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Atmospheric Heavy Metal Accumulation in Epiphytic Lichens and Their Phorophytes in the Brahmaputra Valley

Rebecca Daimari, Raza Rafiqul Hoque*, Sanjeeva Nayaka[1] and Dalip K. Upreti[1]

Department of Environmental Science, Tezpur University, Tezpur – 784028, India

[1]Lichenology Laboratory, National Botanical Research Institute (CSIR), Lucknow – 226001, India

✉ rrh@tezu.ernet.in

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Abstract: Lichens are indicator species of air quality of a locality. Estimate of heavy metal (HM) accumulation in lichens offers an indirect measure of their levels in the atmosphere. Accumulated HMs of lichen *thalli of* 16 species belonging to 10 genera and their phorophytes of two characteristic areas of Brahmaputra valley were studied. Acid digested samples of *thalli* and phorophytes were analysed for Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb by ICP-OES. Mean concentrations of the HMs were found to be higher in lichens at the area situated close to the downtown area of the city and the Brahmaputra River. Accumulation of Cd, Cu, Fe and Ni were found to be higher in lichen *thalli*; however, leaves accumulated higher levels of Co and Mn. Linear regression analysis shows poor dependency of the *thalli* on their phorophytes indicating accumulation of metals from atmosphere. The extent of enrichment in the lichen *thalli*, which was evaluated by calculating enrichment factors (EFs) revealed moderate enrichment of Cr, Cu, Ni and Pb; however, Cd was found to be highly enriched. Ecological risk posed by the heavy metals were calculated and it was found that Principal Component Analysis (PCA) of the data set identifies three contributing sources: coal-fired industrial emission, crustal dust blown from dry river bed and vehicular emission.

Key words: Air pollution, biomonitoring, lichen, Tezpur, source apportionment.

Introduction

Atmospheric pollution has become a ubiquitous phenomenon. Pollutants from urban centres are often carried far to the remote rural and forest areas by atmospheric processes. Deposition of the pollutants far from the source affects biota, land and water environment. Air pollution, therefore, is a matter of concern today for scientists, engineers and planners.

Spatial and temporal distribution of atmospheric pollutants varies greatly over a region. As a result, it becomes physically strenuous and expensive to monitor atmospheric pollution over a large area using conventional methods. Consequently, in recent years, the use of biomonitoring of atmospheric pollutants, especially with lichens, has gained increasing acceptance among pollution researchers (Mishra et al., 2003). For regions that are economically underdeveloped or developing may not have pollution data. Accumulation of pollutants on the lichens can provide basic idea of the atmospheric levels of the pollutants like the heavy metals.

Often as a part of Environmental Impact Assessment (EIA) studies, survey and controls of biological indicators like lichens could be handy to evaluate emission sources.

A number of traits of lichens such as large geographical range, lack of cuticle and stomata, direct dependence

*Corresponding Author

on atmosphere for nutrients, a stable morphology and longevity, perennial condition of *thalli* and rapid uptake and accumulation of cations (James et al., 1973; Puckett, 1988) make them effective biomonitors.

Lichens are efficient accumulators of many elements, particularly heavy metals and radionuclides (Tuominen and Jaakkola, 1973). Heavy metals such as Cd, Cr, Cu, Hg, Ni, Pb, and Zn, considered to be toxic for many other living organisms, may be accumulated simultaneously in a lichen species, which may appear to be harmless in many cases (Bajpai et al., 2004). The accumulation of metals in them, from the atmosphere, primarily follows three mechanisms—ion exchange, intracellular uptake and particulate entrapment (Brown and Beckett, 1984).

Also, lichens are very sensitive population of the biota. They are, especially, very sensitive to air pollution and particularly to high levels of SO_2. Lichens have widely been explored for monitoring the heavy metal pollution in the western countries (Mendil et al., 2009; Saiki et al., 2007) and there are a few attempts from India as well (Begum and Harikrishna, 2010; Bajpai et al., 2009; Begum et al., 2009; Nayaka et al., 2003).

The northeastern region (NE) of India is fast growing economically and, therefore, environmental issues like air pollution is slowly becoming a matter of concern. More so, for many projects those are coming up in the region need to address mandatory EIA for the environmental clearance. Therefore, environmental data is very vital for the region for planning and governance.

The NE region represents a geographical area bigger than the United Kingdom (UK); yet, unfortunately, the region could be termed as an 'environmental black box' for lack of air pollution data and scientific studies.

Tezpur, a city in the middle Brahmaputra plain, is one such area in the NE region which is in a fast pace of development. Since there are no studies in the region, the present study was carried out to address a few very primary issues: (i) Do we still have good lichen diversity in Tezpur city? A good diversity would mean that the city is still within safe limit and possesses a good air quality. (ii) What could be the level of accumulation of metallic pollutants in the lichen species? (iii) Do the levels of accumulation vary spatially? and (iv) What could be the possible sources of the metallic pollutant species? An attempt was also made to understand whether the concentration of metallic pollutants in the lichen *thalli* depend on their concentrations in the respective phorophytes.

The present study is the first ever study from the Brahmaputra plain in Assam. The study, therefore, should provide a baseline for the future researchers and planners.

Study Area

Tezpur is situated on the north bank of the Brahmaputra River, geographically positioned around 26.63^{o}N and 92.8^{o}E and at an elevation of 48 m above mean sea level. The region falls in the subtropical climatic zone and enjoys a monsoon type of climate. Tezpur receives an average annual rainfall of 160 cm and the temperature here ranges between 10 and 37ºC. The region falls within the 'North Bank Landscape' designated by The World Wide Fund for Nature (WWF) and, therefore, the region has lots of relevance with respect to conservation.

Tezpur city is an ancient, mythical city. As per the 2011 census of Government of India, the population of Tezpur is just above 100 thousand. There are no major industries in and around Tezpur; however, the city is fast growing with increased number of small to medium industries.

Based on the prevalent anthropogenic activities and distance from the city centre, two sites were chosen for the present study (Figure 1). Tezpur University (TU) Campus, site 1, is 15 km away from the city centre. The TU campus of today was an agricultural field which was subsequently replaced by vegetation as the boundary wall of the University came up about two decades ago. Agnigarh Hill (AH), site 2, is a small hill located close to the city centre overlooking the Brahmaputra River. A major highway (NH 37A) separates these two sites by about half the distance between each other.

Methodology

Sampling

An area of ~3 sq km was taken from each site and epiphytic lichen samples were collected from trees available in the sites. Collections were made from a height of 1-1.5 metres. The bark and leaf samples of the respective phorophytes were also collected simultaneously. In order to avoid fungal infection, samples collected were air dried properly before storing them into paper packets (Nayaka, 2005). Freezing was also done for a period of five days; as this prevents the lichens from being damaged by most arthropods. Important field records such as substrate, collection date, locality, altitude etc. were noted down at the time of collection.

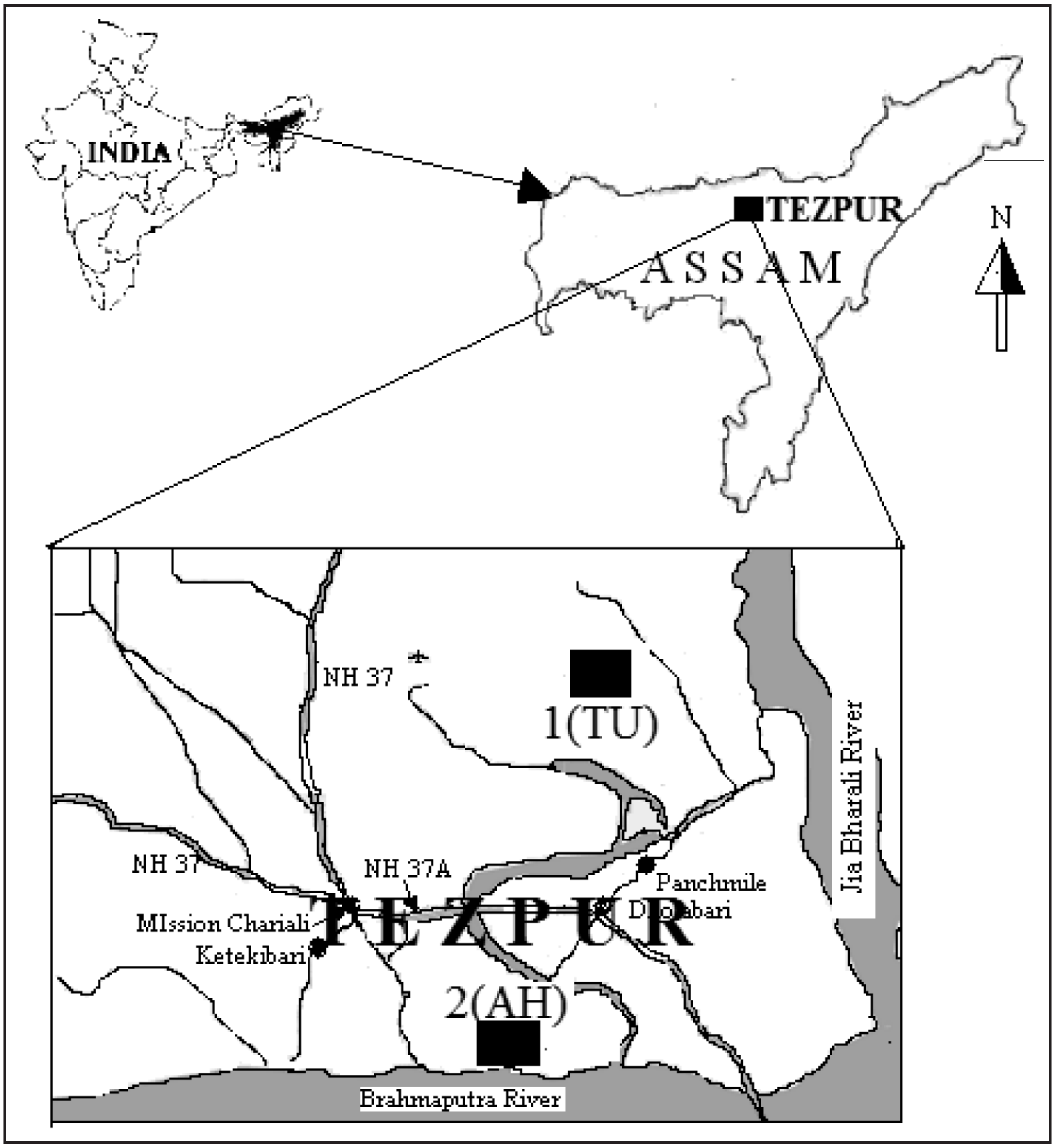

Figure 1: Sketch of study area – 1. Tezpur University (TU) and 2. Agnigarh Hill (AH).

Identification

Identification of the lichen species was done on the basis of morphological, anatomical and chemical tests at National Botanical Research Institute (NBRI), Lucknow (Awasthi, 2007, 1991). Chemical tests include colour tests, with K (5% KOH), paraphenylene diamine (PD), and aqueous calcium hypochlorite, and thin layer chromatographic (TLC). The TLC was run using a solvent regime of toluene, 1,4-dioxane and acetic acid in the ratio of 180:60:8 (Walker and James, 1980). The lichens were placed under different families according to recent classification proposed by Lumbsch and Huhndorf (2007).

The identified specimens have been housed in the Department of Environmental Science, Tezpur University and a set of voucher specimens have been deposited to the herbarium of National Botanical Research Institute.

Chemical Analysis

Lichen *thalli*, substrates and leaves were cleaned with brush to remove extraneous material deposited on the surface. The samples were not washed so as to avoid removal of particles trapped on the lichen surface as there are evidences that washing can alter the elemental composition of lichens (Bettinelli et al., 1996). All samples were oven dried for 24 h at 60ºC. Dried samples were separately ground and aliquot (0.1 gm) of the individual samples were acid digested in a closed Teflon bomb. The digestion was done in a 3:1 (v/v) acid mix of HNO_3 and $HClO_4$ (V/V 3:1) at 70ºC for eight hours. Digested samples were filtered and the filtrate volumes were made up to 10.0 ml. Metal concentrations was determined by ICP-OES (Perkin Elmer-Optima 2100 DV). Care was taken to ensure accuracy and precision of the measurements. The instrument was calibrated by a liquid standard for ICP supplied by Perkin Elmer. All dilutions were made in ultra-pure water.

Assessment of Pollution Load

Enrichment Factor

Double normalization of the elemental concentration in lichens is done to see the level of enrichment of the elements. Enrichment factors (EF) were computed for each element discriminated by collection sites and growth form. Enrichment factors were calculated as follows:

$$EF = ([X]/[\mathrm{Fe}])/([X]_{\mathrm{crust}}/[\mathrm{Fe}]_{\mathrm{crust}})$$

where $[X]$ and [Fe] are the mean concentration of the respective element and Fe, respectively, in the *thalli*; and $[\mathrm{X}]_{\mathrm{crust}}$ and $[\mathrm{Fe}]_{\mathrm{crust}}$ are the mean concentration of the respective element and Fe, respectively, in the earth's crust.

Average elemental concentrations of earth crust were taken from the literature (Fyfe, 1974).

Assessment of Contamination by Heavy Metals

In order to evaluate the contamination of the lichens by heavy metals, contamination factor and degree of contamination were calculated. A modification of contamination factor and degree of contamination suggested by Hakanson (1980) was applied. The contamination factor (C_f^i) was defined as:

$$C_f^i = C_{0-1}^i / C_n^i$$

where C_{0-1}^i is the mean content of metal and C_n^i is the concentration of each individual metal of a background lichen sample. In the present, C_n^i values represent the concentration of heavy metals of samples taken from remote forest located in the foothill of Easter Himalayas.

Four classes of C_f^i were suggested by Hakanson (1980) to evaluate contamination of heavy metals, which are as per the following:

$C_f^i < 1$: low

$C_f^i \leq 1 < 3$: moderate

$3 \leq C_f^i < 6$: considerable

$C_f^i \geq 6$: very high

The degree of contamination (C_D) is the sum of contamination factors for all the elements. We defined the degree of contamination by eight metals in the lichens for the study as suggested by Hakanson (1980) as follows:

$$C_D = \sum_{i=1}^{8} C_f^i$$

Handling of the Data

For the multivariate analysis of the data, *thalli* elemental concentrations were standardized against concentrations of a reference plant (RP). This was done because the samples of the lichen *thalli* were from different species. Standardization of the elemental concentrations was done to bring the concentrations in the same scale. Deviation from the reference material (Dev_x) is calculated as follows after Caivelo et al. (1997). The elemental concentration of the substrate of *P. cocoes* is taken as the reference plant.

$$\mathrm{Dev}_x = 100 \times ([X]_{\mathrm{lichen}} - [X]_{\mathrm{RP}})/[X]_{\mathrm{RP}}$$

where $[X]_{\mathrm{lichen}}$ is the concentration of the respective elements in the respective *thalli* and $[X]_{\mathrm{RP}}$ is the concentration of the respective elements in the reference plant.

Results and Discussion

Lichen Diversity

In the present study 16 lichen taxa belonging to 10 genera and eight families were identified. Site 1 recorded a total of 10 lichen taxa—five crustose, four foliose and a leprose and Site 2 represents a total of six species with five foliose and a crustose species (Table 1). Physciaceae with six species is the most dominant family in the present study. Foliose lichens are more prominent in the study area and are represented by nine species. Comparatively, greater number of foliose lichens has been recorded from Site 2 than Site 1. The reason for this could be that Site 1 was an agricultural field till two decades ago and hence failed to establish suitable substrates for the growth of lichens. However, tree species, *Gmelina arborea* available in Site 1 supports good number of lichen species, which we would like to comment as a good substrate for the lichens. *Gmelina arborea* plantation was done along roadside locations within TU campus as a part of its beautification. Luxuriant growth of lichens was also observed in the tree species, *Bombax malabaricum*, exhibiting suitability for a good substrate for lichens growth.

Table 1: Lichen species, their growth form, family and presence at two sites of Tezpur

Sl.no.	*Species*	*Family*	*GF*	*Site 1*	*Site 2*
1	**Cryptothecia lunulata* (Zahlbr.) Makh. and Patw.	Arthoniaceae	C	−	+
2	*Chrysothrix candelaris* (L) Laundon	Chrysotrichaceae	L	+	−
3	*Leptogium* sp.	Collemataceae	F	−	+
4	**Graphis capillacea* Stirton	Graphidaceae	C	+	−
5	**G. subasahinae* Nag. and Patw.	Graphidaceae	C	+	−
6	**Lecanora leprosa* Fée	Lecanoraceae	F	+	−
7	**Parmotrema praesorediosum* (Nyl.) Hale	Parmeliaceae	F	−	+
8	**P. saccatilobum* (Tailor) Hale	Parmeliaceae	F	−	+
9	**P. tinctorum* (Despr. ex Nyl.) Hale	Parmeliaceae	F	−	+
10	*Dirinaria* sp.	Physciaceae	F	+	−
11	**D. applanata* (Fée) D.D. Awasthi	Physciaceae	F	+	−
12	*D. consimilis* (Sirton) D.D. Awasthi	Physciaceae	F	+	−
13	*Diplotomma lauricassiae* (Fée) Szat.	Physciaceae	C	+	−
14	**Pyxine cocoes* (Sw.) Nyl.	Physciaceae	F	+	−
15	**P. subcinerea* Stirton	Physciaceae	F	−	+
16	**Bacidia mellegrana* (Tailor) Müll. Arg	Ramalinaceae	C	+	−

C: Crustose, F: Foliose, L: Leprose
*Analysed for heavy metal concentration

Several species found in the present study are also reported from other regions of India. Species such as *C. lunulata* and *P. tinctorum* were also reported from Along town of West Siang district of Arunachal Pradesh (Dubey et al., 2007). *P. cocoes, D. applanata* and *Phaeophyscia hispidula* are common foliose lichens in tropical region of India and have well known pollution tolerance (Nayaka et al., 2003) and also found in our study.

Metal Accumulation

The concentration of heavy metals in the lichen *thalli,* substrates and leaves of the two sampling sites are put up in Table 2.

Cadmium and Pb was not detected in most of the samples whether lichen *thalli*, substrate or leaves. Concentration of Cr ranged from 51.4 to 107.6 μgg^{-1} in thallus, 7.8 to 677.6 μgg^{-1} in substrates and 15.1 to 150.5 μgg^{-1}dry wt. in leaves. Fe accumulations in all the samples were relatively higher ranging from 261.6 to 9167 μgg^{-1}. Accumulation of Fe was highest in the *thalli* of *P. subcinerea* with the concentration of 9167 μgg^{-1} of dry weight. Higher concentration of Fe were also observed in studies in other parts of India (Begum and Harikrishna, 2010; Bajpai et al., 2009; Mendil et al., 2009), which is because lichens have a special affinity for Fe. According to Gailey and Lloyd (1983), Fe saturates the absorptive capacity of the lichens at the absorption sites and blocks the uptake of the other metals such as Zn, Cr and Cu.

Concentration of Mn ranges from 8.3 to 275.3 μgg^{-1} in *thalli*, 57.1 to 179.6 μgg^{-1} in substrates and 16.2 to 441 μgg^{-1} in leaves. Pb was not detectable in most of the samples. Puckett et al. (1973) reported the competitive uptake of metals by the lichens to be in the sequence of Fe>>Pb>Cu>>Ni, Zn>Co. In our study, selectivity sequence of metals in the lichen *thalli* was found to be in the order: Fe>>Mn>Cr>Ni>Cu>Co>Cd>Pb.

Quantity of metal accumulation is influenced by the growth form of lichen (Garty, 2001). Mean concentration of Fe, Mn and Ni were highest in crustose lichens, while Cd, Co, Cr, Cu and Pb were highly accumulated in foliose lichens. Among the crustose lichens, *Graphis capillacea* accumulates highest concentration of Co, Cu and Ni and lowest concentration of Fe and among the foliose lichens accumulation of Cd, Co and Cu was highest in *Parmotrema praesorediosum* and that of Cr, Fe and Mn was highest in *Pyxine subcinerea*.

A vivid spatial variation in the metal accumulation was observed. Mean concentrations of Cd, Co, Cr, Cu, Mn and Pb were higher in lichen *thalli* of Site 2, whereas Fe and Ni were higher in lichens of Site 1 (Table 2). Accumulation of metals in lichens of Site 2 was greater than those of Site 1, which could be due to proximity of Site 2 to the polluted city centre. The State Transport buses ply from a point near to Site 2. Pb in lichens of Site 2 also had higher concentrations than their background level, which could be due to the input from the vehicular emissions. Mean concentrations of Cr, Cu, Fe, Mn and Ni in lichens from both sites were

Table 2: Metal concentration (µgg^{-1} dry wt.) in lichen thalli (T), substratum (S) and phorophyte leaves (L): (a) Site 1 and (b) Site 2

(a)

Species		*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*
P. cocoes	T	BDL	1.4	51.4	31	4598	108.2	21.7	BDL
	S	2.1	0.8	30.5	27.7	2038	122.8	24.9	BDL
	L	BDL	0.5	42.5	BDL	1025	16.2	29.1	BDL
G. subasahinae	T	1.3	1.8	63.1	57.9	5124	120.3	28.3	BDL
	S	2.1	0.8	30.5	27.7	2038	122.8	24.9	BDL
	L	BDL	0.5	42.5	BDL	1025	16.2	29.1	BDL
D. applanata	T	0.2	2	61.2	28.8	7022	137.4	31.2	BDL
	S	1.5	1.4	37.5	32.4	1792	179.6	20.1	BDL
	L	0.2	1	111.5	49.4	1681	441	68.2	BDL
B. mellegrana	T	BDL	2.1	87.1	48.3	6831	148.4	48.6	BDL
	S	1.5	1.4	37.5	32.4	1792	179.6	20.1	BDL
	L	0.2	1	111.5	49.4	1681	441	68.2	BDL
G. capillaceae	T	0.1	8.5	51.5	86.3	2384	214.9	528.2	BDL
	S	0.4	0.1	30.7	28.9	1320	68.5	8.3	BDL
	L	BDL	0.1	15.1	BDL	430.3	21.5	11.4	BDL
L. leprosa	T	0.5	2.4	64.4	45	3251	146.3	30.7	BDL
	S	0.4	0.1	30.7	28.9	1320	68.5	8.3	BDL
	L	BDL	0.1	15.1	BDL	430.3	21.5	11.4	BDL
P. cocoes	T	0.6	1.4	97.4	63.2	4465	83.3	46.4	14.3
	S*	0.6	1.3	59	86.6	3450	57.1	34.9	0.8
	L	0.9	0.5	34.5	84	1412	99.9	19.6	2.7

*Substrate used for the standardization of the data.

(b)

Species		*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*
P. subcinerea	T	6.5	1.3	81.7	112.9	1360	105.1	25.4	15.2
	S	6.1	2.6	214.4	129.3	2150	94.9	14.9	1.7
	L	3	0.7	109.1	74.7	4251	119.5	81.7	BDL
P. praesorediosum	T	17.1	9.6	86.1	138.4	2827	153.1	15.6	8.5
	S	10.8	15.7	677.6	154	1068	157	34.3	18.1
	L	10.2	11.8	150.5	144.2	1204	221.7	32.4	5.9
P. tinctorum	T	12.8	8.4	64.5	106.1	2173	137.2	16.3	9.9
	S	10.8	15.7	677.6	154	1068	157	34.3	18.1
	L	10.2	11.8	150.5	144.2	1204	221.7	32.4	5.9
P. saccatilobum	T	1.6	1.7	82.7	67	1944	127.2	46.8	BDL
	S	BDL	0.3	7.8	8	1819	56.3	3.7	BDL
	L	12.8	16.1	68.5	181.3	261.6	91.2	7.5	33.3
P. subcinerea	T	BDL	2.8	107.6	54.9	9167	275.3	38.9	10.9
	S	BDL	1.6	56.9	23	6429	165.8	40	BDL
	L	BDL	0.7	59.4	52.8	3567	152.6	36	BDL
C. lunulata	T	BDL	1.6	71.2	52.6	7270	223.5	24	BDL
	S	BDL	1.6	56.9	23	6429	165.8	40	BDL
	L	BDL	0.7	59.4	52.8	3567	152.6	36	BDL

BDL = Below detectable limit

far above their typical background levels (Table 3) as per Nieboer et al. (1978).

Table 3: Background concentrations of heavy metals in lichen thalli in μg/g dry wt

Metals	*Concentrations (in μg/g dry wt.)*
Cd	1 to 30
Cr	0 to 10
Cu	1 to 50
Fe	50 to 1600
Mn	10 to 130
Ni	0 to 5
Pb	5 to 100

Nieboer et al., 1978

Thallus-phorophyte Relationship

A comparative account of abundance (mean of all samples) of metallic species in *thalli*, substrates and leaves has been illustrated using error bar (Figure 2). The mean concentrations of Cd, Cu, Fe and Ni were higher in *thalli* than their respective bark and leaves. In an earlier study, Bajpai et al. (2009) observed greater accumulation of metals in the *thalli* compared to the substrates. They found insignificant concentrations in the substrates. The standard deviation of the means observed in our study was large, which could be due to differential accumulation capacities of metals among various species of lichens.

The role of the substratum in lichen nutrition is largely unknown (Bargagli and Mikhailova, 2002). However, substrate specificity of most lichens and higher concentration of elements on the lower surface of the thallus and rhizinae underline such interactions (Goyal et al., 1982). Thus the role of substratum on the elemental composition of lichen thallus depends on the lichen species, bark properties, intensity of pollution and the concern element (Bargagli and Mikhailova, 2002).

The dependency of thallus metal concentrations on substrate metal concentrations was tested by a linear regression analysis (Figure 3). Except for Cd ($r^2 = 0.926$), Co ($r^2 = 0.563$) and Cu ($r^2 = 0.692$), other metal concentrations in the thallus did not show any dependency on the levels in substrate. This shows that metals accumulated in the *thalli* could be mainly from the atmosphere.

Assessment of Pollution

Enrichment Factor

Usually an EF above 10 is considered to have input from anthropogenic activities. Elements with EF values 10 to 100 are said to be moderately enriched (Tuncel and Sarakas, 2003).

Enrichment factors are put up in Table 4. The EFs at Site 2 were found to be much higher than those of Site 1. This could be explained in terms of the pollution load of these two sites, which vary due to one being closer to the pollution source.

Table 4: Enrichment and contaminating factors of HMs

HMs	*Enrichment factor (EF)*		*Contamination factor* (C_f^i)		*Background** (C_n^i)
	Site I	*Site II*	*Site I*	*Site II*	
Cd	31.07	595.17	2.44	**39.56**	0.16
Co	1.24	2.19	4.75	7.17	0.59
Cr	7.18	10.14	1.95	2.36	34.85
Cu	9.76	19.6	**6.42**	**11.05**	8.02
Fe			4.04	3.46	1191.7
Mn	1.67	2.41	4.99	**6.2**	27.47
Ni	13.67	4.23	**8.92**	2.36	11.77
Pb	2.03	8.58	2.53	1.31	5.65
Deg of contamination (CD)			36.03	73.48	

*Background levels analysed concentrations of metals in samples collected from forest about 60 km away from the sampling locations.

The EF of Cd was found to be 31 and 595 in Site 1 and 2 respectively, which is extraordinarily high. This explains that there are stronger anthropogenic emissions of metals which get deposited in the lichen *thalli*.

Contamination Factor (C_D)

Contamination factors of heavy metals are calculated and put up in Table 4. It was found that contamination factors of Cd, Ni and Cu were on the higher side. At Site 2 the C_D of Cd and Cu is high. The C_D of Site 2 is higher than Site 1, which indicates that site is a receptor of greater pollution load as compared to Site 1. The C_{Ds} were found to be considerable at Site 2 and moderate at Site 1. This again confirms that there are anthropogenic emission sources of heavy metals in Tezpur region.

Probable Sources of Atmospheric Metals

Associations between the metal pairs could be explained in terms of a common source or chemical similarity (Knudson et al., 1977). Therefore, Pearson's correlations between metal species were built to understand the relationships. The correlation matrix has been put up in Table 5. Metals pairs showing positive significant correlation could indicate a common source for the pairs.

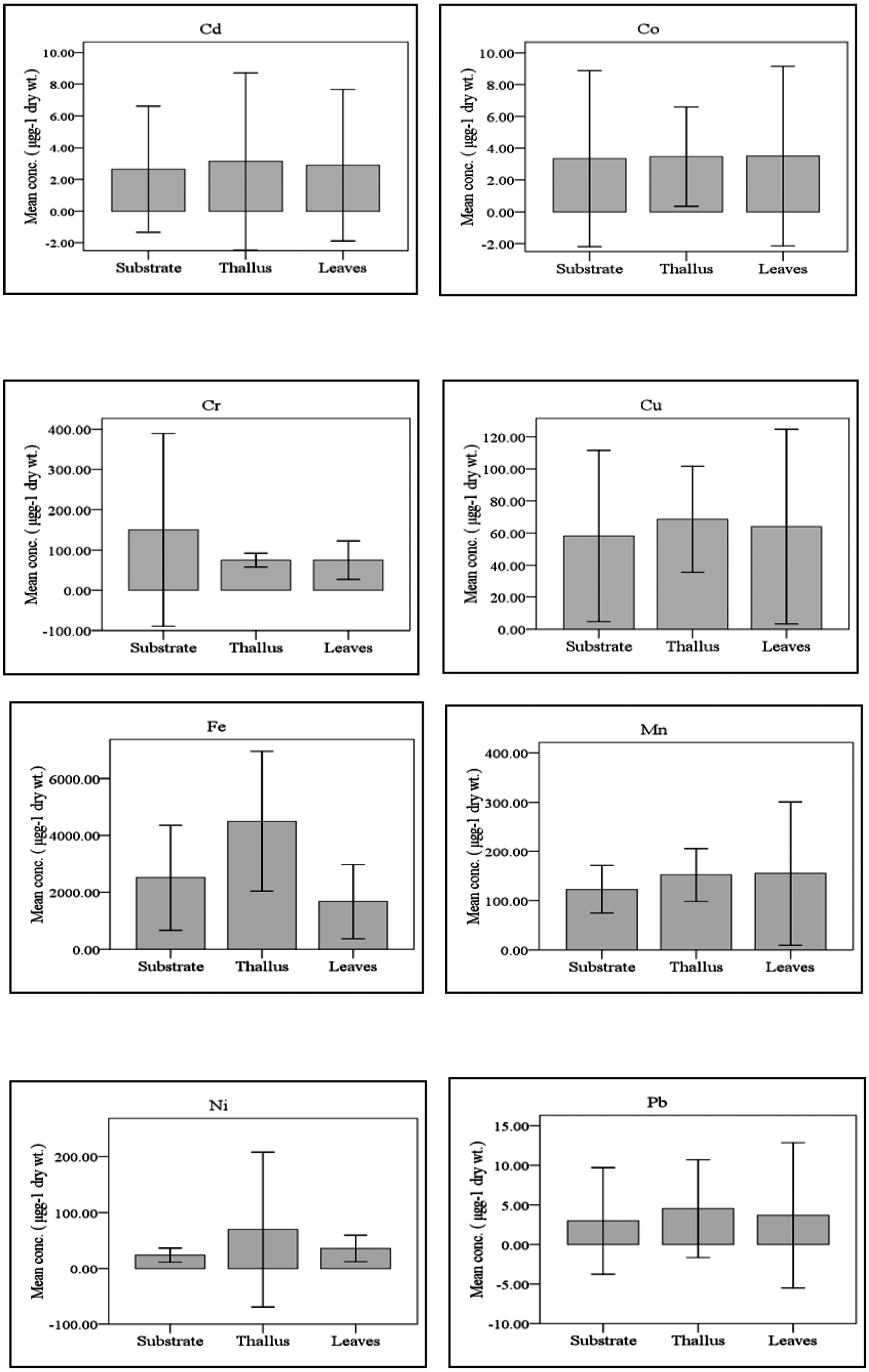

Figure 2: Mean metal accumulation in *thalli* and their respective phorophyte.

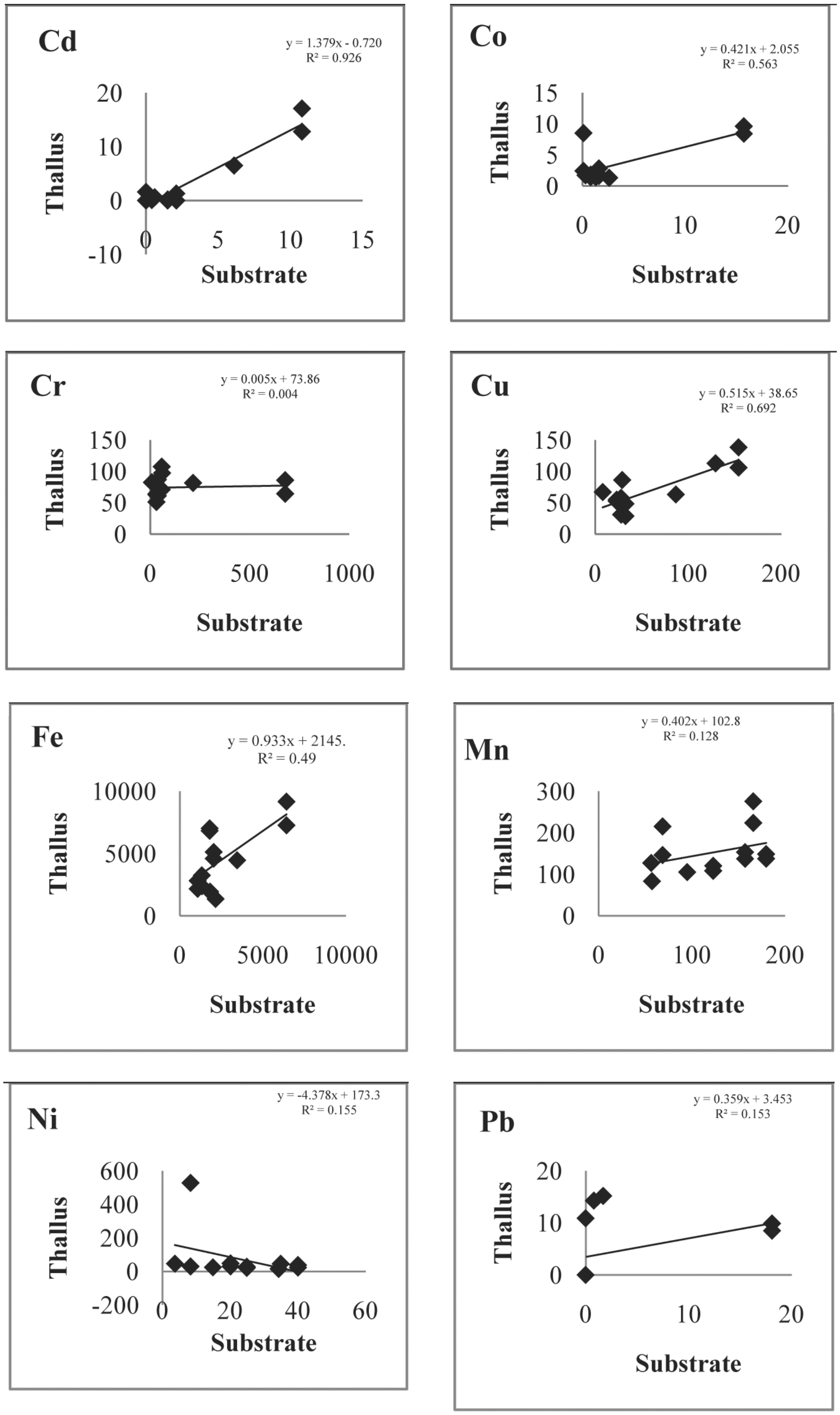

Figure 3: Dependency of the concentrations of metals in *thalli* (T) on the concentraion in substrate (S).

Table 5: Pearson's correlation matrix of metallic species

	Cd	*Co*	*Cr*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*
Cd	1.00							
Co	**0.71**	1.00						
Cr	0.08	-0.17	1.00					
Cu	**0.87**	**0.70**	0.19	1.00				
Fe	-0.52	-0.39	**0.30**	-0.63	1.00			
Mn	-0.19	0.25	0.18	-0.05	**0.52**	1.00		
Ni	-0.20	**0.45**	-0.36	0.12	-0.23	**0.35**	1.00	
Pb	**0.34**	0.11	**0.31**	**0.31**	0.16	-0.01	-0.27	1.00

Positive correlation $r > 0.3$ are in bold.

Further, Principal Component Analysis (Table 6) was performed to ascertain the possible contributing factors of the atmospheric metals. By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors and the percent of variance explained by each of them were calculated.

Table 6: Principal component analysis of the metal data showing components and loadings

	Components		
	1	*2*	*3*
Cd	**0.896**	0.262	-0.211
Co	**0.861**	-0.171	0.359
Cr	-0.02	**0.781**	0.145
Cu	**0.949**	0.159	-0.027
Fe	-0.668	**0.44**	**0.49**
Mn	-0.061	0.091	**0.945**
Ni	0.224	-0.683	**0.548**
Pb	0.276	**0.702**	0.019
Eigen value	3.022	1.894	1.629
%Variance	37.775	23.674	20.369
Cumulative variance	37.775	61.449	81.818
Probable source	Coal-fired industries	Vehicular emission	Crustal dust

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Rotation converged in four iterations.

Three eigenvalues were found to be >1 that explained ~84% of variance. The first three eigenvalues were selected for further analysis and the other small but non-zero eigenvalues were discarded to establishing a probable number of contributing sources. The initial eigenvalues extracted were 'cleaned up' by Varimax rotation.

The principal component 1 amounts for ~38% of variance and includes Cd, Co and Cu with high loadings. Co is attributed to emission from coal-fired industries and Cu from metal working factories. Emission of Cd in the air is mainly due to combustion of fossil fuel. Over the last few years there has been a growth in the number of brick-kilns and small scale industires around Tezpur by the side of highways. These brick-kilns are based on coal-fired heating, which could be a possible source of these heavy metals. Coal is also used as a source of energy in the tea processing units of the tea gardens around Tezpur.

The principal component 2 explains ~25.4% of variance and showed high loading for Cr and Pb. Since Cr and Pb in the urban atmosphere originate from vehicular contribution (Khillare et al., 2004; Shah et al., 2006), this component could be attributed to vehicular emissions.

The principal component 3 explains ~20.5% of variance and showed high loading for Fe, Mn and Ni. Since Fe and Mn naturally occur in higher percentage in the earth's crust (Bowen 1979), they together could come from dusts of crustal origin. Crustal dust from agricultural activities and wind blown dust from Brahmaputra River in the drier season could be, therefore, attributed to these metals.

Conclusions

Rich diversity of lichens was seen in Tezpur region of Brahmaputra valley. Presence of the lichen species *P. cocoes* and *D. applanata* in Tezpur eases pollution monitoring studies in the area with comparable results as they are the common foliose lichens in the tropical climatic regions of India and have well-known pollution tolerance. Metal accumulations in the *thalli* and their enrichment suggest that the region is moderately polluted. The PCA suggests three major sources of atmospheric metals in the study area viz., coal-fired industries, vehicular emission and crustal dust from agricultural sources. The present study being the first report, these findings should provide a baseline information for future studies in the region.

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