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Biomonitoring and interspecies comparison of metal precipitation through bryophytes at petrol pumps on Kumaon hill.

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Abstract

The number of pollution sources raises heavy metal contamination of the environment and become increasingly higher in Kumaon hill. This problem particularly manifests itself around the petrol pump. The objective of our investigation was to measure the pollution load of Pb, Zn, Cu and Cd in near by area of Kumaon hill. Keeping this in mind present investigation was undertaken to study the adverse effect of intensity of these metal load on the ecology and human population in near by area of respective study site. Moss sample were collected from pure and undisturbed habitat in Mukteswar and were transplanted on four petrol pumps and one control site Analysis of harvested transplants shows a significant seasonal increase in the metal in moss, which could be due to automobile exhaust and petroleum product consumption.

Key Words: *Biomonitoring, Metal, interspecies comparison, Petrol pump, Ecology.*

Introduction

The significance of heavy metal deposition in different cryptogam at petrol pump can be looked from different viewpoint. Because their potential to bioaccumulate heavy metal from respective source varies from species to species and also their contribution in environmental pollution rescue is increasing. Due to no other source of transport, dangerously petroleum consumption and automobile exhaust are the major source to put pollution load on the atmospheric condition in the near by area of petrol pumps (Krishnayya & Bedi 1986; Huang *et al.* 1994; Xuolong *et al.* 1994; Saxena *et al.* 2000a).

Monitoring of air contaminant at petrol pumps is necessary to determine upon locality of the near by population. Bryophytes have a long history to use as biological indicators of air quality. High deposition of heavy metal through dry deposition is a specific biology of cryptogams in biomonitoring studies (Saxena *et al.* 2000; Ruhling *et al.* 1987; Ferguson *et al.* 1984).Despite the large number of publication dealing with interaction of cryptogam with heavy metal (Nash 1989; Meenk and Tuba 1992; Saxena and Saxena 1998, 2000, 2001), detail knowledge on environmental condition of the petrol pump of Kumaon hill is in need of more attention.

Indirect or transplant bag method is best-suited technique to study the atmospheric condition (i.e. heavy metal) of petrol pumps (Saxena *et al.* 2000, Kirchoff and Rudolph 1989). The main objective of present work was to gain understanding of the metal accumulation potential of three different experimental species i.e. *Racomitrium crispulum*, *Bryum cellulare* and *Plagiochasma appendiculatum* and pollution load at different petrol pumps of Kumaon hill.

Materials and methods

The area of our investigation is located on the Western Himalaya i.e. Kumaon hill. Catchment areas are the four petrol pumps of Almora, Nainital, Ranikhet and Pithoragarh of Kumaon hill. The moss species

Racomitrium crispulum, Plagiochasma appendiculatum, Bryum cellulare was applied in our investigation. The seasonal and annual transplantation were started in year 2003 with the start of winter season (i.e. in the month of November). Seasonal transplantation was carried out for the fixed period of four months (i.e. 120 days, which represents the exposure of only one season and there is no intermittent mixing of seasonal harvesting of transplant). Sampling and transplantation were carried out by the method of Saxena and Saxena (2000). The catchment site of same height were chosen, to avoid the misleading of data. Samples were digested and analyzed using HNO_3 and $HClO_4$ (4:1 V/V) analysis by atomic absorption spectrophotometer (Model no. E 4139) by following the method of Bengston (1982).

The percent heavy metal loading of each location in proportion to control were calculated using the formula of Tuba and Csintalan (1993). Grodzinska *et al.* (1993) put forwarded the formula for PI (Pollution Index) value, on the basis of each metal, total number of metals, total amount of metals and number of sampling stations. The analysis of experimental heavy metal (i.e. Pb, Zn, Cu and Cd) for every study area were carried out in triplicate and data were presented with ± S.E. Significance (*) differs from control site (Pd" 0.05).

Results

Table 1, 2 and 3 shows the result of metal analysis of three different species i.e. *Plagiochasma appendiculatum*, *Bryum cellulare* and *Racomitrium crispulum* harvested periodically after a fixed period of exposure in Kumaon hill. Experimental site i.e. petrol pumps of Almora, Nainital, Ranikhet and Pithoragarh, are highly populated area of Kumaon hill. Data obtained after every seasonal exposure transplant shows comparative variability in seasonal deposition as well as in interspecies variation in metal accumulation. There is a high accumulation of lead observed i.e. 211 ppm in winter exposure in both bryophyte *Plagiochasma appendiculatum* and *Racomitrium crispulum* in Nainital. *Racomitrium crispulum* shows a significant high value of Cu i.e 142 ppm in Nainital under comparative study with *Bryum cellulare* and *Plagiochasma appendiculatum* in winter season. There is no such significant variability in the Cd content in any of the catchment area of the Kumaon hill and same is observed in all the experimental species.

Summer is the season for the higher vehicular input in the tourist place i.e. in the present experimental sites. A significant high value of Pb were observed in summer in *Plagiochasma appendiculatum* (335.84 ppm) in Nainital, while the highly populated area of Kumaon hill i.e. Almora shows maximum value of Pb input, which were observed in all the three experimental cryptogams. There is no such significant difference in Cd content all the three seasons; while it is striking that rain exposed experimental bryophytes transplant impart Cd in non-detectable limit. There is a positive correlation between metal accumulation and vehicular input in the catchment site (data not shown).

Significant variability in the metal content of annual transplant and summation of seasonal transplant, treated as annual fall out data was observed only in the transplant of *Plagiochasma appendiculatum* (Table- 4, 5, 6).

Undertaken metals i.e. Pb, Zn, Cu and Cd accumulation are the index of vehicular pollution and were useful to indices the vehicular input, in particular area. Percent metal loading at each location signifies that the study area is highly loaded with experimental metal. While the inter species comparison implicit that *Racomitrium crispulum* is much better accumulator than *Bryum cellular* and *Plagiochasma appendiculatum* respectively. It is in doubt that the undertaken control site Mukteswar forest is free from metal load and need more attention in further studies. The site Almora which were observed to be highly loaded with metal is justifiable through % loading value (Fig- 1, 2, 3).

The percent decrease in the metal content in winter season with respect to summer in *indirect* biomonitoring study, through experimental bryophytes imparts that Cu and Cd value decrease up to the range of 80-90 %. While there is no such significant difference in metal concentration observed in case of Pb and Zn in all the three species of bryophytes in winter with respect to summer (Fig- 5). There is an up to 100 % decrease in Cd were observed in rainy season under comparative study with summer (Fig- 6). We can not over rule the role of rain in pollutant leaching. Same could be the reason for decrease in Pb, Zn and Cu value up to 70-80 % in rainy season in all the three experimental cryptogams.

There is a statistically significant correlation found between metal accumulation, an increment in their source type and intensity of source with respect to PI (pollution index) value. The PI value were observed highly positive at Almora i.e. + 4.965 in *Bryum cellulare* signifies that the pollutant intensity among other petrol pump catchment area, while the site of Pithoragarh petrol pump shows negative value – 2.4406, -2.48094, -1.60022 in *Racomitrium crispulum, Plagiochasma appendiculatum, Bryum cellulare* respectively (Fig- 4).

Discussion

We have seen that the study and comparison of the moss transplant of petrol pumps of different site in Kumaon hills give more authentic picture of atmospheric surrounding of petrol pumps and near by areas. The experimental data of seasonal and annual exposure demonstrate that all the three experimental bryophytes have positive potential to accumulate and retain heavy metal pollutant of petrol pumps. However, there efficiencies vary from species to species.

Present study also demonstrate that seasonal transplant of moss bag technique for liverwort is more reliable than annual transplant one. Chlorosis, thallus degradation, ageing, and low surface area by mass ratio could be the reason for lower metal input value in annual transplant of *Plagiochasma appendiculatum*. Ranikhet is relatively clean site as compared to Almora and Nainital, though that the catchment area is in the heart of the city. This further supported by lower % metal loading.

Cu industry in Kumaon region is also a probable additional reason for high metal input value in Almora. Kerosene mixing is also one of the addition facts for increment in Cu in the petrol pump transplants, as $CuSO_4$ is mixed as an impurity in kerosene. Perhaps Cd is also present as a mining impurity in petrol. High input of these two metals (i.e. Cu and Cd) in summer season in all the three experimental bryophytes were reasonable.

The relative cleanness of control site i.e. Mukteswar is over ruled by the metal concentration observed in respective transplant in all the three bryophytes. Though their concentration is low and comparable with the other study areas. Increment in the use of Cu, Zn and Cd fertilizers could be the reason for this high value of metal in Mukteswar. Percent loading value of Nainital and Almora signifies that there is an abrupt increment of consumption of diesel and petrol. This is a matter of serious concern, as the ecosystem flora may not be able to bear the burden of increasing metal level and other pollutant, released on the consumption of petrol and diesel.

Genetic constituent may be assumed to have considerable significance in respect to heavy metal uptake and excretion. The different uptake capacity of heavy metal and retention / excretion by interspecies survey shows variability (Ruhling *et al.* 1987; Ross 1990; Birg *et al.* 1995). This need further harmonization and research in Kumaon region. Research is in continuation by present authors in the survey area of Kumaon hill. Accumulation of heavy metal especially lead through various cryptogams is well known study and several authors described the moss capability to accumulate vehicular pollution (Ruhling and Tyler, 1968; Onianwa and Eunyomi, 1983; Ferguson *et al.* 1984; Makinen 1987; Ross, 1990; Steinnes *et al.* 1994; Saxena 1995).

High Pb value i.e. 600 - 800 mg / L in petrol is a direct evidence of their high concentration in bryophyte transplanted at petrol pumps. Study has also confirmed that the relationship between the environmental quality and metal accumulation in bryophytes. Present investigation confirms that *Bryum cellulare* had a lower potential to monitor the metal, while *Racomitrium crispulum* has the maximum capability to absorb the vehicular pollution on petrol pumps and might be due to this they maintained their physiology throughout the year of transplantation. This was confirmed by the non-significant difference in annual transplant metal data and summation of the seasonal transplant metal data which were treated as annual precipitation data.Seasonal and annual transplantation data of *Plagiochasma appendiculatum* further recommends that biomonitoring by liverworts is better through seasonal way.

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Table 1: Seasonal variation in metal precipitation in winter, summer and rain in year 2003-04 in moss *Plagiochasma appendiculaum*. Each value is mean of 3 replicates ± S.E. Significance (*) differs from control (Pd"0.05).

SITE No.	CATCHMENT AREA	WINTER EXPOSURE				SUMMER EXPOSURE				RAIN EXPOSURE			
		Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
1	MUKTESWAR FOREST	32.42±0.12	3.15±0.02	22.4±0.15	1.124±0.21	41.25±0.24	10.49±0.6	40.3±0.54	6.32±0.22	41.5±0.14	93.95±0.65	8.59±0.25	2.66±0.01
2	ALMORA	318.5*±0.24	25.2*±0.05	46.93*±0.3	0.62*±0.05	298.4*±3.5	173.2*±5.6	50.33*±0.6	1.9*±0.05	33.9*±0.3	18.1*±0.42	41.6*±0.3	ND
3	RANIKHET	42.04*±0.52	42.1*±0.32	62.1*±0.56	1.3*±0.2	54.9*±1.25	56.6*±0.98	83.4*±1.25	2.2*±0.05	37.7*±0.1	36.8*±0.25	47.6*±0.5	ND
4	NAINITAL	211.05*±0.3	59.07*±0.2	44.2*±0.58	2.42*±0.2	335.4*±7.5	60.93*±0.8	69.72*±1.0	3.6*±0.09	33.9*±0.2	14.2*±0.84	32.0*±0.2	1.9*±0.05
5	PITHORAGARH	47.3*±0.35	62.1*±0.5	26.3*±0.25	0.12*±0.02	57.2*±0.22	72.1*±0.65	32.4*±0.36	0.3*±0.01	52.8*±0.5	ND	25.5*±0.9	ND

Table 2: Seasonal variation in metal precipitation in winter, summer and rain in year 2003-04 in moss *Bryum cellulare*. Each value is mean of 3 replicates ± S.E. Significance (*) differs from control (Pd" 0.05).

SITE No.	CATCHMENT AREA	WINTER EXPOSURE				SUMMER EXPOSURE				RAIN EXPOSURE			
		Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
1	MUKTESWAR FOREST	32.42±0.12	3.15±0.02	22.4±0.15	1.124±0.21	41.25±0.24	10.49±0.6	40.3±0.54	6.32±0.22	41.5±0.14	93.95±0.65	8.59±0.25	2.66±0.01
2	ALMORA	318.5*±0.24	25.2*±0.05	46.93*±0.3	0.62*±0.05	298.4*±3.5	173.2*±5.6	50.33*±0.6	1.9*±0.05	33.9*±0.3	18.1*±0.42	41.6*±0.3	ND
3	RANIKHET	42.04*±0.52	42.1*±0.32	62.1*±0.56	1.3*±0.2	54.9*±1.25	56.6*±0.98	83.4*±1.25	2.2*±0.05	37.7*±0.1	36.8*±0.25	47.6*±0.5	ND
4	NAINITAL	211.05*±0.3	59.07*±0.2	44.2*±0.58	2.42*±0.2	335.4*±7.5	60.93*±0.8	69.72*±1.0	3.6*±0.09	33.9*±0.2	14.2*±0.84	32.0*±0.2	1.9*±0.05
5	PITHORAGARH	47.3*±0.35	62.1*±0.5	26.3*±0.25	0.12*±0.02	57.2*±0.22	72.1*±0.65	32.4*±0.36	0.3*±0.01	52.8*±0.5	ND	25.5*±0.9	ND

Table 3: Seasonal variation in metal precipitation in winter, summer and rain in year 2003-04 in moss *Racomitrium crispulum*. Each value is mean of 3 replicates ± S.E. Significance (*) differs from control (Pd" 0.05).

SITE No.	CATCHMENT AREA	WINTER EXPOSURE				SUMMER EXPOSURE				RAIN EXPOSURE			
		Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
1	MUKTESWAR FOREST	35.42±0.21	3.15±0.03	23.65±0.25	0.321±0.54	61.25±0.15	6.49±0.28	32.65±0.24	0.40±0.02	39.62±0.2	ND	9.12±0.24	ND
2	ALMORA	318.5*±9.25	342*±8.645	5.43*±0.55	2.57*±0.05	224.4*±5.3	173.2*±0.5	59.46*±0.4	3.6*±0.32	35.8*±0.1	8.79*±0.24	50.81*±0.5	ND
3	RANIKHET	46.32*±0.55	43.16*±4.5	69.3*±0.13	1.06*±0.05	53.4*±0.65	53.26*±0.9	88.9*±0.54	1.9*±0.05	35.8*±0.5	ND	42.73*±0.6	ND
4	NAINITAL	22.10*±0.54	59.07*±0.5	63.48*±9.5	0.3*±0.004	33.54*±2.2	68.93*±0.9	84.74*±0.4	4.7*±0.14	14.6*±0.5	32.9*±0.33	52.74*±0.5	1.25±0.66
5	PITHORAGARH	42.64*±0.41	60.26*±0.2	20.4*±0.24	0.25*±0.06	57.7*±0.24	78.2*±0.84	25.46*±1.5	0.92*±0.2	43.3*±1.5	ND	18.5*±0.5	ND

Table 4: Variation in metal precipitation value in annual transplant and summation value of three seasons in year 2003-04 in moss *Plagiochasma appendiculaum*. Each value is mean of 3 replicates ± S.E. Significance (*) differs from control (Pd" 0.05).

SITE No.	CATCHMENT AREA	SUMMETION OF SEASONAL TRANSPLANT DATA TREATED AS ANNUAL PRECIPITATION				ANNUAL EXPOSURE OF MOSS BAGS METAL DATA			
		Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
1	MUKTESWAR FOREST	115.17±0.2	107.59±1.22	71.29±2.33	10.11±1.25	95.17±0.65	79.61±3.25	52.64±2.65	7.11±0.32
2	ALMORA	650.86*±9.6	216.62*±6.42	138.95*±1.35	2.58*±0.35	425.01*±8.32	198.6*±4.2	99.64*±4.65	3.58*±0.63
3	RANIKHET	134.67*±2.3	135.51*±2.35	193.18*±5.65	3.5*±0.33	101.94*±4.35	100.2*±2.3	159.67*±2.65	2.7*±0.36
4	NAINITAL	580.49*±5.6	134.29*±2.35	145.97*±3.65	7.96*±0.62	420.16*±5.65	98.64*±2.2	111.94*±6.35	6.46*±0.55
5	PITHORAGARH	157.33*±1.2	134.2*±1.65	84.23*±4.25	0.44*±0.03	133.21*±4.94	98.66*±3.2	89.64*±5.656	0.39*±0.05

Table 5: Variation in metal precipitation value in annual transplant and summation value of three seasons in year 2003-04 in moss *Bryum cellulare* Each value is mean of 3 replicates ± S.E. Significance (*) differs from control (Pd" 0.05).

SITE No.	CATCHMENT AREA	SUMMETION OF SEASONAL TRANSPLANT DATA TREATED AS ANNUAL PRECIPITATION				ANNUAL EXPOSURE OF MOSS BAGS METAL DATA			
		Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
1	MUKTESWAR FOREST	136.29±0.3	9.64±0.34	65.43±0.74	0.72±0.33	131.24±0.1	8.94±0.32	62.23±0.233	0.7*±0.001
2	ALMORA	578.74*±0.3	524.08*±0.5	115.71*±0.51	6.171*±0.35	572.24*±5.25	520.7*±0.2	111.11*±2.33	5.24*±0.04
3	RANIKHET	135.57*±0.5	96.42*±0.51	200.93*±0.69	2.96*±0.098	130.52*±3.25	95.02*±0.6	193.54*±4.22	2.96*±0.3
4	NAINITAL	70.25*±0.5	160.90*±0.73	200.98*±0.54	6.25*±0.25	69.25*±2.54	158.9*±0.3	192.98*±0.35	6.75*±0.32
5	PITHORAGARH	143.74*±0.7	138.46*±0.54	64.36*±0.254	1.17*±0.5	139.74*±0.65	135.4*±0.6	59.37*±0.35	1.34*±0.03

Table 6: Variation in metal precipitation value in annual transplant and summation value of three seasons in year 2003-04 in moss *Racomitrium crispulum*. Each value is mean of 3 replicates ± S.E. Significance (*) differs from control (Pd" 0.05).

SITE No.	CATCHMENT AREA	SUMMETION OF SEASONAL TRANSPLANT DATA TREATED AS ANNUAL PRECIPITATION				ANNUAL EXPOSURE OF MOSS BAGS METAL DATA			
		Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
1	MUKTESWAR FOREST	128.17±0.3	17.48±2.65	75.10±2.34	0.68±0.02	124.47±0.21	14.48±4.35	73.17±1.22	1.25±0.02
2	ALMORA	760.29*±8.6	537.37*±6.35	153.12*±0.25	0.32*±0.02	755.79*±9.66	529.7*±2.3	150.12*±0.5	1.49*±0.05
3	RANIKHET	133.54*±3.2	102.27*±4.35	225.46*±0.55	2.3*±0.23	125.44*±0.55	99.27*±5.3	220.46*±2.35	2.3*±0.05
4	NAINITAL	500.49*±7.6	138.48*±2.325	327.00*±6.35	7.17*±0.35	489.47*±4.2	135.4*±0.5	320.4*±0.512	7.07*±0.04
5	PITHORAGARH	109.23*±4.2	159.29*±2.35	74.80*±2.1	0.9*±0.025	100.24*±2.32	149.7*±0.5	77.80*±4.5	0.9*±0.03

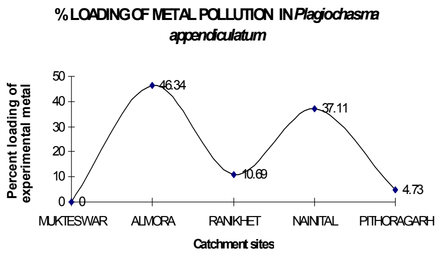

Fig 1: Percent metal loading in Plagiochasma appendiculaum in the experimental catchment area of Kumaon Hill in year 2003-04.

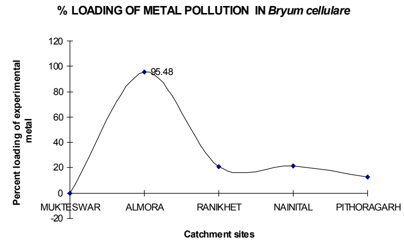

Fig 2: Percent metal loading in *Bryum cellulare* Hook. in the experimental catchment area of Kumaon Hill in year 2003-04

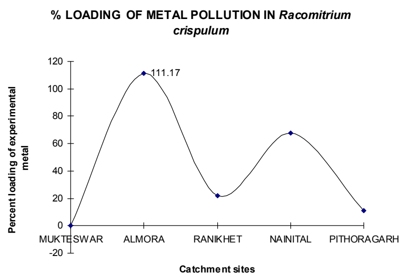

Fig 3: Percent metal loading in *Racomitrium crispulum* in the experimental catchment area of Kumaon Hill in year 2003-04

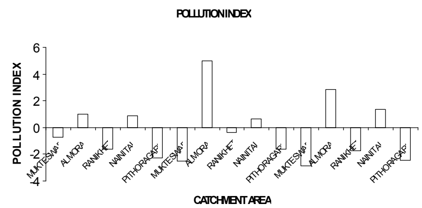

Fig 4: Pollution index value by undertaken bryophytes in the experimental catchment area in year 2003-04

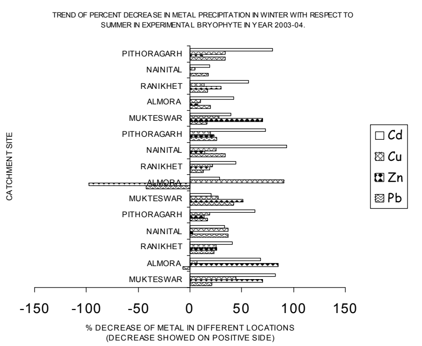

Fig 5: Trend of percent decrease in metal recipitation in winter with respect to summer in experimental catchment areas in experimental bryophytes in year 2003-04.

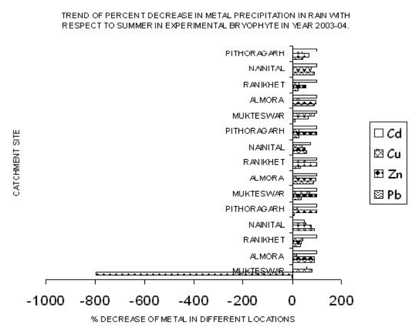

Fig 6: Trend of percent decrease in metal precipitation in rain with respect to summer in experimental catchment areas in experimental bryophytes in year 2003-04