Bull Environ Contam Toxicol (2009) 82:1–5
DOI 10.1007/s00128-008-9491-9

Comparison of Epigeic Moss (*Hypnum cupressiforme*) and Lichen (*Cladonia rangiformis*) as Biomonitor Species of Atmospheric Metal Deposition

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Received: 7 January 2008 / Accepted: 6 June 2008 / Published online: 1 July 2008

Abstract In the present work epigeic moss (*Hypnum cupressiforme Hedw.*) and epigeic lichen (*Cladonia rangiformis Hoffm.*) samples were collected simultaneously in the Thrace region, Turkey according to a regular sampling grid. Whereas the moss was found at all 68 sampling sites, the lichen could be collected only at 25 of the sites, presumably because lichens are more sensitive than mosses with respect to air pollution and climatic variations. All elements showed higher accumulation in the moss than in the lichen whereas element inter-correlations were generally higher in the lichen. All considered the moss was judged to be a better choice than the lichen for biomonitoring of atmospheric deposition of metals in this case, and it is argued that mosses may be generally more suited than lichens for this purpose.

Keywords Biomonitors · Metals · Lichen · Moss · Atmospheric deposition

Biomonitoring of atmospheric deposition of air pollutants using mosses and lichens was first introduced in Sweden about 40 years ago (Svensson and Liden 1965; Rühling and Tyler 1968; Holm and Persson 1975). Over the years this technique has become very popular especially for the monitoring of trace metals, as evident from several reviews (e.g. Tyler 1989; Steinnes 1989; Tyler 1990; Conti and Ceccetti 2001; Onianawa 2006). Although lichens, as different from mosses, are symbiotic organisms composed of fungi (mycobiont) and green algae or cyanobacteria, both organisms tend to prefer the same habitats, and frequently occur together either in epiphytic (on trees) or epigeic (on the ground) form. Investigators thus often have a choice between several lichen and moss species for studies related to atmospheric deposition. Among the very extensive number of investigations reported in the literature on the use of either mosses or lichens as biomonitors, however, there appears to be very few that compare species of the two groups and discuss their feasibility (Steinnes 1977; Boileau et al. 1982; Reimann et al. 1999; Bargagli et al. 2002).

In the present work epigeic moss (*Hypnum cupressiforme Hedw.*) and epigeic lichen (*Cladonia rangiformis Hoffm.*) samples were collected simultaneously in the Thrace region, Turkey and analyzed for some metals frequently encountered in air pollution studies. The main purpose of this paper is to compare the feasibility of the moss and lichen species used here as apparent from the present data. The geographical distribution of metal pollution in Thrace based on the present moss data is described in detail elsewhere (Coskun et al. 2005).

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Materials and Methods

The Thrace region was divided into 68 squares according to a 20 × 20 km grid and samples were collected in the center or near the center of each square in September 2001. This resulted in 68 moss and 25 lichen samples, as shown

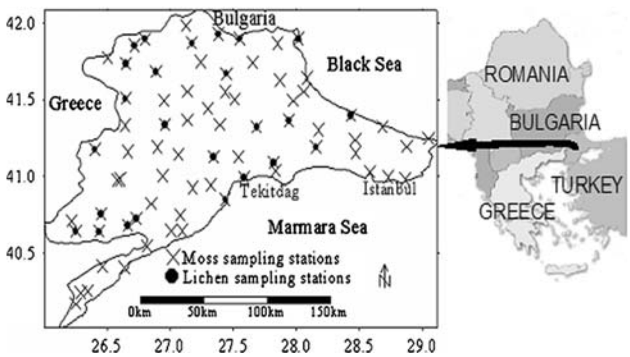

Fig. 1 Sampling stations of moss and liken in Thrace region

Table 1 Certified and obtained results (mg/kg) for Cd, Cr, Cu, Pb, and Zn in pine needles (NIST 1575)

	Certified	Present work	Recovery (%)
As	0.21	0.194	92
Cd	<(0.5)[a]	0.20	na
Cu	3.0	2.92	97
Pb	10.8	10.7	99
Zn	–[b]	88.2	na

[a] not certified

[b] na: not applicable

in the map in Fig. 1. *Hypnum cupressiforme* and *Cladonia rangiformis* were chosen as biomonitors because of their general presence in the Thrace region. Sampling sites were selected at appropriate distances from main roads, populated areas, and single houses. Samples were collected in open areas to reflect atmospheric deposition and to eliminate canopy effect. The samples were stored in plastic bags, and the same procedure was applied for preparation of moss and lichen samples for analysis. In the laboratory the moss or lichen was separated from other materials and dried to constant weight at 40°C.

Unwashed 0.4 g portions of green and greenish shoots of mosses and 1–2 cm of lichen thalli were digested with concentrated nitric acid in a microwave digestion unit. After appropriate dilution of the resulting solution the elements Cu, Mn, and Zn were determined by flame AAS, and As, Cd, and Pb by graphite furnace AAS, respectively. The detection limits of As, Pb, Cd, Cu, Mn and Zn were 0.001, 0.004, 0.04, 0.01, 0.02, and 0.004 mg/kg, respectively. The reported concentrations are mean values of three replicates and the results are presented in mg/kg. The relative standard deviation (RSD) of replicates was generally less than 5%. SPSS 11.0 for Windows was used for the data analysis. The accuracy of the analyses was checked by simultaneous analysis of the standard reference material Pine Needles SRM 1575 (NIST, USA).

Table 2 Correlation coefficients for same elements in moss (*Hypnum cupressiforme*) and lichen (*Cladonia rangiformis*) and for different element in same species

	As		Cd		Cu		Mn		Pb		Zn	
	Moss	Lichen	Moss	Lichen	Moss	Lichen	Moss	Lichen	Moss	Lichen	Moss	Lichen
As												
Moss	1.00											
Lichen	0.72	1.00										
Cd												
Moss	0.02	0.53	1.00									
Lichen	0.17	0.72	0.80	1.00								
Cu												
Moss	0.62	0.48	0.12	0.31	1.00							
Lichen	0.48	0.85	0.60	0.83	0.54	1.00						
Mn												
Moss	0.02	0.17	0.23	0.19	0.11	0.14	1.00					
Lichen	0.00	0.29	0.66	0.63	0.21	0.53	0.33	1.00				
Pb												
Moss	0.50	0.29	0.01	0.03	0.58	0.37	0.12	0.04	1.00			
Lichen	0.59	0.71	0.31	0.61	0.52	0.79	0.10	0.38	0.54	1.00		
Zn												
Moss	0.68	0.33	0.14	0.01	0.59	0.35	0.01	0.04	0.78	0.57	1.00	
Lichen	0.39	0.63	0.48	0.74	0.49	0.83	0.11	0.51	0.36	0.77	0.43	1.00

Results and Discussion

As evident from Table 1 there were no significant differences between certified and obtained values for the reference material ($p > 0.05$). The highest concentrations of As, Cu, Pb, and Zn in moss were found in the Istanbul region. It would not be possible to derive the same conclusion from the lichen data because no *Cladonia* lichen was found at sites near Istanbul, presumably because lichens are generally sensitive to gaseous air pollutants such as SO_2, NO_2, HF, H_2S, and ozone. They are also generally sensitive to high concentrations of heavy metals (Nash III 1975, 1976; Kapu et al. 1991; Bargagli et al. 2002; Jeran et al. 2002). Bargagli et al. (2002) pointed out that epigeic moss (*Hypnum cupressiforme*) was more tolerant to exposure to sulfur compounds than epiphytic lichen (*Parmelia caperata*). Apparently mosses are preferable to lichens as monitors of metal deposition in areas where the air pollution is high.

In general concentrations of the above four elements gradually decrease from the vicinity of big cities to rural areas both in the lichen and the moss, indicating that the sources of metals are the same in moss and lichen. The correlation coefficients between moss and lichen contents for each of the elements As, Cd, Cu, Mn, Pb, and Zn are 0.72, 0.72, 0.54, 0.33, 0.54, and 0.42, respectively. The correlation coefficients of elements in lichens are consistently rather high but much more variable in moss (Table 2). Concentrations and concentration ratios of the six elements in moss and lichen samples collected at same station and the corresponding moss/lichen ratios are given in Tables 3 and 4, respectively. From the observed ratios it appears that the moss (*H. cupressiforme*) accumulates these elements to a greater extent than the lichen

Table 3 Concentrations of elements in moss and lichen collected at the same site (mg/kg)

Station No.	As		Cd		Cu		Mn		Pb		Zn	
	Moss	Lichen	Moss	Lichen	Moss	Lichen	Moss	Lichen	Moss	Lichen	Moss	Lichen
5	0.72	0.70	0.27	0.10	6.09	2.21	445	98	18.5	7.69	23.5	19.8
7	0.99	1.28	0.21	0.12	5.66	2.19	168	50	9.99	5.98	39.4	17.4
13	1.19	0.76	0.20	0.07	6.01	1.83	477	118	11.6	4.29	29.3	14.8
15	0.95	0.83	0.16	0.09	15.2	2.73	88	18	20.3	3.70	26.5	17.3
22	0.86	0.90	0.16	0.07	7.10	1.74	116	23	8.12	7.95	24.7	17.7
24	0.70	0.79	0.18	0.09	5.99	3.84	261	48	7.85	7.68	22.8	26.4
25	1.34	1.25	0.15	0.07	6.72	3.13	173	58	8.82	13.3	24.7	21.3
26	2.79	1.87	0.17	0.09	12.5	3.25	166	57	7.86	7.21	40.7	21.2
32	1.44	1.38	0.23	0.08	7.49	3.36	492	92	16.8	8.03	28.6	16.3
39	2.07	1.62	0.21	0.15	8.72	3.13	118	41	9.65	13.5	35.4	23.8
41	1.19	0.81	0.11	0.06	8.63	3.08	139	36	5.45	6.24	33.1	17.7
43	1.90	1.04	0.15	0.07	10.9	2.18	400	88	8.31	13.7	32.9	19.2
45	3.46	2.47	0.15	0.11	16.4	7.07	180	68	50.6	28.7	107.8	30.7
46	1.32	1.32	0.10	0.09	5.44	2.99	122	32	8.66	11.7	23.9	20.0
49	1.13	0.92	0.14	0.05	4.54	1.75	143	43	7.78	4.34	18.6	13.2
52	1.11	2.31	0.36	0.30	12.3	8.52	182	358	9.71	21.5	23.2	33.8
53	2.37	3.48	0.31	0.25	9.27	8.06	135	52	10.4	18.7	23.9	26.4
55	1.23	0.95	0.18	0.12	5.61	3.13	301	134	14.0	13.0	28.8	21.8
57	1.25	1.28	0.20	0.12	6.32	3.41	88	31	8.50	12.9	28.1	20.3
60	0.78	0.81	0.16	0.12	9.18	3.38	165	30	15.9	15.9	36.5	19.5
62	1.29	0.69	0.15	0.05	6.81	2.29	202	56	13.2	4.67	26.8	14.3
64	0.94	0.97	0.19	0.07	5.59	3.03	194	34	8.50	5.95	24.5	17.1
66	1.30	0.93	0.19	0.12	7.99	3.41	204	56	7.86	10.3	59.0	23.7
67	0.60	0.76	0.18	0.12	6.01	3.03	98	57	13.9	7.34	25.2	24.3
68	0.90	0.80	0.17	0.08	5.01	1.64	78	27	5.14	7.05	17.3	11.1
Mean	1.35	1.24	0.19	0.11	8.06	3.37	205	68	12.3	10.5	32.2	20.4
Maximum	3.46	3.48	0.36	0.30	16.4	8.52	492	358	50.6	28.7	107.8	33.8
Minimum	0.60	0.69	0.10	0.05	4.54	1.64	78	18	5.14	3.70	17.3	11.1

Table 4 Concentration ratios of elements in moss and lichen collected at same station (n = 25)

Moss/Lichen concentration ratio						
Station No.	As	Cd	Cu	Mn	Pb	Zn
5	1.03	2.82	2.75	4.52	2.41	1.19
7	0.77	1.71	2.59	3.35	1.67	2.27
13	1.57	2.98	3.28	4.03	2.71	1.97
15	1.15	1.76	5.57	4.92	5.48	1.53
22	0.96	2.29	4.09	5.12	1.02	1.40
24	0.88	1.93	1.56	5.39	1.02	0.87
25	1.07	1.96	2.15	3.01	0.66	1.16
26	1.49	1.99	3.84	2.92	1.09	1.92
32	1.04	3.02	2.23	5.37	2.09	1.76
39	1.28	1.40	2.78	2.84	0.72	1.49
41	1.47	1.76	2.80	3.83	0.87	1.87
43	1.83	2.05	5.01	4.56	0.61	1.72
45	1.40	1.41	2.31	2.64	1.76	3.51
46	1.00	1.11	1.82	3.83	0.74	1.19
49	1.23	2.82	2.59	3.33	1.79	1.40
52	0.48	1.18	1.44	0.51	0.45	0.69
53	0.68	1.24	1.15	2.62	0.55	0.91
55	1.30	1.51	1.79	2.25	1.08	1.32
57	0.97	1.60	1.85	2.82	0.66	1.39
60	0.97	1.39	2.71	5.51	1.00	1.87
62	1.87	3.02	2.98	3.63	2.82	1.87
64	0.97	2.84	1.85	5.65	1.43	1.43
66	1.40	1.69	2.34	3.62	0.76	2.49
67	0.78	1.49	1.98	1.71	1.89	1.03
68	1.13	2.22	3.06	2.84	0.73	1.56
Mean	1.09	1.77	2.39	3.01	1.18	1.58
Maximum	0.99	1.18	1.92	1.38	1.76	3.18
Minimum	0.86	2.11	2.77	4.36	1.39	1.56

(*C. rangiformis*). This is in agreement with experience from previous work (Steinnes 1977). From the literature it is evident that sources other than atmospheric deposition contribute to the element contents in epigeic moss, such as re-suspension of soil particles, major ion composition of precipitation, and uptake from the substrate under certain conditions (Steinnes 1995; Økland et al. 1999; Reimann et al. 2001; Poikolainen et al. 2004). Moreover the uptake efficiency varies considerably among the elements and depends on their chemical speciation. Among the elements included in the present work it is highly questionable if the Mn content of the moss bears any relation with atmospheric deposition (Steinnes 1995), except perhaps in situations with high deposition rates. The closer correlations observed between some of the elements in the lichen compared to the moss may indicate that the elemental composition of epigeic lichens is less affected by resuspention, precipitation and uptake from soil than is the case for corresponding mosses.

Nevertheless epigeic moss has shown to reflect very well the relative atmospheric deposition of some elements, such as Pb, Cd, and As (Berg and Steinnes 1997). Also the deposition of an element such as Zn can be well predicted from moss data if proper correction is made for the natural content in the moss. Although epigeic lichens have also been frequently used for monitoring of metal deposition corresponding evidence does not exist to the same extent for the lichens as for the mosses.

In spite of the negative factors mentioned above, moss may still be considered a good biomonitor for determination of spatial distribution of many metals from atmospheric deposition. In the present work moss samples were easily found at all sampling stations. Lichen samples on the other hand could not be sampled in the surroundings of Istanbul city and in the southwest part of the Thrace region, in the latter case probably because of sea-spray effects. In the present case, therefore, the moss obviously was the preferred choice. The higher sensitivity of lichens with respect to air pollution and climate should presumably make them less suitable biomonitors than mosses in general, at least in areas with high air pollution or strong marine influence. This statement is supported by the fact that less quantitative evidence exists so far for lichens than for mosses regarding their relation to atmospheric deposition.

Although both species obtain nutrients mainly from the atmosphere in wet and dry deposition, they have plenty of morphological and physiological differences, which effect their heavy metal accumulation. Both species were collected in same sites, so many environmental factors such as vegetation, quality of the substrate, dust derived from soil, altitude etc. were similar for the moss and lichen species. In spite of these similar conditions, distinct differences were observed between heavy metal concentrations in moss and lichen, presumably depending on properties of the moss and lichen species themselves.

Acknowledgements This work was supported by The Research Fund of The University of Istanbul, Project number 1672/30042001, Mahmut Coşkun is grateful to the Norwegian Government for a Scholarship 2002/2003, and to the Scientific and Technical Research Council of Turkey (TUBITAK-NATO B2) for a Science Fellowship.

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