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RESEARCH ARTICLE

Potential of Epiphytic Lichen *Pyxine cocoes,* as an Indicator of Air Pollution in Kolkata, India

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Abstract The accumulation of trace elements in the thalli of epiphytic lichens can reveal levels of trace elements in the ambient air. This study assessed the trace elements in lichen species *Pyxine cocoes* found in the urban and peri-urban areas of Kolkata. Trace elemental analysis was carried out using energy-dispersive X-ray fluorescence and proton-induced X-ray emission spectroscopy. Variable levels of elements like Mn, Fe, Cu, Zn, Cr, V and Pb, are detected in the thalli of *P. cocoes* collected from repressentative locations. Localization of trace elements in the thalli was confirmed by analysis using scanning electron microscope attached with EDX spectrometer. Several pollution indices such as enrichment factor, contamination factor (Cf) and pollution load index were estimated to evaluate the trace element contamination level of the ambient air at the sampling spots. PLI and Cf and values suggest deterioration or air quality that varies from moderate to high level of contamination. Ca, S, Pb, Sr and Cr, are highly enriched at urban sampling spots (1–9). High coefficient of variation values for Ca, S, Pb, Sr and Cr confirm their accumulation from local anthropogenic sources in the urban sampling spots (1–9). However, results of principal component analysis analysis have shown that sources of trace elements in the samples from urban areas include both vehicular emissions and anthropogenic activities. Higher concentration of trace elements in the lichen thalli collected from peri-urban locations is attributed to vehicular emissions from the highways and expressways running through these areas.

Keywords Biomonitor · Epiphytic · Lichen · Trace element · Air pollution · Environment

This work unravels the potential of a specific epiphytic lichen, *Pyxine cocoes* to trap heavy metals from the atmosphere in their thalli and thereby portray the pollution status in and around the places they are collected from. The research highlights how *Pyxine cocoes*, collected from the different urban and peri-urban areas in and around the megacity Kolkata, India, have been instrumental in providing an idea about the air pollution status without actively involving any cumbersome power-consuming monitoring techniques.

Introduction

Air pollution is a global issue yet to be solved. Air quality deterioration has started postindustrial revolution. Such deterioration in air quality has further enhanced due to increase in uncontrolled emissions from transportation, industrial and domestic activities. These emissions contain both gaseous and particulate pollutants which are hazardous to human health. Hence, an increase in pollution has

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resulted in numerous health effects in general and respiratory problems in particular. A study has estimated that air pollution contributes to approximately 800,000 deaths and loss in average years of lives of 4.6 million people annually [1]. It has been observed that the developing countries of Asia are predominantly affected by air pollution. India is one of the most polluted countries in Asia. Atmospheric particulate matter is one of the leading causes of health problems in India [1]. These particulate matters contain heavy metals which have been classified hazardous pollutants due to their toxicity and persistence in the environment. Consequently, the evaluation of the levels of heavy metal deposition is of vital importance for the assessment of human exposure. There is a pressing need to design strategies for effective air pollution management. The foremost requirements for designing management strategies include continuous monitoring of the ambient pollution level and information about the sources of pollutants.

Monitoring air quality is a difficult and complicated process due to several reasons, such as diversity of potentially hazardous substances (pollutants), spatial and temporal variations of pollutants and multiple sources of pollutants [2]. In addition, active air sampling is expensive and requires technical expertise. Thus, several passive air pollution monitoring techniques have been devised. Passive biomonitoring of air pollution is being carried out using several organism. Biomonitoring techniques utilize the ability of living organisms to accumulate pollutants in their tissues as well as organism's sensitivity to pollution. Epiphytic lichens are frequently used for passive biomonitoring of air quality. Several studies have established the usage of lichen as an important tool for biomonitoring atmospheric deposition of trace elements [3]. Perennial life, lack of protective cuticle, lack of roots and absence of well-differentiated vascular system enable lichens to absorb trace elements directly from the atmosphere. Lichens trap atmospheric particulates contaminated with trace elements in a non-selective manner in their thalli. The elemental concentration in the lichen thalli is found to bear correlations with the atmospheric metal level (metal content in the aerosols) which increases with distance from the source [4]. The sensitivity of lichens to pollution is related to the degree of dependency of the mycobiont (fungal partner) on the photobiont (algal partner) for metabolic energy. The stronger the dependency, more sensitive would be the lichen. Lichens have been employed to draw inferences about large-scale spatial and long-term temporal patterns of atmospheric metal deposition. Pollution-tolerant lichens hence can manifest the spatial and temporal variations in atmospheric elemental deposition.

A joint study by the British Deputy High Commission, UKAID and Kolkata Municipal Corporation in 2016 reported that around 70% of the city's 15 million inhabitants suffer from some form of respiratory problems caused by air pollution, which comes mainly from automobile exhausts and industrial emissions. Thus, the present work has been designed to study spatial variations in accumulation, enrichments and interaction patterns of elements in epiphytic lichen growing in and around Kolkata, which is one of the most polluted cities in India/South Asia. Among the various lichen species collected, *Pyxine cocoes* has been identified to be the most dominant species, and hence, it is chosen as the model organism of the present study.

Material and Methods

Study Area

The present work has been designed to study spatial variations in accumulation, enrichments and interaction patterns of elements in epiphytic lichens growing at different locations in and around Kolkata, which is now among the most polluted cities of India/South Asia. A joint study by the British Deputy High Commission, UKAID and Kolkata Municipal Corporation in 2016 reported that around 70% of the city's 15 million inhabitants suffer from some form of respiratory problems caused by air pollution, which comes mainly from automobile exhausts and industrial emissions. Among the various lichen species collected, *P. cocoes* has been identified to be the most dominant species and hence chosen as the study organism of the present study.

Figure 1 (Map showing the 22 sampling spots in and around Kolkata) shows the study area in and around Kolkata (22.5726° N, 88.3639° E) which is one of the most densely populated megacities in India. Kolkata is located on the east bank of the Hooghly River and is characterized with a tropical wet and dry climate with norwesters or summer monsoons. The annual mean temperature is 26.8 °C; monthly mean temperature ranges from 19 to 30 °C, and the maximum temperature sometimes exceeds 40 °C during summer months. Summers are hot and humid; winters are cold and dry. Rainfall ranges from 1580 to 1600 mm mainly during June to September with occasional showers in autumn

The sampling area was chosen as the northern boundaries of Kolkata and also around the city within a radius of 100 kms keeping Salt Lake as the starting point. Sampling was carried out from 22 spots which comprises of 9 urban and 13 peri-urban areas. Samples were collectively gathered from 22 sampling spots that are described in supplementary Table 1.

Collection and Preparation of Samples

Lichen samples (*P. cocoes)* were collected from 22 spots in and around Kolkata, India. The samples of about the same

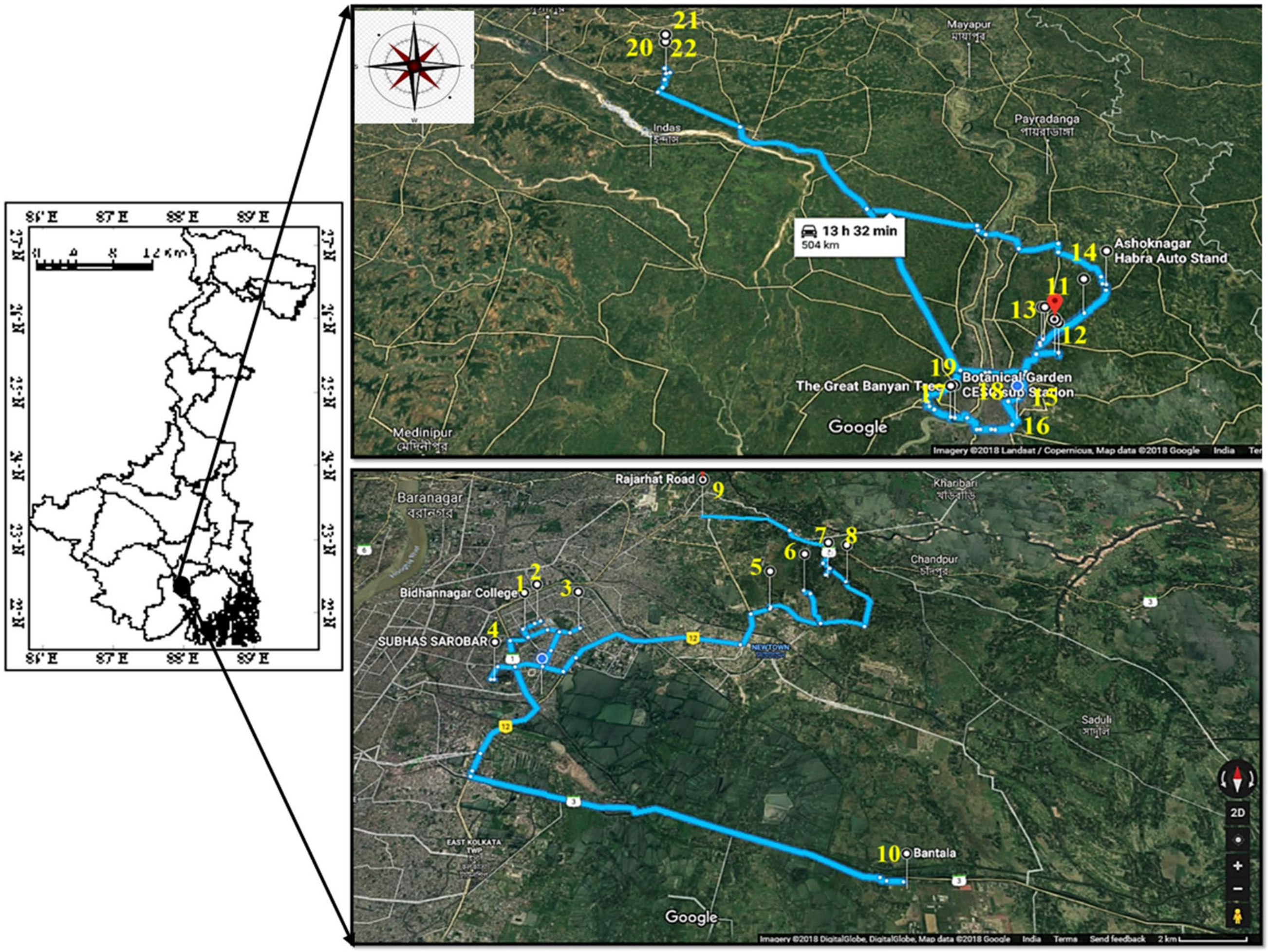


Fig. 1 Map showing the 22 sampling spots in and around Kolkata

size of thalli (~ 3–5 cm in diameter) were collected in triplicates from a height 3 to 5 feet above the ground, from the barks of trees like areca nut, jackfruit, mango, nerium, neem, tamarind, coconut and palm. After removing the dust from the surface using a small brush, the lichen thalli were freeze dried. Dried lichen samples (in triplicates) were ground to a fine powder using a mortar and pestle and stored for further use. Three pellets for each sample collected from a given sampling spot were prepared using press pelletizer.

Analytical Procedures

Due to differential detection limits, two different techniques were used for the elemental analysis. Both of these techniques are based on the same principle, i.e., use of photons to excite the atoms in the samples to produce characteristic secondary X-ray fluorescence. The energy of the secondary X-ray confirms the element, and the intensity of X-ray specifies the quantity of the element present in the sample. Photons used in EDXRF technique are primary X-rays, whereas proton are used as photon in PIXE technique. Differential detection limits can be ascribed to source of photons, sample matrix and type of detectors used for detection of X-rays.

Analysis of Elements Using PIXE

PIXE measurements were taken using a 3 MeV Pelletron facility (3.0 MV Pelletron Accelerator (NEC-made)—MCS-NICS ion source, Ion Beam Laboratory: Beam lines for PIXE). The sample pellets were prepared using graphite for PIXE analysis. Pellets were mounted in a scattering chamber at a pressure of 10^{-6} Torr and subsequently exposed to a 2 mm collimated beam of 3 MeV protons. The beam current was maintained between 1.5 and 3.0 nA for a count rate of 400–600 cps during spectra collection. SRM 1515 (apple leaves), SRM 1547 (peach leaves) and CTA-OTL-1 (tobacco leaves) were used for quantification of the elements and checking the reliability of the data obtained by the system. PIXE was employed to detect heavy metals like Cu, Zn, V, Ti, Ni, Cr and Pb.

Table 1 Sampling locations and their details

Spot number	Sampling points	Latitude (N)	Longitude (E)	Elevation (in m)
1	Salt lake City Center	22.58784212°	88.40794802°	5
2	Salt lake Bidhan Nagar college	22.5844913°	88.4053353°	7
3	Karunamayee	22.5921709°	88.42827648°	6
4	Subhas Sarovar	22.56859371°	88.40383351°	7
5	Rajarhat Main Road	22.61071777°	88.51965934°	7
6	Rajarhat Mohammadpur	22.5894°	88.4748°	9
7	Rajarhat Kadampukur	22.61°	88.52°	4
8	Rajarhat CC pur	22.6138°	88.4931°	9
9	Rajarhat Jamalpara	22.6041°	88.5056°	8
10	Bantala	22.5057°	88.5082°	11
11	Madhyamgram	22.6924°	88.4653°	15
12	N-24 Pgs, Bira	22.7834°	88.5734°	10
13	N-24 Pgs, Torulia	22.848854°	88.663956°	14
14	Ashokenagar	22.833°	88.633°	13
15	Indian Botanic Garden (Ibg)- Palm line	22.5565°	88.2855°	7
16	IBG Main Gate	22.55695750136148°	88.30070433283291°	7
17	IBG	22.56138889°	88.29222222°	16
18	IBG	22.556475°	88.28554166666666°	13
19	IBG Andul Road	22.58°	88.24°	9
20	Jamunadighi	23.4286111°	87.62333333333332°	55
21	Bhalukimachan	23.4560°	87.6263°	76
22	Jamunadighi fisheries	23.430234°	87.6228048°	55

Analysis of Elements Using EDXRF

EDXRF study was carried out using a Xenemetrix Ex-3600 spectrometer having an oil-cooled Rh anode X-ray tube (operating at a maximum voltage of 50 kV and a maximum current of 1 mA). The measurements were taken in vacuum condition. The X-rays were detected using a liquid nitrogen-cooled 12.5 mm^2 Si (Li) semiconductor detector (resolution 150 eV at 5.9 keV). To optimize the signal-to-noise ratio, different filters were used between the source of photon and sample. The X-ray fluorescence spectra were quantitatively analyzed by the software next Integrated with the system. Standard reference materials (SRM) from the National Institute of Standards and Technology (NIST) were used for quantification of the elements and checking the reliability of the data obtained by the system. In this study, SRM 1515 (apple leaves), SRM 1547 (peach leaves) and CTA-OTL-1 (tobacco leaves) were used as standards.

Environmental Quality Indices

To understand the origin of the elements accumulated in the lichens and to assess the pollutant status in the ambient habitat of the lichens, environmental quality indices like enrichment factor (EF), contamination factor (CF) and pollution level index (PLI) were calculated from the data procured by analyzing the elemental profile of the lichen samples of the respective locations.

Enrichment Factor (EF)

In this study, the EF was calculated by normalizing elemental concentrations to the corresponding baseline values of trace elements in foliose lichens in Northern Hemisphere, using the formula:

$$\mathrm{EF} = \frac{([\mathrm{EI}]/[\mathrm{X}])\mathrm{Lichen}}{([\mathrm{EI}]/[\mathrm{X}])\mathrm{Baseline\ values\ for\ foliose\ lichens\ from\ Northern\ Hemisphere}}$$

where X is the concentration of the reference element chosen for normalization and EI corresponds to the element of interest whose enrichment were assessed in the present study. The subscripts denote the type of the sample. The concentrations of elements in the baseline values for foliose lichens in the Northern Hemisphere have been referred from the literature [5].

Contamination Factor (CF)

In order to evaluate the degree of contamination in an ecosystem, or to carry out biomonitoring operations, it is necessary to have the background or baseline values of the contaminant. The background elemental concentrations refer to natural range in concentration of the elements which exists in an ecosystem prior to contamination through anthropogenic sources, whereas baseline concentrations can be higher than those background values as they represent the levels that are measured in samples from a given area suitable enough to serve as reference values. Here, the baseline values of foliose lichens [5] reflected the relationship between the levels of contaminants found in the lichens to the baseline concentration of the contaminant were calculated as follows:

$$\mathrm{CF} = \frac{\text{(Concentration of the contaminant in Lichens)}}{\text{(Baseline Concentration of the contaminant)}}$$

This calculation of contamination factor determines the situation or the environmental conditions of the sampling location.

Pollution Load Index (PLI)

The air pollution status of the study area was quantified using the pollution load index (PLI) to estimate degree of contamination and pollution in lichens following the standard methods [6]. PLI values were calculated as:

$$PLI = (CF1 \times CF2 \times \ldots \times CFn)^{1/n}$$

where CF is the contamination factor or pollution index factor (PIF).

Analysis of Particle Entrapment Using SEM

In order to characterize the particulate matter (PM) morphology before quantifying its elemental composition, small thalli were cut. Such small samples that include the deposited particles on its surface were mounted on an Aluminum plate and carbon coated, which was designed to avoid altering particle morphology. Particles were identified by a Phillips model XL30 scanning electron microscopy (SEM). Measurements validated the entrapment of particles PM 10 and PM 2.5 within the lichen thalli.

Statistical Analysis

Three measurements were taken for each sampling spot. Hierarchical cluster analysis was performed on the lichen data set by MINITAB using Ward's method of linkage with squared Euclidean distance shown as level of significance of similarity within a range of 100% to evaluate similarity if any between the sampling spots. Pearson's correlation and principal component analysis were done with Origin 8.0 and SPSS 20, and the level of statistical significance was set at $p \leq 0.05$.

Results and Discussion

Lichen Diversity and Abundance

In recent years, the air pollution scenario in Kolkata has drastically worsened. The report, Global Urban Ambient Air Pollution Database (update 2016), released by World Health Organization (WHO), shows that the toxicity in air is increasing most rapidly in Kolkata with a sharp increase in, both ultra-fine particulate and nitrogen oxides. The annual average $PM_{2.5}$ level increased to 61 μg per cubic meter in 2016 from 43 in 201. It was worse across the Hooghly River in Howrah–100 μg per cubic meter in 2016 from 47 in 2014, the national permissible limit being 40 μg per cubic meter.

Lichens show decline in their diversity, absence of sensitive species, morphological, anatomical and physiological changes as a result of increasing pollution due to increased anthropogenic activities. A study in 2014 reported *Parmelia caperata* to be the most abundant as well as a pollution-tolerant species in Kolkata [7]. It was proposed in another study [7] that among the different localities, the boundary areas of Kolkata city have scarce growth of few lichen species, while the heart of the city is devoid of lichens. In the present study, we have investigated this shift in lichen diversity, identification of the tolerant species (as mentioned in supplementary Table 2) that was available at all the sampling locations along with their capacity to accumulate trace elements.

In this study among all the sampling spots, 15, 18, 19 and 21 exhibited greater abundance and luxuriant growth of lichens and showed maximum lichen diversity. A group of earlier researchers working in these sites reported maximum species diversity [7]. Spots 15, 16, 17, 18 and 19 have shown wide variety of species of trees growing in moist, shady conditions and are situated in the less polluted pockets amidst the center of the Botanical Garden that makes

Table 2 Diversity and abundance of the lichen species that were collected across 22 sampling spots

Spot number	Sampling points	*Pyxine cocoes (Siv.) Nyl. (A)*	*Pyxine coccifera (Fee) Nyl.(B)*	*Pyxine subcineria (C)*	*Pyxine himalayensis (D)*	*Graphis cincta (Pers.) Aptroot (E)*	*Cryptothecia lunulata (F)*	*Lecanora achroa Nyl. (G)*	*Bacidia millegrana (Taylor) Mull. Arg(H)*	*Arthonia tumidula (I)*	*Permotrema tinctorum (J)*
1	Salt lake City Center	+	+	–	–	–	–	–	–	–	–
2	Salt lake Bidhan Nagar College	+	–	–	–	–	–	–	–	–	–
3	Karunamayee	+	–	–	–	–	–	–	–	–	–
4	Subhas Sarovar	+	+	+	–	–	–	–	–	+	–
5	Rajarhat Main Road	+	–	–	–	+	+	–	–	–	–
6	Rajarhat Mohammadpur	+	–	–	+	–	+	–	–	–	–
7	Rajarhat Kadampukur	+	–	–	–	+	+	–	–	–	–
8	Rajarhat CC Pur	+	–	+	–	–	+	–	–	–	–
9	Rajarhat Jamalpara	+	–	+	–	–	+	–	–	–	–
10	Bantala	+	+	+	–	–	–	–	–	–	–
11	Madhyamgram	+	–	–	–	–	–	–	–	–	+
12	N-24 Pgs, Bira	+	–	–	–	+	–	–	–	–	–
13	N-24 Pgs, Torulia	+	–	–	–	+	–	–	–	–	–
14	Ashokenagar	+	–	–	–	+	–	–	–	–	–
15	IBG-Palm line	+	–	+	–	+	–	+	–	+	–
16	IBG Main Gate	+	–	+	–	+	+	–	–	–	–
17	IBG	+	+	–	–	+	+	–	–	–	–
18	IBG	+	+	+	–	+	+	–	–	–	–
19	IBG Andul Road	+	–	–	–	–	–	–	–	–	–
20	Jamunadighi	+	–	–	+	+	–	–	–	–	–
21	Bhalukimachan	+	–	–	–	–	–	+	+	+	–
22	Jamunadighi fisheries	+	–	–	+	+	–	–	–	–	–

them suitable for housing abundant lichen species within the area [8]. 20, 21 and 22 spots are located at peri-urban area near a tourist spot with considerable human activity. 20, 21 and 22 also have shady moist microclimate together with open canopies, which allow more sunlight and wind to enter the spots. These spots have comparatively cleaner air than Kolkata city as they are quite far from the city, and showed a variety of five to six species within the protected areas. Observations on abundance and diversity of lichens showed that the spots which are in close proximity to Kolkata or within the city, viz. 1–10 and 11–14, have lesser variety of lichens. This could be due to very less tree coverage owing to the occasional clearing of lands for commercial and residential purposes, construction of buildings and widening of roads. These spots (1–10 and 11–14) have high pollution index which imparts toxicity and/or lethality to the sensitive lichens. Significant loss in diversity and abundance noted in the present study, as compared to the reports by the earlier researchers including the previous group from our laboratory. A minimal presence of avenue trees on the streets of Kolkata reportedly lessened the availability of lichens [7]. Majumder et al. [9] confirmed the presence of *P. caperata* as the pollution resistant lichen in the boundary areas of Kolkata city. Figure 2 (Relative abundance of the lichen species that were collected across 22 sampling spots) shows the relative abundance of the species that were collected from 22 sampling spots as shown in supplementary Table 2. The most abundant species found in all the sampling spots has been identified as *P. cocoes* (foliose) and *Cryptothecia lunulata* (crustose) and no other species are notably observed. In this study, we have also come across significant loss in vegetation cover and consequent loss in lichen diversity in core areas of the Kolkata city. Scarcely growing foliose licshens in the northern and southern fringes of the city (coverage = 0.05% area) were observed. Alongside the fact that lichen growth has already got sparse with relatively small cover value in the heart of the city, a relative shift from foliose to crustose species (that are more tightly adhered to the surface of the bark and needs less water for growth) has also been observed. Thus, over the years and past few decades subsequent shift in availability of certain growth forms of lichens has been noticed which is reportedly now more crustose than foliose in the polluted areas. Therefore, diversity and abundance of lichens growing in any area can potentially indicate the status of pollution in air throughout a considerable period of time.

Particle Entrapment:

SEM observations of exposed lichen thalli are shown in Fig. 3 (Anatomical observations of *Pyxine cocoes* under SEM). SEM analysis of sampling spots (d, e and f) correspond to sampling spots 2 and 3 with vehicular and industrial influences, respectively showing the particulate matter PM 10 and PM 2.5 being entrapped within the thalli. The coarse particles can be associated with pollutants released by metallurgical workshops and other factories in this area. SEM results (c) (Fig. 3) showing more algal cells are taken from sampling spot 15 which is a protected area with plant canopy and less inhibited by anthropogenic activities.

Elemental Analysis

The data from EDXRF and PIXE analysis revealed the presence of elements like P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr and Pb in lichen samples (*P. cocoes*) as shown in Fig. 4 (Concentrations of elements in parts per million (ppm) as analyzed by EDXRF and PIXE). Kar et al. [10] have reported the presence of conspicuously high levels of heavy metals like Fe, Cr, Ni, Cu, Zn and Pb in urban atmospheric particulates from Kolkata Metropolis. Gerdol et al. [11] have reported general negative correlation between lichen abundance and trace metal concentrations in lichens. Likewise, in the present study high concentrations of elements such as Ca, K and Fe were detected in lichens from sampling locations 1–9, where lichen abundance was comparatively lower than the other spots. The high concentrations of S and Fe in lichens from 1 to 4 and 5 to 9 may be attributed to heavy vehicular load and congested traffic at these spots. In addition, lichens from the site 5–9 presented highest accumulation of Ti and Rb. High Ca concentrations was observed in the samples of these spots is expected considering the large-scale civil construction works going on there (including road repair and metro rail construction). However, the highest concentration of Ca was observed in samples of spot 11, possibly because of the contribution from a cement ash factory, located very near to this site. This complies with the findings of Caggiano et al. [12] that showed significant accumulation of several trace elements which were higher when in close proximity to a treatment plant and were subsequently removed upon transplantation in a place away from the plant. Elements which are usually known to accumulate quite frequently on the thalli include Cu, Hg, Na, Ti and Zn [13]. Cd, Fe and Pb were accumulated preferably by lichens as compared to mosses [13]. This is in parallel to observations of the present study. Spot 11 showed highest accumulation of Zn, which is nearly 50% higher than that observed in spots 20, 21 and 22 with lowest accumulation of Zn. Highest accumulation of Pb was observed in the thalli of lichens collected from spot 11 (58 ppm) which was 2–threefold more than that at other spots. The source of Pb is automobile exhaust, whereas sources of Cu and Zn are wearing machine parts, automobile tires and brake pads. Cu

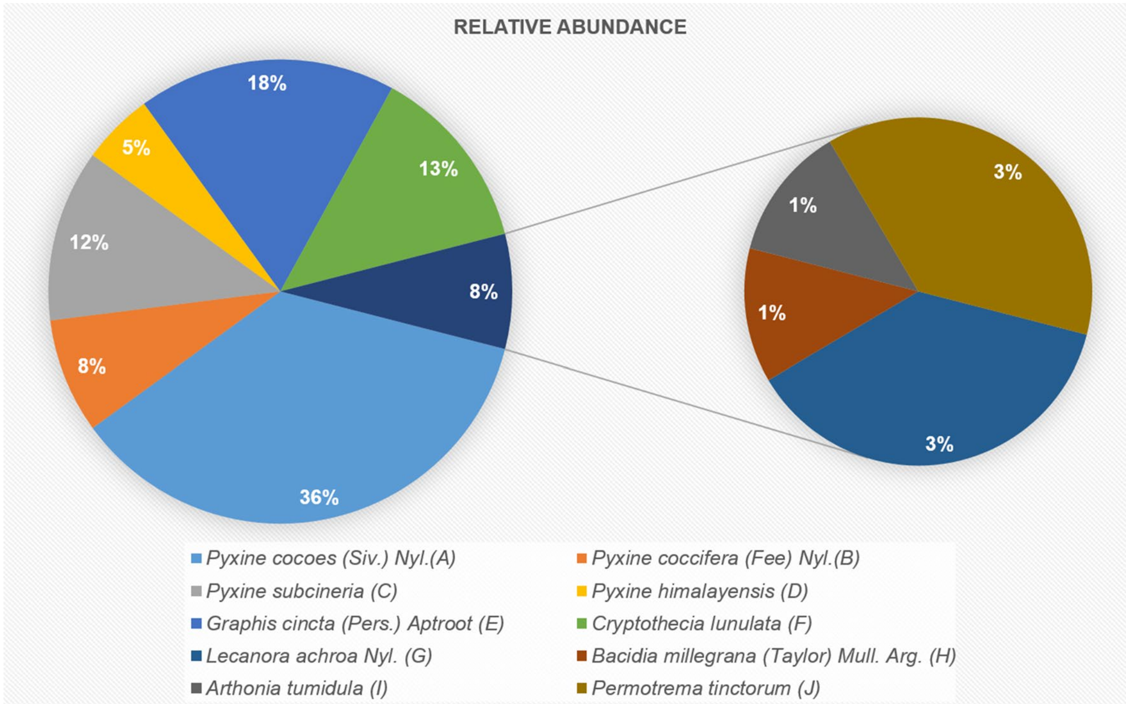


Fig. 2 Relative Abundance of the lichen species that were collected across 22 sampling spots

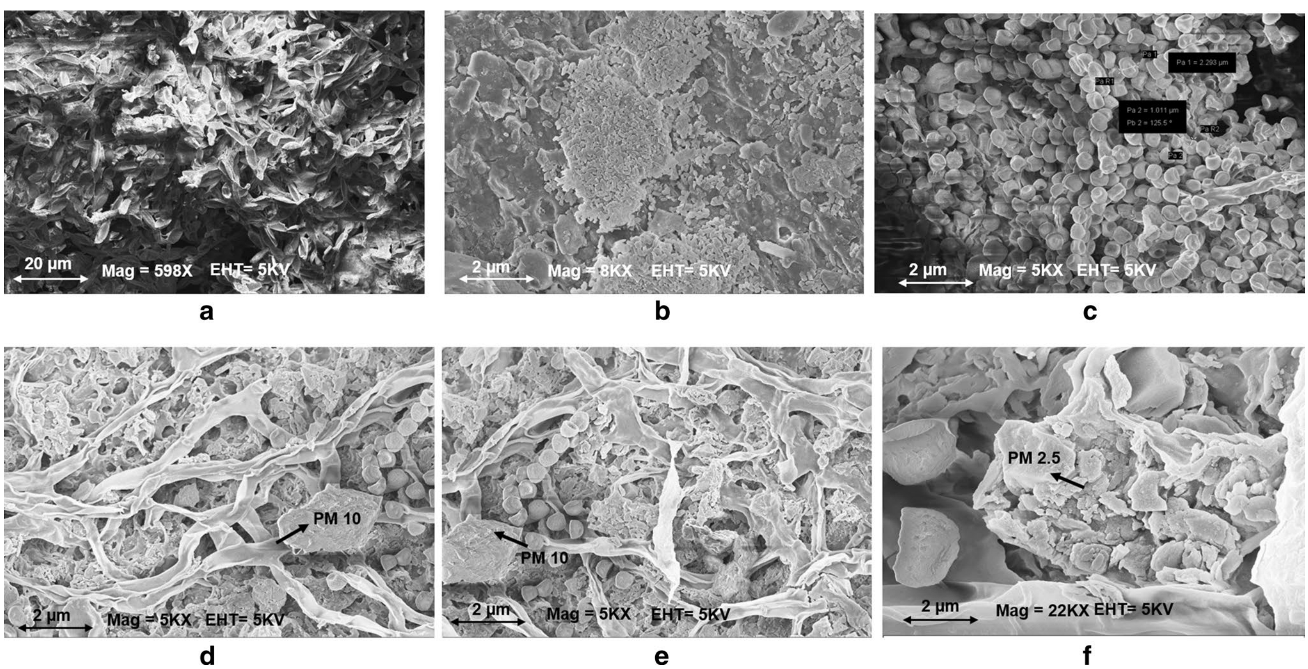


Fig. 3 Anatomical observations of *Pyxine cocoes* under SEM: **a** lichen thalli (higher magnification), **b** lichen thalli (lower magnification), **c** lichen thalli from sampling spot 15 (unpolluted area showing more algal cells, healthy *thallus*), **d** and **e** entrapment of particulate matter (PM 10) in lichen sample collected from sampling spot 2, and **f** entrapment of particulate matter (PM 2.5) in lichen sample collected from sampling spot 3 (partially damaged)

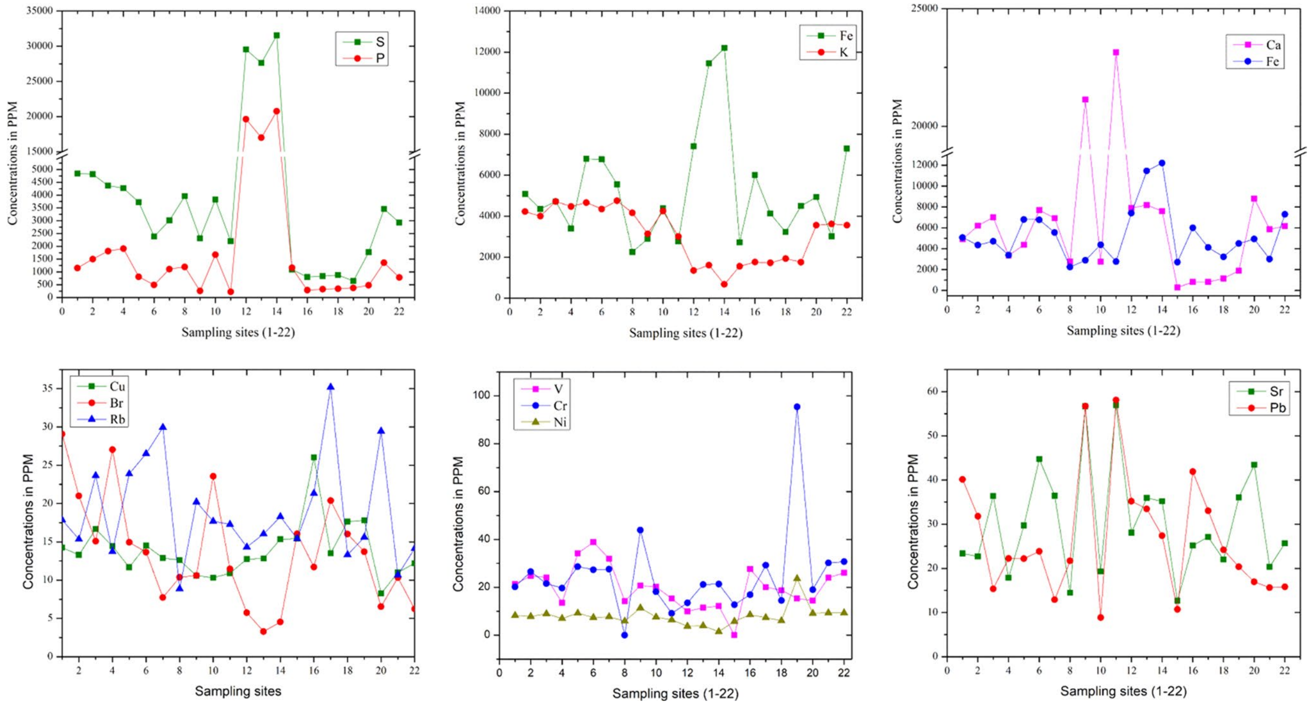


Fig. 4 Concentrations of elements in parts per million (ppm) as analyzed by EDXRF and PIXE

is used in brakes for controlling the transfer of excess heat. Cu can also be present in diesel. Zn arises from the wear and tear of galvanized automobile parts and vulcanized vehicle tires [14].

Concentrations of airborne vanadium have increased in recent years, probably because of the increase in direct combustion of crude oil residues in power plants and community-heating systems that are widely in use. Significantly higher accumulation of V was observed in lichen thalli from spots 1 to 7. Maximum accumulation in lichen thalli collected from spot 6, 5 and 7. Samples of site 11 have highest concentrations of Mn and Sr. In contrast, concentrations of Fe and Cr were lowest in the samples from spot 11. Overall, lichen thalli collected from all the other spots exhibited higher concentration of Fe than any other metal detected, indicating Fe to be one of the most abundant elements. In vitro experiments demonstrated high affinity of lichen toward Fe [15]. High concentration of Fe in samples could be through trapping of soil particles and also due to contribution from the metallurgical industries present near the sampling spots.

Ni was observed to be in the range of 3–23 ppm, while concentration of Cu varied from 8 to 26 ppm. Highest concentrations of Ni, a non-redox active metal is found in location 19, which also shows a comparatively lesser accumulation of Cu. Similarly, spot number 16 that shows the highest accumulation of Cu, a redox active metal, exhibits a lesser accumulation of Ni. Overall, in all the sampling spots, however, Ni and Cu show an antagonist accumulation patterns by epiphytic lichen *P. coces*. The sources of Cu include use of fungicides containing Cu, welding and electroplating materials, and combustion of fossil fuels in factories [16]. Accumulation of Cu in lichen thalli from spots 15–19 may be due to the contribution from application of pesticides and chemical fertilizers in the botanic garden [9]. In contrast, concentration of S is less in spots 15, 16, 17, 18 and 19 because of the dense plant cover that can act as a cleansing mechanism. The spots 20, 21 and 22 showed considerably greater range of concentration of S, Fe, Mn and Zn and moderate range of Ti concentration. Spots 20, 21 and 22 being peri-urban tourist spots, support anthropogenic activities like farming and fisheries. However, these spots are considerably less populated than the other peri-urban sampling points. Zn, Pb and Fe appeared to be closely associated with industry sources. Ni and Cr are typically used as indicators of residual fuel oil combustion, which occurs in oil-fired power plants and steam boilers [17].

Correlation Analysis

The supplementary Table 3 shows the correlation of metals in the 22 sampling points. All the element pairs are correlated at $p > 0.05$ level. The table shows the interaction between metals in terms of their correlation coefficients. Strong positive to moderately positive to significantly positive r values are coded in shades of blue and strong negative to moderately negative to significantly negative *r* values are coded in shades of red. Pearson correlation analysis in this study showed significant correlation among the elements and their site-wise variation. High correlations among trace elements observed in the present study reflect strong biogeochemical influences as has been reported elsewhere [18]. In all the sampling spots, *P* bears a strong positive correlation with S and Fe (*r* values P:: S-0.995; P::Fe-0.776). S and Mn bear a strong positive correlation with Fe ($r = 0.787$). This is possibly due to the high abundance of Fe and geogenic origin of Mn. Fe and Mn are common metallic elements found in the earth's crust occurring naturally in soils, rocks and minerals. The particles of Fe and Mn enter the air mainly through crustal weathering. The influence of industrial emission on higher Fe levels has been reported earlier [19].

Coefficient of Variation

Coefficient of variation (CV) is calculated as the ratio of the standard deviation to the mean of the metal concentrations of the metals that were measured to assess the source of pollutants in the ambient air. Higher coefficients of variation suggest localized deposition of coarse particles and low CVs refer to accumulation through an even suspension or soluble phases [20]. In contrast to the finer particles, heavier, large and coarse particles generally settle down closest to the source of emission. The higher the CV value, the more are the probabilities of effects from local sources, and the lower the value, the more are the chances of having dispersion from sources at a larger distance or from a greater radius indicating larger dispersion of pollutants. Results of the present study show higher coefficient of variation (CV) in Ca (0.93), S (0.50), Pb (0.5), Sr (0.38) and Cr (0.39) and lesser in Cu (0.12), Ni (0.15) and Rb (0.11). Higher CVs may indicate that there is no equilibrium between the element concentrations inherent in lichens and that of atmospheric deposition [21]. Lower CV suggests greater dispersion of metal associated particles and their subsequent trapping by lichens [20].

Pollution Indices

The EF values are characterized by a significant variability, mainly spot-specific. Elements with $EF > 5$, including P, S, Ca and Cr in certain sampling spots, were found to be in surplus. In case of Ca the EF is very high (4–5) in spots 9 and 11. Sampling spots 20 and 21 also showed $EF > 1$ for Ca (1.09–1.19), in contrast to all other locations which showed minor enrichment for Ca (0.1–0.9). The reason for minor enrichment in these spots is the geogenic origin of Ca. However, the sampling spot 11 had a cement factory that complies with high enrichment of Ca which is solely due to the emission from the industry. Similarly, EF of Mn indicates its anthropogenic origin in spots 9, 11, 20, 21 and 22. The highly enriched V (except in 12, 13 and 14) and Cr (except spots 8, 12, 13 and 14) and high EFs of Ca, Mn and Pb and S clearly indicate high contribution from anthropogenic activities. Both V and Cr showed a similar trend in enrichment pattern while Ni showed an $EF \leq 1$ in all the spots other than spots 7, 8, 19 and 21. High enrichment was observed for Pb in spots 9 and 11 (2.04–2.17), whereas the rest of the spots showed $EF < 1$. The transportation of polluted soil from urban and industrial areas may also be considered as important contributors for the enriched elements in lichens. The analysis of atmospheric deposition of trace metals shoed significant levels of chromium, zinc, lead, cadmium, nickel, manganese and iron in PM 10 particulates [22]. This complies with the observations from our present study. Cu is likely to have a mixed origin because the majority of its EF values fall within 0.1–0.9 and is not found to be greater than 1 anywhere among the selected sampling spots. The lower EF (< 1) for the remaining elements gives the basis for the assumption that they were predominantly originated from crustal material. Cong et al. [23] suggested that a very high EF of Cr indicates that Cr is very sensitive to the increasing pollution of the atmosphere. The variation of selected enrichment factors of some metals is shown in Fig. 5 (Enrichment factors for the elements accumulated in the lichen *Pyxine cocoes* and distribution of enrichment values in each of the 22 sampling spots shown in a stacked bar chart), and the mean range of site-wise distribution of enrichment factors are shown in Fig. 6 (Box and whisker plot showing mean range of site-wise distribution of enrichment factors).

The contamination factor denotes the level of contamination manifested in each sampling spot in relation to the background and the contribution of each element or contaminant subsequently affecting the air quality of that place. The risk index approach to get a uniform way of describing the contamination factor is: $Cf < 1$ = low contamination; $1 \leq Cf < 3$ = moderate contamination; $3 \leq Cf < 6$ = considerable contamination; and $Cf \geq 6$ = very high contamination. Comparing lichens from all the spots, contamination due to S is observed to be very high in samples collected from spots 12, 13 and 14, while considerable contamination due to S is observed in spots 1, 2, 3, 4 and 5. P, S, Fe, Mn, Cr and V are included in the hazardous pollutants category ($CF > 3$) [24]. Our results showed that Ni, Pb and Cr get introduced into the environment less intensely than other elements. Very high contamination by V is observed in spots 5, 6 and 7 which are in close proximity to each other. Considerable pollution due to V is also observed in spots 1, 2, 3, 9, 10 and 11. In spots 9 and 11, considerable contamination is seen from Ca which may be attributed to localized anthropogenic activities. The contamination due to Pb is observed to be more in spot 11 as compared to the other sampling spots. Vanadium emission

Table 3 Correlation amongst metals in the 22 sampling points calculated showing data values significant at $p \leq 0.05$ (significant data values are denoted by * for $p \leq 0.05$ and ** for strongly significant data values significant at $p \leq .01$)

Pearson's correlation coeff. (r)	P	S	K	Ca	Mn	Fe	Cu	Zn	Br	Rb	Sr	Ti	V	Cr	Ni	Pb
P	–	0.995**	−0.554*	0.082	0.181	0.776*	−0.029	−0.274	−0.48*	−0.193	0.039	−0.702**	−0.408	−0.16	−0.506*	0.11
S	0.995**	–	−0.491*	0.119	0.205	0.787*	−0.07	−0.312	−0.465*	−0.203	0.056	−0.685**	−0.368	−0.177	−0.518*	0.135
K	0.554*	−0.491*	–	0.09	−0.017	−0.358	−0.367	−0.276	0.378	0.122	−0.008	0.592*	0.583*	−0.113	0.122	−0.267
Ca	0.082	0.119	0.09	–	0.599*	−0.01	−0.46	−0.253	−0.33	0.047	0.831**	−0.09	0.022	−0.03	−0.069	0.649*
Mn	0.181	0.205	−0.017	0.599	–	0.493*	−0.164	−0.385	−0.576*	0.182	0.74*	0.176	0.409	0.267	0.085	0.263
Fe	0.776*	0.787*	−0.358	−0.01	0.493*	–	0.091	−0.367	−0.488*	0.121	0.162	−0.265	0.051	0.013	−0.334	−0.001
Cu	−0.029	−0.07	−0.367	−0.46	−0.164	0.091	–	0.411	0.104	−0.047	−0.238	0.164	0.075	0.113	0.135	0.077
Zn	−0.274	−0.312	−0.276	−0.253	−0.385	−0.367	0.411	–	0.346	−0.216	−0.32	−0.001	−0.344	0.017	0.1	0.018
Br	−0.48*	−0.465*	0.378	−0.33	−0.576*	−0.488*	0.104	0.346	–	0	−0.405	0.217	0.081	−0.006	0.141	−0.032
Rb	−0.193	−0.203	0.122	0.047	0.182	0.121	−0.047	−0.216	0	–	0.423	0.424	0.417	0.093	0.043	0.007
Sr	0.039	0.056	−0.008	0.831**	0.74*	0.162	−0.238	−0.32	−0.405	0.423	–	0.077	0.21	0.264	0.175	0.537
Ti	0.702**	−0.685**	0.592*	−0.09	0.176	−0.265	0.164	−0.001	0.217	0.424	0.077	–	0.862**	0.189	0.361	−0.134
V	−0.408	−0.368	0.583*	0.022	0.409	0.051	0.075	−0.344	0.081	0.417	0.21	0.862**	–	0.154	0.191	−0.036
Cr	−0.16	−0.177	−0.113	−0.03	0.267	0.013	0.113	0.017	−0.006	0.093	0.264	0.189	0.154	–	0.88**	−0.048
Ni	−0.506*	−0.518*	0.122	−0.069	0.085	−0.334	0.135	0.1	0.141	0.043	0.175	0.361	0.191	0.88**	–	−0.084
Pb	0.11	0.135	−0.267	0.649*	0.263	−0.001	0.077	0.018	−0.032	0.007	0.537*	−0.134	−0.036	−0.048	−0.084	–

comes from both anthropogenic and natural sources, but the anthropogenic contribution dominates especially in densely populated areas and these particles can travel over long distances, making it relevant even for trans-boundary air pollution [25]. The dendrogram built from the hierarchical cluster analysis which is illustrated in Fig. 7 (A dendrogram showing clustering of analyzed lichen samples based on the contamination factors of several trace elements showing similarities between the sampling spots) shows the underlying similarities in the pollution pattern among the sampling spots 1–22. Results depict greater than 50% level of significance in similarity between the pollution patterns of spots 1, 2, 3, 10, 21, 4 and greater than 90% level of significance in similarity between spots 1, 2, 3, 10 and 21. Thus two distinct clusters comprising spots 12, 13, 14, 15 and 19 were observed with negative similarity. On the other hand, spot 8 is completely separated from other clusters as it has shown low pollution index. The spots 8, 15, 17 and 18 that shows less pollution form separate cluster in the diagram.

Based on the PLI values, observed in the present study, it may be postulated that contamination by particulate forms of elements is more pronounced in the urban areas due to significant dust load. The pollution load index (PLI) for the specific sampling spots calculated based on the contamination factors of various elements shows the mean PLI of spots 1, 2, 3, 5, 6, 9, 12, 13 and 14 is greater than 1.5 while that of spots

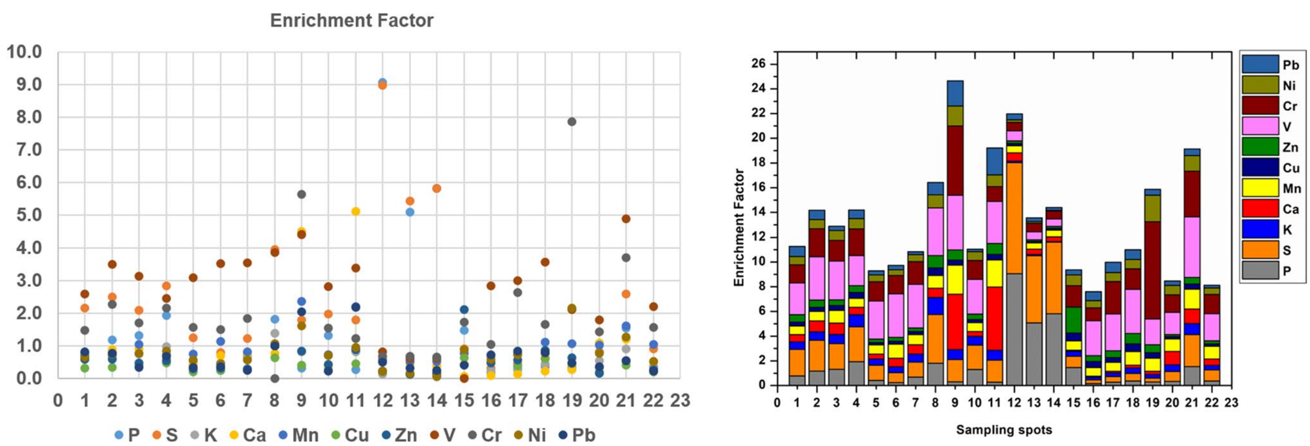
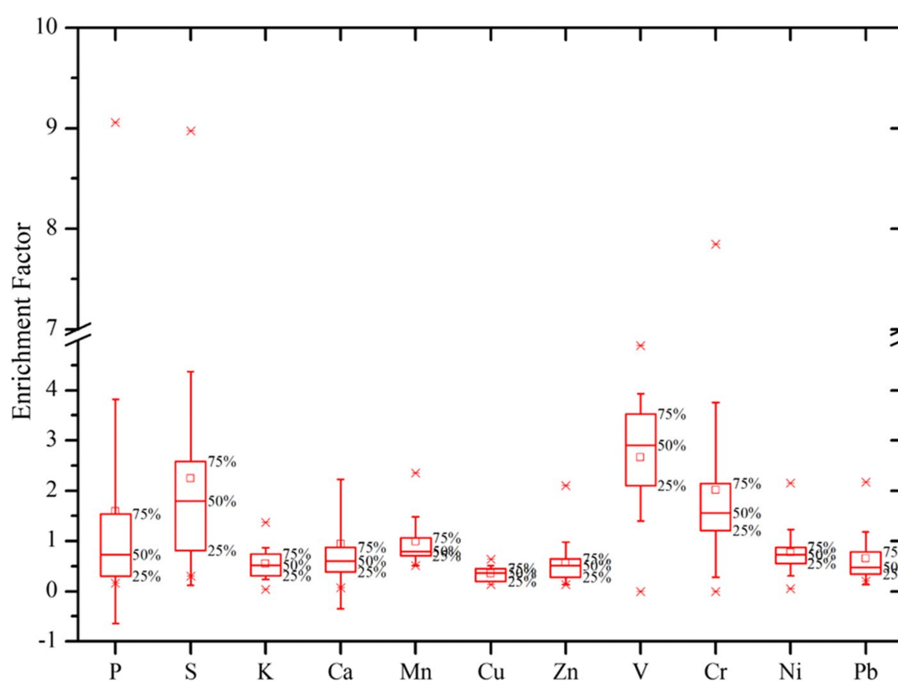


Fig. 5 Enrichment factors for the elements accumulated in the lichen *Pyxine cocoes* and distribution of enrichment values in each of the 22 sampling spots shown in a stacked bar chart

Fig. 6 Box and whisker plot showing mean range of site-wise distribution of enrichment factors



4, 7, 11, 19 and 22 is nearly 1.5. In contrast, PLI of spots 8, 15, 17 and 18 is less than 1, spot 8 being the lowest (Fig. 8 Pollution Load Indices of the sampling spots). Sampling spots 15, 17 and 18 were located at a garden with innumerable plants and big trees. The air of these spots was cleaner with respect to the other sampling spots. The growth and abundance of lichens observed in these areas complement the findings. The spots 20, 21 and 22 located approximately 160 kms away from the main city have lesser anthropogenic activities compared to other sampling locations. Further, the presence of a large number of water bodies accounts for the comparatively low PLI of these spots.

Principal Component Analysis (*PCA*)

In order to understand the possible sources of the trace elements that act as potential pollutants, principal component analysis was carried out. Principal factors with eigenvalues greater than 1 were considered as significant. The PCA revealed 5 components which explained $r=$ 83% of total variance (supplementary Table 4). These 5 components were selected for further analysis, whereas the other nonzero values were discarded to establish the idea of a probable number of sources that are contributive (supplementary Table 5). Initial eigenvalues were cleaned up by Varimax rotation with Kaiser normalization. Each component thus groups the major contribution of elements that impact air quality. Principal Component 1 (PC1) explained ~ 28% of variance and was loaded with elements Fe, P, S and Mn. This component altogether represented the influence of combustion sources mainly the burning of fossil fuels and also from the dusts of crustal origin as Fe and Mn. Principal Component 2 (PC2) amounted for ~ 22% of variance and showed higher variance of Ca, Sr, Pb and Mn. The higher covariance validated the probability of a nearby source and hence determines the contamination to be local either from vehicular or industrial contribution or both. Several construction sites and industries involving brick cement can contribute Ca to the local atmosphere. Pb accumulation can also be from both vehicular emission and road dust [26, 27]. Principal Component 3 (PC3) showed ~ 13% of the variance and was loaded with Mn, V, Rb and K. Additives like organo-manganese compounds in diesel, are most likely to increase the Mn concentration in the urban atmosphere where diesel driven vehicles are common [28]. Thus, PC3 can be ascribed to diesel exhaust. Principal Component 4 (PC4) explained ~ 11% of the variance with high loadings of Cr and Ni. Cr. PC4 can

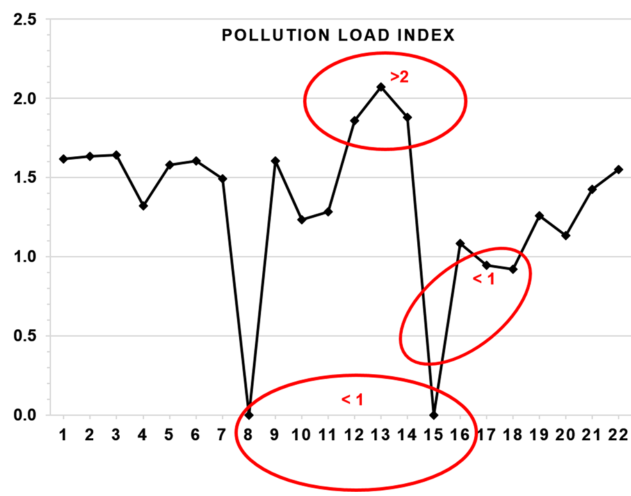


Fig. 8 Pollution Load Indices of the sampling spots

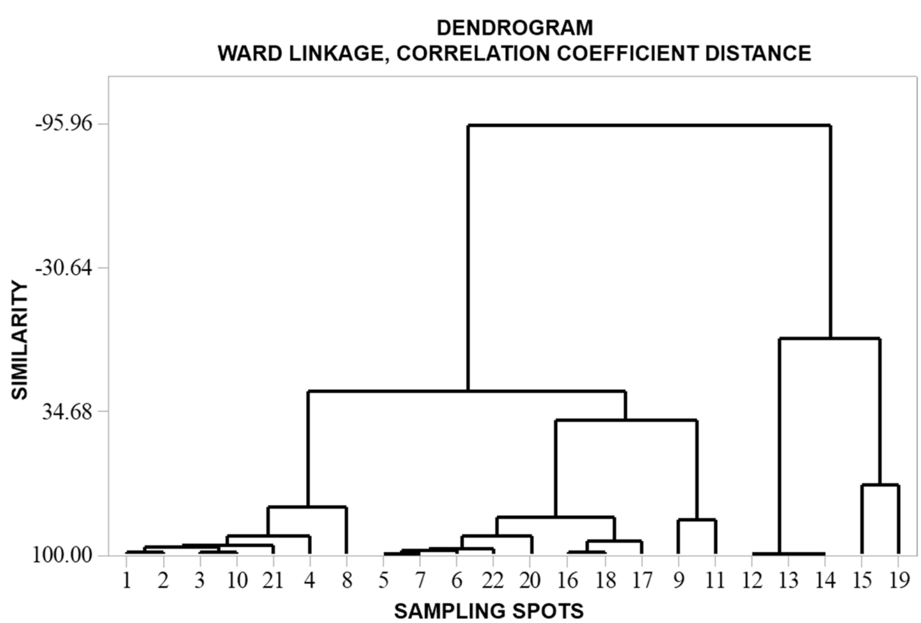


Fig. 7 A dendrogram showing clustering of analyzed lichen samples based on the contamination factors of several trace elements showing similarities between the sampling spots

be attributed to vehicular exhausts [29]. Coal combustion is the main anthropogenic emission source of Ni which is an essential constituent of fly ash from coal-fired industries [30]. Principal Component 5 (PC5) explaining ~ 8% of the variance was loaded with Cu and Zn. Usually, Cu and Zn can be attributed to coal combustion and automobile sources. Zn, together with copper, are from the brake linings' deposition and wear and tear. Copper particles exhibit an unconventional behavior and are also founds as runoff from roofs covered with copper sheeting [31]. Re-suspended dust from the road can also be attributed to these two metals. Cu in the urban atmosphere is generally released from vehicular wear and tear [29]. PCA suggested multiple sources such as vehicular and industrial emissions, burning of fossil fuel, re-suspended road dust, wear and tear of vehicles, and construction activities, for atmospheric elemental contamination.

Table 5 Principal component analysis showing 5 principal components

	Component				
	1	2	3	4	5
Fe	0.912	−0.038	0.241	−0.060	0.077
P	0.898	0.023	−0.275	−0.237	0.032
S	0.891	0.043	−0.251	−0.259	−0.018
Br	−0.689	−0.275	0.004	−0.136	0.161
Ca	0.050	0.914	−0.025	−0.035	−0.360
Sr	0.173	0.848	0.305	0.243	−0.165
Pb	−0.014	0.840	−0.058	−0.161	0.286
Mn	0.454	0.552	0.408	0.296	−0.213
V	−0.160	−0.008	0.883	0.118	−0.133
Rb	−0.022	0.142	0.724	−0.002	0.070
Cr	0.029	0.034	0.056	0.954	0.086
Ni	−0.329	0.000	0.047	0.921	0.038
Cu	0.019	−0.189	0.151	0.089	0.873
Zn	−0.421	−0.055	−0.388	0.016	0.620
K	−0.524	−0.147	0.428	−0.079	−0.605

Extraction method principal component analysis, rotation method varimax with kaiser normalization a rotation converged in 6 iterations

Conclusion

The present results of biomonitoring studies utilizing the lichen *P. cocoes* provide significant information on the level of environmental pollution, directions of pollutant propagation and transport, and bioavailability of pollutants in and around Kolkata. A steep decline in the vegetation cover, increased urbanization and increased industrialization has changed species-specific habitats for lichens resulting in loss of diversity of lichens in Kolkata. Several other factors like changing climatic and microclimatic conditions, rain water drainage, dust accumulation, increased pollution levels (SO_2, SPM, RSPM, etc.) might have also influenced depletion of lichen abundance. Findings of the present study shown that *P. cocoes* is the dominant species in Kolkata metropolis which can function as a bioalarm for predicting air quality deterioration from the perspective of metal contamination of air. This particular lichen species was found to be extremely tolerant to the heavy pollution load of the urban areas. The study showed differential accumulation of trace elements like P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr and Pb in *P. cocoes*. Different pollution indices indicated enrichment of trace elements due to their crustal as well as anthropogenic origin. Low to moderate contamination atmospheric air with trace elements in urban as well as peri-urban areas was noticed. Further principal component analysis has suggested multiple sources for the trace elements detected in the lichen thali collected from the urban and peri-urban sites. The major sources include crustal origin, emissions from vehicles, industries, wear and tear of vehicles and re-suspended road dust. Therefore, it can be recommended that in future integrated biomonitoring approach can be used to monitor the low pollutant thresholds and assess the overall spatial variability of air quality in a complex peri-urban area. Such integrated biomonitoring approach can likely contribute to assess historical patterns of air quality and, thus, to the implementation of environmental policies on atmospheric pollution control.

Table 4 Eigen values rotated component matrix a total variance

Component	Initial eigen values			Extraction sums of squared	
	Total	% of Variance	Cumulative %		
1	4.217	28.110	28.110	4.217	28.110
2	3.338	22.254	50.365	3.338	22.254
3	1.986	13.238	63.603	1.986	13.238
4	1.786	11.906	75.509	1.786	11.906
5	1.225	8.167	83.676	1.225	8.167
6	0.797	5.313	88.989		
7	0.702	4.677	93.667		
8	0.440	2.930	96.597		
9	0.215	1.432	98.029		
10	0.142	0.947	98.976		
11	0.092	0.612	99.588		
12	0.025	0.166	99.754		
13	0.024	0.158	99.912		
14	0.013	0.086	99.998		
15	0.000	0.002	100.00		

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Authors' Contributions SB performed all the fieldwork, sample collection, sample preparations, experiments, and analysis and prepared the manuscript. SSR was involved in helping SB with the EDXRF & PIXE experiment set up, data acquisition and data analysis. AM provided valuable guidance with the field work and sample collection. NJ helped in the outline and concept of the study. MS was involved in experiments and analysis and manuscript correction. AC was involved in designing experiments and analysis and manuscript preparation. All authors read and approved the final manuscript.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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