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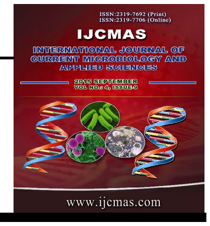

Original Research Article

Air Quality Assessment by *Rinodina sophodes* with Reference to Seasonal Variation and Traffic Influence in India

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ABSTRACT

Keywords

Macro micro elements, *Rinodina sophodes*, Seasonal variation, Traffic level, India

The aim of this study was to assess the seasonal variation in accumulation of macro-elements (C, N and S) and to elucidate influence of traffic load on accumulation pattern of micro-elements (Mn, Cu, Zn, Cr, Fe, Ni and Pb) by lichen *Rinodina sophodes* in North India. Lichen samples were collected from ten *Mangifera indica* tree trunk from the height of 1.5 to 2 m above the ground. The estimation of macro and micro elements were carried out by using Fisons 1108 Elemental Analyzer and Atomic Absorption Spectrophotometer, respectively. The result indicated that during winter thalli gradually accumulated carbon and nitrogen. Correlation analyses revealed that carbon content was significantly correlated (1%) with Cr (r=0.9198). Nitrogen was negatively correlated with Cu (-0.3817) and Zn (-0.1834). All studied macro elements were showed significant difference at 5 %. The highest concentration of Mn, Zn, Cr, Fe, Ni and Pb were found at highly polluted areas with heavy traffic. Mn was positively correlated between Fe (r=0.9752) and Ni (r=0.9668) while Cu and Zn negatively correlated with Pb (r=-0.4719, -0.0764). Zn was positively correlated with Cr (r=0.9534) while Cr was positively correlated with Fe (r=0.9643). The present study has established that utility of crustose lichen; *R. sophodes* in monitoring of environmental health in North India.

Introduction

Lichens depend mainly on atmospheric deposition for their nutrition. The intake of mineral nutrition depends on wet or dry deposition in lichens. Lichens are sensitive to sulphur dioxide because their efficient absorption systems result in rapid accumulation of sulphur when exposed to high levels of sulphur dioxide pollution. The algal partner seems to be most affected by the sulphur dioxide, chlorophyll is destroyed and photosynthesis is inhibited. In general lichens are employed worldwide for air quality assessment by determination of heavy metals, polycyclic hydrocarbons (Guidotti *et al.*, 2009; Protano *et al.*, 2014; Paoli *et al.*, 2012).

In pollution-enhanced environments, lichens can accumulate nitrogen, sulphur, metals and other pollutants well in excess of their nutritional needs (Sochting, 1995; Glavich Geiser, 2008). The effects of many climatic and other environmental factors on the physiological process in lichens, including those related to their carbon (C), nitrogen (N) and sulphur (S) accumulation have been investigated (Tretiach *et al*,. 2007). The impact of C,N,S on lichen flora remains poorly understood (Purvis *et al.* 2003; Cont Cecchetti, 2001; Sujetoviene, 2010). Variation in the rate of N accumulation may be due to changes in the deposition rates or to the increased, the level of N capture due to metabolism dependent nitrate-uptake (Crittenden, 1996). Humans are altering the global cycle of N via combustion of fossil fuels, traffic, production of N-based fertilizers, cultivation of N-fixing legumes, and other actions (Galloway *et al.*, 1995; Gilbert et al; and 2007). The major sources of deposited atmospheric N are ammonia (NH_3), in rural environments, and nitrogen oxides (NOx), in urban environment which are close to roads and motorways.

In particular, lichens and mosses have been widely used as bioindicators for assessing the atmospheric deposition of heavy metals and/or biological effects of airborne contaminants (Klos *et al.* 2011; Ite *et al.*, 2014).

A large number of microelements such as heavy-metal accumulation studies with foliose lichens are available in India (Shukla and Upreti, 2007b; 2008a; 2012; Bajpai *et al.*, 2012; & 2013). In areas, particularly highly industrialized and urban region, foliose lichens do not occur. In these areas crustose lichen supervenes frequently. In such regions, the discretion of pollution monitoring remains with crustose lichens. Very few studies have been carried out on heavy metals and PAHs accumulation by crustose lichens in India (Nayaka *et al.*, 2003; Saxena *et al.*, 2007; Satya and Upreti, 2009; Satya *et al.*, 2012).

The main objective of this study was (1) to compare the seasonal variation in accumulation of macro elements (C, N and S) shown by *R. sophodes* in two different season i.e. in post Manson (September, 2008) and winter (December, 2008), in North India. (2) to evaluate an influence of traffic load on the accumulation of microelements (Mn, Cu, Zn, Cr, Fe, Ni, Pb) by *Rinodina sophodes* in North India (3) The correlation variances among micro and macro elements were analyzed to evaluate the impact of air quality with group of elements accumulated by *R. sophodes*.

Materials and Methods

Description of site

The studies areas are part of Kanpur city (Fig. 1 and Table 1). Kanpur is second largest industrial city in North India. It is also the largest populated city in the State.

The study area is situated in the zone of humid subtropical climate and the year is divided into three seasons: the coal season (November–February), the hot season (March–June) and the monsoon season (July–October). Heavy rainfall occurs during the monsoon season in the months of July, August and September. Generally 70–80% of the total rainfall occurs during this period (Chowdhury *et al.*, 1982). According to final report of Kanpur City Development Plan under Jawaharlal Nehru National Urban Renewal Mission (2006), on an average day a total 89,4,68 vehicles in Kanpur city enter and exit at the outer corridors. The lichens were collected from two different pollution level sites i.e. highly polluted and moderately polluted area (Table 1).

Sampling methodology

The area in and around the Kanpur city was surveyed for collection of lichen species in December (winter), 2008. At each site, samples were taken from ten *Mangifera indica* tree trunks facing towards the road. From each tree, 3-5 whole thalli of *R. sophodes* were collected. Lichen thalli were collected from a height of 1.5 to 2 m above the ground.

Estimation of total carbon, nitrogen, sulphur (macro elements)

The air dried samples were divided in aliquots of ca. 500 mg and stored in petri dishes at -32^0 C until use for analysis of C, N, S elements. Total C, N and S content was measured according to the flash combustion procedure with a Fisons 1108 Elemental Analyzer in triplicates of 10 mg (triplicate) of lichen thalli. In order to avoid H_2O-SO_2 signals overlapping, a trap system of Mg $(ClO_4)_2$ was employed to remove the excess of H_2O from the gases produced by combustion. Accuracy and recovery of elements were checked analyzing a sample of sulphanilamide was used as standard (Tretiach *et al.*, 2007) for the analysis of C, N and S (macro-elements). The reagent used from Merck. Accuracy and recovery level was ± 0.5 % and nil, respectively.

Estimation of micro elements

For the analysis of the micro-elements, the lichen thalli were removed from the bark with sharp snapper blade avoiding coming out of bark with it. The samples were oven dried for 2 days at 65° C. The dried lichen samples (triplicate) were powdered (1.0 g each) with pestle and mortar and digested in mixture of concentrated HNO_3 and $HClO_4$ (v/v 5:1) for 1 hour. Residues were filtered through Whatman Filter Paper No. 42 and diluted to 10 ml with double distilled water and metal contents were analyzed using a Perkin Elmer 2380 Atomic Absorption Spectrophotometer. Stock standards were used from Merck India, traceable to NIST (National Institute of Standards Technology), to establish calibration curves that covered the region from 1, 2 and 3 μgg^{-1} for all the metals detected (Shukla *et al.*, 2007).

The quality tests were conducted vide certification of analysis of Resource Technology Corporation (RTC) Laramie, WY, USA, Catalog no., CRM 028-050, lot no., IH028. The acid used for digestion were all analytical grade Merck Germeny and blank were used for both celebrating the instrument '0' before measuring the unknown samples.

Statistical analysis

The experiment was done as randomized block design. One-way analysis of variance (ANOVA) and Correlation of variance was done with all the data to confirm the variability of data and significant difference between parameters (Gomez and Gomez, 1984).

Results and Discussion

Seasonal variation in macro elements shown by R. sophodes

The current study was repeated in the same site to check for possible seasonal variation in accumulation pattern of macro-elements (C, N, and S) concentration in *R. sophodes* thalli in December, 2008 (winter). The data were compared with previous study, which was taken during post monsoon season in September, 2008 (Satya and Upreti, 2009) in Kanpur City, India.

Table 2 showed decreased concentration of C content with 32.06 to 36.11 µg g^{-1} DW in current study sites. It suggested that the C was acquired through photosynthesis in the photobions which is active when the lichen is wet and exposed to light (Palmqvist, 2000). Though, Máguas (2013) concluded that the carbon acquisition of the lichen depends on the water content, light intensity and CO_2 fixation of the photobiont. Signal factor ANOVA was also showed significance difference at 5%.

The current study revealed that the concentration of N was lower during winter season (Table 2). It ranged between 2.27 to 2.74 µg g^{-1} DW in study sites (Table 2). It has been noticed that the physiological activity of the plant is usually slow during winter due to low light and reduced availability of water, which indicates low uptake of N in the current study area (Hovenden, 2000). Lichen thalli shows seasonal changes in the concentration of N which indicates a temporal pattern in the uptake of elements for the lichen growth. In contrast, higher concentration was found in previous study which was done in monsoon season, it may be due to the maximum photosynthesis and transpiration rate which increased the water absorption capacity in plant, thereby, increase in N uptake. Signal factor ANOVA was also showed significance difference at 5%.

The S concentration did not showed found in current study sites. Signal factor ANOVA was also showed significance difference at 5%. The assessments of S content in lichens provide a good estimate of the atmospheric SO_2 concentration in rural, suburban and urban sites (Garty, 1988). SO_2 is a byproduct of coal or fuel oil combustion, many other industrial processes and vehicular exhausts. In the present study, all four sites do not show any concentration of Sulphur. The previous data on atmospheric SO_2 level in the Kanpur area was analyzed decreasing. The SO_2 level in 1987 was 11µg/m^3, however in 1994 and 1996 it abruptly went down to 7.0 and 8.0 µg/m^3 [http://www.usc.edu/dept/polsci/sellers/Recent%20Projects/AMIS/Assets/Kanpur.pdf]. After a long gap of about 11 years the accumulation potential of *R. sophodes* has shown null concentration. This study reveals that the SO_2 level might have decreased by any one of the variable parameters, which are to be further investigated. A study also ascertains that amount of S accumulation was species dependent and did not found in all species from the same site which would contain the same amount of sulphur (Takala *et al.*, 1985).

Correlation matrix (Table 3, all significant at 1 %) of the macro-micro elements indicates that C content was significantly correlated with Cr (r= 0.9198), while Mn positively correlated with Fe (r = 0.9759) and Ni (r = 0.9668). However, Zn was favorably correlated with Cr (r= 0.9534) while Cr was positively correlated with Fe (r = 0.9643). The negative correlation was found among N-Cu-Zn, Cu-Pb and Zn-Pb (Table 3).

Influence of traffic load on microelements contents in R. sophodes

The Concentration of micro-elements contents (Mn, Cu, Zn, Cr, Fe, Ni, Pb) were also investigated to determine the influence of traffic load on distribution pattern of micro-elements, which were accumulated by *R. sophodes* in the study area (Table-2).

The data represented that the sites having high-traffic load, (Table-1) shows maximum concentration of six micro-elements (Mn, Zn, Cr, Fe, Ni and Pb) except Cu (Table 2). The study indicated that the concentration of Fe was found highest (1152.56 µg g^{-1} DW to 4962.86 µg g^{-1} DW) in comparison to other micro-elements. Some reports showed that traffic activities enrich the roadside soil Fe content (Monaci *et al.,* 2000). However, Oliva and Espinosa (2007) concluded that the enrichment of Fe in roadside soil was attributed to the natural sources. Fernandez *et al.,* (2000) reported that the Fe is emitted from iron steel plant and during the combustion of fossil fuel such as coal. However, Pb is second most accumulated element (492.76 µg g^{-1} DW) in the study area. High level of these elements may be representing to industries like Tanneries, Fertilizers, Paints as well as traffic load.

The average value of Mn content in the study area ranged from 43.44 to 103.14 µg g^{-1} DW (Table 2). The site 1 and 2 (Table 1) were located close to major motor vehicle traffic manifested the highest level of Mn having 103.14 µg g^{-1} DW and 95.81 µg g^{-1} DW, respectively. Motor vehicles are known to be a source of Mn in urban areas (Monaci *et al.,* 2000).

The Cu content in *R. sophodes* ranged from 5.53 µg g^{-1} DW to 9.76 µg g^{-1} DW in the study area. Table 2 indicated that the highest concentration of Cu was found at site 1 (Highly polluted) with 9.76 µg g^{-1} DW followed by site 3 and 4 (Moderately polluted) with 7.96 µg g^{-1} DW and 6.02 µg g^{-1} DW, respectively. However, a lot of literatures showed strong evidence that traffic activity is one of the Cu pollution source on roadside soil (Monaci *et al.,* 2000), while de Vries *et al.* (2002) reported that the Cu pollution from the traffic activities, but it cannot ignore Cu pollution from the fertilizer and manure. Hence, the concentration of Cu in site 3 & 4 can be correlated with use of fertilizer and manure for the agricultural purpose.

The highest level of Zn in the *R. sophodes* was found in the site-1 (53.83 µg g^{-1} DW), then site-2 (32.71 µg g^{-1} DW) and site-3 (31.00 µg g^{-1} DW). Zn belongs to a group of trace metals, which is essential for the growth of humans, animals & plants and is potentially dangerous for the biosphere when present in high concentrations (Gowd *et al.,* 2010). The vehicular traffic and industrial emissions are supposed to be the main source of Zn in the study area. Romic and Romic (2003) reported that the main sources of the Zn pollution are industries and the huge of liquid manure, composted materials and agro chemicals such as fertilizers and pesticides in agriculture. The present study is represented to 300 tanneries along the bank of river Ganga. It is a prominent center for leather processing, especially for the manufacture of saddler products (Gupta *et al.,* 2011). The Cr content in the present study was correlated with industrial as well as traffic influence. The Cr concentration was found highest at the site-1 with 13.22 µg g^{-1} DW. However, it was observed that the average concentration of Cr in *R. sophodes* was decreased with the increase of distance from the road site (Table 1 & 2). Similarly, Aslam *et al.,* (2011) reported that the concentration of total Cr in soil was decreased with the increase of destination from the road side. Lee (1972) reported that Cr was much used in Cr plating plant in paint's production, tanneries, paper factories, dye-works and steel industries.

The concentration of Ni in lichen thalli can be regarded as good tracers of fossil-fuel combustion (Minganti *et al.,* 2003a). In the current study, the highest concentration of Ni was found at road sides, which give a strong support to conclude that traffic activity contributed to Ni pollution (Aslam *et al.,* 2011).

In the present study, the higher concentration of Pb was recorded in traffic area (Table 1& 2). The increase in Pb concentration in traffic/urban area is probably confirmed by the amount of this metal deriving from the exhaust gases. A notably higher Pb concentration was also characteristic of the industrial sites (Biolonskan Dayan, 2005). Site-2 (Table 1) with maximum human activities, together with motor garage, high vehicular density congestion showed the highest Pb level with the value of 492.76 µg g^{-1} DW. Duman *et al.,* (2009) concluded that maximum concentration of Pb indicated highest vehicular density.

The results of the present study indicated that the accumulation patterns of macro-elements (C, N and S) are much more affected by their immediate microclimate. The finding suggests that the vehicular traffic is generally the main source of micro-elements in the Kanpur city. Some industrial activity in and around the city sites may also have a contribution to the urban pollution. Highest concentration of Mn, Zn, Cr, Fe, Ni and Pb content at highly polluted areas are directly indicated that the city is suffering from vehicular emissions. On the other hand, it is possible to differentiate the effect of traffic released pollutants on the different studied sites, which helps raise the issue of the need to carry out better controls on the quality of the air in our country, as well as to control the level of pollutant emissions in the vehicles circulating. The results confirm the ability of crustose lichen of *R. sophodes* is a suitable tool for monitoring of macro and micro-elements in urban environment.

Table.1 Description of the sites selected for the collection of *R. sophodes* at Kanpur city, North India

S. No.	Localities	Vegetations	Site directions	Pollution level
1.	Ramnagar	*Mangifera indica*	50 v/hr (G. T. road, highly traffic activity, railway track with maximum human interference) urban area	Highly polluted
2.	Tatiyaganj	*Mangifera indica*	50 v/hr (G. T. road, high traffic activity, site having motor garage with maximum human interference) urban area	Highly polluted
3.	Raghunathpur	*Mangifera indica*	10 v/hr (Light vehicles, village, livestock forming animal wastes, agricultural area) rural area	Moderate polluted
4.	Maharajpur	*Mangifera indica*	10 v/hr (Mostly light vehicles, village area with low human interference) rural area	Moderate polluted

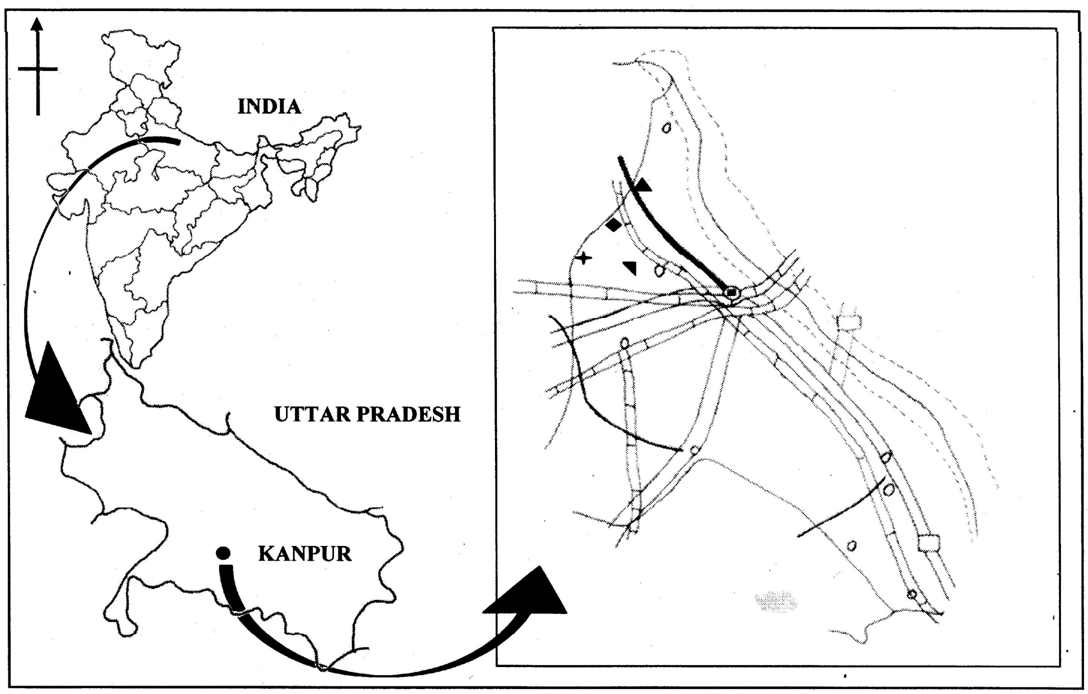
Table.2 Macro elements (%) and Micro elements concentration (µg g^{-1} DW) quantified in R. sophodes at different sites of Kanpur city, North India

Sites	Macro elements						Micro elements						
	Current study			Previous study (Satya and Upreti, 2009)									
	C	**N**	**S**	**C**	**N**	**S**	**Mn**	**Cu**	**Zn**	**Cr**	**Fe**	**Ni**	**Pb**
Ramnagar	36.1 ± 0.48	2.38 ± 0.31	0	33.91 ± 1.54	2.43 ± 0.33	0	103.14 ± 0.46	9.76 ± 0.38	53.83 ± 0.43	13.22 ± 0.40	4962.86 ± 0.46	5.56 ± 0.29	271.86 ± 0.461
Tatiyaganj	34.19 ± 0.42	2.74 ± 0.37	0	36.74 ± 0.53	2.75 ± 0.15	0	95.81 ± 0.42	5.53 ± 0.29	32.71 ± 0.35	11.18 ± 0.43	3592.82 ± 0.43	6.15 ± 0.45	492.76 ± 0.38
Raghunathpur	33.96 ± 0.54	2.48 ± 0.28	0	35.5 ± 1.92	2.99 ± 0.10	0	47.92 ± 0.50	7.69 ± 0.34	31± 0	10.00 ± 0.56	1152.56 ± 0.29	3.36 ± 0.32	229.18 ± 0.430
Maharajpur	32.06 ± 0.52	2.27 ± 0.28	0	35.6 ± 1.77	2.33 ± 0.37	0.22 ± 0.22	43.40 ± 0.29	6.02 ± 0.56	29.64 ± 0.32	9.69 ± 0.34	1242.32 ± 0.34	2.78 ± 0.402	226.73 ± 0.369

Table.3 Correlation variance between the macro and micro elements in R. sophodes. Correlation variance shows ** Significant at 1 %

Elements	C	N	S	Mn	Cu	Zn	Cr	Fe	Ni	Pb
C	1	0.2502	0	0.8140	0.7725	0.8681	0.9198**	0.8443	0.7282	0.1914
N		1	0	0.4832	-0.3817	-0.1834	0.1053	0.2792	0.6890	0.8974
S			1	0	0	0	0	0	0	0
Mn				1	0.3444	0.7253	0.8982	0.9759**	0.9668**	0.6307
Cu					1	0.8550	0.7041	0.4914	0.1524	-0.4719
Zn						1	0.9534**	0.8494	0.5367	-0.0764
Cr							1	0.9643**	0.7662	0.2258
Fe								1	0.8865	0.4568
Ni									1	0.7932
Pb										1

Figure.1 Map of Kanpur city showing localities explored for lichen and its location within Uttar Pradesh, India



◥ Ramnagar, ✦ Tatiyaganj, ◆ Raghunathpur, ▲ Maharajpur

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