Atmospheric Heavy Metal Deposition in Garhwal Hill Area (India): Estimation Based on Native Moss Analysis

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Abstract

Atmospheric distribution of metals was evaluated throughout the Garhwal Hills region of Uttaranchal, India by analysis of native moss species, Rhodobryum giganteum and Hypnum cupressiforme. The performance of these two mosses as biomonitors was studied in relation to the accumulation of atmophile elements. The elements Cd, Zn, Cu and Pb were surveyed at 33 sampling sites by conducting a passive monitoring technique using these mosses. Sampling was carried out from March 2004 to February 2005 for three different seasons (summer, monsoon and winter) in four directions nearly equidistant from a control site (Chamba Forest) where the moss samples were originally collected. Bioaccumulative ability in these two mosses was evaluated statistically using Dunkun’s Multiple Range test. Results indicate that summer has a significantly higher concentration of the metals Zn, Pb, Cu, Cd than winter and monsoon. Similarly, significant distance and seasonal differences were calculated and are presented on contour maps. The novel aspect of this study is that it actually delivered any information at all on atmospheric deposition in India and Asia, where very limited information is available in this field. Therefore, this finding is a gap filling one.

Keywords: Biomonitoring; Moss; Metal precipitation; Rhodobryum giganteum; Hypnum cupressiforme; Garhwal Hills.

INTRODUCTION

The presence of elements in ecosystem is due to both natural and anthropogenic causes, while natural forms are usually found in relatively low concentrations. Major pollutants persisting in the environment are very widely dispersed by man-made emission sources (Giordano et al., 2005). In recent decades, the number and intensity of anthropogenic sources, such as waste burning, fertilizers, vehicle emissions, and agricultural and sewage sludge have...
increased the overall concentration of elements in the environment (Bargagli, 1998). Automated, continuous monitoring is a useful tool for determining levels of atmospheric precipitation and for forming implications for future management; but it suffers from certain limitations, including involvement of a number of instruments, and the continual requirement and high cost of power and manpower to run them (Fernandez and Carballeira, 2002). An advantage to using mosses is that it allows several sites to be monitored simultaneously and around the clock at costs much lower than using more sophisticated instrumentation.

In addition, unlike conventionally used instruments, bryophytes, which lack well-developed root systems, can integrate pollutants over a long time. A number of studies have shown the ability of bryophytes to intercept, retain and accumulate pollutants, including metals. It is well-documented that mosses obtain most of their nutrients via atmospheric deposition; therefore, the elements present in their tissues may reflect the presence of elements in the atmosphere. Moreover, moss surveys may describe regional differences and time trends in metal deposition, as well as being valuable for possible identification of sources of airborne metal pollution (Berg and Steinnes, 1997). In this study, the mosses *Rhodobryum giganteum* and *Hypnum cupressiforme* were selected for the study because they are distributed widely in the Garhwal Hills. No one has explored the tolerance potential of these mosses (Saxena et al., in press), nor their application for biomapping.

This study of metals in mosses was carried out from two prospective views. Firstly, to examine how distance affects the accumulation of metals. Secondly, to examine the effect of seasonal variations on metal concentration in mosses. The study also provides a suitable and cost-effective method for determining the extent of an area affected by deposition of metals emitted from different sources. We also aimed to determine possible differences in the capacity of these two species to accumulate elements.

**MATERIAL AND METHODS**

**Study area**

A map of the study area and the location of sampling sites are shown in Fig. 1. Mussoorie city is an easily accessible, beautiful and highly crowded hill station in northern India located at an altitude of 2005.5 meters, with an area of 6.425 km², and is renowned for its salubrious atmosphere that helps to revive ailing visitors. The city remains overcrowded throughout the year due to increasing tourist activity. The numbers of vehicles are also increasing.

Dhanaulti is a woody paradise, located about 30 km away from Mussoorie at an altitude of 1676 meters. It is covered with the thick virgin forest of deodar, rhododendron, oak, apple, pear, plum, peach, apricot and litchi gardens.
The Chamba forest cover was selected as a control site. The area, situated at an altitude of 1524 meters, is tucked in by an evergreen subtropical forest having trees of oak, conifer, rhododendron, pine, deodar, etc. Moss samples were collected from the interior forest area of Chamba (unpolluted site) for control samples.

The Garhwal climate is cool from April to October, with monsoon showers between June and August. Conditions are moderate from September to November and snowfall is seldom observed in January. The maximum and minimum temperature hovers around 25.6°C–31.7°C and 7.2°C–12.8°C, respectively, during summer. Maximum winter temperatures range from 7.2°C–2.2°C and the minimum from 1.0°C–4.4°C. However, during this study great variation was observed during monsoon season, probably due to humidity. Maximum rainfall was measured from July–October (702 mm), and minimum March-June (182.5 mm). High relative humidity was measured in July and August at about 90%; whereas, it was lowest in January at about 60%.

Sampling was carried out for three different seasons of the year in accordance with Indian weather conditions (summer, winter and monsoon). Each season represents nearly four months. In contrast, biomonitoring in Europe may be carried out during four seasons—autumn, winter, summer and spring (Fernandez and Carballeira, 2002).
Sampling

Branches of the mosses *R. giganteum* and *H. cupressiforme* were cut and collected in four directions from center of the city (east, west, north and south) nearly equidistant (1 km, 3 km, 5 km, 10 km) in July 2004 (after summer), then again from the same spots in November 2004 (after monsoon). In March 2005 (after winter) samples were collected from a variety of roadside sites in both rural and urban areas. Care was taken to collect samples during different seasons and from the same spot each time. All 33 sites had abundant individuals of the two species used in the study.

Area of sampling

On each site, 3 quadrates of 1 meter were plotted in different directions and nearly 50 gm of moss samples were collected, followed by control in triplicate.

Analytical procedures

The unwashed green, or greenish brown, part of freshly collected plant material was used for the analysis. The moss samples were manually cleaned to remove all foreign material and other higher plant material. Afterwards, dry cleaning was done by mild air pressure to remove other foreign material, including soil and dust particles that had adhered to samples. After drying at 70°C, 1 gm of plant material was digested with 5 mL of concentrated HNO_3_ and with 2 mL of HClO_4_. The digested samples were filtered using Whatman No. 42, and the solution was diluted to 50 mL with bi-distilled water and analyzed by atomic absorption spectrophotometer. A suitable blank was used to check for possible contamination during extraction.

Data analysis

Samples were harvested in triplicate to conduct the statistical analysis. Value was represented as mean ± standard error (Snedecor and Cochran, 1967). ANOVA revealed significant differences in the metal concentration at different distances and seasons (for p ≤ 0.01, p ≤ 0.05) utilizing Dunkun’s Multiple Range Test (Karmer, 1956). Cartographic representation of the results was performed with the program package Surfer (Golden Software Inc., USA).

RESULTS

*Xylophyllum giganteum*

Zinc: The control values of zinc at the end of different seasons in harvested moss branches were measured at 42.506 ppm in summer, 22.191 ppm in monsoon and 25.901 ppm in winter season. Monsoon and winter do not show significantly different values. Seasonally, values were found significantly different in all the four directions. During summer, zinc was measured maximum at 5 km Mussoorie east (105.010 ppm), at 10 km in Mussoorie west (45.420 ppm) during monsoon, and at 5 km for Mussoorie south (73.154 ppm) during winter (Table 1). Minimum zinc concentrations were all found at Dhanaulti east: at 5 km, (50.030 ppm) in summer, at 3 km in monsoon (11.531 ppm) and in winter (23.531 ppm) (Table 2).
| Distance | Zinc | Lead | Copper | Cadmium | Zinc | Lead | Copper | Cadmium |
|----------|------|------|--------|---------|------|------|--------|---------|
| Control  | 42.506 | 21.912 | 7.972 | 0.374 | 41.593 | 20.812 | 7.762 | 0.362 |
| 1 km     | 81.800 | 22.110 | 15.140 | 0.364 | 22.000 | 14.800 | 14.700 | 0.364 |
| 3 km     | 78.000 | 15.780 | 7.962 | 0.364 | 78.200 | 15.780 | 7.962 | 0.364 |
| 5 km     | 82.000 | 19.800 | 1.750 | 0.364 | 82.000 | 19.800 | 1.750 | 0.364 |
| 10 km    | 85.000 | 21.912 | 7.972 | 0.374 | 85.000 | 21.912 | 7.972 | 0.374 |
| Control  | 42.506 | 21.912 | 7.972 | 0.374 | 41.593 | 20.812 | 7.762 | 0.362 |
| 1 km     | 81.800 | 22.110 | 15.140 | 0.364 | 22.000 | 14.800 | 14.700 | 0.364 |
| 3 km     | 78.000 | 15.780 | 7.962 | 0.364 | 78.200 | 15.780 | 7.962 | 0.364 |
| 5 km     | 82.000 | 19.800 | 1.750 | 0.364 | 82.000 | 19.800 | 1.750 | 0.364 |
| 10 km    | 85.000 | 21.912 | 7.972 | 0.374 | 85.000 | 21.912 | 7.972 | 0.374 |

**Notes:**
- Value superscripted same alphabet in horizontal row are seasonally not significantly different 1% & 5% level.
- *P ≤ 0.05*
- *NS = Non-significant as compared to control site*
Table 2. Metals concentration (ppm) in native samples of *Rhodobryum giganteum* at different distances from Dhanauli during summer, monsoon and winter season (2004-2005).

| Distance | Rhodobryum giganteum (Dhanauli-East) | | Rhodobryum giganteum (Dhanauli-West) | | Rhodobryum giganteum (Dhanauli-North) | | Rhodobryum giganteum (Dhanauli-South) |
|----------|----------------------------------------|-----------------|----------------------------------------|-----------------|----------------------------------------|-----------------|
| Metals   | Zinc | Lead | Copper | Cadmium | Zinc | Lead | Copper | Cadmium | Zinc | Lead | Copper | Cadmium | Zinc | Lead | Copper | Cadmium |
|          | Summer | Monsoon | Winter | Summer | Monsoon | Winter | Summer | Monsoon | Winter | Summer | Monsoon | Winter | Summer | Monsoon | Winter |
| Control  | 42.506 ± 1.989 | 22.191 ± 2.759 | 25.920 ± 0.881 | 22.191 ± 1.514 | 19.899 | 7.785 | 0.20 | 8.988 | 0.213 | 9.098 | 0.223 | 3.965 | 0.026 |
| 1 km     | 86.123 ± 0.577 | 23.196 ± 0.549 | 26.602 ± 0.190 | 15.612 ± 0.577 | 34.612 | 6.767 | 0.25 | 21.729 | 0.056 | 2.507 | 0.089 | 1.597 | 0.057 |
| 3 km     | 73.021 ± 1.744 | 11.531 ± 0.653 | 23.531 ± 1.137 | 18.299 ± 0.577 | 19.899 | 1.439 | 0.20 | 18.299 | 0.576 | 1.539 | 0.056 | 2.040 | 0.589 |
| 5 km     | 50.030 ± 0.560 | 31.336 ± 0.590 | 30.336 ± 0.387 | 15.523 ± 0.221 | 19.523 | 0.103 | 0.20 | 29.707 | 0.694 | 18.727 | 0.066 | 26.727 | 0.105 |
| 10 km    | 61.203 ± 0.626 | 20.570 ± 0.642 | 31.570 ± 0.565 | 16.019 ± 0.574 | 18.019 | 0.574 | 0.15 | 29.790 | 0.529 | 13.598 | 0.083 | 5.507 | 0.578 |

- *P* ≤ 0.01  
- NS = Non-significant as compared to control site  
- Value superscripted same alphabet in horizontal row are seasonally not significantly different 1% & 5% levels.
Furthermore, zinc turned out to be significantly higher ($p \leq 0.05$) between monsoon and winter at Mussoorie north (5 km).

Lead: Lead concentration in control site samples was analyzed at 22.191 ppm, 12.469 ppm and 16.224 ppm in summer, monsoon and in winter season, respectively.

However, a significantly different ($p \leq 0.05$) value was found in samples collected during summer and winter; whereas, the same seasons exhibited non-significant trend at few sites in comparison to control samples of lead. The highest values of lead evaluated in summer, monsoon and winter were 55.020 ppm at Mussoorie east (3 km), 26.018 ppm (3 km) and 36.018 ppm (1 Km) at Dhanaulti west, respectively (Tables 1 and 2). Lowest contamination was found at: 10 km, Dhanaulti north (18.112 ppm) in summer; at 3 km, Dhanaulti east (10.299 ppm) in monsoon; and at 3 km, Dhanaulti west (16.105 ppm) in winter (Table 2).

In addition, Mussoorie east exhibited significant variation ($p \leq 0.05$) in different seasons at 1 km and 3 km, and also towards Dhanaulti north at 3 km.

Copper: The level of copper in moss from the control site (i.e., Chamba forest) during summer was 14.313 ppm, during monsoon, 7.785 ppm, and at the end of winter, 8.898 ppm.

The value of copper rose to the concentration of 35.460 ppm at Mussoorie east (5 km) in summer, 25.216 ppm at Mussoorie north (3 km) in monsoon, and 33.475 ppm at Dhanaulti south (10 km) in winter (Tables 1 and 2). However, concentration of this metal declined down to 16.056 ppm at Dhanaulti west (10 km) during summer, 9.528 ppm at Mussoorie south (5 km) during monsoon, and 12.050 ppm at Dhanaulti west (10 km) during winter (Tables 1 and 2).

Statistically significant variation was detected ($p \leq 0.05$) at 3 km and 10 km in Dhanaulti north and at 10 km Dhanaulti south; whereas, at Mussoorie the same was calculated in west and north directions at 5 km and 3 km, respectively, in different seasons.

Cadmium: The control site concentration of cadmium was found to be 0.908 ppm, 0.004 ppm and 0.365 ppm in summer, monsoon and winter, respectively.

The peak concentrations of Cd were 6.903 ppm and 6.871 ppm at Mussoorie south (10 km) in summer and winter, respectively, and 4.397 ppm at Mussoorie north (1 km) in monsoon (Table 1). Minimum concentrations of Cd were measured in moss samples harvested 3 km east from Mussoorie during summer (1.002 ppm) and winter (0.008 ppm), with 0.001 ppm found at many Dhanaulti sites in monsoon (Table 2).

A significant difference ($p \leq 0.05$) was calculated for Cd in moss samples collected from the three directions excluding east of Mussoorie, at the distances of 1, 3, and 10 km during different seasons. Values for Cd were found significantly different across seasons at Dhanaulti east and west.

Hypnum cupressiforme

Zinc: The concentration of zinc in the moss species Hypnum cupressiforme harvested from Chamba forest was 24.401 ppm in summer, 12.856 ppm in monsoon and 17.348 ppm in winter season.

Zinc levels were analyzed maximum at
5 km in Mussoorie south (148.883 ppm) during summer (Table 3), and at 5 km Dhanaulti north (52.982 ppm) and east (52.299 ppm). Nearly the same results were observed at 10 km Dhanaulti south (52.699 ppm) during monsoon (Table 4) and at 5 km Mussoorie west (79.024 ppm) during winter (Table 3). A decline in zinc values in moss collected from Dhanaulti east (5 km), and Dhanaulti north (3 km) and west (10 km) showed contamination of 42.298 ppm in summer, 11.732 ppm in monsoon and 19.777 ppm in winter, respectively (Table 4).

In addition, significant difference ($p \leq 0.05$) was found at 1 km in Mussoorie west and south, and at Dhanaulti north; while variation was also calculated at Dhanaulti west (5 km) and south (3 km) across seasons.

Lead: The contamination level of lead in control-site moss samples was 0.763 ppm in summer, 3.241 ppm in monsoon, and 5.360 ppm in winter.

Lead was found high at 1 km in all three seasons at different sites (Tables 3 and 4). Maximum values were found at Dhanaulti south 1 Km (55.986 ppm) in summer and at Mussoorie west 1 Km in monsoon (22.514 ppm) and winter (31.004 ppm). Minimum loads were found at 10 km, Dhanaulti north (14.672 ppm) in summer, at 3 km, Mussoorie north (7.540 ppm) in monsoon, and at 3 km, Mussoorie south (11.705 ppm) in winter (Table 3).

The significant difference of $p \leq 0.05$ was shared in monsoon and winter at Mussoorie east (10 km), north (5 km) and south (3 km). At Dhanaulti, significant variation at that same level was observed in east, west and north directions at 3, 1, and 10 km, respectively, in different seasons.

Copper: The moss collected from the Chamba control site showed concentrations of 8.733 ppm during summer, 2.924 ppm during monsoon, and 6.273 ppm during winter season.

The maximum concentration of copper in summer was found to be 32.934 ppm at Mussoorie south (3 km), in monsoon at 23.253 ppm at Dhanaulti south (1 km), and during winter at 24.000 ppm at Mussoorie north (3 km). Decline in Cu values was observed at 10 km (11.695 ppm) during summer and 5 km (6.861 ppm) during monsoon at Dhanaulti north, and at 3 km, Mussoorie south (9.034 ppm) during winter (Tables 3 and 4).

A significant difference ($p \leq 0.05$) was found at 1 km east and north at Mussoorie and at 5 km east at Dhanaulti during summer, monsoon and winter.

Cadmium: Cadmium values at the control site in different seasons were calculated as 0.127 ppm in summer, 0.001 ppm in monsoon and 0.003 ppm in winter.

Cadmium concentration was found maximum at Dhanaulti south, at 3 km (6.694 ppm) in summer, while at Dhanaulti east at 5 km (6.772 ppm) in monsoon, and 10 km (6.650 ppm) during winter (Table 4). The lowest values were obtained from 1 km, Dhanaulti east (0.374 ppm) in summer. Decreased cadmium values were measured at two distances: 1 km and 10 km towards Dhanaulti north (0.001 ppm) in monsoon (Table 4) and from the same site at 10 km in winter (0.006 ppm).
| Distance | Zinc       | Lead       | Copper      | Cadmium     |
|----------|------------|------------|-------------|-------------|
|          | Summer     | Monsoon    | Winter      | Summer      | Monsoon    | Winter      | Summer      | Monsoon    | Winter      | Summer      | Monsoon    | Winter      |
| Control  | 24.401     | 12.856     | 1.536*      | 5.360*      | 0.664*      | 8.733*      | 0.654*      | 2.924      | 0.563      | 6.273       | 0.127       | 0.001       | 0.000       | 0.003       | 0.001       |
| 1 km     | 95.057     | 95.057     | 10.269      | 10.269      | 10.269      | 10.269      | 10.269      | 10.269     | 10.269     | 10.269      | 10.269      | 10.269      | 10.269      | 10.269      | 10.269      |
| 5 km     | 110.916    | 110.916    | 110.916     | 110.916     | 110.916     | 110.916     | 110.916     | 110.916    | 110.916    | 110.916     | 110.916     | 110.916     | 110.916     | 110.916     | 110.916     |
| 10 km    | 120.425    | 120.425    | 120.425     | 120.425     | 120.425     | 120.425     | 120.425     | 120.425    | 120.425    | 120.425     | 120.425     | 120.425     | 120.425     | 120.425     | 120.425     |

* P ≤ 0.01  * P ≤ 0.05  
NS = Non-significant as compared to control site  
Value superscripted same alphabet in horizontal row are seasonally not significantly different 1 % & 5 % level.
Table 4. Metals concentration (ppm) in native samples of *Hypnum cupressiforme* at different distances from Dhanaulti (East and West) during summer, monsoon and winter season (2004-2005).

| Location | Control | 1 km | 3 km | 5 km | 10 km |
|----------|---------|------|------|------|-------|
| Zinc     | 24.401  | 12.856 | 24.401 | 12.856 | 24.401 |
| Lead     | 0.879   | 1.091  | 1.091  | 1.091  | 1.091  |
| Copper   | 5.390   | 5.390   | 5.390   | 5.390   | 5.390   |
| Cadmium  | 7.833   | 7.833   | 7.833   | 7.833   | 7.833   |

- *P* ≤ 0.01
- *P* ≤ 0.05
- NS = Non-significant as compared to control site
- Value superscripted same alphabet in horizontal row are seasonally not significantly different 1% & 5% level.
Fig. 2a-1. Distribution map of Zn content \( R. \) giganteum (ppm) in summer at Mussoorie.

Fig. 2b-1. Distribution map of Pb content \( R. \) giganteum (ppm) in summer at Mussoorie.

Fig. 2c-1. Distribution map of Cu content \( R. \) giganteum (ppm) in summer at Mussoorie.

Fig. 2d-1. Distribution map of Cd content \( R. \) giganteum (ppm) in summer at Mussoorie.

Fig. 2a-2. Distribution map of Zn content \( R. \) giganteum (ppm) in monsoon at Mussoorie.

Fig. 2b-2. Distribution map of Pb content \( R. \) giganteum (ppm) in monsoon at Mussoorie.

Fig. 2c-2. Distribution map of Cu content \( R. \) giganteum (ppm) in monsoon at Mussoorie.

Fig. 2d-2. Distribution map of Cd content \( R. \) giganteum (ppm) in monsoon at Mussoorie.

Fig. 2a-3. Distribution map of Zn content \( R. \) giganteum (ppm) in winter at Mussoorie.

Fig. 2b-3. Distribution map of Pb content \( R. \) giganteum (ppm) in winter at Mussoorie.

Fig. 2c-3. Distribution map of Cu content \( R. \) giganteum (ppm) in winter at Mussoorie.

Fig. 2d-3. Distribution map of Cd content \( R. \) giganteum (ppm) in winter at Mussoorie.
Fig. 3a-1. Distribution map of Zn content \( R. \ giganteum \) (ppm) in summer at Dhanaulti.

Fig. 3a-2. Distribution map of Zn content \( R. \ giganteum \) (ppm) in monsoon at Dhanaulti.

Fig. 3a-3. Distribution map of Zn content \( R. \ giganteum \) (ppm) in winter at Dhanaulti.

Fig. 3b-1. Distribution map of Pb content \( R. \ giganteum \) (ppm) in summer at Dhanaulti.

Fig. 3b-2. Distribution map of Pb content \( R. \ giganteum \) (ppm) in monsoon at Dhanaulti.

Fig. 3b-3. Distribution map of Pb content \( R. \ giganteum \) (ppm) in winter at Dhanaulti.

Fig. 3c-1. Distribution map of Cu content \( R. \ giganteum \) (ppm) in summer at Dhanaulti.

Fig. 3c-2. Distribution map of Cu content \( R. \ giganteum \) (ppm) in monsoon at Dhanaulti.

Fig. 3c-3. Distribution map of Cu content \( R. \ giganteum \) (ppm) in winter at Dhanaulti.

Fig. 3d-1. Distribution map of Cd content \( R. \ giganteum \) (ppm) in summer at Dhanaulti.

Fig. 3d-2. Distribution map of Cd content \( R. \ giganteum \) (ppm) in monsoon at Dhanaulti.

Fig. 3d-3. Distribution map of Cd content \( R. \ giganteum \) (ppm) in winter at Dhanaulti.
Fig. 4a-1. Distribution map of Zn content \textit{H. cupressiforme} (ppm) in summer at Mussoorie.

Fig. 4a-2. Distribution map of Zn content \textit{H. cupressiforme} (ppm) in monsoon at Mussoorie.

Fig. 4a-3. Distribution map of Zn content \textit{H. cupressiforme} (ppm) in winter at Mussoorie.

Fig. 4b-1. Distribution map of Pb content \textit{H. cupressiforme} (ppm) in summer at Mussoorie.

Fig. 4b-2. Distribution map of Pb content \textit{H. cupressiforme} (ppm) in monsoon at Mussoorie.

Fig. 4b-3. Distribution map of Pb content \textit{H. cupressiforme} (ppm) in winter at Mussoorie.

Fig. 4c-1. Distribution map of Cu content \textit{H. cupressiforme} (ppm) in summer at Mussoorie.

Fig. 4c-2. Distribution map of Cu content \textit{H. cupressiforme} (ppm) in monsoon at Mussoorie.

Fig. 4c-3. Distribution map of Cu content \textit{H. cupressiforme} (ppm) in winter at Mussoorie.

Fig. 4d-1. Distribution map of Cd content \textit{H. cupressiforme} (ppm) in summer at Mussoorie.

Fig. 4d-2. Distribution map of Cd content \textit{H. cupressiforme} (ppm) in monsoon at Mussoorie.

Fig. 4d-3. Distribution map of Cd content \textit{H. cupressiforme} (ppm) in winter at Mussoorie.
Fig. 5a-1. Distribution map of Zn content \textit{H. cupressiforme} (ppm) in summer at Dhanaulti.

Fig. 5a-2. Distribution map of Zn content \textit{H. cupressiforme} (ppm) in monsoon at Dhanaulti.

Fig. 5a-3. Distribution map of Zn content \textit{H. cupressiforme} (ppm) in winter at Dhanaulti.

Fig. 5b-1. Distribution map of Pb content \textit{H. cupressiforme} (ppm) in summer at Dhanaulti.

Fig. 5b-2. Distribution map of Pb content \textit{H. cupressiforme} (ppm) in monsoon at Dhanaulti.

Fig. 5b-3. Distribution map of Pb content \textit{H. cupressiforme} (ppm) in winter at Dhanaulti.

Fig. 5c-1. Distribution map of Cu content \textit{H. cupressiforme} (ppm) in summer at Dhanaulti.

Fig. 5c-2. Distribution map of Cu content \textit{H. cupressiforme} (ppm) in monsoon at Dhanaulti.

Fig. 5c-3. Distribution map of Cu content \textit{H. cupressiforme} (ppm) in winter at Dhanaulti.

Fig. 5d-1. Distribution map of Cd content \textit{H. cupressiforme} (ppm) in summer at Dhanaulti.

Fig. 5d-2. Distribution map of Cd content \textit{H. cupressiforme} (ppm) in monsoon at Dhanaulti.

Fig. 5d-3. Distribution map of Cd content \textit{H. cupressiforme} (ppm) in winter at Dhanaulti.
Significant differences for Cd at the p ≤ 0.05 level was shared by three different seasons at 5 km in Dhanaulti north and west, and at 1 km in Dhanaulti east; while at Mussoorie, statistical variation was calculated at 3 and 1 km east, and at 1 and 5 km north. However, at Mussoorie south, significant variability (p ≤ 0.05) was found between monsoon and winter at 1 km and 3 km.

MAPPING

The mapping pattern of different metals shows fluctuation in distribution at Mussoorie and Dhanaulti during different seasons and directions for both moss species as shown in Figs. 2 through 5. The reason could be due to different sources of metal emission and their impact in a particular direction. In addition, at some places, samples get direct exposure of metals, while not so in other areas. We cannot ignore meteorological factors and prevailing wind directions, which may be additional causes for variation in the distribution pattern.

DISCUSSION

The two moss species, *Rhodobryum giganteum* and *Hypnum cupressiforme*, studied here were used in combination as biomonitors, because: they are widespread, occur commonly in the same environments, and are considered to behave similarly with respect to sorption and retention of atmospheric input of several elements. The results of this study were determined on the basis of statistical variability in metal concentration levels with respect to three seasons and distances in relation to and compared to the control site.

At the control site, concentrations of elements undertaken in both species showed significant variation (p ≤ 0.01, p ≤ 0.05) between the three seasons in most cases. This may be due to the fact that the samples used as controls might have undergone changes in the concentration of elements over time, or variation occurred naturally due to environmental conditions and seasonal variations (Fernandez and Carballeira, 2002). Moss physiology is independent of the source of contamination (Couto et al., 2004) and depicts a level of tolerance. Besides this, in a few cases, the control site showed elevated concentrations in comparison to Dhanaulti. The reason could be that Dhanaulti is tucked away in the midst of deep forests where mosses do not get direct exposure to the metal load. Secondly, the dominant lithology of the sampling sites was studied as another factor of possible influence on the levels of elements accumulated in the mosses, including the use of insecticides and pesticides as growth promoters to increase agricultural productivity in rural areas.

The concentration of different metals analyzed in moss samples of *R. giganteum* and *H. cupressiforme* from Mussoorie and Dhanaulti were not consistent in different seasons and distances. Variation was observed in the distribution patterns shown in Figs. 2–5. The summer season shows higher concentration of all studied metals compared to monsoon and winter. The reason could be a continuous upsurge of tourists at other hill stations,
accompanied by a many-fold increase in the number of automobiles. An important source of Pb, Zn, Cu, and Cd in these areas was the dry deposition of metals dust spewed out from automobiles (Imperato et al., 2003), as well as from the use of insecticides and pesticides in the area. A sharp decline in concentration during the monsoon season was observed, possibly due to the leaching of these as a result of rainfall. However, in a few cases, with zinc and copper, significant variability was minor between monsoon and winter. This might be due to fewer tourists, thus fewer automobiles, during these seasons.

The contamination level of Zn, Cu and Cd was found to be 2-3 times higher, and that of Pb approximately two times higher, as compared to the control. However, comparison of contaminant concentration in mosses growing in the forest cover (Chamba) shows higher values only in few cases with those growing in open areas, could be the reason that at these places elements are washed off from the tree cover, thus providing an extra ionic source. This finding is in agreement with Berthelsen et al. (1995).

Zinc in moss samples was significantly different in all the seasons and distances. This may be due to the proximity of sampling sites to roadsides, traffic density, use of fertilizers for growth of crops and orchards (Saxena and Saxena, 2000).

Lead is an integral constituent of steel and automobile industries, as well. While concentration of lead and copper exhibited significant variation in most cases, the main source of Pb is vehicular emission. It is also found associated with anthropogenic variables in the environment. Sites have been found to have high values of lead in relations to inland areas and towns corresponding to motorway intersections, or near bus stops and taxi stands. Since Cu at low levels provokes plant growth, it is used in fertilizers. In contrast, it is also used in fungicides and pesticides (Gerdol et al., 2000; Otvos et al., 2003). Higher values in domestic waste were reported due to their improper dispersal in atmosphere.

Road traffic emissions of Cd were maximum at Mussoorie, suggesting that automobile exhausts may be a source of higher concentrations (Stefano and Bonini, 2000) of this metal at some Mussoorie and Dhanaulti sites. The source of contamination may also come from the use of metallic or plastic pipes, sewage sludge, abrasion of automobile tires and from domestic wastes in urban areas (Markert et al., 1996; Scharova and Suchara, 1998; Grodzinska and Szarek-Lukaszewska, 2001).

This study was also based on distance-wise sampling (1, 3, 5, and 10 km) in four directions (east, west, north, south). Fluctuation in the distribution pattern map at different distances was observed, showing concentrations gradually decreasing at some distances, but not in all cases. This could be due to different environmental factors in correlation with the distribution of emission sources. Furthermore, traffic density, proximity to other roads, precipitation, meteorological factors, seasons, time of sampling, and prevailing wind directions may be other factors. Previous studies have reported mineral transport practices from local soils (largely in the form of
dust carried by the wind) to be one of the sources of various elements in mosses (Santelmann and Gorham, 1988; Steinnes, 1995).

An attempt was also made to show possible differences in the capacity of these two species to accumulate elements. Comparison of total and normalized concentrations of elements in both mosses collected from the same sites of Mussoorie and Dhanaulti showed overall higher values for Zn, Pb, Cu and Cd in *R. giganteum*; whereas, *H. cupressiforme* had the highest values of Zn and Cd at some study area sites during all three seasons. This distinctive pattern is probably due to the high capacity for variation in metal-precipitation sources, possibly due to pollutants subjected to long transport ranges, as well (Berg *et al.*, 1995). This study suggests that the two mosses undertaken have bioaccumulation potential and are strongly suited for biomapping studies.

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