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Determination of atmospheric heavy metals using two lichen species in Katni and Rewa cities, India

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Abstract

A biomonitoring study was conducted to assess the levels of atmospheric heavy metal pollution in Katni and Rewa cities of Madhya Pradesh, state in central India. The *Pyxine cocoes* and *Phaeophyscia hispidula*, two epiphytic foliose lichen were used as bioindicators in the present study and seven metals (As, Al, Cd, Cr, Fe, Zn, Pb) were analyzed in naturally growing thallus. The concentrations of these metals was observed to be in higher range as maximum values of Al, Cd, Cr and Zn were reported from the lichen samples from Rewa city which was 561.8±2.4, 6.8±0.8, 35.2±1.4, 214.6±2.0 $\mu g\ g^{-1}$ dry weight respectively. Whereas As, Fe and Pb were reported maximum in the lichen samples collected from Katni city areas with 33.4±0.05, 689.4±2.6, 13.3±0.5 $\mu g\ g^{-1}$ dry weight respectively. However the accumulation of Cd and Pb from both the cities are more or less similar in concentration. The selectivity sequence of metals were Fe>Al>Zn>As>Cr>Pb>Cd in Katni city, and Al>Fe>Zn>Cr>As>Pb>Cd in Rewa city. The findings of this study indicates that extent of heavy metal pollution in the atmosphere of the two cities which may lead to adverse health affects.

Key words

Biomonitoring, Heavy metal pollution, Lichen, Bioindicator

Introduction

Industrialization and urbanization have promoted socio-economic development. However, they have also led to variety of environmental hazards. Several pollutants are released into the atmosphere from different sources in the form of nitrogenoxides, sulphuroxides, pesticides, herbicides, suspended particulates and heavy metals. Out of these, the heavy metals are emitted into the atmosphere from industrial and many other anthropogenic sources. These pollutants threaten not only human health but also the structure of the ecosystem. Pollutants emitted from a source fall either in the area immediately surrounding the source or are carried to remote areas. Biomonitoring studies provide valuable information about the quantity and quality of pollutants in the atmosphere and can be very effective as an early warning system to detect environmental changes (Seaward, 2004). Therefore, many studies have been devoted to show the distribution of atmospheric air pollutants (Loppi and Bonini, 2000; Garty *et al.,* 2002). Different bioindicator organisms have been used for the monitoring of atmospheric air pollution (Steinnes, 1977; Sloof, 1995; Coskun, 2006), among them moss and lichens occupy first place showing local and regional variations in heavy metal pollution. They have no real root system but accumulate heavy metal cations supplied by dry and wet deposition (Ruhling and Tyler, 1971).

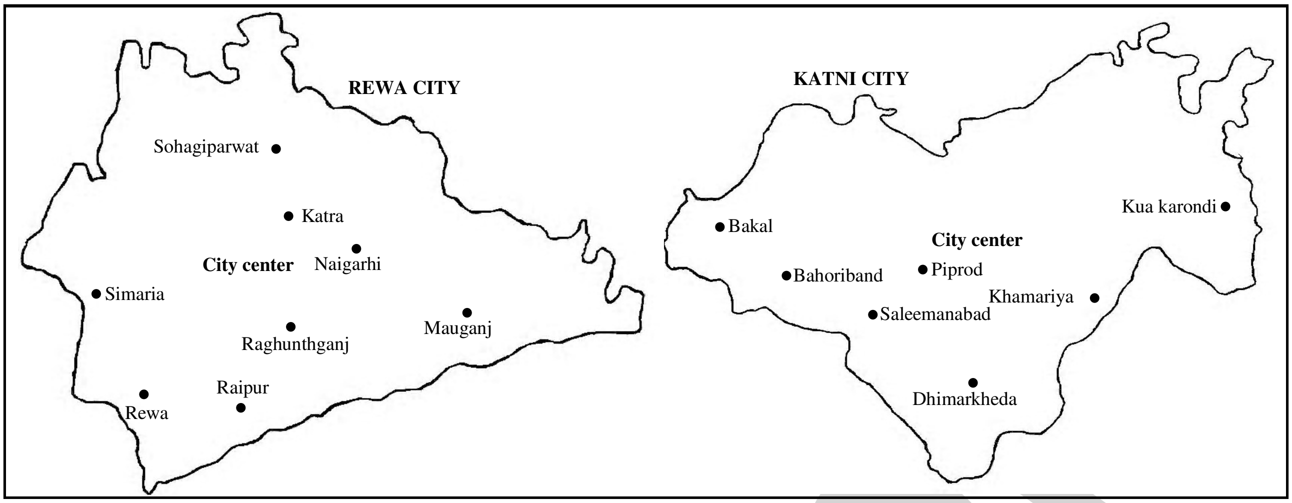

Fig. 1: Location of studied sites in the Katni and Rewa cities of Central India

Several studies have shown that, lichens are among first organisms used as bioindicators for assessment of chemical pollution (Garty, 1993). Many studies have demonstrated their ability to absorb and accumulate persistent contaminants and are routinely employed to monitor radionuclides, metals, nonmetals and other compounds present in the atmosphere (Goldsmith, 1991). Lichen flora have been used as indicators for monitoring sources of pollution at industrial levels and from vast areas (Sloof, 1995; Guidetti and Stefanetti, 1996) or by transplantation from uncontaminated areas to places devoid of spontaneous colonization (Bajpai *et al.*, 2004; Garty *et al.*, 1996; Jeran *et al.*, 1995; Levin and Pignata, 1995). Consequently, various workers have monitored the heavy metals using different growth forms of lichen in different geographical area with varied climate (Godinho *et al.*, 2008; Bergamaschi *et al.*, 2004; Carreras and Pignata, 2002; Upreti and Pandey, 2000). In, India studies on the use of lichens as biomonitoring was adopted in different climatic zones by several workers (Dubey *et al.*, 1999; Nayaka *et al.*, 2003; Bajpai *et al.*, 2004, 2009; Shukla and Upreti, 2007). The foliose lichen species *Pyxine cocoes* (Sw.) Nyl., and *Phaeophyscia hispidula* (Ach.) Essl., are abundantly found in Katni and Rewa cities respectively. The aim of the present study was to obtain the first hand data about the heavy metal concentrations in these two lichens growing in the vicinity of pollution sources.

Materials and Methods

Study area, sample collection and metal analysis: Katni and Rewa cities are located in Madhya Pradesh state of central India and have more or less dry and warm climate. The temperature varies from 6 to 20°C in winter and 21 to 48°C in summer; while receives a rainfall of 75-85 cm during rainy season. The sites were selected due to the anthropogenic activities like agricultural, mining, stone crushers, automobile and also preserving some forest areas.

Specimens of *P. cocoes* were collected from 3 to 6 points in each sampling sites and a total seven sites were investigated in Katni city. Whereas specimens of *P. hispidula* were collected from 3 to 5 points in each sampling sites of Rewa city and eight sampling sites were investigated (Fig. 1). The collections were made in triplicates from tree trunk of *Mangifera indica* with the help of chisel and knife and approximately 3-4 gm of the thallus (of similar size up to 4 cm) was taken from each point. The lichen samples were identified and voucher specimens are deposited in the herbarium of National Botanical Research Institute, Lucknow.

Collected, lichen samples were cleaned for dust, leaf debris, fungus contamination and degraded material by brush. Lichens thallus was then oven dried for 24 hr at 60°C temperature. The dried lichen samples were separately grinded to powder and 0.5 gm of this grinded sample was digested in mixture of concentrated HNO_3: $HCLO_4$; (V/V 9:1) for 2 hr (APHA, 1992). Residues were filtered through Whatman filter paper no. 42 and diluted to 10.0 ml with double distilled water. Concentration of heavy metals in the digested samples was analyzed by using Flame Atomic Absorption Spectrophometer (*Perkin Elmer, model A Analyst 300- Australia*). Stock standards and chemicals used were from Merck India. Working standards were prepared from the stock using deionised water.

Stastical analysis: The results of heavy metal accumulation in lichen thallus were evaluated by analysis of varience (ANOVA) together with mean, standard deviation, standard error of each metal. Student-Newman-Keuls (SNK) test was also performed to check the significant variation between the each metals and sites.

Results and Discussion

Results obtained in the analysis of lichens from Katni and Rewa cities are presented in Table 1,2. The tables shows the mean and ANOVA for each of the seven metals analyzed in thallus of lichen which found to be significant at 0.01% between the sites as well as metals. The SNK test also exhibited significant comparison between the each metal (Table 3 and 4).

Table - 1: Metal accumulation (µg g^{-1} dry weight) in lichen thallus of *Pyxine cocoes* at Katni city

Metals	Sites							Total	*f*
	1	2	3	4	5	6	7		
As	N.D.	21.8±1.2	10.0±1.0	8.3±0.8	2.3±0.4	5.1±1.0	33.4±0.5	81.1	15.6**
Al	78.2±1.3	230.9±0.6	145.0±1.9	213.4±0.8	118.7±1.3	95.2±0.2	365.1±2.0	1246.8	
Cd	N.D.	6.3±0.5	3.8±0.8	N.D.	N.D.	0.9±0.4	5.8±0.2	16.9	
Cr	0.8±0.0	15.1±1.0	1.3±0.2	1.5±0.1	2.5±0.2	4.5±0.4	26.2±0.3	52.0	
Fe	103.0±2.5	564.0±0.9	138.7±2.0	410.3±2.5	119.5±1.9	369.8±1.4	689.4±2.6	2394.8	
Pb	0.9±0.1	5.6±0.0	6.9±0.4	1.0±0.6	N.D.	0.1±0.0	13.3±0.5	28.0	
Zn	64.9±1.7	187.3±1.9	117.7±2.7	146.7±1.6	79.7±0.4	57.3±1.9	194.4±2.5	848.3	
Total	247.9	1030.9	423.7	781.5	322.8	533.2	1327.8		
Two-way ANOVA									
f	3.0								

Mean ± S.D.; n=3; S.D. = Standard deviation; N.D.= not detectable (detection limit >0.05 ppm); **Significant at 0.01%, Sampling sites: 1. Kua Karondi forest, 2. Saleemanabad, 3. Khamriya, 4. Dhimar Kheda, 5. Bahoriband, 6. Bakal, 7. Piprod (City centre)

Table - 2: Metal accumulation (µg g^{-1} dry weight) in lichen thallus of *Phaeophyscia hispidula* at Rewa city

Metals	Sites								Total	*f*
	1	2	3	4	5	6	7	8		
As	17.4±1.2	19.6±1.6	5.7±0.5	11.6±0.9	3.6±0.0	1.5±0.0	N.D.	8.5±1.0	68.3	28.7**
Al	499.0±2.5	561.8±2.4	345.8±2.0	541.2±2.6	260.6±1.8	169.8±1.0	92.7±0.9	123.8±1.7	2595.1	
Cd	6.8±0.8	5.9±0.4	1.0±0.0	2.0±0.9	1.1±0.0	0.9±0.0	N.D.	0.8±0.2	18.7	
Cr	25.2±1.0	35.2±1.4	9.3±0.7	14.2±0.8	5.3±0.0	3.4±0.8	N.D.	4.9±0.1	97.9	
Fe	419.4±2.2	307.0±2.4	257.3±1.6	225.6±2.0	317.0±1.8	201.0±1.6	176.5±2.7	181.3±2.0	2085.4	
Pb	11.7±0.9	11.7±0.8	N.D.	4.4±0.0	6.2±0.6	11.2±0.4	N.D.	N.D.	45.4	
Zn	214.6±2.0	203.7±1.8	127.9±1.4	178.5±2.1	168.3±0.9	103.1±1.3	115.6±1.6	136.0±2.0	1248.0	
Total	1194.5	1145.3	747.2	977.8	762.4	491.2	384.9	455.5		
Two-way ANOVA										
f	2.6									

Mean ± S.D.; n=3; S.D. = Standard deviation; N.D.= Not detectable (detection limit >0.05 ppm); **Significant at 0.01%, Sampling sites: 1. city centre, 2. Raipur, 3. Raghunathganj, 4. Mauganj, 5. Naigarhi, 6. Katra,7. Sohagiparwat, 8. Simariya

Arsenic (As) is a ubiquitous element and it ranged from 2.3±0.4 to 33.4±0.5 and 1.5±0.0 to 19.6±1.6 µg g^{-1} dry weight (DW) in the air of Katni and Rewa Cities respectively. Maximum amount of As was reported from city centre and its surrounding where commercial and industrial activities are more. As is also released unintentionally as a result of many human activities like smelting, industrial applications and with combustion of fossil fuels. Rapid leaching of As has been observed in case of exposed wastes of ores and mining, as well as soil erosion (Al and Blowes, 1999; Madhwan and Subramanian, 2000). In this study maximum As 33.4±0.5 µg g^{-1} DW was reported from Piprod locality where the main pollution source are automobile and stone crushers. In an earlier study Bajpai *et al*., (2009), reported maximum concentration of 51.9±0.1 µg g^{-1} DW of As in thallus of *Phaeophyscia hispidula* from a sites having past mining activities.

Aluminum (Al), metal is widely accumulated in thallus of lichens and it ranged from 78.2±1.3 to 365.1±2.0 and 92.7±0.9 to 561.8±2.4 µg g^{-1} DW in Katni and Rewa cities respectively. In both the cities samples collected from city centre having mixed pollution source like automobile exhausts, coal burning, and electroplating, paint and pesticide application generally influenced the concentration of Al in lichen thallus.

Cadmium (Cd), content was very less in lichen thallus when compared to other heavy metals and ranged from 0.9±0.4 to 6.3±0.5 and 0.8±0.2 to 6.8±0.8 µg g^{-1} DW in Katni and Rewa respectively. At Katni in most of the sampling sites it was not detected, whereas, at Rewa it was found in small quantities in all the sampling sites except, Sohagiparwat which is more than 750 mt away from the road. According to Nimis *et al*. (1990), the burning of fossil fuel, incineration of solid waste, paint and phosphate fertilizers are the main source of the Cd in the air. In the present study, most of Cd was detected at roadside samples, clearly indicating its origin from vehicular as well as agricultural applications.

The presence of Chromium (Cr) in lichen thallus exhibits its airborne origin. It ranged 0.8±0.0 to 26.2±0.3 µg g^{-1} DW in the lichen samples at Katni city whereas it ranged from 3.4±0.8 to 35.2±1.4 µg g^{-1} DW in the samples of Rewa city. Maximum amount of Cr was reported in the samples collected from roadside areas having heavy vehicular activities in both the cities. According to Nriagu and Pacyana (1988); Shtiza *et al*. (2008), Cr is emitted to

Table - 3: SNK test between the different metals in lichen samples collected from Katni city

Comparison	q_{cal}	q_{tab} (0.01)	q_{tab} (0.05)	*P* value
Fe~Cd	9.15**	5.26	4.38	7
Fe~Pb	9.11**	5.11	4.23	6
Fe~Cr	9.01**	4.93	4.03	5
Fe~As	8.90**	4.69	3.79	4
Fe~Zn	5.95**	4.36	3.44	3
Fe~Al	4.41**	3.82	2.85	2
Al~Cd	4.73*	5.11	4.23	6
Al~Pb	4.69*	4.93	4.03	5
Al~Cr	4.59*	4.69	3.79	4
Al~As	4.48*	4.36	3.44	3
Zn~As	2.95*	3.82	2.85	2

q_{cal} = value calculated; q_{tab} = tabulate value according to degree of freedom and *p; p* step between two values; (~) versus; ** significant at 0.01% ; * significant at 0.05%

Table - 4: SNK test between the different metals in lichen samples collected from Rewa city

Comparison	q_{cal}	q_{tab} (0.01)	q_{tab} (0.05)	*P* value
Al~Cd	11.29**	5.26	4.38	7
Al~Pb	11.18**	5.11	4.23	6
Al~As	11.07**	4.93	4.03	5
Al~Cr	10.94**	4.69	3.79	4
Al~Zn	5.90**	4.36	3.44	3
Fe~Cd	9.06**	5.11	4.23	6
Fe~Pb	8.94**	4.93	4.03	5
Fe~As	8.84**	4.69	3.79	4
Fe~Cr	8.71**	4.36	3.44	3
Fe~Zn	3.67*	3.82	2.85	2
Zn~Cd	5.39**	4.93	4.03	5
Zn~Pb	5.27**	4.69	3.79	4
Zn~As	5.17**	4.36	3.44	3
Zn~Cr	5.17**	3.82	2.85	2

q_{cal} = value calculated; q_{tab} = tabulate value according to degree of freedom and *p; p* step between two values; (~) versus; ** significant at 0.01% ; * significant at 0.05%

the atmosphere due to coal and oil combustion especially by diesel-fed vehicles, refuge incineration and frequent use in stainless steel production. The huge amount of Cr in the study area are indicated its mixed sources such as automobile exhaust, incineration of waste and agricultural applications.

Iron (Fe) was accumulated in huge amount in all the sampling sites of both the cities and it ranged from 103.0±2.5 to 689.4±2.6 and 176.5±2.7 to 419.4±2.2 µg g^{-1} DW at Katni and Rewa Cities respectively. Fe was most abundant in the samples collected from areas having mixed pollution sources (city centre), while moderate in localities having less vehicular and agricultural activities. The data clearly indicates the origin of Fe is from vehicular, crushers, coal and oil burning activities. According to Baptista *et al*. (2008), the Fe content in lichens is evidently affected by iron originating from fuel and soil dust.

The main source of Lead (Pb) in the atmosphere is the automobile fuel, batteries industries and their use in pesticide manufacturing. In this study the Pb was accumulated in very less quantities in the lichen thallus and it ranged from 0.1±0.0 to 13.3±0.5 and 4.4±0.0 to 11.7±0.9 µg g^{-1} DW at Katni and Rewa cities respectively. Maximum amount of this element was found in lichens growing in the higher traffic areas and absent in unpolluted areas. Pb was not detected at three localities of Rewa city and in one locality of Katni city. This metal clearly indicates the traffic volume of a particular area. Takala and Okkonen (1981) correlated the Pb content with traffic volume by a lichen *Hypogymnia physodes* and concluded that traffic load is directly proportional to Pb accumulation in lichen thallus.

Zinc (Zn) content varied from 57.3±1.9 to 194.4±2.5 µg g^{-1} DW in the lichen samples collected from Katni city, whereas 103.1±1.3 to 214.6±2.0 µg g^{-1} DW in the samples of Rewa city. The higher concentration of Zn was recorded from the samples collected along roadside having heavy vehicular activities. Higher Zn concentration was associated with automobile tire and incomplete combustion of fossil fuel (Ward and Sampson, 1989). According to Harte *et al*. (1991), Zn level may be elevated near motorways due to tyre wear. The maximum concentration of Zn in the study areas recorded from city centre with traffic signals.

The selectivity sequence of metal analyzed from the all seven localities for Katni city is found to be Fe>Al>Zn>As>Cr>Pb>Cd, whereas for Rewa City Al>Fe>Zn>Cr>As>Pb>Cd for all eight localities. Most of the carcinogenic metals (Cr, Cd, Pb, As) (Nrigu and Pacyana, 1988) were found in maximum amount at Katni city localities followed by Rewa city. The mean concentration of heavy metals was maximum for Al, Fe, Zn with 178.1, 342.1, 121.1 µg g^{-1} DW for Katni and 324.3, 260.6, 156.0 µg g^{-1} DW for Rewa City respectively. Above data indicates that the *Phaeophyscia hispidula* accumulated maximum quantities of metals than the *Pyxine cocoes.* According to Garty, (2001) morphology of lichen thallus may play an important role in accumulation of most of the metals. Shukla and Upreti (2007), also proven the *P. hispidula* a potential bioaccumulator of heavy metals in Pauri city of India. The mean concentration of heavy metals at a particular sites it is found that city centre has maximum concentration followed outskirts area like Saleemnabad, Dhimarkheda and Bakal with 189.6, 147.2, 111.6 and 76.1 µg g^{-1} DW respectively at Katni city while, at Rewa city concentration of heavy metals was maximum at city centre followed by Raipur, Mauganj and Naigarhi it represented with 170.6, 163.6, 139.7 and 108.9 respectively. Among these the Sohagiparwat and Simariya of Rewa city and Kuakarondi forest and Bahoriband of Katni have less pollution. It indicates the dispersion of pollutants from city centre to outerskirts. According to Garty (2001) and Pignata *et al*. (2007), distribution of some elements allowed the detection of their emission sources and their range of dispersion within the study area.

The comparison between metals was found significant in both the cities. The concentration of Fe in lichen thallus significantly differs from all other metals at $p<0.01$ except for Al, remaining metals not significant in Katni City localities. Whereas, in case of Rewa city accumulation of Al, Fe and Zn are significant at 0.01%, which indicates these metals originates from a same sources.

It is clear from the study that the lichen samples from Katni City accumulated Fe, Al, Zn and As in higher concentration, whereas the Rewa City has higher level of Al, Fe, Zn, Cr though the vehicular activities, stone crushers and agricultural applications are the main source of pollution in both the cities.

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