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RESEARCH ARTICLE

STUDY OF AIRBORNE METAL DEPOSITION ON SOME PLANT SPECIES AT VARIOUS DISTANCES FROM NATIONAL HIGHWAY 24 AND PARKS OF URBAN MORADABAD, INDIA

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ABSTRACT

The present investigation is carried out at two urban parks to assess the soil metal and atmospheric heavy metals in plant species which are commonly growing at varying distances from heavily trafficked National Highway 24 in Moradabad city. Emission of heavy metals from the automobile exhaust and brassware industries nearby the highway contaminates the soil and surrounding plants. Unwashed leaves samples were used to assess the of total metal concentration (Cr, Cu, Cd, Fe, Ni, Zn, Pb) and for the purpose six common plant species i.e. *Ficus rumphii, Polyalthia longifolia, Bauhinia variegata, Delonix regia, Alstonia scholaris and Anthocephalus kadamba* were collected from both sites and were analyzed by Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES). The results indicate that the plants species such as *Bauhinia variegata* is sensitive among all the species having highest concentration of heavy metals at both of the sites and *Ficus rumphii* with lowest concentration, is tolerant among all the species. It possibly may be due to differences in plant morphology and leaf surface and apparently particulate size decides the extent of solubility providing the bioavailability of metals to primary consumers. Univariate (correlation study) and Multivariate statistical analysis were adopted including; factor analysis, cluster analysis and enrichment factor analysis to identify the sources and their contribution to urban soil. The major source of airborne trace metals identified were brassware industries, illegal e-waste burning automobile emissions and combustion processes.

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INTRODUCTION

Heavy metals are integrated components of the biosphere and occur naturally in soil and plants (Ali *et al*., 2013; Zan *et al*., 2014). Frequently, the heavy metals, causing toxicity in plants, are biologically non-essential and these include cadmium (Cd), Lead (Pb), and chromium (Cr). These non-essential heavy metals could be immensely harmful to plants even in very small amount of the potentially toxic heavy metals likely to occur in the soil (Moinuddin and Iqbal, 2010). The metals Cu, Zn, Pb and Cd are often associated with high traffic density, originating from exhaust emissions, tyre, brakes, vehicles and engine wear or the re-suspension of road dusts (He and Lu 2010; Allen *et al*., 2011; Gurugubelli *et al*., 2013). Industrial activities like burning of fossil fuel and smelting of metallic wastes have added large quantity of pollutants such as suspended particulate matter (SPM) and it serves as a media for the transfer or distribution of metals across various environmental reservoir on earths system (Tripathi *et al*., 1999; Pacyna *et al*., 2009; Peachey *et al*., 2009; Vianna *et al*., 2011). When heavy metals are carried into the soil, they will accumulate there and by the time enter into the biosphere or the food chain causing harm to human health (Balakrishnan *et al*. 2013). Almost all the trace elements that contaminate the biosphere firstly absorbed by plants and then to animals which are very toxic as it are above the level of requirement for maintaining normal metabolic activities of the body (Sharma *et al*., 2008; Patel *et al*., 2010). The maximum proportion of metals was recorded in plants leaves as reported by Naveed *et al*. (2010) and Yusuf *et al*. (2011). The role of urban trees in improving air quality has been given increasing attention in recent years due to their relatively high capturing efficiencies compared to other types of vegetation and land use (Mohamed *et al*., 2012; Zaidi *et al*., 2012). The heavy metals above the certain concentration when transferred to the food chain through vegetations or plants are harmful to all the animals and consequently harm to the vegetation itself (Vianna *et al*., 2011; Orisakwe *et al*., 2012). This Brass city has been facing

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unprecedented urban and vehicular population growth and causing serious degradations of air quality of city. Plants grown in the region of non-ferrous smelters display increased foliar orientation of heavy metal (Tripathi *et al*., 2010). Thus to extend the scope of work based on the previous findings and relevant studies the objectives of this research is to investigate the characterization and deposition of heavy metals i.e. Cd, Cr, Cu, Fe, Ni, Pb and Zn in leaves by growing species commonly planted in the urban roadside and the variation in deposition of metals between distance from road and plant species. The total metals within the plant tissue are presented to provide an indication of their bioavailability to primary consumer. Since plants are sensitive to air pollutants they are often used as warning devices to indicate the presence of a pollutant. Thus characteristic injuries to certain plants can be interpreted to show not only the presence but also the relative concentration, of the air pollutants.

MATERIALS AND METHODS

About the study location

Moradabad is known as 'Peetal nagri' as it is famous for brassware industries and contains around 47 lac population. Moradabad is located in the north- west of India with extreme summer and winter conditions. Moradabad is situated at the bank of Ramganga river and many seasonal tributaries of Ramganga cross the region. It covers the total area of 3493Sq.km and is located at an average height of 76.19 meter above sea level in the western gangetic plain of Indian subcontinent at latitude 28.15 N and longitude 74.49 E

Site Selection

Gandhi Park

This park is situated in the centre of residential region of Gandhi Nagar 1km away from railway station maintained privately by the residents of this area. The soil is planted with a lawn, small trees, shrubs and large ornamental trees located one Km from main bus stand. It is located at the national highway 24 and surrounded by narrow road causing traffic jam leading to slow movement of traffic. On the other hand it is a very dense industrial area having a slaughter house in adjoining area. Traffic exhaust and industrial emission are the main source of heavy metals in this region.

Deer Park

This site is situated at the roadside of NH-24 nearly 8 km. away from the railway station in north direction. It consist a very large area having small and large trees, shrubs, herbs, ornamental and wild varieties of vegetation. The main source of air pollution is the traffic density on highway.

Police Training Centre (PTC)

Additional plants were kept at a rural site 5 km away from the railway station. These plants were used as a control to relate measured metal concentrations to a background range.

Analysis of Heavy Metal in Soil samples

Soil samples were collected at various distances from highway and metal concentrations were also determined through Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) from samples collected for each site.

Plant Species Selection and Analysis of Heavy metal in leaves

Six locally available avenue tree species such as *Ficus rumphii, Anthocephalus kadamba, Alstonia scholaris, Delonix regia, Bauhinia variegata* and *Polyalthia longifolia* in and around the various sites, were selected for the study. All the species have very dense foliage and this combined with the fact that it is in leaf throughout the year result in a very high particulate capturing efficiency. The fresh leaf samples of selected trees from different sites were carried aseptically to the laboratory and airborne metal pollution was determined by the following method. The unwashed leaf samples were digested in concentrated nitric acid overnight and the samples were heated slowly until red fumes of NO_2 ceased. After cooling for few minutes, 70% perchloric acid was added and the samples were heated to reduce its volume. These samples were filtered through Whatman number 42 filter paper and the filtrate was diluted to 50 ml. using deionised water and kept at room temperature for further analysis of heavy metals. The concentration of lead in filtered samples was analyzed with ICP-OES. Five Replicates of each sample were analyzed and average Pb concentration was calculated.

Quality Assurance

Blank (5% tri-acid mixture) and quality control standards were measured at every five samples to detect contamination and drift. The elemental concentrations of procedural blanks were generally <5% of the mean analyses were also ensured through replicate analyses of samples against standards reference material (SRM-1570) of National Institute of Standard and Technology for all the heavy metals. The results were found to be within ±2% of certified values.

Statistical Analysis

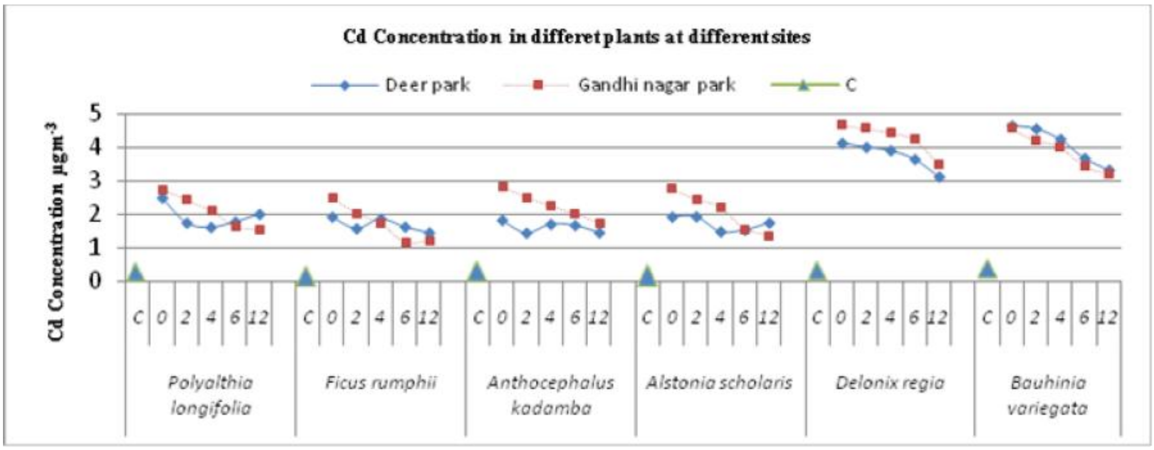
Obtained data were processed for statistical analysis including univariate and multivariate methods. Basic statistical parameters such as mean and standard deviation are computed along with correlation analysis, while multivariate statistics in terms of Principal Component Analysis (PCA) and Cluster Analysis (CA) as given by Lee and Hieu, 2011. Calculation of Enrichment Factors (EFs) was also performed using the SPSS version 16.0 statistical software.

RESULTS

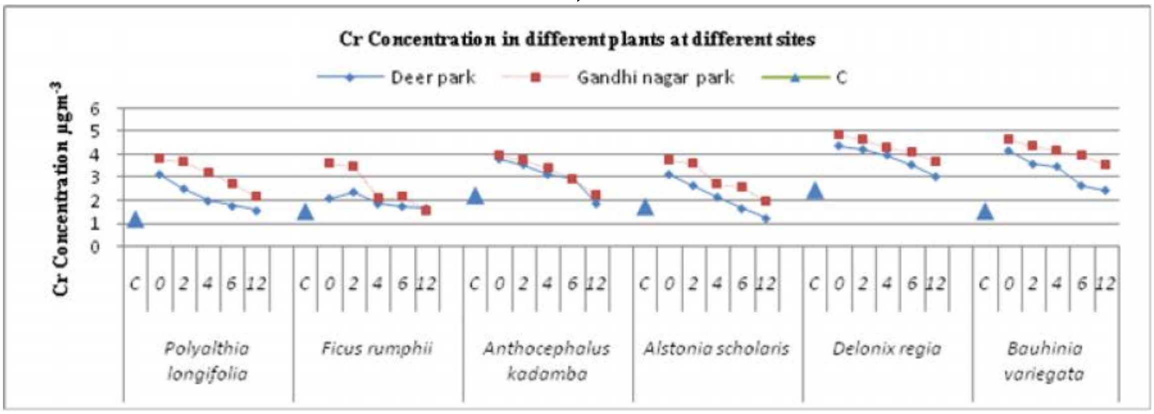
Total metal concentrations in plant leaves

Total metal concentrations i.e. Cd, Cr, Cu, Ni, Fe, Zn and Pb in selected six plant species at two heavily trafficked roads of Moradabad city is summarized in Fig. 1 (A-G).

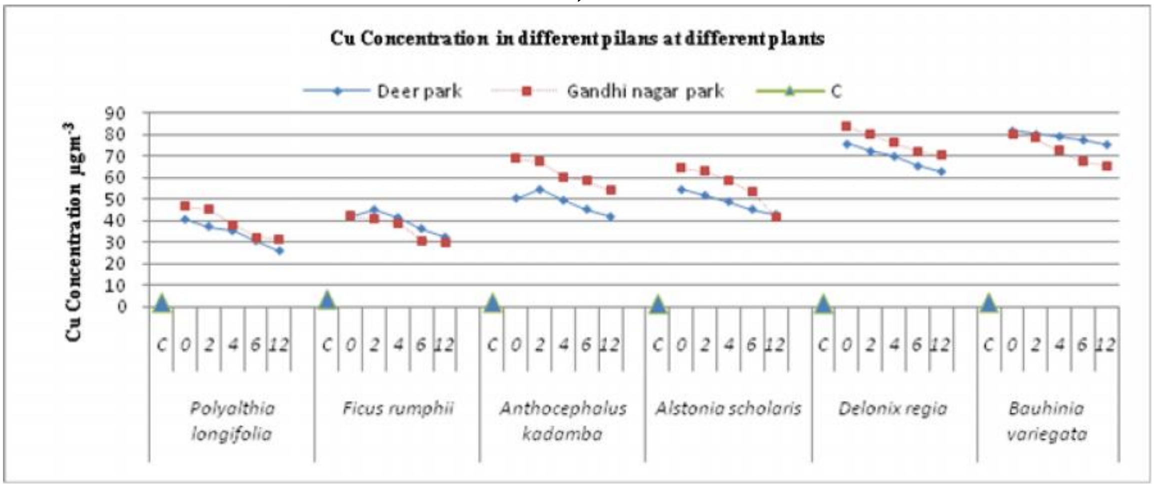
It was observed that Cd concentration (4.67µg/g) was found maximum in *Bauhinia variegata* and Cu (83.58 µg/g), Fe (48.53 µg/g), Ni (47.63 µg/g), Cr (4.86 µg/g), Pb (2.50 µg/g) and Zn (96.76 µg/g) were found in *Delonix regia* at Gandhi Park site.


Cd Concentration in differet plants at different sites
Deer park
Gandhi nagar park
C
Cd Concentration µgm-3
Polyalthia longifolia
Ficus rumphii
Anthocephalus kadamba
Alstonia scholaris
Delonix regia
Bauhinia variegata

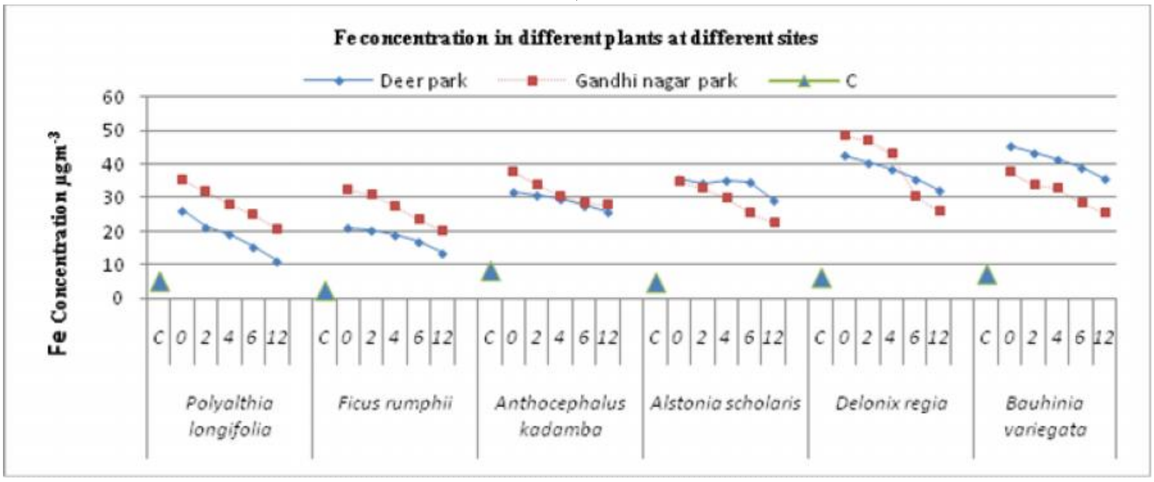
a)


Cr Concentration in different plants at different sites
Deer park
Gandhi nagar park
C
Cr Concentration µgm-3
Polyalthia longifolia
Ficus rumphii
Anthocephalus kadamba
Alstonia scholaris
Delonix regia
Bauhinia variegata

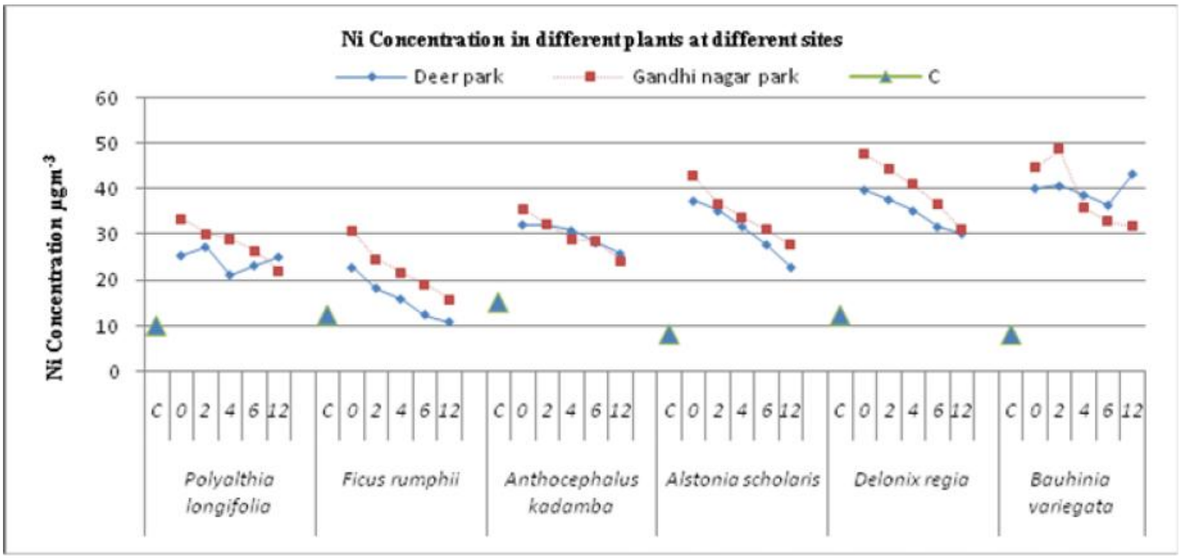
b)


Cu Concentration in different pilans at different plants
Deer park
Gandhi nagar park
C
Cu Concentration µgm-3
Polyalthia longifolia
Ficus rumphii
Anthocephalus kadamba
Alstonia scholaris
Delonix regia
Bauhinia variegata

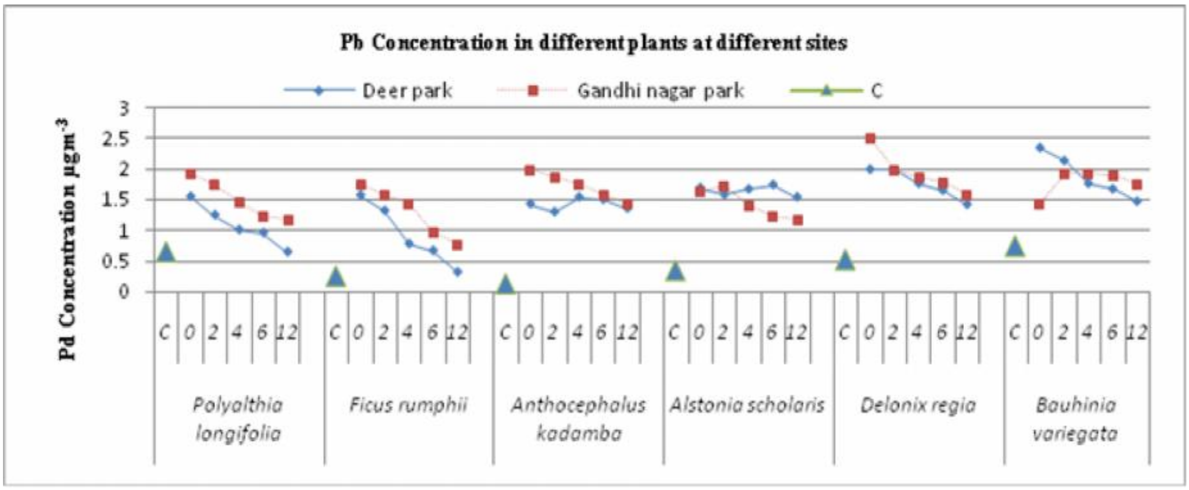
c)


Fe concentration in different plants at different sites
Deer park
Gandhi nagar park
C
Fe Concentration µgm-3
Polyalthia longifolia
Ficus rumphii
Anthocephalus kadamba
Alstonia scholaris
Delonix regia
Bauhinia variegata

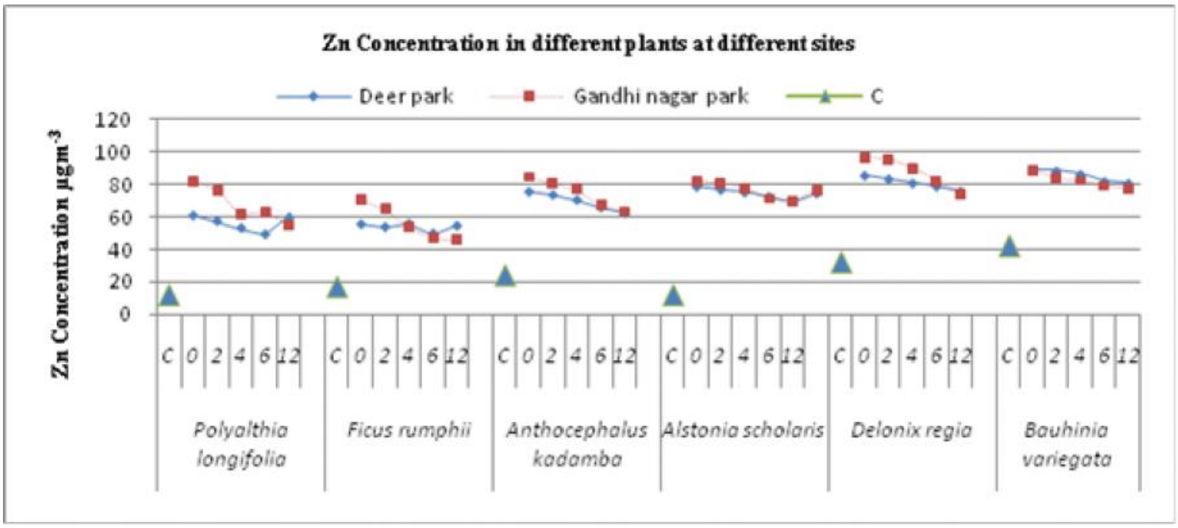
d)



e)



f)



g)

Fig. 1(A-G). Total metal concentration in plant leaves at various distances from different sites of Moradabad city

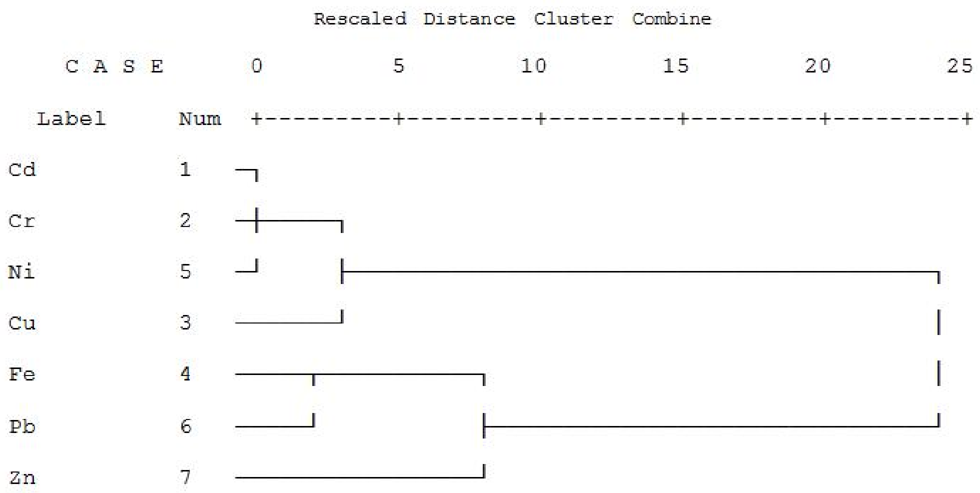


Fig. 2. Cluster Analysis Dendrogram using Ward Method

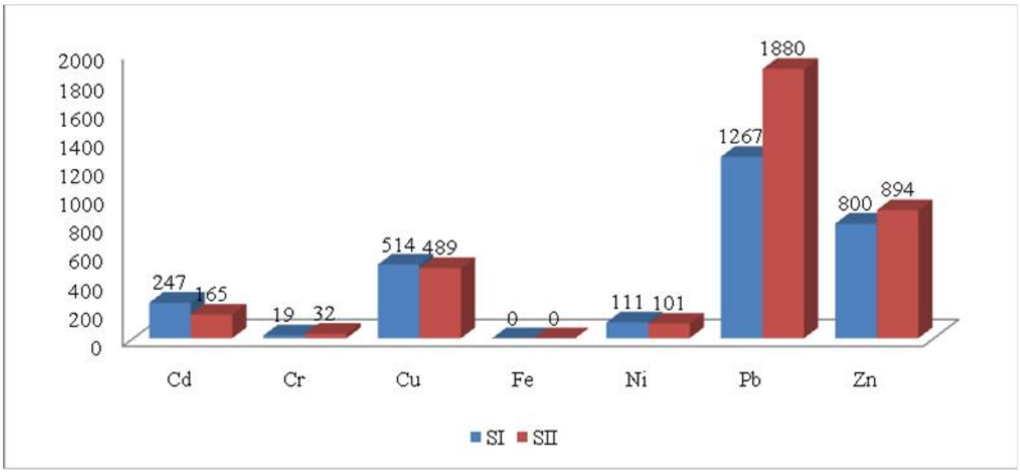


Fig.3. Enrichment Fector for heavy metal in soil samples

Table 1. Pearson Correlation co-efficient between the metal concentrations measured in different plant species at various distances at different sites of Moradabad city

Cd	1.00						
Cr	0.84**	1.00					
Cu	0.36^{ns}	0.38^{ns}	1.00				
Fe	0.64*	0.76**	0.05^{ns}	1.00			
Ni	0.23^{ns}	0.50*	0.48^{ns}	0.42^{ns}	1.00		
Pb	0.73*	0.79**	0.04^{ns}	0.91**	0.46^{ns}	1.00	
Zn	0.03^{ns}	0.11^{ns}	0.84**	0.19^{ns}	0.3^{ns}	0.29^{ns}	1.00
	Cd	Cr	Cu	Fe	Ni	Pb	Zn

Note : ** p<0.01, *p<0.05, ns = non significant

Table 2. Mean±SD Soil metal concentrations (mg/kg) at Gandhi nagar Park and Deer park Distance from road (m)

Gandhi nagar park	n	1	7	12	25	50
Cd (mg/kg)	98	5.2±4.52	3.15±7.25	4.48±2.25	2.53±0.28	1.57±0.85
Cr(mg/kg)	98	36.25±11.2	25.87±2.58	20.12±0.25	18.19±2.36	14.86±1.25
Cu(mg/kg)	98	231.15±2.56	286.27±0.58	129.58±4.25	141.27±1.25	110.78±3.25
Fe(mg/kg)	98	625.28±6.25	532.7±0.58	504.28±0.54	348.94±0.38	438.28±0.05
Ni(mg/kg)	98	82.22±14.2	75.24±12.25	86.24±0.58	48.57±0.39	49.14±0.58
Pb(mg/kg)	98	453.15±26.25	434.68±4.25	348.46±4.26	378.15±0.28	123.28±0.69
Zn(mg/kg)	98	945.15±48.25	845.24±0.58	751.28±0.18	648.29±0.49	785.96±1.26
Deer Park		1	5	10	25	55
Cd (mg/kg)	98	3.245±0.28	2.28±2.39	1.48±0.25	1.2±0.025	0.97±0.24
Cr(mg/kg)	98	34.25±0.25	45.25±1.2	26.28±0.35	27.26±0.27	19.18±0.48
Cu(mg/kg)	98	244.66±1.52	151.21±4.25	145.54±0.54	86.56±0.5	65.55±0.48
Fe(mg/kg)	98	516.48±2.35	533.89±6.25	365.32±0.36	345.25±1.25	225.58±5.52
Ni(mg/kg)	98	54.26±0.36	63.25±5.24	48.26±0.8	51.28±1.21	34.29±1.25
Pb(mg/kg)	98	545.25±0.063	424.18±12.5	532.28±0.45	348.17±2.36	284.55±1.25
Zn(mg/kg)	98	759.26±0.26	842.2±31.25	726.26±0.37	654.64±3.2	621.84±6.35

Table 3. Pearson Correlation co-efficient between the soil metal concentrations measured at various distances at different sites of Moradabad city

Cd	1.00						
Cr	0.296	1.00					
Cu	0.633*	0.436	1.00				
Fe	0.812**	0.583	0.754*	1.00			
Ni	0.881**	0.322	0.564	0.839**	1.00		
Pb	0.392	0.610	0.598	0.361	0.300	1.00	
Zn	0.677*	0.568	0.693*	0.924**	0.731*	0.239	1.00
	Cd	Cr	Cu	Fe	Ni	Pb	Zn

Note : N=10, *. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

Table 4. Principal component analysis after Varimax rotation for the trace elements analyzed in soil samples

	Components		
	1	2	3
Cd	0.913	0.011	0.271
Cr	0.140	0.878	0.395
Cu	0.634	0.250	0.542
Fe	0.852	0.474	0.144
Ni	0.925	0.107	0.122
Pb	0.137	0.238	0.948
Zn	0.773	0.582	0.008
Eigen values	3.454	1.465	1.457
% of Variance	49.346	20.925	20.818
% of Cumulative	49.436	70.271	91.088
Possible Sources	Industrial emission	Anthropogenic exhaust	Automobile activity

The ranking between metal concentrations was consistent between species and is in the order i.e. Zn>Cu>Fe>Ni>Cr>Cd>Pb. In *Ficus rumphii* Cd (1.2 µg/g), Ni (10.76 µg/g), Pb (0.32 µg/g) and Zn (45.54 µg/g) was found lowest whereas Cu (25.78 µg/g) and Fe (11.03 µg/g) in *Polyalthia longifolia* and Cr (1.45 µg/g) in *Anthocephalus kadamba* (Tripathi *et al*., 2009). The Pearson correlation coefficient between the metal concentrations was measured in different plant species following exposure to particulate pollution on two urban roads (Table 2). The correlation statistics reveal strong positive correlation between Cr with Cd ($r = 0.84$), Fe ($r = 0.76$), Pb ($r = 0.79$) and Cu with Zn ($r = 0.84$) suggesting the presence of some common sources which would be verified by using multivariate analysis. Considering all metals together, distance from the road had a significant effect on leaf concentrations, but the interaction between distance and metal was significant ($P<0.01$) for leaf concentration (Peachey *et al*., 2009). Pb concentrations in samples were found highly correlated with distance and their correlation coefficients with Cd ($r = 0.73$) and Cu ($r = 0.79$) are shown in Table 1.

Heavy metal concentration in soil

Soil monitoring was carried out at both of the trafficked road at various distances during the study period in Moradabad city. The soil sampling indicated that concentrations of metals generally decreased with distance from the road (Table 2). The soil data suggested that the distance from the road was a factor varied between metal and site, however the decline in metal concentrations was generally sharper within 10-12 m of the road and more gradual between 12m and 50m. Among the heavy metals, Zn was found highest (945.15mg/kg) in soil of Gandhi Park site, may be due to its various sources i.e. Brassware industries, coal combustion, in nearby areas, incineration and wood combustion followed by Pb (845.25mg/kg), Fe (625.28mg/kg), Cu (531.15mg/kg), Ni (82.22mg/kg), Cr (36.25mg/kg) and Cd (5.2mg/kg). High concentration of Pb at this site may be attributed to nearby Bus stand and Railway station (Nyangabado *et al*. 2005; Xu *et al*. 2012). Heavy metal toxicity varies greatly with element, element concentrations and plant species. The heavy metals that are translocated slowly accumulated in the roots, affecting the overall plant growth primarily through root damage. In plants that are unable to exclude or inactivate heavy metals, continuous accumulation of their ions leads to severe metabolic damages causing necrotic lesions on the leaf margins or blades, leading sometimes to death of the plant (Moinuddin and Iqbal 2010). Inter-elemental relationships provide interesting information on heavy metal sources and pathways. Fe demonstrates strong and positive correlation ($p<0.01$) with Zn ($r=0.924$), Cd ($r=0.882$) and Ni ($r=0.839$). Highly significant correlation was found between Cd and Ni ($r=0.881$) (Table 3). These high correlations show that the origin of the metals in the investigated areas is highly related to the industrial activities, heavy traffic and street dust emission. Very week correlation was found between Pb - Zn ($r=0.239$) and Cd - Cr ($r=0.296$). Heavy metal enrichment factors (EFs) for the soil samples were calculated by assuming the mean metal concentrations in earth's crust given by Taylor and McLennan (1995) (enrichment factors were calculated based on Fe). The results are presented in Figures 4. The highest EF values for Cd (247), Cu (514) and Ni (111) were determined in the soil samples at site SI whereas Cr (32), Pb (1880) and Zn (894) were at SII.

DISCUSSION

The largest anthropogenic sources of metals, however, originate locally as dry-deposited particulate matter from roadways and deposition typically decreases with distance from road (Peachey *et al*., 2009). Road density values within census tracts in urban area of Moradabad are four to five folds greater than those in other developing and rural census tracts, respectively. On the other hand at Gandhi park the concentrations of almost all the metals found high in comparison to Deer park. High values may be due to its location in dense area and nearby Bus stand. The metal levels in plant samples are rather high and their interpretation is not simple as plants receive fallout metals via wet and dry deposition directly on leaves. As a result of direct deposition on soil from the atmosphere and indirect deposition via stem flow, heavy metals may enter the plants from the soil solution through the root system (Opoluwa *et al*., 2012). At each step towards plant accumulation of the heavy metals, some of them may be lost. Hence the plant metal content is a measure of the total metal input minus what is lost before the metals enter the plant tissues. However, it has been shown that plants grown on soil of high metal content take up only small amounts into their aerial parts and that abnormal metal level in the aerial parts are indicative of enhanced levels in the surrounding atmosphere (Horaginamani and Ravichandran 2010; Dev and Herbert 2013). The results indicate that the plants species such as *Bauhinia variegata* is sensitive among all the species having highest concentration of heavy metals at both of the sites and *Ficus rumphii* with lowest concentration, is tolerant among all the species. It possibly may be due to differences in plant morphology and leaf surface and apparently particulate size decides the extent of solubility providing the bioavailability of metals to primary consumers (Misra *et al*., 2010; Dev and Herbert 2013). The metal, plant species, distance from the road ($P<0.01$) and the interactions between them all had a significant effect on the leaf concentrations (Table 1). The value of experimental plants were examined, there was a great variation between pollution level of individual plants within as well as between sites and found that there was a significant difference between plants and metals at a given particular site. Different metal pollution levels among plants were due to the different deposition levels of airborne metals and similar work is also reported by Aksoy and Sahin (1999) and Feng *et al*. (2011).

Source of particulates from roadside is responsible for metal deposition include tire wear (Cd, Pb, Zn) brake wear (Cr, Cu, Pb, Zn), vehicle body degradation (Ni), engine fluid spills (Cr, Ni, Zn) and exhaust emissions (Cu, Cr, Pb, Zn) and deposition is typically greater where braking and /or accelerating are greatest (Sabir *et al*., 2006). The deposition of airborne particulates decreases the light availability for photosynthesis and cause stomata clogging (Sun *et al*. 2009). Thus supported the fact that Particles having diameters less than the diameter of stomata cause the partial clogging which those having equal diameter to that of stomata completely clogged them. This order generally follows a similar pattern to that for total metals, except Fe concentration which are greater than Cu, suggesting a greater proportion of Fe and Zn in soluble form. The biologically essential heavy metals such as Fe, Zn and Cu or those which are essential only to a limited number of species such as Ni can be toxic when they accumulated in plants in relatively high concentrations. This fact is also supported by many workers (Yusuf *et al*., 2011). The essential heavy metals are required in small quantities (micronutrients) normal for metabolism and growth of the plants and their deficiency or excess can impair these phenomena, rendering the plants with low yield and quality (Pandey, 2010). Although natural sources cannot be eliminated, high concentration may be attributed to greater emissions in urban areas, as a greater number of stationary and mobile sources are usually found in cities (Pitcaira *et al*., 2006; Fenn *et al*., 2007) these findings illustrated the utility of the urban-to-rural gradient approach, since analysis suggest that elemental concentrations observed may be related to pollution exposure.

High heavy metal concentrations of trees reflect their strong ability for absorbing and accumulating heavy metals from atmosphere and soil. Low heavy metal concentrations of some trees are probably due to these species having some resistance to heavy metal pollution. Other possible explanations include low exposure or low uptake. It may also reflect variations in the physical nature of the cuticle and epicuticular wax which have been shown to determine deposition and uptake at the leaf surface. The difference between leaf content for Pb between park and road locations is probably because the tree leaves at the roadside were polluted by automobile exhaust emissions. PCA was applied to determine the correlation between pollutants and to identify the source profile of heavy metals in soil. Table 4 describes the Principal Component (PC) loadings for the metal data of the study period with corresponding Eigen values and variances. The Ist PC explains 49.346% of data variance and it is characterized by Cd, Ni, Fe, Zn and Cu. These heavy metals are mainly related to the Industrial emissions, especially the metallurgical/ electroplating and e-waste burning units located in the industrial area of the city (Wang *et al*., 2001; Quiterio *et al*., 2004; Shah and Shaheen 2008). The IInd and IIIrd factor characterized by Cr and Pb. These metals are well known to be associated with the automobiles (Ayras and Kaushilina, 2000). The extracted components explain nearly 90.088% of the variability in the original 7 variables. The results of CA for the variables, trace elements in soil, were obtained as dendograms displaying four main clusters. In the dendogram for soil (Fig. 2) the first group containing the variables Cd and Cr with Ni, is associated with traffic emissions; the second group includes Fe, Pb and Zn mostly originating from abrasion of mechanical parts of road vehicles. All groups are connected at some distance, suggesting that the main sources of metals in soil are fossil fuel combustion (traffic or stationary units) and resuspended dust, which is a mixture of soil and road dust.

In the present study, large variation of EF values was found for different metals in the soil samples. The highest EF values for Pb, Zn, Cu, Cd and Ni were determined highly enriched ($EF > 100$) whereas Cr was intermediately enriched (EF between 10-100) at both sites in the soil samples, may be due to brassware industries, illegal e-waste burning automobile emissions and combustion processes (Fig 3). The higher EF values of these metals showed the anthropogenic sources (industrial, automobile and combustion emission) contributed a substantial amount of the metals in atmospheric particulates, which otherwise were difficult to justify on the basis of normal crustal weathering process. In contrast the less enriched metals were dominantly derived from earth crust, and re-suspension of soil dust. On the whole, all metals revealed EF greater than unity, thus predominantly contributed by the anthropogenic source.

Conclusion

It is concluded that heavy traffic load, dust material, condition of vehicle engine cause deterioration in the quality of air that results in the desiccation of leaf moisture and early senescence leading to poor growth in roadside plant. On the basis of low heavy metal accumulation in *Ficus rumphii* it may be considered as a tolerant plant and used as a roadsides plantation. The high heavy metal concentration in urban soil and plant samples are mostly due to the density of the traffic which is considered as one of the major sources of heavy metal concentration. In terms of soils heavy metal concentrations at roadside locations were higher and their coefficients of variation larger than those samples obtained from urban park. The data suggest that urban area, that is to say roadside verses park location, can influence metal concentrations. Roadside locations gave rise to higher level compared to samples from urban parks, a location where one might expect less pollution due to a lack of vehicular traffic and industry. As we know unleaded gasoline is expensive and mostly drivers prefer leaded gasoline which is the major source of high Pb pollution alongside the roads on these sites. Factor analysis cumulatively indicate that high level of heavy metals may be ascribed to industrial emission followed by automobile exhaust, tyres, brake wear, resuspention of road dust e-waste burning and other anthropogenic activities. Certain control measures can be undertaken to abate air pollution viz., introduction of improved test procedures like transient loaded test and stringent emission standards for diesel commercial vehicles, private vehicles should be tested regularly to comply with emission standards and certified use of alternative fuels like CNG in public transport systems. Preparing and implementing an effective urban air pollution control strategy in Moradabad city requires educating at all levels including policymakers, implementing agencies, manufacturing industries and general public.

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