leaf vs. foliar dust and road dust of both *S. siamea* and *A. scholaris*. In a previous study, leaves showed active accumulation of selected metals (Pb, Cd, and Cu) from foliar dust with highly significant correlation (Liu *et al.*, 2013). Leaves of *Nerium oleander* showed significant correlation with PM_{10} for Cu and Fe (Espinosa and Oliva, 2006). The correlation analysis between toxic metal concentrations in foliar dust is used as an efficient approach to assessing the source of airborne toxic metal pollution (Liang *et al.*, 2017). The concentration of metals in leaves is directly connected to urbanization with traffic and industrial activities (Mori *et al.*, 2015). Moreover, the correlation results of leaf vs. road dust of both plants were better than those of leaf vs. foliar dust in terms of level of significance. If we

compare the correlation between plants, *S. siamea* showed better results than *A. scholaris*. Based on the above results, it is evident that PM-bound Pb was partitioned in plant leaves from foliar dust/road dust resuspension (airborne sources) and enrichment from soil was insignificant.

4 CONCLUSIONS

Based on concentration values found in different sample types (soil, road dust, foliar dust, and leaf), correlation analyses, and EF observations, it can be concluded that Pb, Cd, and Cu accumulate in the leaves of the selected plants by an airborne route. The airborne foliar transfer of selected toxic metals is considered a less common route for accumulation of toxic metals in plants. *S. siamea* showed relatively better accumulation potential than *A. scholaris*. Evergreen tree species such as *S. siamea* and *A. scholaris* can be used as effective phytomonitors for toxic metals in the environment. They can also be used as a suitable means to reduce airborne PM and PM-bound metals. However, one needs to determine the critical/toxic levels of metals for a given plant species and should restrict use of the plants and/or plant parts growing in affected areas.

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SUPPLEMENTARY MATERIAL

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REFERENCES

Al-Khashman, O.A., Shawabkeh, R.A. (2006). Metals distribution in soils around the cement factory in southern Jordan. Environ. Pollut. 140, 387–394. https://doi.org/10.1016/j.envpol.2005.08.023

Aničić, M., Spasić, T., Tomašević, M., Rajšić, S., Tasić, M. (2011). Trace elements accumulation and temporal trends in leaves of urban deciduous trees (*Aesculus hippocastanum* and *Tilia spp.*). Ecol. Indic. 11, 824–830. https://doi.org/10.1016/j.ecolind.2010.10.009

Ayo, G.O. (2013). Proximate and mineral compositions of the leaves and stem bark of *Cassia nigricans* Vahl. Int. J. Med. Plant Res. 2, 242–246. https://www.internationalscholarsjournals.com/articles/proximate-and-mineral-compositions-of-the-leaves-and-stem-bark-of-cassia-nigricans-vahl.pdf

Baycu, G.I., Tolunay, D., Ozden, H., Gunebakan, S. (2006). Ecophysiological and seasonal variations in Cd, Pb, Zn, and Ni concentrations in the leaves of urban deciduous trees in Istanbul. Environ. Pollut. 143, 545–554. https://doi.org/10.1016/j.envpol.2005.10.050

Chhattisgarh State Industrial Development Corporation Ltd. (CSIDC) (20119). Industrial Growth Centre Sirgitti. https://csidc.in/home2/index.php/en/2015-01-25-07-31-44/2015-01-25-07-32-27/igc-sirgitti (accessed 6 January 2019).

Cho-Ruk, K., Kurukote, J., Supprung, P., Vetayasuporn, S. (2006). Perennial plants in the phytoremediation of lead-contaminated soils. Biotechnology 5, 1–4. https://doi.org/10.3923/biotech.2006.1.4

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. https://doi.org/10.1016/j.geoderma.2009.04.016

Espinosa, A.F., Oliva, S.R. (2006). The composition and relationships between trace element levels in inhalable atmospheric particles (PM_{10}) and in leaves of *Nerium oleander L.* and *Lantana camara L.* Chemosphere 62, 1665–1672. https://doi.org/10.1016/j.chemosphere.2005.06.038

Gajbhiye, T., Kim, K.H., Pandey, S.K., Brown, R.J. (2016a). Foliar transfer of Dust and Heavy Metals on roadside Plants in a subtropical Environment. Asian J. Atmos. Environ. 10, 137–145. https://doi.org/10.5572/ajae.2016.10.3.137

Gajbhiye, T., Pandey, S.K., Kim, K.H. (2016b). Factors controlling the Deposition of Airborne Metals on Plant Leaves in a subtropical Industrial Environment. Asian J. Atmos. Environ. 10, 162–167. https://doi.org/10.5572/ajae.2016.10.3.162

Gajbhiye, T., Pandey, S.K., Kim, K.H., Szulejko, J.E., Prasad, S. (2016c). Airborne foliar transfer of PM bound heavy metals in *Cassia siamea*: A less common route of heavy metal accumulation. Sci. Total Environ. 573, 123–130. https://doi.org/10.1016/j.scitotenv.2016.08.099

Gajbhiye, T., Pandey, S.K., Lee, S.S., Kim, K.H. (2019). Size fractionated phytomonitoring of airborne particulate matter (PM) and speciation of PM bound toxic metals pollution through *Calotropis procera* in an urban environment. Ecol. Indic. 104, 32–40. https://doi.org/10.1016/j.ecolind.2019.04.072

Ho, H.H., Swennen, R., Van Damme, A. (2010). Distribution and contamination status of heavy metals in estuarine sediments near Cua Ong Harbor, Ha Long Bay, Vietnam. Geol. Belg. 37–47. https://popups.uliege.be/1374-8505/index.php?id=2844

Kim, N.D., Fergusson, J.E. (1994). Seasonal variations in the concentrations of cadmium, copper, lead and zinc in leaves of the horse chesnut (*Aesculus hippocastanum* L.). Environ. Pollut. 86, 89–97. https://doi.org/10.1016/0269-7491(94)90010-8

Li, X., Liu, L., Wang, Y., Luo, G., Chen, X., Yang, X., Hall, M.H., Guo, R., Wang, H., Cui, J., He, X. (2013). Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China. Geoderma 192, 50–58. https://doi.org/10.1016/j.geoderma.2012.08.011

Liang, J., Fang, H.L., Zhang, T.L., Wang, X.X., Liu, Y.D. (2017). Heavy metal in leaves of twelve plant species from seven different areas in Shanghai, China. Urban For. Urban Greening 27, 390–398. https://doi.org/10.1016/j.ufug.2017.03.006

Liu, L., Fang, Y.M., Wang, S.C., Xie, Y., Yang, D.D. (2013). Leaf micro-morphology and features in adsorbing air suspended particulate matter and accumulating heavy metals in seven trees species. Environ. Sci. 34, 2361–2367. (in Chinese)

Lorenzini, G., Grassi, C., Nali, C., Petiti, A., Loppi, S. Tognotti, L. (2006). Leaves of Pittosporum tobira as indicators of airborne trace element and PM_{10} distribution in central Italy. Atmos. Environ. 40, 4025–4036. https://doi.org/10.1016/j.atmosenv.2006.03.032

Mijic, Z., Stojic, A., Perisic, M., Rajsic, S., Tasic, M., Radenkovic, M., Joksic, J. (2010). Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade. Atmos. Environ. 44, 3630–3637. https://doi.org/10.1016/j.atmosenv.2010.06.045

Mori, J., Hanslin, H.M., Burchi, G., Sæbø, A. (2015). Particulate matter and element accumulation on coniferous trees at different distances from a highway. Urban For. Urban Greening 14, 170–177. https://doi.org/10.1016/j.ufug.2014.09.005

Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., Friedrich, R. (2007). Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. Atmos. Environ. 41, 8557–8566. https://doi.org/10.1016/j.atmosenv.2007.07.040

Piczak, K., Leśniewicz, A., Żyrnicki, W. (2003). Metal concentrations in deciduous tree leaves from urban areas in Poland. Environ. Monit. Assess. 86, 273–287. https://doi.org/10.1023/A:1024076504099

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. Sci. Total Environ. 481, 360–369. https://doi.org/10.1016/j.scitotenv.2014.02.072

Sawidis, T., Breuste, J., Mitrovic, M., Pavlovic, P., Tsigaridas, K. (2011). Trees as bioindicator of heavy metal pollution in three European cities. Environ. Pollut. 159, 3560–3570. https://doi.org/10.1016/j.envpol.2011.08.008

Simon, E., Baranyai, E., Braun, M., Cserháti, C., Fábián, I., Tóthmérész, B. (2014). Elemental concentrations in deposited dust on leaves along an urbanization gradient. Sci. Total Environ.

490, 514–520. https://doi.org/10.1016/j.scitotenv.2014.05.028

Simon, E., Harangi, S., Baranyai, E., Fábián, I., Tóthmérész, B. (2016). Influence of past industry and urbanization on elemental concentrations in deposited dust and tree leaf tissue. Urban For. Urban Greening 20, 12–19. https://doi.org/10.1016/j.ufug.2016.07.017

Škrbić, B., Milovac, S., Matavulj, M. (2012). Multielement profiles of soil, road dust, tree bark and wood-rotten fungi collected at various distances from high-frequency road in urban area. Ecol. Indic. 13, 168–177. https://doi.org/10.1016/j.ecolind.2011.05.023

Sutherland, R.A., Tolosa, C.A. (2000). Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu, Hawaii. Environ. Pollut. 110, 483–495. https://doi.org/10.1016/S0269-7491(99)00311-5

Taylor, S.R., McLennan, S.M. (1995). The geochemical evolution of the continental crust. Rev. Geophys. 33, 241–265. https://doi.org/10.1029/95RG00262

Thomaidis, N.S., Bakeas, E.B., Siskos, P.A. (2003). Characterization of lead, cadmium, arsenic and nickel in $PM_{2.5}$ particles in the Athens atmosphere, Greece. Chemosphere 52, 959–966. https://doi.org/10.1016/S0045-6535(03)00295-9

U.S. Environmental Protection Agency (U.S. EPA) (1996). Method 3050B: Acid Digestion of Sediments, Sludges, and Soils. https://www.epa.gov/sites/default/files/2015-12/documents/3050b.pdf (accessed 30 August 2018).

U.S. Environmental Protection Agency (U.S. EPA) (2016). Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. EPA 821-R-16-006. https://www.epa.gov/sites/production/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf (accessed 1 August 2018).

Voutsa, D., Samara, C., Kouimtzis, T., Ochsenkühn, K. (2002). Elemental composition of airborne particulate matter in the multi-impacted urban area of Thessaloniki, Greece. Atmos. Environ. 36, 4453–4462. https://doi.org/10.1016/S1352-2310(02)00411-9

Zheng, N., Liu, J., Wang, Q., Liang, Z. (2010). Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China. Sci. Total Environ. 408, 726–733. https://doi.org/10.1016/j.scitotenv.2009.10.075