Biomonitoring of Atmospheric Heavy Metal Deposition by using Moss species *Bryum Argenteum*

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1 Introduction

Air pollution has become a major contributor to environmental degradation. Air pollution is caused by emissions from industrial chimneys and automobile exhausts. Rapid developments in the industrial and transportation sectors, combined with rising human population demand, have become significant sources of air pollution [1]. Human activities are responsible for the release of chemical compounds or metallic elements such as heavy metals, sulfur, and nitrogen compounds into the atmosphere, which causes damage to the health of human beings and the environment [2–4]. The intensity with which emissions are distributed is determined by the type of emission source, the composition of emissions, and the weather conditions [5, 6]. The majority of emissions occur very close to the source, but some emissions can travel thousands of kilometers [7–9].

Air quality can be monitored by directly measuring pollutants in the air or deposition, building models depicting the spread of contaminants, or using biomonitors

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[10–13]. Direct air quality measurements provide information about pollutant levels, but they are very expensive, and there is a risk of contamination when determining low concentrations [14].

Biomonitors provide data on the number of pollutants as well as their impact on the occurrence and condition of biomonitors [14]. Despite the fact that the methods are quick and inexpensive, they may only provide a rough picture of air quality and pollutant deposition.

Biomonitors/bioindicators are organisms or parts of organisms that depict the presence of pollutants based on specific symptoms, reactions, morphological changes, or concentrations [15–19]. There is a lot of variation in the terms biomonitor and bioindicator. However, bioindicator refers to all organisms that provide information on the quality of environmental changes, whereas biomonitor refers to organisms that provide quantitative data on the domain's quality [20–22].

In general, organisms are classified based on their origin into passive biomonitors, which monitor organisms that naturally occur in the study area. Active biomonitors are organisms that are brought into the research area for a specific period of time under controlled conditions [17, 20, 23, 24].

Visakhapatnam's industrial development is conspicuous to urban agglomeration, and the city is situated in a topographical bowl formed by two hill ranges. A significant portion of the town is located within the bowl area, where the majority of the industrial and commercial activities are concentrated within a 10-km radius of the Bay of Bengal's shore. Because of the city's unusual geographical location, wind movement is either eastern or western and is engulfed within the hill ranges. As a result, there is a chance that air pollution levels will rise within the city. The town has witnessed an influx of people from neighboring places for their livelihood. It has increased the concentration of industries, traffic over time. Therefore, this work aimed to appraise the concentrations of trace metals in Bryumargenteum, which is grown in different areas of Visakhapatnam, to ascertain the metal pollution levels.

2 Materials and Methods

2.1 Study Area

Visakhapatnam city was selected as a study area for estimation of heavy metal concentrations by using mosses as bioindicators. Visakhapatnam city is situated in North coastal Andhra Pradesh. It lies between latitude 17,040′30″–170 45′N and longitudes 83,010′–820 21′E, covers above 160km^2 in the Survey of India Topographic Map of 65 O/1 and 65 O/2, and is located in Andhra Pradesh, India. The climate in Visakhapatnam is generally tropical humid with mean daily maximum temperatures is in the range of 27–34 degrees centigrade and mean daily minimum temperatures varies between 140 and 280 C. The annual mean humidity is 77%, and the wind direction is generally from the Southwest toward North West. And it is 0.8 m below mean sea level (MSL). Due to the peculiar geographical location of the city, wind movement is either eastern or western and is engulfed within the hill ranges. Hence, there is a possibility of the buildup of air pollution levels within the city. Visakhapatnam is selected for the case study since numerous sources emit air pollutants, including several major and minor industries like steel, refinery, fertilizers, port activities, etc., located within the city study area. The study was carried out in industrial and urban areas characterized by heavy industrial activity and traffic density.

2.2 Sampling

Both moss and air samples were collected from three industrial areas, like Autonagar area (BHPV), Parawada industrial area (NTPC), Gajuwaka area. And a control sample was collected from Rushikonda (GITAM) area. The sampling region from Autonagar is 13 km, Parawada is 10 km, Gajuwaka is 12 km, and Rushikonda (control area) is 2 km away from the seafloor. The primary objective of establishing the sample plots was to monitor concentration changes in different industrial areas concerning the control area. Moss samples were collected from four regions and mixed to get a composite and representative sample. Moss samples were taken from old walls of the sampling regions. The principal moss species sample was Bryumargenteum. Air samples were collected by using a Respirable Dust Sampler on filter papers in respective sampling areas.

2.3 Sample Preparation

Samples were collected manually, free from solid litter, dust, and other unwanted material. The specimens dried in a hot air oven for 24 h at 400C. Then the material was taken and crushed with a mortar and sieved (UNECE 2001). As per Rühling [25], 0.5 g of sieved moss material was taken in Teflon beakers, and 30 ml of concentrated Nitric acid (HNO3) was added in each beaker and kept for overnight digestion by closing the lids. The next day, these beakers were heated on a hot plate at 130–1400C for 2 h by keeping the tops. The acid content should be maintained at 10 ml in the beakers. Toward the end, about 4–5 ml of hydrogen peroxide (H_2O_2) must be added drop-wise and heated further, and the volume was reduced to about 10 ml. All organic material gets oxidized during this entire process, and the inorganic contents are extracted into the solution. The digested solutions were transferred to a 250 ml volumetric flask and diluted to 250 ml with deionized water [26, 27, 28].

For air samples, filter papers were collected from the different areas were taken and cut into small pieces. These pieces were taken in Teflon beakers, and 30 ml of concentrated Nitric acid (HNO_3) was added to each beaker and kept for overnight digestion by closing the lids. The next day, these beakers were heated on a hot plate at 130–1400C for two hours, keeping the lids. When the solution comes to about

10 ml, heating was stopped and transferred to a 250 ml volumetric flask and diluted to 250 ml with deionized water.

2.4 Analysis

The concentrations of different metals Chromium (Cr), Manganese (Mn), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Selenium (Se), Cadmium (Cd), and Lead (Pb) were analyzed by ICP-MS (Inductive Coupled Plasma Mass Spectroscopy) (Perkin-Elmer Sciex Instrument, Model ELAN DRAC II, USA). For calibration and to check the accuracy of the analysis of filter paper and moss material, NIST 1643e reference material is used for quality control. Reagent blanks were used wherever appropriate to ensure accuracy and precision. Further details of ICP-MS are presented elsewhere [29].

3 Results and Discussion

Several works have been proved the significant role of mosses as bioindicators for monitoring heavy metals [30, 31]. In the present study, the significant uptake of elements by mosses is relatively straightforward for heavy metals. The heavy metal concentrations such as Chromium (Cr), Manganese (Mn), Iron (Fe), Zinc (Zn), Arsenic (As), Selenium (Se), Nickel (Ni), Copper (Cu), Cadmium (Cd), and Lead (Pb) determined in mosses collected from sampling sites are higher than air concentrations in respective sampling sites. The assessment of toxic elements deposition at different areas by bryophytes shows variation in content. The increased amount of metal accumulation in moss Bryumargenteum resulted from its lifetime deposition [32]. A significant source of heavy metal in the urban area is metallurgical process, automobile exhaust emission, oil combustion, and processing of crustal material [33, 34]. The trace metal concentration at different sampling sites was shown in Fig. 1. The trace metal concentration in moss samples at various sampling sites was shown in Fig. 2.

In the discussion, described each trace metal concentration at different sampling sites.

3.1 Chromium

Chromium concentrations in moss samples were showed in Tables 1 and 2. The chromium concentrations in air samples were 14.573 ng/g–19.078 ng/g, whereas Cr concentrations in the moss samples range are 646.4 ng/g–787.76 ng/g. High chromium concentrations were observed in the air sample of the control area

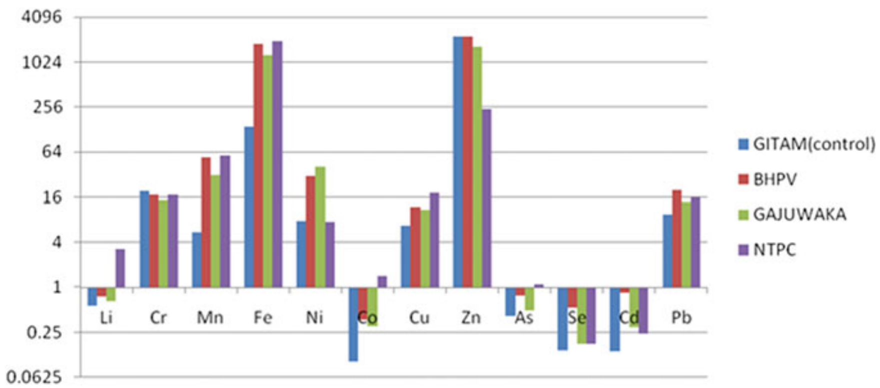

Fig. 1 Trace metal concentrations in air samples at different sampling sites of Visakhapatnam

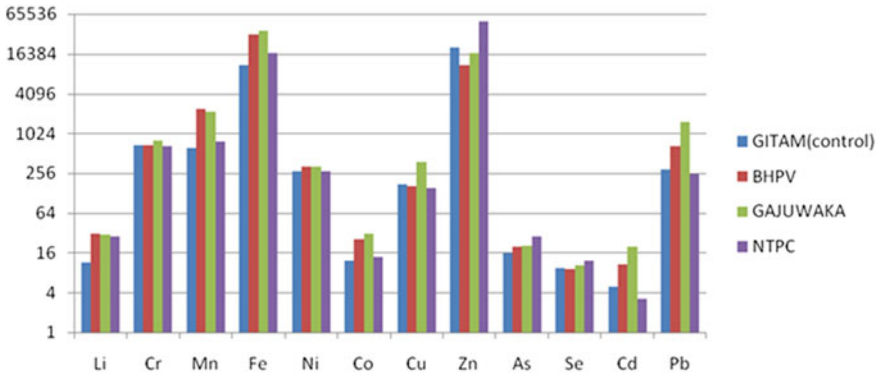

Fig. 2 Trace metal concentrations in moss (*Bryum argenteum*) samples at different sampling sites of Visakhapatnam

Table 1 The Bio concentration factor values for heavy metals in the study areas

Location	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Cd	Pb
Rushikonda	34.97	113.6	78.69	34.74	26.16	9.11	37.59	65.35	34.85	31.3
Autonagar	39.85	45.11	18.16	10.34	13.88	4.88	25.02	17.01	12.84	33.11
Industrial area	54.05	69.00	28.86	7.95	35.08	10.06	41.97	58.28	66.21	111.47
Parawada	37.4	13.45	8.61	35.67	8.5	206.47	26.03	72.23	13.91	15.7

(GITAM) (19.078 ng/g). Accumulation of Cr metal in moss species Bryumargenteum was highly regarded in Gajuwaka (787.76 ng/g). The lowest absorption was

Table 2 Trace elemental concentration (in ng/g dry wt.) of moss samples collected from sampling sites of Visakhapatnam

Location	Sample	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Cd	Pb
Rushikonda (control area)	Air	19.078	5.453	137.981	7.776	6.593	2233.659	0.415	0.142	0.14	9.407
	Moss	667	619.16	10,858.48	270.2	172.48	20,361.68	15.6	9.28	4.88	294.44
Autonagar (industrial area)	Air	17.256	53.622	1791.55	30.784	11.808	2240.132	0.788	0.529	0.841	19.871
	Moss	687.68	2419.24	32,548.84	318.44	164	10,942.28	19.72	9	10.8	658.08
Gajuwaka (industrial area)	Air	14.573	31.27	1272.492	40.187	10.859	1650.459	0.486	0.175	0.296	13.573
	Moss	787.76	2157.72	36,730.08	319.68	380.96	16,616.8	20.4	10.2	19.6	1513
Parawada industrial area	Air	17.28	57.02	1958.86	7.59	17.99	241.23	1.10	0.17	0.23	15.55
	Moss	646.4	767.48	16,871.92	270.8	153.08	49,807.56	28.64	12.28	3.2	244.24

observed in the sampling site of the Parawada industrial area (646.4 ng/g). The significant sources of chromium emissions are from the steel industry, combustion of tires [35–37].

3.2 Manganese

In the moss sample, concentrations of Manganese were represented in Tables 1 & 2. The Manganese concentrations in air samples ranged from 5.5 ng/g to 57.02 ng/g. The significant sources of Manganese are vehicular movement and combustion of coal [37, 38].

Parawada industrial area moss samples show a lower accumulation of Mn. The maximum and minimum Manganese concentrations in moss samples found were 619.16 ng/g and 2419.24 ng/g.

3.3 Iron

The observed iron concentrations in air samples range is from 137.981 ng/g to 1958.863 ng/g. A substantial amount of iron was found in the air sample collected in Parawada industrial area (1958.863 ng/g). The familiar sources for the iron emissions are the steel industries, traffic emissions, and combustion [16].

The maximum and minimum concentrations of Iron in moss samples found were 36,730.08 ng/g and 10,858.48 ng/g. Maximum accumulation of Iron in Bryumargenteum was found in the area of Gajuwaka. Minimum accretion of Iron in moss species was found in the control area due to low atmospheric concentration.

3.4 Nickel

Nickel concentrations in air samples in all sampling sites range from 7.594 ng/g to 40.187 ng/g. The maximum value of air samples was found in the sampling site of Gajuwaka, whereas the minimum value was observed at the site Parawada industrial area, which was less than the control area air concentration. Nickel was emitted as an air pollutant from thermal power stations, where the combustion of coal was significant activity [31].

Nickel's maximum and minimum concentrations in moss samples found were 319.6 ng/g and 270.2 ng/g. Accumulation of Nickel in moss Bryumargenteum was highest in the Gajuwaka sampling site due to increased atmospheric concentration. Minimum nickel concentration in moss samples was found in the control sampling site.

3.5 Copper

The observed copper concentrations in air samples range is 6.593 ng/g to 17.994 ng/g. Minimum copper concentration was found in the control area GITAM. Maximum copper concentration was observed in the Parawada industrial area. The copper concentration in the air observed was not at an objectionable level. The atmospheric deposition of copper may be due to coal combustion and from smelters and metallurgic industries [30].

The long-term accumulation of moss for copper metal ranges from 153.08 ng/g to 380.96 ng/g. Minimum accumulation of copper metal was observed in the Parawada site, which has the highest atmospheric copper concentration. Maximum copper accumulation was observed in the Gajuwaka sampling site.

3.6 Zinc

Zinc levels in air samples were found between 241.237 and 2233.659 ng/g. Minimum zinc concentration in air was found in the Parawada industrial area site. The maximum concentration was observed in the Control area. The primary sources for zinc emission are smelters and the combustion of fossil fuels [30].

The moss zinc accumulations range between 10,942.28 ng/g and 49,807.56 ng/g. The highest accumulation of zinc element was found in Parawada industrial area, where the lowest atmospheric zinc concentration was found. This is due to the impairment of the accumulation capacity of moss due to high concentrations. The lowest accumulation of zinc in the moss sample was observed in the Autonagar area.

3.7 Arsenic

Arsenic was highly toxic to the environment. The air concentrations of arsenic range between 0.415 ng/g and 1.104 ng/g. The lowest air concentration of arsenic was found in Control (0.415 ng/g), a control site. Maximum arsenic concentration in air samples was observed in the Parawad industrial area. Arsenic emissions may be from coal and tires, and glass manufacturing industries [39].

The Arsenic concentration of the moss sample was recorded between 15.6 ng/g and 28.64 ng/g. The maximum Arsenic concentration in Bryumargenteum was observed in Parawada industrial area, which has a high atmospheric arsenic concentration. And the minimum Arsenic concentration in moss was found in the control site due to low arsenic concentration in the atmosphere.

3.8 Selenium

Selenium concentration in air samples of different sampling sites ranges between 0.142 ng/g and 0.529 ng/g and toxic. Minimum air selenium concentration was found in the area 0.142 ng/g. Maximum air selenium concentrations were found in the Autonagar area. Minor emissions of Selenium were due to thermal power stations and coke oven batteries [31].

Accumulation of Selenium was dependent on the atmospheric selenium concentrations and climatic factors. The maximum deposition in moss was found in Parawada industrial area, and the minimum deposit was observed in the Autonagar area. High concentration in the atmosphere may retard the uptake of Selenium by moss species Bryumargenteum. The moss selenium concentration ranges between 9 ng/g and 12.28 ng/g.

3.9 Cadmium

Cadmium is the most toxic metal, and it is primarily present as industrial cadmium dust or fume. The Cd concentrations in the air range between 0.14 ng/g and 0.841 ng/g. Maximum atmospheric concentration was found in the Autonagar site, whereas minimum concentration was found in Rushikonda (GITAM), i.e., the control area. The familiar sources of Cadmium emissions are fertilizer industry, combustion, and vehicular emissions [40].

The accumulation of cadmium in moss species Bryumargenteum was ranging between 3.2 ng/g and 19.6 ng/g. the maximum accretion was found in the Gajuwaka area, whereas minimum accumulation was found in Parawada industrial area.

Lead

Lead concentration in different sampling sites was ranging from 9.407 ng/g to 19.871 ng/g. The lowest atmospheric concentration was found in the Control area, whereas the highest concentration was found in the Autonagar area. The primary emission sources for lead elements were smelters, traffic, and combustion of fossil fuels and tires [30].

The accumulation concentration of lead was between 244.24 ng/g and 1513 ng/g. The maximum accumulation concentration in moss was found in the Gajuwaka area, while the minimum was observed in Parawada industrial area.

The Bioconcentration factor (BCF) of heavy metal(s) was calculated as shown below.

BCF = Metal concentration in moss (mgkg-1)/Metal concentration in air environment (mgL-1 or mgkg-1).

It is clearly observed that the accumulation of trace metals in moss samples was comparatively high in all the industrial areas than the control site. Compared to other moss samples collected from industrial areas, Autonagar moss samples show high levels of heavy metals. In Parawada industrial area, where high atmospheric concentrations were found, significant accumulation in moss (Bryumargenteum) was not observed. The concentrations of heavy metal in the air are in the order of Fe > Zn > Mn > Ni > Pb > Cr > Cu > Cd > As > Se. The uptake efficiency of studied heavy metals in the moss species Bryumargenteum is in the order Fe > Zn > Mn > Pb > Cr > Ni > Cu > As > Cd > Se.

Bryumargenteumcan is used as a bioindicator for atmospheric pollution [41]. The uptake efficiency of the majority heavy metals follows the order Pb > Co, Cr > Cu, Cd, Mo, Ni, V > Zn > As in most studies [42].

Analyte	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Cd	Pb
% increase in industrial area to control area	15	74	70	15	54	59	45	24	75	80

The amount, duration, and intensity of heavy metals in the atmosphere influence moss accumulation [22]. If there are large levels of certain cations in the depositions, these affect the uptake of other cations due to ion competition.

4 Conclusion

The ease of sampling, the lack of complex and expensive elevated equipment and the consolidated and time-integrative behavior patterns of the moss biomonitor provides the advantages for future biomonitoring of atmospheric trace elements, particularly in large-scale surveys.

Biomonitoring is a critical method for determining the source. It is a simple and straightforward process to collect mosses in specific areas ranging from pollution-free background regions to highly polluted areas. By collecting mosses during the pre-monsoon, monsoon, and post-monsoon seasons, it is possible to determine the specific trace element pollution area. This research can also predict the appropriate moss species, which can be used as a biomonitor for a single trace element or a group of trace elements.

The present study reveals the content of heavy metals (Cr, Mn, Zn, As, Fe, Ni, Cu, Se, Cd, and Pb) in moss Bryumargenteum collected in the industrial zones of Visakhapatnam. The species grows prominently in the urban areas and forms dense carpet in moist and shady places, particularly in the winter months. The results show that these species can accumulate high amounts of trace metals present in particulate matter of its surrounding atmosphere. Thus, the moss Bryumargenteum can be used as a heavy metal indicator in regional studies as follows.

Other approaches have a great difficulty to obtain such detailed and accurate variations in time and space at a reasonable cost. Since the current study was preliminary, and a systematic protocol needs to be developed.

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