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# Identification of heavy metals in some cryptogams in Uttarkashi district, Uttarakhand

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## Abstract

As compared to terrestrial bryophytes, epiphytic mosses are more exposed to pollutants. Their widespread distribution and high accumulative capacity have led to their use for monitoring purposes. In the present study six species of epiphytic mosses namely, *Trachypodopsis serrulata* (P. Beauv) M. Fleisch., *Papillaria fuscescens* (Hook.) A. Jaeger, *Barbella turgida* Nog., *Meteoriopsis reclinata* (Müll. Hal.) M. Fleisch., *M. Squarrosa* (Hook. ex Harv.) M. Fleisch. and *Homalothecium sericeum* (Hedw.) Schimp. were collected from Uttarkashi district in different localities and analyzed for Cd, Cr, Cu, Pb, and Ni concentration in naturally growing mosses. Results depicted that Cr, Ni and Cd concentrations in epiphytic bryophyte tissues as well as in their substratum was very high followed by Cu and Pb. The highest concentration of Cd and Cu was found to be in *Meteoriopsis reclinata*, in both the plant sample as well as the substratum whereas the highest concentration of Cr, Pb and Ni was found to be highest in *Trachypodopsis serrulata, Meteoriopsis squarrosa*, *Homalothecium sericeum* and *Barbella turgida* respectively.

**Keywords:** Biodiversity, Metal, Uttarakhand.

## Introduction

Heavy metals such as Cd, Cr, Cu, Pb and Ni, are sometimes extremely toxic to organisms when present in higher than their trace concentrations. The detailed experimental studies have provided some insight into the complex responses of plants to heavy metal toxins. Mosses act as good sinks of heavy metals and are also reliable indices of the level of pollution. Pleurocarpous mosses mainly acquire nutrients from their surroundings through the surface cells of the plant. They efficiently intercept and absorbe solutes in rain water, fog and mist droplets and airborne dust. During such absorption, many of the undesired elements also enter in the tissue of mosses (Bates 2000; Czarnowska 1974; Le Blanc et al. 1974). Mosses have been used to measure atmospheric heavy metal deposition because of they have specific features, like unistratose leaves, high ion-exchange capacity, and uptake of nutrients directly from the atmosphere which make them useful for monitoring of regional and local patterns of deposition owing to the high accumulation capacity (Samecka-Cymerman et al. 2005; Gramatica et al. 2006). Besides these, they have high counter gradient mechanisms for the accumulation of heavy metals in their tissues (Carginale et al. 2004). One of the main factors influencing cation exchange capacity is the presence of polygalacturonic acids on the external part of the cell wall and proteins in the plasma membrane (Aceto et al. 2003). Chemical analyses of contaminants in moss samples reflect the state of environmental contamination (Ganeva 1998). Epiphytic species are much more exposed to air pollutants and confronted with a larger amount of pollutants than most terrestrial bryophytes.

Metals occur naturally in the environment, with the variations in their concentrations (Maxhuni et al. 2015). The bioavailability of heavy metals in the soil is regulated by many physical, chemical and biological properties and processes (Ernst 1996). The mobility and toxicity of heavy metals are strongly related to the acidity and organic matter content of the soil (Alloway 1995). They come down to earth as dry, wet, or atmospheric occult deposition after either short (local, regional) or long-range (intercontinental) transport, (Nickel et al. 2015). Heavy metal uptake and retention efficiencies differ from species to species according to morphological and physiological variabilities (Wolterbeek et al. 1995; Thöni et al. 1996). Metal concentrations in plant tissues not only depend on atmospheric input but also on mineralogy, humus decomposition, leaching rates, and historical factors. Environmental sources of pollutants could include construction and demolition activities, mining and mineral processing, agricultural activities, sea spray, windblown dust, automobiles and transportation related activities on the road (Melaku et al. 2008). The present study is undertaken to assess heavy metal deposition in the epiphytic mosses of an urban locality to see the effect of anthropogenic activities.

## Materials and Methods

Six taxa of epiphytic mosses, *Trachypodopsis serrulata*, *Papillaria fuscescens*, *Barbella turgida*, *Meteoriopsis reclinata*, *Meteoriopsis squarrosa* and *Homalothecium sericeum* were collected in October 2019 from Uttarkashi (Sankari) to study the accumulation of five heavy metals (Cd, Cr, Cu, Pb and Ni). This is a cool period (average day temperature $16^0$Cto $18^0$C and average humidity 36%) and moss growth is higher. Each of these species was supposed to obtain moisture and nutrients mainly from the air and stem through fall. Moss samples were carefully cleaned of foreign matter, air-dried immediately at the site and collected in polyethene bags. They were washed and dried at room temperature in the laboratory. The moss samples were identified using moss floras (Chopra 1975; Gangulee 1969 & 1980). The pH of the substrate was determined by using a glass electrode on a Beckman's pH meter. The samples of plant materials and their substrata were analyzed for exchangeable metallic cations- Cd, Cr, Cu, Pb and Ni. The samples were cleaned, purified to rule out the mixing of other species, washed, dried at room temperature between folds of blotting sheets and then crushed in pestle and mortar and sieved. The samples were digested in triplicates in a ratio of 6:1 in nitric acid and perchloric acid in an Erlenmeyer flask on a hot plate with mild heating, under a fume hood. Estimation of the heavy metals in the plant samples as well as in the substratum was done by atomic absorption spectroscopy according to Allen (1989), using AAS ZEEnit 60/65.

## Results and Discussion

In the recent years the anthropogenic activities have been increased in the Uttarkashi area because of the more and more tourists. Industrial development and some other activities have been releasing the heavy metals in the environment and causing degradation of soil (Macedo‑Miranda et al. 2016). We recorded the concentration of metal contents in the selected mosses as well in their substrata to assess the accumulation capacities of selected plants. A considerable amount of metals were found accumulated in the samples (Table 1), though the metal concentration was found to be higher in the substrata (Table 2). Values of the pH of the substrata were found to affect the metal accumulation. The metal concentration (µg/g) of five different heavy metals (Cd, Cr, Cu, Pb and Ni) in the substrata of mosses showed higher values relative to those observed in the moss samples. As is evident from the tables (1 and 2) and graphs, Cr, Ni & Cd are present in considerably higher concentration while Pb & Cu are generally in lower concentration. The pH of the substratum was also determined and it was found to be slightly acidic to slightly alkaline in the range of 5.78 – 8.14.

Table 1: Showing details of heavy metal content (in µg/g) of various epiphytic taxa.

| S.No. | Name of the taxon | Cadmium (Cd) | Chromium (Cr) | Copper (Cu) | Lead (Pb) | Nickel (Ni) | pH** |
|---|---|---|---|---|---|---|---|
| 1. | ***Trachypodopsis serrulata* (P. Beauv.) Fleisch** | * 28.30<br>**234.48 | 43.28<br>329.16 | 8.76<br>124.53 | 13.35<br>51.01 | 40.20<br>495.94 | 8.14 |
| 2. | ***Papillaria fuscescens* (Hook.) Jaeg.** | * 18.40<br>**255.03 | 39.67<br>324.65 | 11.05<br>97.51 | 10.60<br>81.71 | 22.04<br>492.51 | 6.5 |
| 3. | ***Barbella turgida* Nog.** | * 25.85<br>** 66.57 | 30.66<br>423.84 | 11.87<br>100.52 | 5.10<br>120.00 | 45.03<br>232.57 | 7.82 |
| 4. | ***Meteoriopsis reclinata* (C. Muell.) Fleisch.** | * 28.11<br>**239.99 | 32.46<br>396.79 | 12.42<br>105.97 | 5.55<br>124.50 | 43.25<br>449.00 | 6.5 |
| 5. | ***Meteoriopsis squarrosa* (Hook.) Fleisch.** | * 20.74<br>** 2.10 | 25.85<br>396.79 | 6.40<br>133.51 | 18.63<br>87.00 | 13.50<br>475.96 | 6.5 |
| 6. | ***Homalothecium sericeum* (Hedw.) B.S.G.** | * 23.44<br>**247.59 | 36.07<br>441.88 | 7.80<br>112.50 | 18.63<br>261.52 | 26.40<br>225.81 | 5.78 |

* Plant Samples ** Substratum

Table 2: Showing range of metals present in the plants samples and substrata of presently studied epiphytic bryophytes.

| Heavy Metal | Conc. In Plant Samples («g/g) | Conc. in Substratum («g/g) |
|---|---|---|
| Cd | 20.44 – 31.11 | 2.10 – 297.59 |
| Cr | 25.85 – 43.28 | 324.65 – 441.88 |
| Cu | 6.40 – 12.42 | 97.51 – 133.51 |
| Pb | 5.10 – 18.63 | 51.01 – 261.52 |
| Ni | 13.50 – 45.03 | 225.81 – 495.94 |

Epiphytic bryophytes have long been known to be very sensitive to the effects of various forms of atmospheric pollution. Chen et al. (2010) and Macedo‐Miranda et al. (2016) studied accumulation efficiency of different species of mosses. The trace metals Cd, Cr, Cu, Pb and Ni are of greater interest due to their potential toxicity of biota (Saxena et al. 2013). Present data revealed that the plant samples as well as substrata of all six species contained a higher content of Cr while Cu was found to be in the least concentration. Mosses are capable of taking up Cd from soil solution (Rühling and Tyler 1970) and can act to intercept and accumulate airborne Cd (Goodman and Roberts 1971). Presently highest concentration of Cd in the plant sample was found in *Meteoriopsis reclinata* (31.11µg/g$^{-1}$) whereas in Meteoriopsis *squarrosa* the concentration of Cd in the plant material (20.74µg/g$^{-1}$) was higher than that of their substrata (2.10µg/g$^{-1}$) (Table 1 and Fig.1&2). Chromium is one of the most widely element present in the Earth's crust. The most stable oxidation states and common forms are Cr (III) and Cr (VI). The relatively insoluble and less mobile Cr (III) form predominates in the majority of soils and it generally occurs as insoluble hydroxides and oxides. Emission of Cr in both air and water occurs at the highest rate in the metallurgy industry. The present data indicate that the concentration of Cr is highest in the plant material as well as in the substrata. *Trachypodopsis serrulata* (43.28µg/g$^{-1}$) contained the maximum amount of Cr while *Meteoriopsis squarrosa* (25.85µg/g$^{-1}$) was found to be in the least concentration in the plant material (Table 1 and Fig.1& 2).

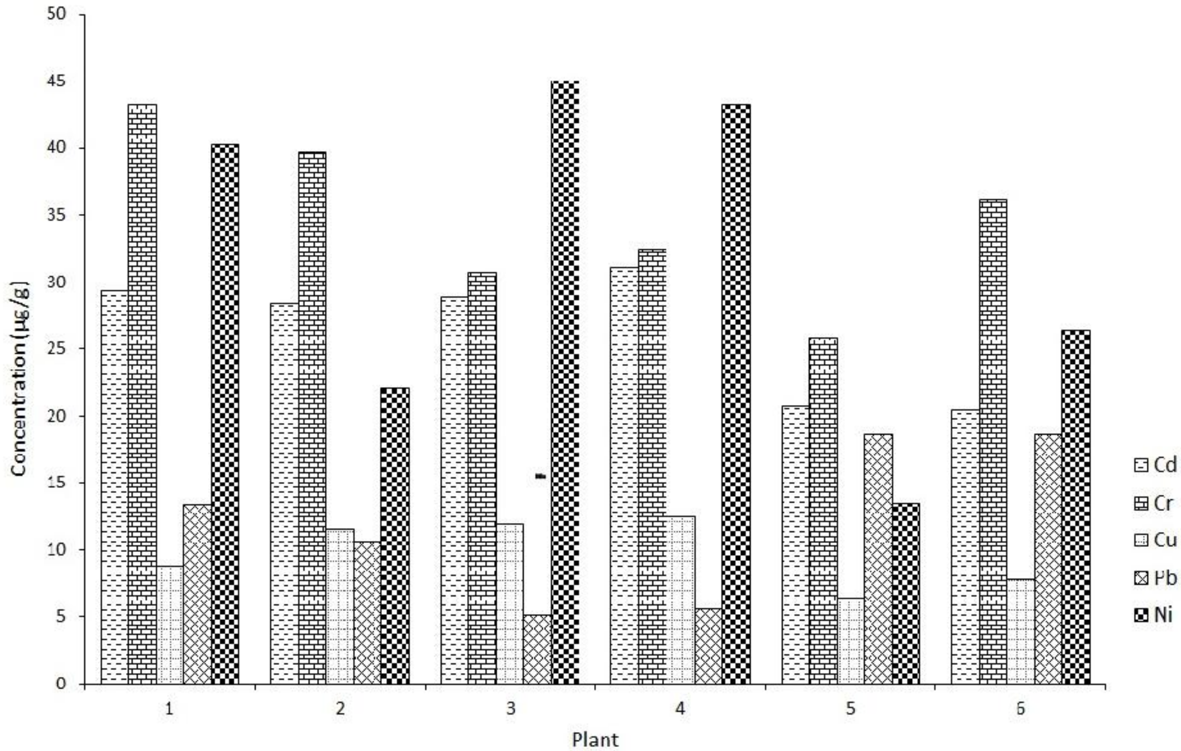


**Fig- 1.** Concentration (µg/g) of heavy metals (a) Cd (b) Cr (c) Cu (d) Pb (e) Ni in different epiphytic mosses. The digits on the horizontal axis of the graph correspond to the name of the taxon as given in the Table1.

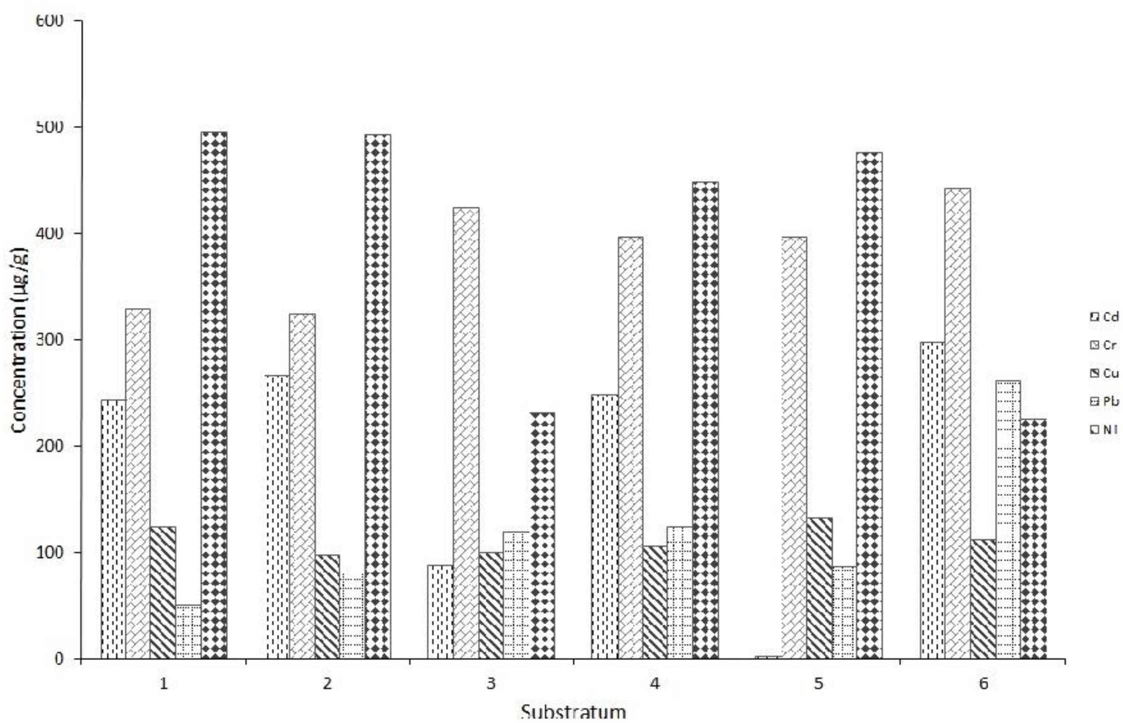


**Fig- 2.** Concentration (µg/g) of heavy metals (a) Cd (b) Cr (c) Cu (d) Pb (e) Ni in the substratum. The digits on the horizontal axis of the graph correspond to the name of the taxon as given in the Table1.

Copper is an essential plant micronutrient, but it is toxic when present in excessive amounts. Overall, the content of Cu was found to be in lower amounts in plant material as well as in their supporting substrate as compared to other metals studied. The content of Cu in the plant sample was found to be lowest in *Meteoriopsis squarrosa* (6.40$\mu g/g^{-1}$) while *Meteoriopsis reclinata* (12.42$\mu g/g^{-1}$) contained the highest concentration of Cu (Table 1 and Fig.1 & 2). The average Cu content of the upper lithosphere is 70 ppm.

Lead is a widespread soil contaminant. As compared to vascular plants, mosses have almost no possibility of utilising Pb directly. Lead binds ionically with the cell walls, thus preventing its penetration into the cytoplasm in lethal amounts (Brown and Bates 1972). Skaar et al. (1973) observed electron dense inclusion in the nuclei, and several damages in the nuclear envelope of polluted leaf cells of *Rhytidiadelphus squarrosus*. In the present study the content of Pb was found to be highest in *Meteoriopsis squarrosa* **(**18.63 $\mu g/g^{-1}$) and *Homalothecium sericeum* **(**18.63$\mu g/g^{-1}$) and lowest in *Barbella turgida* (5.10$\mu g/g^{-1}$). The high concentration of Pb ions in the substratum (261.52$\mu g/g^{-1}$) may be an additional factor to promote higher uptake by the moss which was also supported by the slightly acidic pH (5.78-6.5) (Table 1 and Fig.1&2).

Nickel is recognized as a potentially phytotoxic element (Misra and Kar 1974; Hutchinson 1981). *Meteoriopsis squarrosa* (13.50$\mu g/g^{-1}$) shown to contain a lower concentration of Ni whereas *Barbella turgida* (45.03$\mu g/g^{-1}$) was found to contain Ni in higher concentration (Table 1 and Fig.1 & 2). Also, the content of Ni in the substratum was found to be sufficiently in higher concentration as compared to Cd, Cu and Pb. Elevated soil nickel levels can arise as a result of applying metal-contaminated sewage sludges to farmland (Freedman and Hutchinson 1981).

Low pH increases the metal availability since the hydrogen ion has a higher affinity for negative charges on the colloids, thus competing with the metal ions of these sites, thus releasing metals. An increase in pH results in higher adsorption of Cd, Zn, and Cu to soil particles and reduces the uptake of Cd, Zn, and Pb by plants (Kuo et al. 1985). On the other hand, acidification increases the metal absorption by plants through a reduction of metal adsorption to soil particles (Chaney et al. 1995; Huang and Cunningham 1996). *Trachypodopsis serrulata* which is an obligate epiphyte was found growing on oak tree bark with slightly alkaline nature with pH value 8.14. *Papillaria fuscescens*, *Barbella turgida*, *Meteoriopsis reclinata*, *M. squarrosa* and *Homalothecium sericeum* were found to be grown on slightly acidic to neutral pH values (5.78 – 7.82).

The metal concentrations in mosses are influenced by many factors such as concentrations of emitted metals and the chemical and physical properties of the metal-containing particles, for instance their size and acidity. The solubility of heavy metals usually increases with decreasing pH. Some metals can also be substituted for others by ion exchange (Rühling and Tyler 1970). The relative accumulation of different metals in a particular species may also vary with the total metal load (Ward et al. 1977). The uptake of heavy metals in mosses may certainly be influenced by climate, especially humidity and wind velocity. The following gradation in the trace element content was found in both plant sample as well as their supporting substratum: Cr > Ni > Cd > Pb > Cu [Tables (1&2) and Fig. 1&2].

## Conclusion

In the present study six taxa of epiphytic mosses *Trachypodopsis serrulata*, *Papillaria fuscescens*, *Barbella turgida*, *Meteoriopsis reclinata*, *M. squarrosa* and *Homalothecium sericeum*, proved that mosses are useful for monitoring of regional and local patterns of deposition of pollutants and are also proved to be the indicator of kind of contaminants. Chemical analyses of heavy metals (Cd, Cr, Cu, Pb and Ni) in moss samples reflect the state of environmental contamination. As compared with the permissible limits of these metals (Kabata-Pendias and Pendias 2001), these metals are present within the tolerant limits of the various species as large amount of element content did not show any toxicity symptoms. However, the presence of these elements may seriously retard colonization of such potential sites by bryophytes and other plants. In our study, Cr was found to be in the highest range, both in the plant material (25.25 – 43.28$\mu g/g^{-1}$) as well as in the substratum (324.65 – 441.88 $\mu g/g^{-1}$), as compared to Cd, Cu, Pb and Ni, which shows likely the presence of metallurgical industries in the form of particles e.g. from electric arc furnaces, refractory brick production, combustion of coal, iron and steel industry in the nearby area of our study.

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