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ORIGINAL PAPER

Deposition of anthropogenic secondary anions through indoor dust on *Ficus elastica* plants in Delhi, India

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Abstract

The tolerance against air pollution in plants depends on the nature of air particles and gases. This study was carried out to determine chemical composition of indoor dust and to assess its impact on the biochemical properties of foliage of *Ficus elastica* in two households with different characteristics of Delhi (India). The dustfall fluxe data of major cations and anions were analyzed to understand the spatial variations in the chemical composition and sources of the deposited particles onto the foliage. The fluxes of anionic species ($SO_4^{2-} + NO_3^-$) were higher at MH (industrial) site as compared to the DH (residential) site. The physiological response of *F. elastica* was investigated by studying the biochemical constituents, i.e., ascorbic acid, soluble sugars, carotenoids, and chlorophyll *a* and *b*, in foliage and variations with respect to dustfall fluxes of anionic species ($SO_4^{2-} + NO_3^-$) in the households. Higher ($SO_4^{2-} + NO_3^-$) fluxes had noticeable impacts on biochemical constituents of *F. elastica* indicating indoor air pollution stress. Chemistry of dust particles showed influences from indoor and outdoor anthropogenic activities. The morphological effects of dustfall deposition on the foliage were also studied using SEM–EDX. Indoor plants can serve as a platform to capture dust particles and plant responses are influenced by the chemical composition of deposited dust.

Keywords Air pollution stress · Indoor air pollution · SEM–EDX · Residential · Industrial

Introduction

Outdoor air with high pollution loadings dominant in megacities usually move into the indoor spaces through ventilation and infiltration airflows. Consequently, indoor air pollution has piqued scientific curiosity as people routinely spend maximum time (> 80%) inside built structures, owing to our lifestyle and working environment in modern metropolises (Jenkins et al. 1992). Studies have confirmed that outdoor composition strongly influences the indoor air quality (Leung 2015). Outdoor pollutants such as gases, heavy metals, and particulate matter contaminate indoor air by infiltration and the impact is more in developing countries where particle levels are incessantly increasing (Katoch and Kulshrestha 2021). Indoor concentration of pollutants is often higher than outdoor concentrations and daily exposure to air pollutants inside these buildings may cause the popularly known "sick building syndrome" and "building-related illnesses" which is a silent epidemic (Brilli et al. 2018). Among several available surfaces, plant canopies serve as efficient sinks for both gaseous and particulate pollutants from the atmosphere (Fowler et al. 1989; Weerakkody et al. 2018). Aerial organs such as leaves act as efficient absorbers of airborne particles because of their high surface-to-volume ratio. Dust is present indoors as a composite of particulate matter derived from outdoor as well as from indoor sources such as smoking, incense burning, building materials, furniture, cosmetics, cleaning, and routine occupant activities (Turner and Simmonds 2006). In the Indian context, mineral dust has persisted for several decades, but increasing emissions from industries, transport, biomass burning as well as other anthropogenic activities are known to interact with ambient dust and alter its morphological and chemical characteristics (Mishra and Kulshrestha 2017; Sharma et al. 2018; Mishra et al. 2019). Air Quality Index (AQI) of NCR-Delhi (India) is usually found under poor and very poor categories due to high loadings of particulate matter (Mishra and Kulshrestha 2021). It is known

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that natural ventilation in buildings dilutes the indoor air and simultaneously introduces outdoor pollutants in the indoor spaces (Stabile et al. 2017). Reports suggest that naturally ventilated buildings with manual airing have higher concentrations of particulates due to the influence of outdoor atmospheric conditions as compared to some gaseous indoor pollutants (such as CO_2, VOCs, and radon) (Chithra and Shiva Nagendra 2012) which get diluted with infiltration of outdoor air. Impaction and sedimentation processes occurring indoors help these particles to settle on the foliage and other indoor surfaces. The alkaline nature of mineral dust plays a key role in determining its chemical composition and in the atmospheric acid–base reactions. Alkali and alkaline earth metals present in mineral dust chemically combine with the anthropogenic secondary ions such as SO_4^{2-} and NO_3^- which are formed from precursor gases. The aged dust particles show the abundance of secondary inorganic SO_4^{2-} and NO_3^- species. Previous studies have found that dust deposited onto the foliar surfaces affects surface, stomata, biochemical constituents, and physiology of the plants (Gupta et al. 2015a; Weerakkody 2018; Katoch and Kulshrestha 2023). Chemical composition of dust affects plant health and commonly deposited secondary ions SO_4^{2-} and NO_3^- enter mesophyll cells and may cause indirect injuries to plant tissues and organelles (Fowler et al. 1989; Buchner et al. 2004; Gupta et al. 2015b). In addition to PM, chronic dosage of pollutant gases such as O_3, NO_x, and SO_2 also cause phytotoxicity and aberrations in metabolic processes such as inhibition of photosynthesis, soluble sugars, and gas exchange (Koziol and Jordan 1978; Miller and Davis 1981; Srivastava 1999). These changes involve variations in their biochemical constituents such as chlorophyll, carotenoids, soluble sugars, ascorbic acid, and amino acids. Photosynthetic pigments (chlorophyll and carotenoids) and soluble sugars are sensitive to pollutants and show variations in their concentrations when subjected to damage by air pollution (Gupta et al. 2015a). Dust deposition on the leaves may cause various phytotoxic effects and pollutants such as SO_4^{2-} and NO_3^-, and heavy metals cause air pollution stress in plants (Fowler et al. 1989; Gupta et al. 2015a). Plants do not immediately succumb to injury caused by air pollution as they have the ability to remove and metabolize pollutants through assimilation in cell organelles (Gupta et al. 2016b). Reports suggest that *Ficus elastica* has shown good results in removing some of the major indoor air pollutants such as formaldehyde (Kim et al. 2010; Dela Cruz et al. 2014), benzene (Cornejo et al. 1999), and CO_2 (Cetin and Sevik 2016). Plants in the indoor environment can be good candidates for removal of air pollutants along with providing psychological push through, mood lifting, and enhanced alertness for the occupants. Very limited studies have demonstrated the effect of dust deposition on foliar surfaces in real indoor set-ups (Gawrońska and Bakera 2015; Viecco et al. 2018). This study specifically investigates the chemical composition and ionic fluxes of household dust deposited on the leaves of *F. elastica*, and also the surface morphology and biochemical responses in the leaves of the plant in actual household conditions of a highly polluted megacity (Delhi) in South Asia which makes it unique.

Materials and methods

Study area

Two naturally ventilated households (DH and MH sites—Dwarka Household and Mayapuri Household, respectively) located in Delhi (India) were selected as the sampling sites. Figure S1 shows the geographic representations of MH and DH sampling sites in Delhi. Air Quality Index (AQI) of Delhi is reportedly very high due to ubiquitous presence of particulate matter in the atmosphere (Mishra and Kulshrestha 2021). Background outdoor pollution recorded at the nearby air quality monitoring stations showed the annual average PM_{10} values to be approximately 182 $\mu g/m^3$ site and 240 $\mu g/m^3$ during sampling period at DH and MH sites, respectively. Buildings with natural ventilation show significant presence of particulate matter as compared to other air pollutants commonly monitored indoors (Chithra and Shiva Nagendra 2012). *Ficus elastica* is a popular indoor ornamental plant. It can be grown as an indoor plant as well as a tree which can grow up to 15–17 m tall when planted outdoors. Various reports suggested that *F. elastica* foliar surfaces showed good to moderate particle capture capacity under outdoor and controlled laboratory conditions (Cao et al. 2019). Hence, in this unique study we attempted to investigate the effect of indoor dustfall deposition on the *F. elastica* kept in actual characteristic household conditions. For this study, *F. elastica* potted plants of similar size were placed at each sampling site. DH site was located in the area that represented residential characteristics whereas MH site represented industrial characteristics. However, both DH and MH sites are located approximately 12 km apart in Delhi and, therefore, the outdoor meteorological conditions such as temperature, humidity, and rainfall did not vary a lot from each other. It was also ensured that the plants were kept in uniform conditions for experimental purpose with respect to watering, natural ventilation, temperature, light, and other routine influences by the inhabitants inside the households at both sites. A detailed description of the sites with their characteristic features has been provided elsewhere (Katoch and Kulshrestha 2020, 2021).

Sample collection and chemical analysis

The foliar dustfall was collected from July 2017 to June 2019 on 10 days exposure basis each time. However, due to experimental limitations, a total of 38 sets of leaves were collected from *F. elastica* plants during the sampling period. For sampling purpose, each time healthy and mature leaves were tagged, cleaned, and properly washed with distilled-deionized water before exposure. Following exposure, selected leaves were plucked and washed with 50 ml distilled deionized water using surface washing method (Gupta et al. 2015a) to prepare aqueous dustfall extract samples which were analyzed for major anions (Cl^-, F^-, NO_3^-, and SO_4^{2-}) and cations (Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}) by ion chromatography (Metrohm 883 Basic IC Plus).

The dustfall fluxes were calculated gravimetrically using the method described by Gupta et al. (2015a). The foliar samples were processed and analyzed for various parameters such as chlorophyll *a*, chlorophyll *b*, carotenoids, total chlorophyll (Hiscox and Israelstam 1979), pH (Gupta et al. 2016a), relative water content (Sivakumaran and Hall 1978), total soluble sugar (Gupta et al. 2016a), and ascorbic acid content (Keller and Schwager 1977). Foliar samples were analyzed in triplicates each time to ensure authenticity of the results.

Foliar morphology analysis

Scanning electron microscopic (SEM) (Carl Zeiss EVO 40, Germany) at the Advance Instrumentation Research Facility (AIRF), Jawaharlal Nehru University, was employed to study the morphological characteristics of *F. elastica* leaves. For adaxial and abaxial surface analysis, a piece of area 1 × 1 cm was cut from the collected foliar and immediately fixed in 2.5% glutaraldehyde (phosphate buffer, pH 7.2). Details of step-by-step sample preparation, followed by sputter coating with gold (Sputter coater-Polaron SC7640), have been provided elsewhere (Gupta et al. 2015b). Elemental composition of dust on the *F. elastica* leaves was determined using EDX attached to SEM, at an accelerating voltage of 15 kV. The elements detected were Cr, Zn, Fe, Cu, Si, Al, K, and Ca, and the EDX spectra showing their characteristic X-ray peaks were obtained.

Results and discussion

Dust deposition on the foliar surfaces of *Ficus elastica*

The average dustfall flux on the foliar surfaces of *F. elastica* at the DH site was recorded as 161 mg/m^2/day whereas the average dustfall flux at the MH site was 234 mg/m^2/day. Figure 1 shows the average indoor dust deposition fluxes of major ions on *F. elastica* foliar surfaces at MH and DH sites. Average deposition fluxes (mg/m^2/day) of ions in the dustfall (F^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) were found to be higher at MH site as compared to DH site. Ca^{2+} and K^+ were the dominant ions at both the sites. MH site was exposed to industrial surroundings having more emissions of air pollutants, vehicular movement, and resuspension of dust; therefore, it had higher fluxes of ionic components as compared to the DH site. However, the equivalent abundance order (mEq/m^2/day) of ionic species on the foliar surfaces at the MH site was $Ca^{2+} > K^+ > Mg^{2+} > Na^+ > SO_4^{2-} > Cl^- > NO_3^- > NH_4^+ > F^-$ while at the DH site the order was $Ca^{2+} > K^+ > Mg^{2+} > Cl^- > Na^+ > NO_3^- > SO_4^{2-} > NH_4^+ > F^-$. In case of anions, Cl^- was the most abundant anion at DH site while SO_4^{2-} was the most abundant anion at MH site. Ions such as Cl^- and K^+ are commonly released from combustion activities such as cooking, open plastic burning, and municipal waste burning which are prevalent in residential areas such as DH site (Mishra and Kulshrestha 2017; Jain et al. 1996).

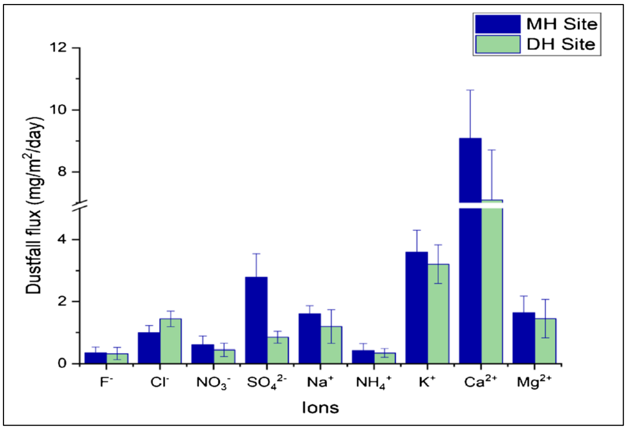


Fig. 1 Dust deposition fluxes of ions on *Ficus elastica* foliar surfaces at MH and DH sites

Figure S2 shows the percent contribution of the major ions to the dustfall composition by mass (mg/m^2/day) on the foliar surfaces which represented the unchanging dynamics for majority of the ionic components between the two indoor sites. Ca^{2+} showed the highest fluxes among cations with average values of 9.1 mg/m^2/day (MH site) and 7.1 mg/m^2/day (DH site). However, among the anionic species, SO_4^{2-} was the highest at MH site with an average flux value of 2.8 mg/m^2/day while Cl^- was the highest at DH site with an average flux value of 1.4 mg/m^2/day. It is observed that at DH site, Cl^- had the maximum percent contribution among anions, whereas Ca^{2+} had the maximum percent contribution among cations in the indoor dustfall on foliar surfaces. Similar findings have been reported for indoor dust in other studies (Zhong et al. 2014). Percentage composition of the indoor foliar dustfall at the two sites varied significantly for SO_4^{2-} flux (MH site at 13%; DH site at 5%) while it remained more or less similar for most of the other ions (Fig. S2). The significant fraction of SO_4^{2-} in dust is contributed by SO_2 oxidation. SO_2 is oxidized to calcium sulfate (Kulshrestha et al. 2003a) via its adsorption onto crustal particles, e.g., $CaCO_3$, and subsequently forms $CaSO_4 \cdot 2H_2O$ as shown below (Kulshrestha 2013).

$$\begin{aligned} CaCO_3 + 1/2O_2 + 3H_2O + SO_2 ===> CaSO_4 \cdot 2H_2O \\ + 2H_2O + CO_2 \end{aligned} \tag{2}$$

SO_4^{2-} fluxes on the foliar surfaces of *F. elastica* at MH site were around three times higher as compared DH site due to the outdoor sources at MH site. The acidity of atmospheric aerosols affects the atmospheric processes and ecosystems. Dry deposition of SO_2 as well as SO_2 adsorption onto the dust particle settled on the foliar surfaces can give rise to $CaSO_4$ (Kulshrestha 2013). Similarly, $CaSO_4$ formation has been reported in case of dust particles settled on the foliar surfaces of plants due to SO_2 adsorption (Gupta et al. 2015b).

In order to see the net ionic balance, the sum of equivalent ionic concentrations of cations and anions were calculated using concentration of individual ion obtained from chromatographic determination (mg/l) as given in Eqs (3) and (4):

$$\begin{aligned} \sum C(mEq/l) = (Na^+/23) + (NH_4{}^+/18) + (K^+/39) \\ + (Mg^{2+}/12) + (Ca^{2+}/20) \end{aligned} \tag{3}$$

$$\begin{aligned} \sum A(mEq/l) = (F^-/19) + (Cl^-/35.5) \\ + (NO_3{}^-/62) + (SO_4{}^{2-}/48) \end{aligned} \tag{4}$$

The ionic fluxes (mEq/m^2/day) for cations and anions were further calculated using the equivalent ionic concentrations (mEq/l) which were multiplied by 0.05 extraction volume (50 ml), and further this value was divided by the product of leaf surface area (in m^2) and number of days of exposure during dustfall collection on leaves. The total C and A fluxes (mEq/m^2/day) in the indoor dustfall on the foliar surfaces were 0.75 and 0.11 at MH site and 0.63 and 0.08 at DH site, respectively. The average ionic flux ratio on the foliar surfaces at the DH site (C/A = 7.8) was higher as compared to the MH site (C/A = 6.8). The C/A ratios indicated anion deficient situation which is common in this region (Kulshrestha et al. 2005). Generally, the anion deficit cases are due to unanalyzed anions such as HCO_3^-, $HCOO^-$, or CH_3COO^- (Kulshrestha et al. 2003a; Park et al. 2015). HCO_3^- is a prevalent anion in the Indian region due to the dominance of $CaCO_3$-rich mineral dust in the atmosphere (Kulshrestha et al. 2003b; Kulshrestha 2013; Gupta et al. 2015b; Tiwari et al. 2016). Following the electroneutrality principle, the C/A ratio should be unity, which means that out of total ion equivalents, 50% ions are contributed by anions and 50% by cations. When the sum of measured cations exceeds that of the measured anions, then this difference is computed as anion deficit (anion deficit = $(\sum C - \sum A)$. Also, the average C/A ratio more than 1 is referred as anion deficit (Beiderwieden et al. 2005; Kulshrestha et al. 1998). When the pH of aqueous sample is more than 5.6, the ion difference can be minimized by careful measurements of HCO_3^- (Satyanarayana et al. 2010; Kulshrestha et al. 2003c). The acceptable ranges of ion difference for a given sum of ions in an aqueous sample have been given in the WMO Report No. 102 (WMO 1994). In this study, the anion deficit is 0.64 and 0.55 at MH and DH sites, respectively. The average pH of deposited dust was observed to be 7.5 and 7.3 at DH and MH sites, respectively. At both sites, the alkaline pH of dustfall can be attributed to the dominance of crustal components such as $CaCO_3$ and $MgCO_3$ contributed by the soil-derived dust. For the pH range recorded at the sites, as mentioned above, the HCO_3^- would explain the anion deficit as $CaCO_3$ and/or $MgCO_3$ dissociation will give rise to HCO_3^- in equilibrium at the measured pH. Therefore, the sum of Ca^{2+} and Mg^{2+} will be equal to the unanalyzed anions, primarily represented by HCO_3^-. Figure S3 shows the linear regression plot of anion deficit $(\sum C - \sum A)$ with respect to $\sum (Ca^{2+} + Mg^{2+})$ equivalents at both sites. Significant R^2 values at DH (0.97) and MH (0.82) indicated the presence of unanalyzed concentrations of HCO_3^- in the aqueous dustfall extract suggesting a crucial role of HCO_3^- in samples in this region.

Interactions of water-soluble inorganic ions in indoor dust

Inter-ionic associations in the indoor dustfall flux occurring on the foliar surfaces of *F. elastica* at both sites were analyzed using correlation coefficients along with the scatter plots. At MH site, Fig. 2a and b show the correlation matrix of inorganic ions at 95% confidence interval ($p = 0.05$) in the dustfall flux deposited on the foliar surfaces of *F. elastica* at MH site and DH sites, respectively. Tables T1 and T2 in supplementary material show the equations for linear regression of major inorganic ions in dustfall with respect to NO_3^- and SO_4^{2-} dustfall fluxes at DH and MH sites. At MH site, high correlation was observed between Ca^{2+} and SO_4^{2-} ($r = 0.80$) and Mg^{2+} and SO_4^{2-} ($r = 0.51$). It might be due to outdoor crustal components and building materials containing sand, cement, gypsum, etc. Jain and co-workers have reported the formation of $CaSO_4$ in dusty atmosphere of Delhi region (Jain et al. 2000). Ca^{2+} also showed a positive correlation with NO_3^- ($r = 0.68$) indicating a significant role of Ca^{2+} in the stoichiometric neutralization reaction of nitrogenous acidic precursors in coarse mode (Tiwari et al. 2016; Mishra and Kulshrestha 2017). The regression analysis for Ca^{2+} fluxes with respect to NO_3^- and SO_4^{2-} showed their moderately strong association with Ca^{2+} indicating formation of their secondary compounds. The Ca^{2+}/SO_4^{2-} and Ca^{2+}/NO_3^- ratios were 3.3 and 8, respectively. NO_3^- also showed high correlation with NH_4^+ ($r = 0.63$) indicating that these are derived from anthropogenic sources such as industrial

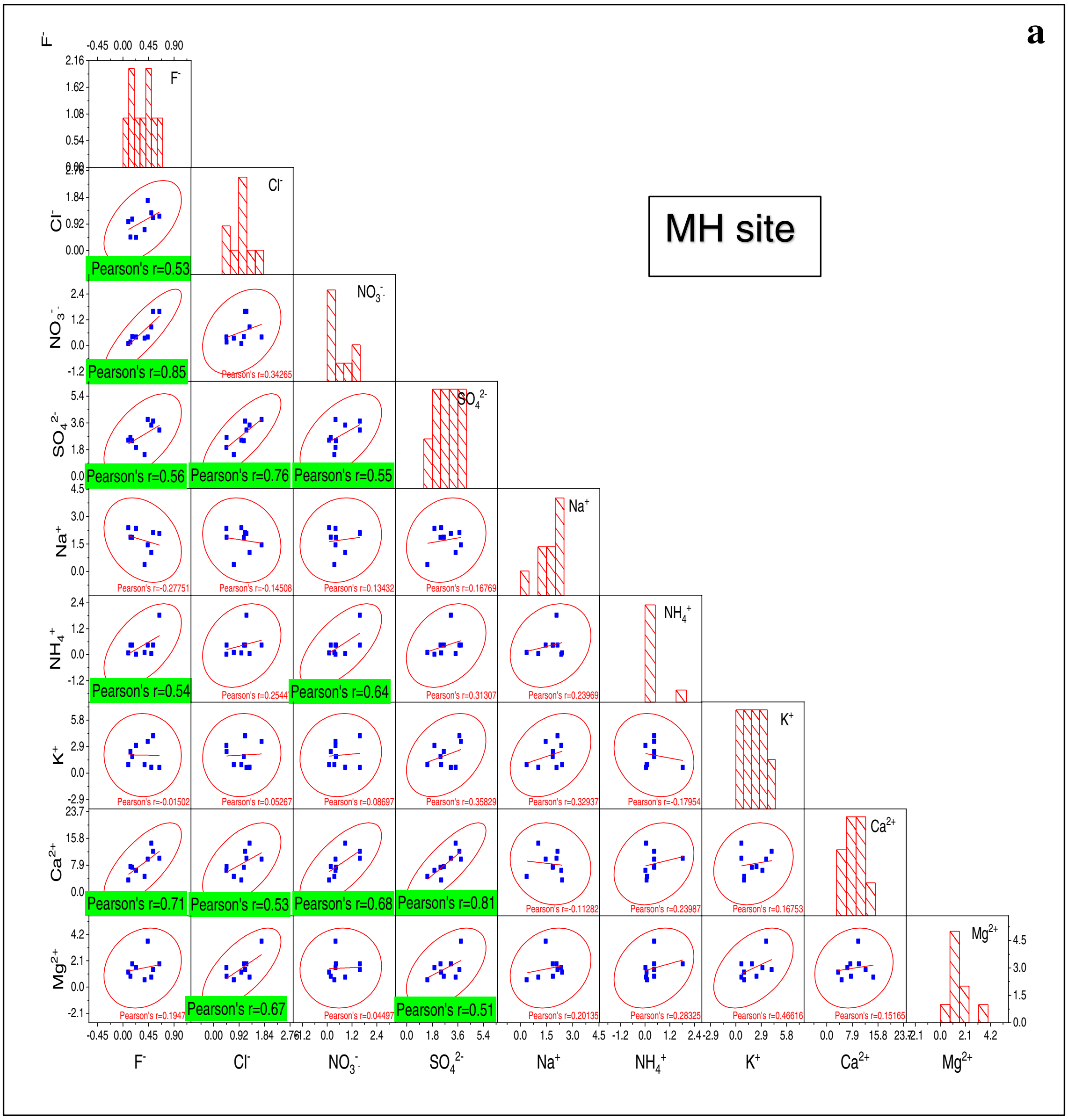


Fig. 2 **a** Correlation matrix of inorganic ions in the dustfall flux deposited on the *Ficus elastica* foliar surfaces at MH site. **b** Correlation matrix of inorganic ions in the dustfall flux deposited on the *Ficus elastica* foliar surfaces at DH site

manufacturing, and wood and biomass burning. Regression analysis indicated moderate association between NO_3^- and NH_4^+. SO_4^{2-}/NO_3^- ratio at MH site was 6.3 which showed higher concentration of SO_4^{2-} as compared to NO_3^- indicating their release from stationary sources such as industries and fossil fuel burning in the surrounding industrial area. Cl^- showed a significant positive correlation with SO_4^{2-} ($r = 0.78$) which supports coal burning as a primary activity in the adjoining local restaurants, shops, banquet halls, and other commercial places. SO_4^{2-}/Cl^- ratio at MH site was 3.1 which indicated more abundance of SO_4^{2-} at MH site. Moreover, R^2 value showed high association between SO_4^{2-} and Cl^- indicating their common emission sources. F^- is released from anthropogenic sources such as industrial activities including aluminum smelters, fertilizer factories, vehicle repair shops, and coal and wood burning (Habil et al. 2015). F^- showed high correlation with NO_3^- ($r = 0.84$), SO_4^{2-} ($r = 0.55$), and Cl^- ($r = 0.53$) due to their common industrial and combustion sources that are prevalent around MH site. Regression analysis also corroborated the linkages of F^- with SO_4^{2-} and NO_3^- emission sources in the dustfall fluxes. At DH site, Fig. 2b shows the correlation matrix of inorganic ions at 95% confidence interval ($p = 0.05$) in the dustfall flux deposited on the foliar surfaces of *F. elastica*

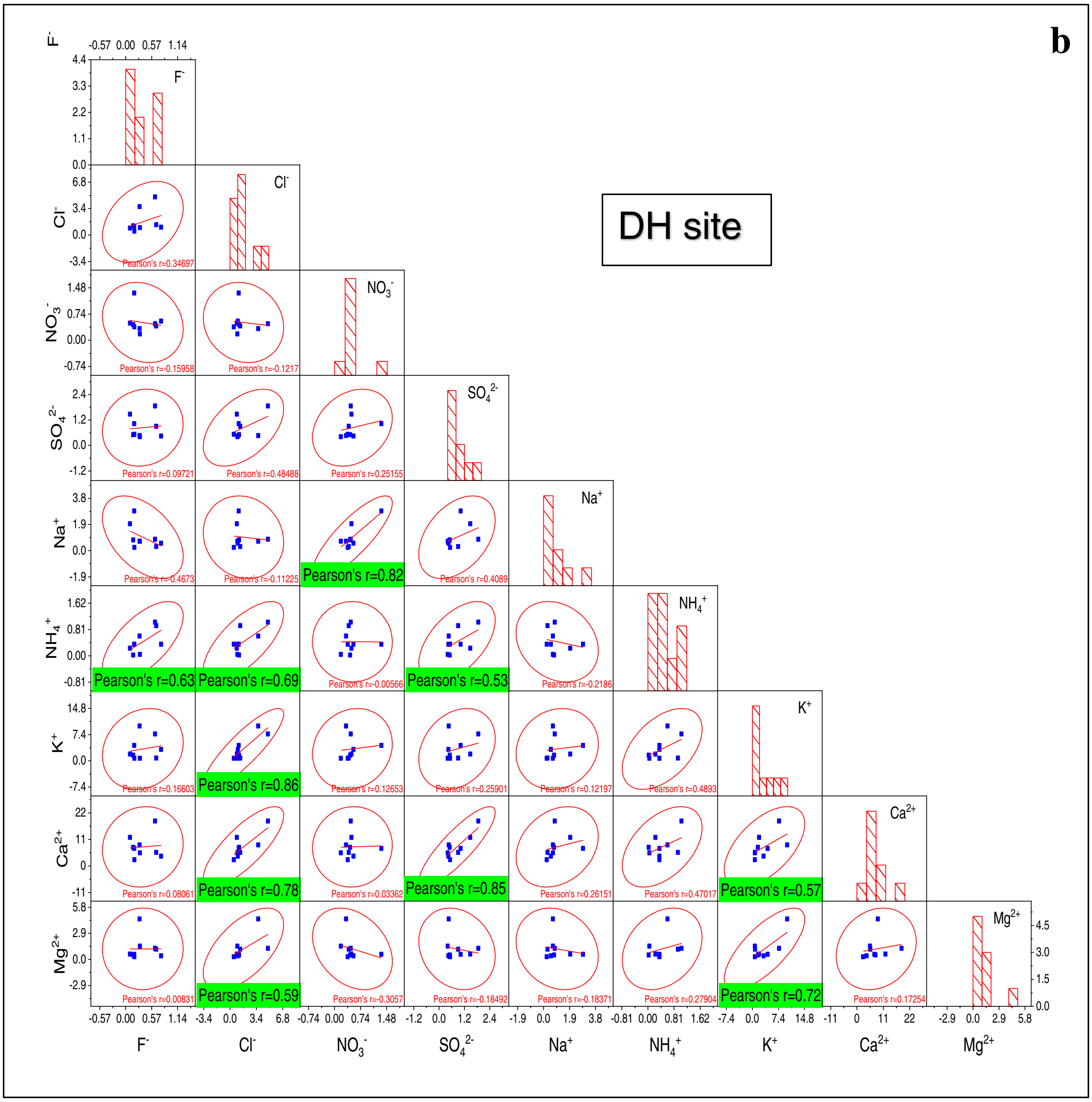


Fig. 2 (continued)

Table 1 Regression equations of the scatter plots of photosynthetic pigments

Parameters	MH site	DH site
Chl *a*	$y=-0.1072x+1.0789$ $R^2=0.6472$	$y=-0.0875x+0.8202$ $R^2=0.2832$
Chl *b*	$y=-0.0704x+0.4714$ $R^2=0.8953$	$y=-0.0487x+0.314$ $R^2=0.4190$
Total Chl	$y=-0.1776x+1.5503$ $R^2=0.8021$	$y=-0.1362x+1.1342$ $R^2=0.4555$
Car	$y=-0.0941x+0.7564$ $R^2=0.5805$	$y=-0.213x+0.8613$ $R^2=0.4844$

at DH site. K^+ showed high correlation with Ca^{2+} ($r=0.56$) and Mg^{2+} ($r=0.72$) that indicated their common crustal sources. Also, K^+ and Cl^- showed significant correlation with each other ($r=0.86$) which indicated the outdoor influence of biomass and municipal waste burning around DH site, as well as indoor sources such as cooking and cleaning activities which release K^+ and Cl^- (Tian et al. 2008; Zhong et al. 2014; Habil et al. 2015; Nazaroff and Weschler 2020). A high correlation was observed between Ca^{2+} and SO_4^{2-} ($r=0.85$) similar to MH site, which indicated the scavenging of SO_4^{2-} through chemical coupling. The regression analysis of Ca^{2+} and SO_4^{2-} also indicated the secondary compound formation. NO_3^- showed high correlation with Na^+ ($r=0.82$) suggesting coarse mode interactions between NO_3^- and Na^+ (Kulshrestha et al. 1998; Satsangi et al. 2002). The Na^+/NO_3^- ratio was approximately 2.6 which indicated abundance of Na^+ arising from local dust. Linear regression analysis also showed the association between NO_3^- and Na^+ at DH site. These strong correlations indicate the influence of road dust and roadside vehicular emissions (in the form of SO_2 and NO_2) on suspended roadside dust and regional soil (Kulshrestha et al. 2003b). During long-range transport in atmosphere, NO_3^- shows enhanced loadings in larger sized coarse particles (Bates et al. 2004; Topping et al. 2004). Linear regression analysis of NO_3^- and SO_4^{2-} also showed no association at DH site. It was due to a decrease in SO_4^{2-} abundance with no industrial activities and very few common sources for SO_4^{2-} and NO_3^- at DH site.

It can be summarized that the C/A ratios and pH of the dustfall extract indicated that the dust was basic in nature at both the sites. Outdoor activities influenced the chemical characteristics of the indoor dustfall fluxes on the foliar surfaces because most of the indoor dust is derived from outdoors.

Variations of biochemical components in response to SO_4^{2-} and NO_3^- fluxes

The degree of resistance to pollutants is strongly dependent on the chemistry of pollutant, and accurate knowledge of their type and concentrations is necessary for the successful pollution abatement using plants (Farmer 1993; Shannigrahi et al. 2004). In the present study, the average dustfall flux of SO_4^{2-} was statistically different between DH and MH sites ($p < 0.05$). SO_4^{2-} abundance in dust is reported to cause a decrease in leaf pH and photosynthetic pigments, cuticle damage, and necrosis in plants which increases under moist conditions (Gheorghe and Ion 2011; Gupta et al. 2016a). SO_4^{2-} and NO_3^- content of the dustfall enhances stress by increasing the foliar acidity which has significant impact on the biochemical constituents of the plant (Gupta et al. 2015a). SO_4^{2-} and NO_3^- gain diffused entry inside the mesophyll cells of the leaves which causes stress when they are not able to get assimilated within cells (Buchner et al. 2004; Gupta et al. 2015b). The ions such as SO_4^{2-} and NO_3^- enter into the cell with cotransport of protons (aided by membrane transporters). NO_3^- is cotransported with one H^+ whereas SO_4^{2-} is cotransported with three H^+ into the cytosol as shown by following simple equations (Buchner et al. 2004; Britto and Kronzucker 2005; Gupta et al. 2015b).

$$NO_3^-(ext) + H^+(ext) ===> NO_3^-(cyt) + H^+(cyt) \quad (5)$$

$$SO_4^{2-}(ext) + 3H^+(ext) ===> SO_4^{2-}(cyt) + 3H^+(cyt) \quad (6)$$

NO_3^- and SO_4^{2-} transport has been shown to initially cause a transient lowering of cytosolic pH which can be enhanced when the concentration is increasing and unassimilated NO_3^- and SO_4^{2-} accumulate to substantial concentrations (Britto and Kronzucker 2005). High NO_3^- concentrations may ultimately lead to NO production (via non-enzymatic reduction of nitrite) which along with O_2^- can be catalyzed by nitrate reductase to produce peroxynitrite ($ONOO^-$) that is potentially toxic to plants. Similarly, SO_4^{2-} is remobilized from mesophyll cells to vascular tissue for assimilation in the sink cells. Translocation of excess SO_4^{2-} results in reactive oxygen species (ROS) that are toxic to biochemical constituents and further affect the physiological activities of plants. In the following sections, we studied the variations in selected biochemical parameters of *F. elastica* foliage with respect to indoor dustfall fluxes of SO_4^{2-} and NO_3^- which are contributed by anthropogenic activities.

Photosynthetic pigments versus SO_4^{2-} and NO_3^-

Chlorophyll *a* (Chl *a*), chlorophyll *b* (Chl *b*), and carotenoids (Car) are found in the chloroplasts that are essential in light harvesting for the photosynthetic activity in green plants. Examination of these pigments is of primary importance to assess the extent of injury in the plants on exposure to pollutants. Figure 3 shows the mean values of total Chl, Chl *a*, Chl *b*, and Car obtained in the *F. elastica* foliage at both sites. Chlorophyll is an indicator of plant injury due to air pollution (Gupta et al. 2016b) and a decrease in chlorophyll content is associated with its oxidation, pheophytinization,

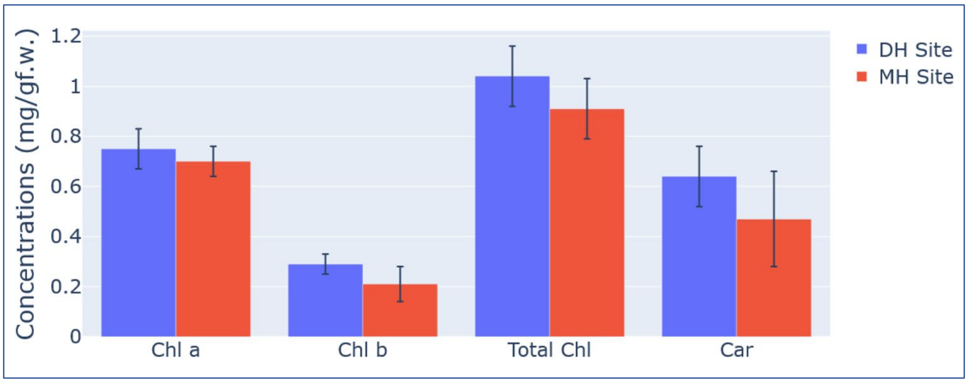


Fig. 3 Average concentrations of photosynthetic pigments

and reversible bleaching processes on exposure to air pollutants. The degradation of Chl *a* to pheophytin occurs through replacement of Mg^{2+} ions from chlorophyll molecules, but degradation of Chl *b* to chlorophyllide is followed by the removal of the phytol group in Chl *b* molecules (Gupta et al. 2015a). SO_2 and NO_2 are known to cause foliar injury and inhibit photosynthesis at high concentrations (White et al. 1974). Similarly, reduction was also observed in Car levels. Higher dustfall fluxes play a destructive role which either catalyzes the breakdown of carotenoids or does not allow its accumulation in the foliage that indicates greater oxidative stress in plants (Mandre and Tuulmets 1997). Photosynthesis process is known to be sensitive to excess SO_4^{2-} concentrations as it is a competitive inhibitor of ribulose-1,5-bisphosphate carboxylase and inhibits the photophosphorylation process. SO_2 gets dissolved in the cell sap to form HSO_3^- and SO_3^{2-} ionic species which are further converted to SO_4^{2-}. When the cell sap pH is between 2 and 3.5, Mg^{2+} gets displaced from the chlorophyll molecule, which in turn leads to the formation of a degradation product of chlorophyll known as phaeophytin. However, if the sap pH is above 3.5, superoxide radicals are generated which oxidize carotenoids pigments and subsequently damage chlorophyll. Excess of NO_3^- causes the photo-oxidation of chlorophyll molecules, thereby changing the chlorophyll *a*/*b* ratios which alters photosynthetic efficiency of the plants (Tüney Kızılkaya and Unal 2018). Figure 4a and b show the variations in the content of photosynthetic pigments with respect to dustfall fluxes of SO_4^{2-} and NO_3^- (mg/m^2/day). Table 1 presents the regression equations associated with the variations in photosynthetic pigments with respect to and SO_4^{2-} and NO_3^- fluxes in dustfall. It was noted that as the anionic flux increased, levels of all the studied photosynthetic parameters such as Chl *a*, Chl *b*, Total Chl, and Car progressively decreased in *F. elastica* leaves and the effect was more pronounced at MH site as compared to DH site.

Ascorbic acid versus SO_4^{2-} and NO_3^-

The average ascorbic acid (AA) content determined in *F. elastica* leaves was 1.32 ± 0.21 and 0.78 ± 0.15 mg/g f.w. at MH and DH sites, respectively, and AA concentrations were observed to be significantly higher at the MH site as compared to DH site ($p < 0.05$). It is reported that the interaction with AA is very critical and plants with higher AA concentration in their leaves have reportedly shown higher rates of NO_2 uptake through their stomata (Teklemariam and Sparks 2006; Xin et al. 2007). During stomatal uptake, NO_2 reacts with ascorbate (AH^-) to form nitrite (NO_2^-) and dehydroascorbate (A^-) (Forni et al. 1986; Ramge et al. 1993).

$$NO_2 + AH^- ===> NO_2^- + A^- + H^+ \tag{7}$$

AA is a natural antioxidant that is produced in the plants for protection against harmful oxidative species. It has the capacity to donate electrons in numerous enzymatic and non-enzymatic reactions in the plant systems and thereby serves as a potent ROS (reactive oxygen species) scavenger, such as by scavenging O_2^- and

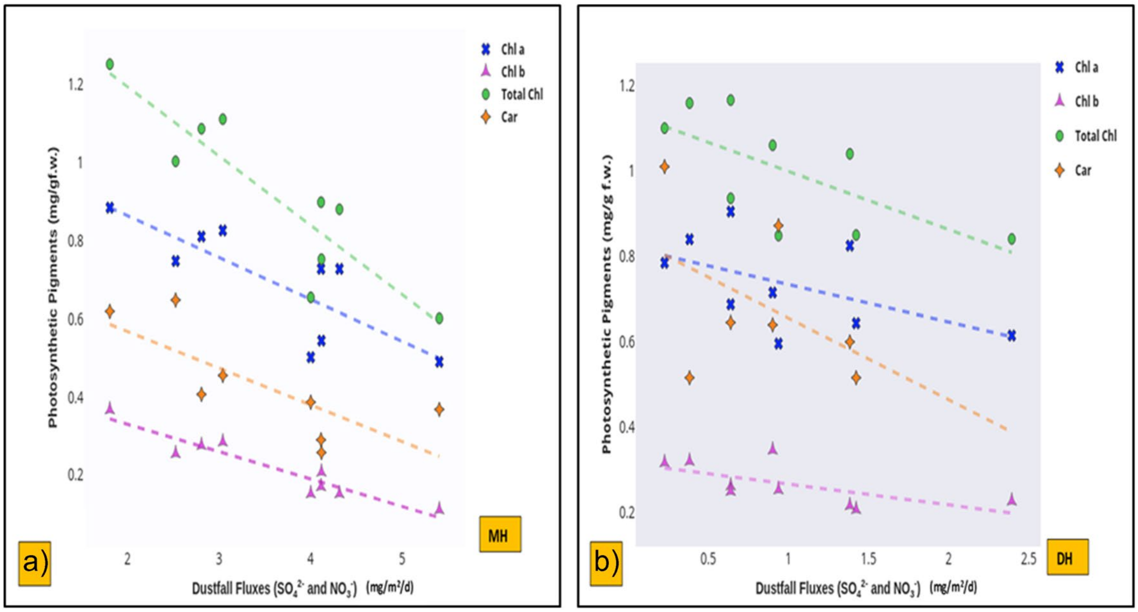


Fig. 4 Scatter plots showing variations in the photosynthetic pigments of *Ficus elastica* leaves with dustfall fluxes of (SO_4^{2-} + NO_3^-) at **a** MH and **b** DH sites

OH$^{\bullet}$ radicals and providing stability to cell membranes (Smirnoff 2000). Figure 5 shows that AA content in the leaves increased with the increase in dustfall fluxes of SO_4^{2-} and NO_3^- which marked stress conditions in plants due to air pollution at both sites.

Total soluble sugar versus SO_4^{2-} and NO_3^-

The average concentrations of total soluble sugar (TSS) were recorded as 87.61 ± 12.2 and 75.82 ± 10.5 mg/g f.w. at DH and MH sites, respectively. They serve as the primary energy source for plants and play key roles in maintaining structure and metabolism at cellular level. It was observed in the present study that as the SO_4^{2-} and NO_3^- dustfall fluxes increased, TSS concentrations dropped in *F. elastica* leaves as depicted in Fig. 6. Lowering of TSS levels under polluted conditions could be due to higher respiration rates and inhibition of photosynthesis which leads to decreased C fixation by plants (Tripathi and Gautam 2007).

Relationship between biochemical parameters

The relationship between biochemical parameters was ascertained by calculating the Pearson correlation coefficients among Chl *a*, Chl *b*, Total Chl, Car, TSS, and AA along with the dustfall fluxes of SO_4^{2-} and NO_3^-. Figure 7a and b indicate that Chl *a*, Chl *b*, Total Chl, Car, and TSS showed negative correlation and AA showed positive correlation with dustfall flux of SO_4^{2-} as well as NO_3^- at both MH and DH sites. It is known that soluble sugars are involved in the biosynthesis of AA (Debolt et al. 2007; Gallie 2013) and a negative correlation between TSS and AA corroborated the fact that TSS decreased with the increasing concentrations of AA. Similarly, AA showed negative correlation with Chl *a*, Chl *b*, Total Chl, and Car because stress conditions produced due to dustfall flux of SO_4^{2-} and NO_3^- reduce the levels of photosynthetic pigments in *F. elastica* leaves and increase AA concentrations. The decrease in photosynthetic pigments adversely affects photosynthesis which influences the formation and availability of soluble sugars. Following this, TSS and the monitored photosynthetic pigments showed

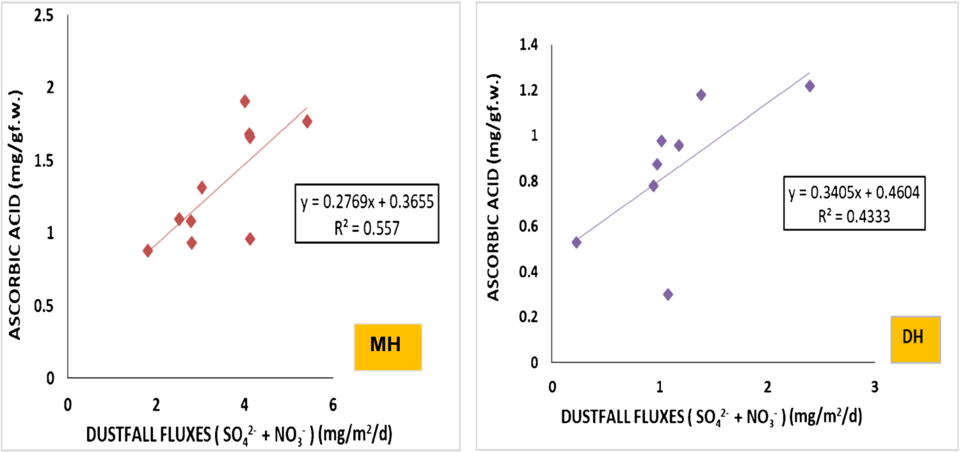


Fig. 5 Variations in ascorbic acid content of *Ficus elastica* leaves with dustfall fluxes of (SO_4^{2-} + NO_3^-) at MH and DH sites

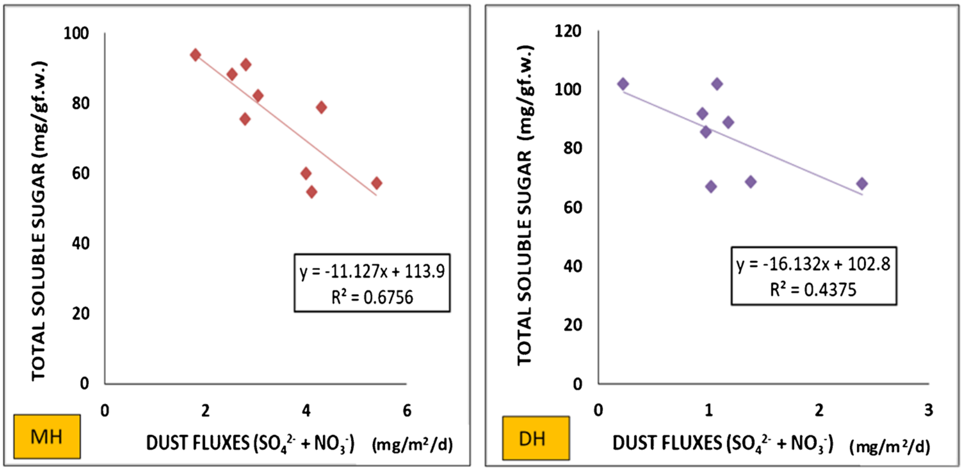
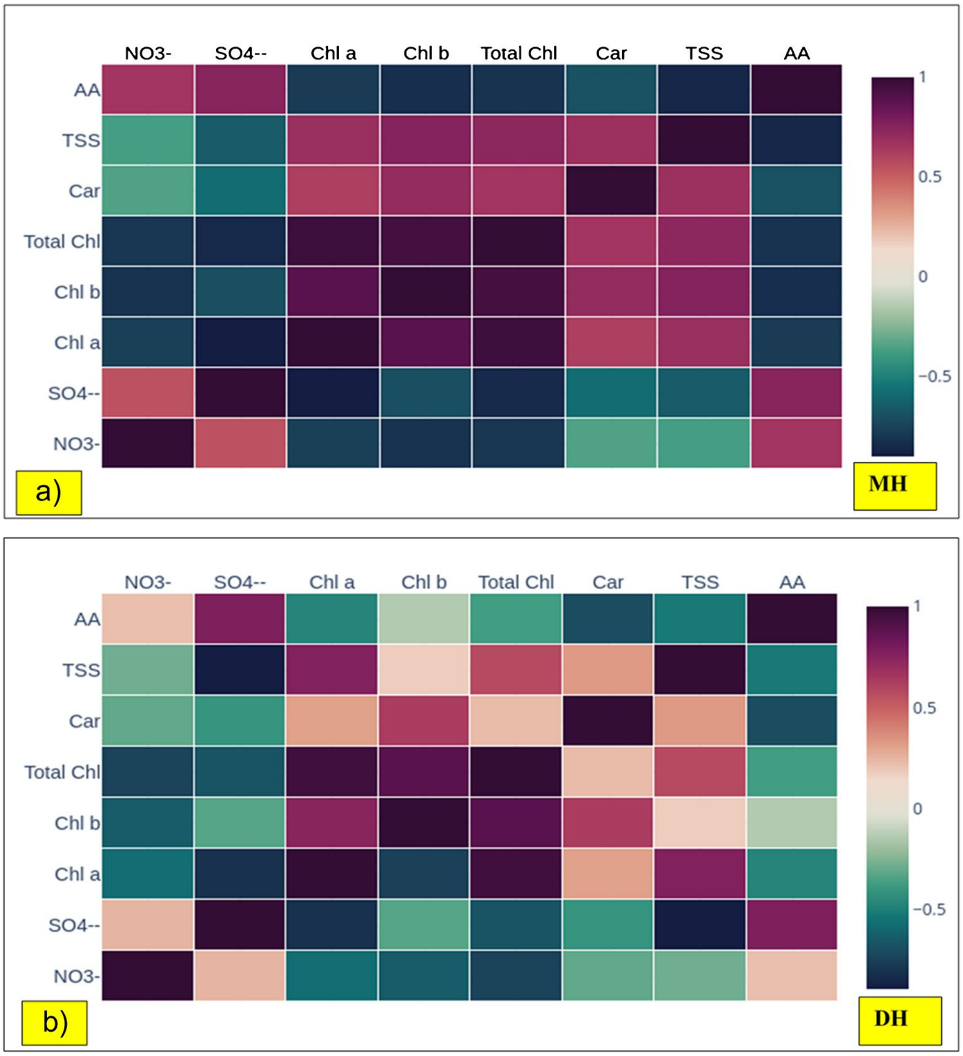


Fig. 6 Variations in total soluble sugar content of *Ficus elastica* leaves with dustfall fluxes of (SO_4^{2-} + NO_3^-) at MH and DH sites

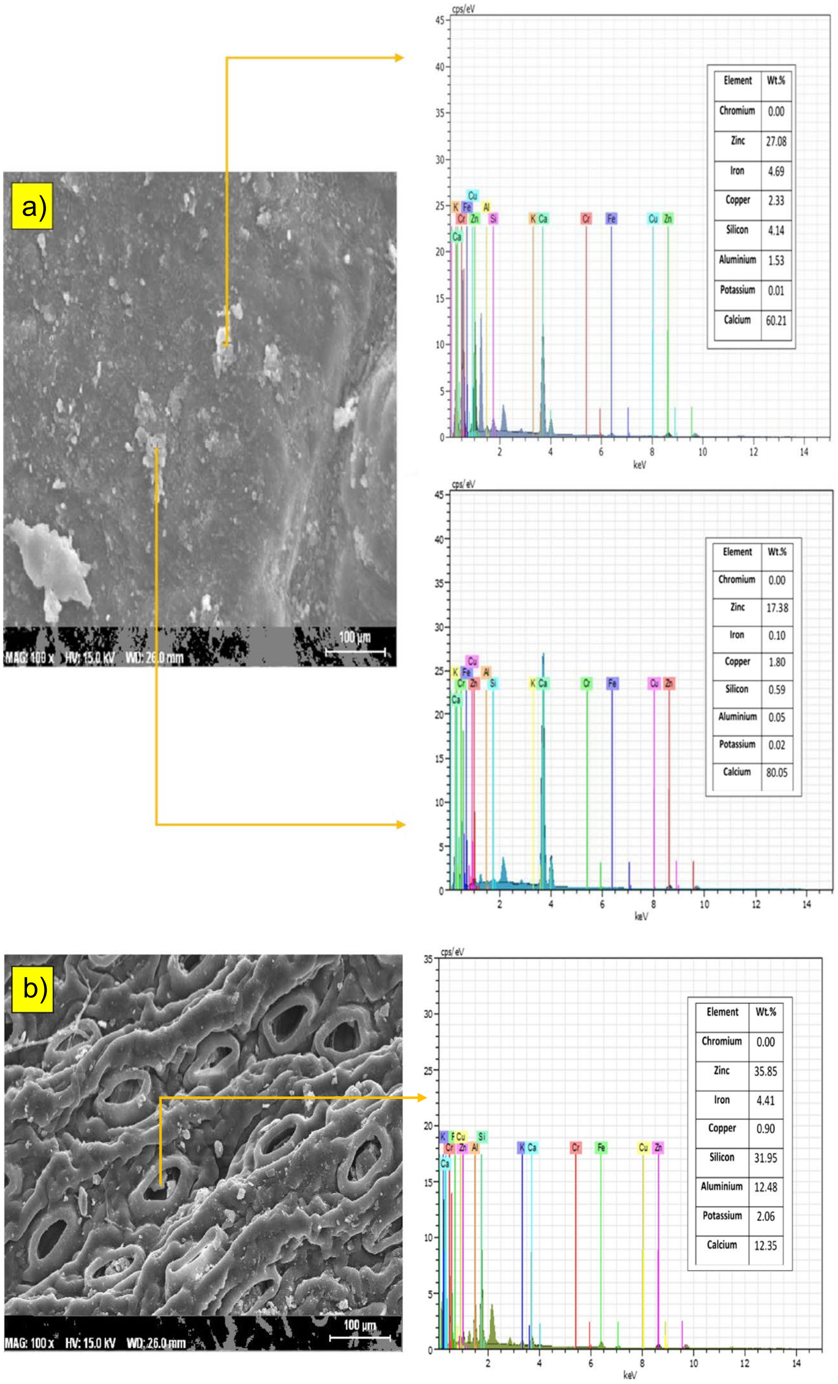
Fig. 7 Correlation between dustfall fluxes of SO_4^{2-}, NO_3^-, and biochemical parameters for *Ficus elastica* leaves at **a** MH and **b** DH sites



positive correlation at both DH and MH sites. Based on the biochemical parameters, viz., ascorbic acid, leaf pH, total chlorophyll content, and relative water content, the Air Pollution Tolerance Index (APTI) of a plant can be calculated. APTI is an effective parameter to assess a plant's ability in the form of its tolerance or susceptibility against air pollutants and to remove them from the surrounding atmosphere. The authors have computed the APTI for *F. elastica* at DH (9.5) and MH (10.1) sites and it has been previously reported elsewhere (Katoch and Kulshrestha 2022).

Morphological analysis of indoor dust

Figures 8 and 9 (SEM images of *F. elastica*) indicate that dust deposition on the *F. elastica* leaves was more at MH site as compared to DH site with greater density of dust particles on the adaxial surface as compared to the abaxial surface of the leaves. Sedimentation of coarse particles has more effect on the adaxial surface of foliage. Similar results have been shown in earlier studies (Gupta et al. 2016b; Katoch and Kulshrestha 2022). Micromorphological features of plants such as stomatal density, trichomes, density of undulations, grooves, and ridges play a key role in capturing dust by foliar surfaces. SEM images of *F. elastica* indicate the absence of trichomes and presence of grooves and ridges on the abaxial surface. Based on the origin and type of dust, the dust particles can be small, individual large, or large aggregates of variable size. Particles with irregular and elongated shapes were observed which have natural mineral sources and are rich in crustal elements. However, particles with smooth surfaces and spherical shapes were also present which could be derived from high-temperature combustion sources such as cooking, engines and tail pipes of vehicles, or abrasion of vehicular components which are commonly present in urban cities like Delhi (Sharma et al. 2018; Mishra et al.



Element	Wt.%
Chromium	0.00
Zinc	27.08
Iron	4.69
Copper	2.33
Silicon	4.14
Aluminium	1.53
Potassium	0.01
Calcium	60.21

Element	Wt.%
Chromium	0.00
Zinc	17.38
Iron	0.10
Copper	1.80
Silicon	0.59
Aluminium	0.05
Potassium	0.02
Calcium	80.05

Element	Wt.%
Chromium	0.00
Zinc	35.85
Iron	4.41
Copper	0.90
Silicon	31.95
Aluminium	12.48
Potassium	2.06
Calcium	12.35

Fig. 8 SEM images and EDX spectra of the indoor dust present on the **a** adaxial and **b** abaxial sides of *Ficus elastica* leaves at DH site

2019). These particles indicate the occurrence of soot particles and fly ash (containing alumino-silicate compounds as shown by EDX analysis) in the indoor dust deposited from outdoor industrial activities. Dust particles covered the leaf surfaces but were not homogenously distributed. Deposition of particles on leaf surfaces can increase leaf temperature and alter stomatal conductance (Gupta et al. 2016b). Plugging of stomata with particles leads to physiological imbalances by altering the gaseous exchange and water regime in the plants.

Elemental analysis of indoor dust

In the elemental analysis of the indoor dustfall deposited on plant leaves, we have focused on the inorganic fraction in the course of present study. Such profiling of elements is helpful in identifying the dominant sources and their contribution to the indoor dust load. Usually, foliar deposition and uptake of heavy metals from the atmosphere are less studied as compared to root transfer in plants (Shahid et al. 2017). Figures 8 and 9 show the SEM–EDX spectra

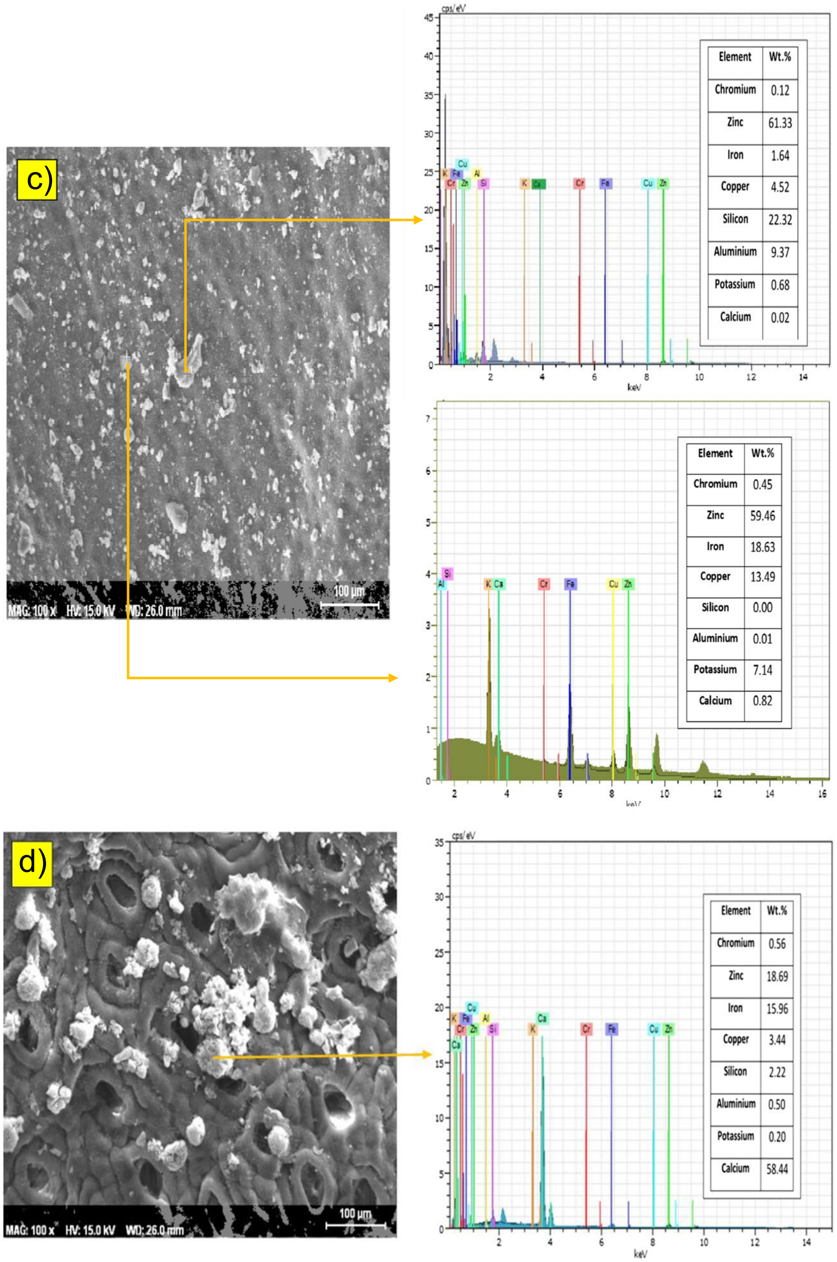


Fig. 9 SEM images and EDX spectra of the indoor dust particles present on the **c** adaxial and **d** abaxial sides of *Ficus elastica* leaves at MH site

Element	Wt.%
Chromium	0.12
Zinc	61.33
Iron	1.64
Copper	4.52
Silicon	22.32
Aluminium	9.37
Potassium	0.68
Calcium	0.02

Element	Wt.%
Chromium	0.45
Zinc	59.46
Iron	18.63
Copper	13.49
Silicon	0.00
Aluminium	0.01
Potassium	7.14
Calcium	0.82

Element	Wt.%
Chromium	0.56
Zinc	18.69
Iron	15.96
Copper	3.44
Silicon	2.22
Aluminium	0.50
Potassium	0.20
Calcium	58.44

to assess the presence of elements such as Cr, Zn, Fe, Cu, Si, Al, K, and Ca in the foliar capture of dust particles on the adaxial and abaxial surfaces of *F. elastica* plants kept in the households at both sites. It was observed that Zn was ubiquitously present as one of the major components of foliar dust. Rapid construction of roads, subways, buildings etc. and dust resuspension are known to amplify the levels of Zn in urban dust (Yang et al. 2020). Yaparla and coworkers (Yaparla et al. 2019) observed higher Zn concentrations than background values in the indoor dust of rural households which used biomass burning as primary fuel type. In the present study, fuel used in the households was LPG. The presence of Zn in urban households was a result of mixed activities such as traffic movement, tire abrasion, fuel burning, cooking fumes, construction activities, and road dust (Yang et al. 2020; Jia et al. 2021). Cu and Cr were observed in the dust on adaxial and abaxial foliar surfaces at MH site. The percentage of Cr present was less, but its occurrence indicated industrial sources (Lin et al. 2017). Cu and Cr are found in automobile components, engine wear, lubricating oil residues, tire abrasion, bearing parts, brake dust, etc. (Wang et al. 2020). Heavy traffic movement and manufacturing activities related to automotive parts and automobile sector are quite prevalent near MH site.

Conclusions

It was observed that the average dustfall flux on *F. elastica* leaves was higher at MH site as compared to DH site. This study shows that apart from the amount of dustfall deposition, chemical composition of the deposited dust plays a key role in driving the plant specific responses. Chemical analysis of dust indicated the effect of industrial sources in the indoor dust at MH site. Ca^{2+} was noted to be the dominant cation at both the sites whereas SO_4^{2-} and Cl^- had highest fluxes among anions at MH and DH sites, respectively. Elements such as Zn, Ca, K, Si, Fe, and Al were present in the dust on foliar surfaces at DH and MH sites indicating crustal and secondary origins in the households. It was observed that with the increase in the dustfall fluxes of ($SO_4^{2-} + NO_3^-$), the content of soluble sugar and photosynthetic pigments decreased and the decrease in these biochemical parameters was more pronounced at MH site as compared to DH site. An increase in ascorbic acid content in *F. elastica* leaves was seen with the increase in SO_4^{2-} and NO_3^- fluxes, and a significant increase at MH site indicated more stress in *F. elastica* leaves at this site. However, as the plants were exposed to natural conditions at the study sites, therefore they can be under the influence of additional factors/elements apart from the observed correlations which needs to be studied further. It can be summarized that *F. elastica* foliage capture dust particles inside buildings and differences in ambient surroundings affect the chemical characteristics of the dust particles as well as the biochemical responses of the plant to dust deposition. More comprehensive studies are needed to ascertain the role of indoor plants in developing a smart and sustainable urban green infrastructure which could be helpful in abating air pollution and improving the quality of life.

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Author contribution Ankita Katoch—sample collection, chemical analysis, data analysis, visualization, manuscript preparation. U.C. Kulshrestha—conceptualization, editing, and content enrichment.

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Data Availability Data can be made available by authors on reasonable request.

Declarations

Conflict of interest The authors declare that they have no competing interests.

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