DISTURBANCES OF IONIC EQUILIBRIUM IN MOSSES OF CONTAMINATED AREAS

PIOTR KOSIBA, KRZYSZTOF KOLON

Department of Ecology and Nature Protection
Institute of Plant Biology, Wrocław University
Kanonia 6/8, 50-328 Wrocław, Poland

(Received: November 5, 2001. Accepted: September: 17, 2002)

ABSTRACT

Mosses are sensitive and precise bioindicators of heavy metals contamination of the environment. They accumulate in their tissues large amounts of these elements than do higher plants. The aim of this study was to present the influence of environmental pollution on quantitative relations of heavy metals and cationic equilibrium in tissues of mosses: *Pleurozium schreberi*, *Hylocomium splendens* and *Hypnum cupressiforme*. Twelve sampling sites were selected in the area of Lower Silesia (Poland), diverse in respect of pollution degree determined for dust fall and contents of metals in dust. The contents of Ca, K, Na, Mg, Al, Mn, Fe, Cu, Pb, Ni, Cd, and Zn have been examined in the mosses. Significant differences in the elements contents of mosses between the examined sites, and between moss species were found. This differentiation affects the cationic equilibrium. It is expressed by weighed sum of square roots of relative cation concentrations. The quantitative relations between contents of elements in mosses depended on species and pollution level. These relations and accumulation of metals in moss tissues is the indicator of environmental pollution, which influences the ecological condition of mosses and their occurrence in the given area. The air contaminated by heavy metals causes stress and the decline of moss populations, and can be of significance for their survival. The results of this type of investigations are of importance for the active protection of mosses and their biotopes.

KEY WORDS: *Pleurozium schreberi*, *Hylocomium splendens*, *Hypnum cupressiforme*, heavy metals, cationic equilibrium, bioindication, environment pollution.

INTRODUCTION

Environmental pollution is usually determined by means of chemical methods, e.g. determination of concentrations of toxic elements in the air. The biological methods are relatively simple, quick and cheap. The various biological materials used in bioindication require ecological investigations, field and laboratory experiments (Fabiszewski 1983; Fabiszewski et al. 1983; Markert 1993). The impact of industrial emissions on various plant species in Lower Silesia was investigated on the basis of bioindication studies, among others by Brej (1998) and Fabiszewski, Brej (2000).

Mosses are precise and sensitive bioindicators of heavy metals' deposition in the environment (Grodzińska et al. 1999; Fernandez, Carballeira 2001). They are used for long-term ecological monitoring in many countries. Air contaminated by heavy metals causes stress and decline of moss populations and can be a significant factor for survival of more moss species (Kosiba 1997). The results of this type of investigations should be taken into account in active protection of mosses and their biotopes. The aim of this paper was to determine the degree of environmental pollu-

tion by dust fall and heavy metals contamination, and how this pollution affects the cationic equilibrium in three moss species *Pleurozium schreberi* (Brid.) Mitt. *Hylocomium splendens* (Hedw.) Br. Eur. and *Hypnum cupressiforme* Hedw.

MATERIALS AND METHODS

The investigations were carried out in Lower Silesia (Poland). Twelve sites of investigated mosses were chosen, differing in respect of the degree of environmental pollution (Fig. 1).

On each site three samples of mosses and dust have been collected. The quantity of dust fall was assessed by means of the sedimentary method (Skinder 1991). The measurements consisted in collecting dust in sedimentary dishes, in monthly intervals. The quantity of dust was determined by weighing; the results were expressed in g/m²/year. The contents of cations in dust and in plants were determined by the flame Atomic Absorption Spectrometer of firm GBC Scientific Equipment Pty Ltd model AVANTA PM. In accordance with Czarnowski (1977) we accepted, that

Site number	Area characteristics	Group number
1, 2, 3	control area (control samples)	I
4, 5, 6	urban area	II
7, 8, 9	copper basin, copper mills	III
10, 11, 12	brown coal basin, power plants	IV

the concentrations of a definite cation in plant tissues is a function of concentration of other cations. The weighted sum of square roots of relative cation concentration is expressed by the equation:

$$\sum C_i \sqrt{\frac{[E_i]}{\sum [E]}} = \text{const.} \quad (\text{cationic equilibrium})$$

where C_i is the interdependent weight of cation E_i .

The cationic equilibrium is a constant value for the plant species. For most plants of temperate climate it equals ca. 12.515. On the basis of the carried out chemical analyses the cationic equilibrium for the examined mosses in all localities has been calculated. The statistical analysis of obtained results was performed. The differentiation of mean values was obtained using the analysis of variance and calculating the Least Significant Difference (LSD). The similarity of objects was determined by constructing tree diagrams using the single linkage method basing on matrixes of City-block (Manhattan) distances (Hartigan 1975). For calculations the computer program Statistica 6.0 (Statsoft, Inc. 2001) was used.

RESULTS AND DISCUSSION

The investigated sites are localized on areas being under influence of different emission sources (Fig. 1):

- 1, 2 and 3 (group I) sites outside immediate influence of emission,
- 4, 5 and 6 (group II) within the range of municipal-agglomeration pollution,
- 7, 8 and 9 (group III) area of output and processing of copper,
- 10, 11 and 12 (group IV) ground of output of lignite and its combustion in ower plants.

The investigated sites of mosses are significantly differing in respect of dust fall (Table 1). The least dust fall has been found on site 3 (137 g/m²/year) and 1 (180 g/m²/year) and the greatest on site 11 (610 g/m²/year). According to Ciechanowicz (1994) allowable dust fall (except of areas specially protected) is 200 g/m²/year. This criterion satisfies site 3 and 1. Dust fall on site 2 is also low, however it slightly exceeds the allowable value. The remaining sites are characterized by an increased or high dust fall, from

TABLE 1. Average values of dust fall and contents of heavy metals in the dust.

Site number	Dust fall [g/m ² /year]	Pb	Cd	Cu	Zn
		[mg/kg]			
1	180	1460	18	810	2870
2	210	1105	14	795	3050
3	137	1640	13	865	2800
4	270	3360	20	1050	3950
5	245	3400	18	1105	3700
6	292	3840	22	1205	3500
7	460	8050	64	7250	12 600
8	520	7960	48	4460	4380
9	485	11260	120	7060	14 700
10	550	2560	32	1601	5700
11	610	3405	38	1540	5205
12	470	3870	31	1860	5110
F	65.7	170.6	42.8	54.2	72.2
F _{0.05}			2.22		
LSD	28	362	3	87	136

Fig. 1. Map of Lower Silesia area, showing the main locations of the examined sites.

Fig. 2. Tree diagram of similarity of examined localities.

245 g/m²/year on site 5 to 610 g/m²/year on site 11. On the basis of chemical analyses of dust it was found that these sites are different in respect of Pb, Cd, Cu and Zn contents (Table 1). The differentiated contents of the particular metals in dust are connected with the character of dust sources. For sites of municipal-agglomeration areas is slightly higher in respect of heavy methods contents (group II) in relation to sites from control areas (group I). Instead, high values and a large differentiation in respect of contents of metals characterize sites from the remaining groups (III, IV). Sites localized on territories of copper processing (7, 8 and 9) are characterized by the highest content of heavy metals, several times higher than in the remaining sites, except Zn on site 8. Sites 10, 11 and 12 are characterized by the highest content of Zn in dust and high contents of Pb and Cu.

On the ground of values of dust fall and contents of heavy metals in dust similarity of sites has been determined (Fig. 2). The applied method of cluster analysis is suitable in exploration geochemistry and is more often used than other classification methods (Hongjin et al. 1995). Clusters of sites in tree similarity have been found. The group formed by sites 7, 8 and 9 strays most from the remaining ones. These sites are characterized by high contents of heavy metals.

All the moss samples occur in one climatic zone, i.e. in southwestern Poland. They were collected at the same time and were subjected to the same chemical analyses. This enabled their comparison in respect of heavy metals contents (Herpin et al. 1996).

Mosses accumulate in their tissues larger amounts of heavy metals than higher plants (Grodzińska et al. 1999; Grodzińska, Szarek-Lukaszewska 2001; Fernandez J.A., Carballeira A. 2001). Chemical analyses have shown, that the chemical composition of gametophytes in mosses *Pleurozium schreberi*, *Hylocomium splendens* and *Hypnum cupressiforme* is related to the pollution of environment with heavy metals and amount of dust fall.

The average contents of elements in mosses is shown in Tables 2, 3 and 4. In all the cases a significant difference in contents of elements between the analysed localities has been recorded. A similar differentiation of elements contents in mosses was described by Steinnes (1995), Fernandez et al. (2000), Fernandez, Carballeira (2001) and Reimann et. al. (2001).

Species of examined mosses from sites 7, 8, 9 (group III) are characterized by higher content of Al, Mn, Fe and Mg than mosses from sites 1, 2, 3 (group I). *Hylocomium splendens* from sites 7, 8, 9 (group III) contains also more Ca and Na in comparison to sites site 1, 2, 3 (group I). *Pleurozium schreberi* and *Hypnum cupressifome* from sites 7, 8 and 9 are characterized by higher content of K in relation to sites 1, 2 and 3 (Table 2, 3 and 4).

Worthy of notice is the contents of Cu, Pb, Ni, Cd and Zn in the examined mosses. Mosses from sites 1, 2 and 3 are characterized by a lower content of these elements than the remaining sites, particularly sites 7, 8 and 9 with the highest contents of these metals, which considerably exceed the values given by Gydysen et al. (1980) for Sweden, Denmark and Greenland, and according to Berg et al. (1995) for most sites in Norway. According to Herpin et al. (1996) and Grodzińska et al. (1999) the mentioned above average content values of of these metals are situated within the range of contents of these elements in mosses from Poland.

Using the cluster analysis, the similarity of populations in respect of metal concentrations in mosses has been de-

TABLE 2. Average concentrations of elements and cationic equilibrium in *Pleurozium schreberi*.

Site number	Ca	K	Na	Mg	Al	Mn	Fe	Cu	Pb	Ni	Cd	Zn	Cationic equilibrium
[mg/kg d.wt.]													
1	1254.23	2640	2460.58	1300.3	350.1	86.52	870	10.2	21	1.2	0.3	42	12.41
2	1864.51	2500	2700.26	1420.7	459.7	62.83	920	14.3	19	2.8	0.4	47	12.70
3	1463.33	1940	2164.55	1200.1	379.8	44.29	765	11.5	23	2.2	0.3	39	12.63
4	2401.00	2950	2468.39	1755.0	870.3	65.92	1640	16.4	47	3.9	0.6	64	12.51
5	2600.50	3120	3045.93	1470.6	950.2	74.16	1700	15.3	51	3.2	0.7	69	12.58
6	2107.24	3505	3210.22	1355.6	1079.8	96.82	1580	12.1	42	3.3	0.6	58	12.44
7	1668.62	2680	2405.63	1750.8	2639.9	185.40	4550	27.4	50	6.4	3.2	107	10.71
8	1945.35	2964	2461.12	1700.2	3100.4	202.91	3890	24.6	57	4.8	3.8	89	11.10
9	2410.27	3210	2764.61	1630.3	2869.7	177.16	4290	19.4	53	4.3	2.9	85	11.28
10	1657.02	3600	3490.25	1450.5	1840.2	97.85	1320	9.2	31	2.1	1.4	74	12.19
11	1952.19	3480	2950.67	1200.7	1640.3	110.21	1405	12.1	27	2.4	1.7	71	12.40
12	2010.74	3260	3280.45	950.3	1569.8	75.19	1935	8.1	24	1.2	0.4	42	12.14
F	98.2	36.5	101.5	35.2	13.3	42.2	8.4	63.1	8.6	10.3	2.5	9.8	67.4
F _{0.05}	2.22												
LSD	594.33	511	596.24	192.5	165.4	28.31	142	5.9	5.6	1.1	0.19	8.2	0.83

TABLE 3. Average concentrations of elements and cationic equilibrium in *Hylocomium splendens*.

Site number	Ca	K	Na	Mg	Al	Mn	Fe	Cu	Pb	Ni	Cd	Zn	Cationic equilibrium
	[mg/kg d.wt.]												
1	1265.24	2824	2464.36	1435.6	512.2	49.31	940	11.2	17	0.9	0.33	39	12.35
2	1792.33	2365	2745.22	1425.5	533.3	59.74	1050	13.5	15	1.9	0.36	43	12.56
3	1515.10	2043	2459.54	1280.4	491.4	47.38	780	12.3	18	2.1	0.54	41	12.60
4	2484.22	2768	2578.30	1730.2	658.3	86.65	1580	14.7	29	3.4	0.58	49	12.57
5	2561.45	3371	3386.75	1510.2	887.2	71.07	1710	16.1	37	3.5	0.82	58	12.55
6	1958.56	3455	3542.66	1420.9	965.4	89.61	1630	11.1	33	2.9	0.67	59	12.32
7	1532.28	2798	3186.21	1985.0	1886.7	197.76	5400	19.5	41	5.9	2.81	94	10.50
8	1847.33	2936	2945.08	1785.7	2854.6	200.85	4840	28.4	45	5.4	3.44	88	10.80
9	2320.67	3132	2854.24	1670.8	2736.3	191.58	5160	21.1	40	6.2	3.13	81	10.98
10	1945.20	3614	3225.23	1440.5	1568.9	105.06	1250	11.6	28	2.1	1.81	69	12.45
11	1655.12	3496	3107.72	1285.4	1610.0	104.03	1530	10.3	25	1.9	1.43	70	12.16
12	1986.84	2987	3256.64	1205.2	1520.3	97.55	1890	8.9	24	1.4	0.82	45	12.14
F	227.9	19.9	96.4	88.1	22.8	17.8	21.9	13.5	11.2	7.9	3.8	27.3	96.7
F _{0.05}	2.22												
LSD	603.26	476	331.65	163.7	49.7	26.45	337	5.8	7.5	1.3	0.24	5.2	1.05

TABLE 4. Average concentrations of elements and cationic equilibrium in *Hypnum cupressiforme*.

Site number	Ca	K	Na	Mg	Al	Mn	Fe	Cu	Pb	Ni	Cd	Zn	Cationic equilibrium
	[mg/kg d.wt.]												
1	1217.84	2640	2341.79	870.2	354.2	44.51	890	15.5	29	1.0	0.36	56	12.44
2	1765.92	2500	2588.99	961.4	474.1	41.23	960	21.5	32	2.0	0.36	61	12.68
3	1477.84	1940	2036.91	794.2	386.9	38.07	785	17.1	34	2.1	0.60	28	12.72
4	2485.60	2950	2350.03	1216.0	921.0	51.02	1820	28.6	61	3.6	0.60	70	12.50
5	2565.68	3120	2944.34	999.4	1008.2	68.60	1760	28.8	75	3.7	0.96	84	12.56
6	1938.56	3505	3114.29	912.0	1149.9	64.21	1690	27.1	69	3.1	0.72	88	12.31
7	1495.52	2680	2285.14	1212.2	2850.3	180.55	5125	42.6	87	6.2	3.36	143	10.36
8	1823.12	2964	2342.82	1174.2	3351.7	184.73	4294	61.4	84	5.8	4.08	130	10.83
9	2315.04	3210	2654.91	1121.0	3101.0	171.11	4501	48.2	81	6.4	3.72	117	11.11
10	1925.04	3600	3402.69	984.2	1978.3	84.29	1284	21.4	61	2.3	2.16	97	12.35
11	1623.44	3480	2846.49	794.2	1760.3	94.08	1645	18.3	47	1.8	1.68	98	12.07
12	1967.68	3260	3186.39	604.2	1684.0	57.43	1896	14.2	42	1.4	0.96	58	12.09
F	183.5	47.2	194.2	73.5	18.9	52.4	68.4	2.3	4.5	3.3	2.9	31.4	71.2
F _{0.05}	2.22												
LSD	512.77	326	363.57	93.8	131.2	19.14	189	6.3	15	1.1	0.32	19	0.92

terminated (Fig. 3, 4 and 5). Populations 7, 8 and 9 showing high contents of metals, particularly Cu, Pb, Ni, Cd and Zn, form a group of least similarity in relation to the remaining populations. Populations 1, 2 and 3 form another group

characterized by lowest contents of these metals. The tree diagrams of population similarity (Fig. 3, 4 and 5) correspond with the diagram of sites' similarity (Fig. 1). The tree diagrams confirm the relation between distribution of

Fig. 3. Tree diagram of similarity of *Pleurozium schreberi* populations.

Fig. 4. Tree diagram of similarity of *Hylocomium splendens* populations.

Fig. 5. Tree diagram of similarity of *Hypnum cupressiforme* populations.

Fig. 6. Values of cationic equilibrium in examined populations of mosses.

emission sources and contents of metals (particularly heavy metals) in mosses from various sites in Lower Silesia. Hence, the investigated populations of *Pleurozium schreberi*, *Hylocomium splendens* and *Hypnum cupressiforme* reflect the difference in environmental pollution, with respect to metals' contamination.

The variable and high contents of metals in plants and their quantitative relations influence the cationic equilibrium. The value of cationic equilibrium for plants growing on non-contaminated areas is 12.515 (Czarnowski 1977). In mosses from sites 7, 8 and 9 (group III) the cationic equilibrium ranges within 10.36 (site 7) to 11.28 (site 9). Sites 10, 11 and 12 (group IV) show higher values of cationic equilibrium, from 12.07 (site 11) to 12.45 (site 10). The values of cationic equilibrium in group I and II are closer to 12.515 (from 12.31 site 6 to 12.72 site 3).

The concentration of one cation in plant tissue is the function of concentration other cations. Thus, the concentration of heavy metals in mosses from populations growing on industrially polluted localities is the reason of changes in cationic equilibrium. This effect has been examined earlier in plants of *Scapania undulata* (Samecka-Cymerman 1988). Therefore, we can state that the calculation of cationic equilibrium value in mosses can be a valuable test of environmental pollution and is of importance for the active protection of mosses and their biotopes.

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ZABURZENIA RÓWNOWAGI JONOWEJ W MCHACH OBSZARÓW SKAŻONYCH

STRESZCZENIE

Mchy są wrażliwymi i precyzyjnymi bioindykatorami skażenia środowiska metalami ciężkimi. Celem badań było określenie stopnia skażenia środowiska opadającym pyłem w szczególności metalami ciężkimi oraz jak to skażenie wpływa na równowagę kationową w mchach *Pleurozium schreberi*, *Hylocomium splendens* i *Hypnum cupressiforme*. Do badań wytypowano 12 stanowisk znajdujących się na terenach przemysłowych, miejskich i pozostających poza bezpośrednim wpływem skażeń na Dolnym Śląsku. Wykazano, że badane stanowiska różnią się istotnie pod względem opadu pyłu i zawartości Pb, Cd, Cu i Zn w pyle. Stwierdzono również zróżnicowanie populacji mchów pod względem zawartości Ca, K, Na, Mg, Al, Mn, Fe, Cu, Pb, Ni, Cd i Zn. Wysoka zawartość Pb, Cd, Cu i Zn w gametofitach mchów odpowiada wysokiej zawartości tych pierwiastków w pyle. Zwiększona zawartość metali ciężkich w mchach na różnych stanowiskach zaburza ich równowagę kationową. Na stanowiskach skażonych wartość równowagi kationowej w roślinach jest niższa, tj. od 10,36 do 11,28. W roślinach ze stanowisk pozostających poza bezpośrednim wpływem emisji wartość ta wynosi od 12,31 do 12,72 i jest bliższa wartości $const. = 12,515$ podawanej jako typowa dla roślin wyższych. Ustalenie wartości równowagi kationowej może być wartościowym testem ukazującym skażenie środowiska.

SŁOWA KLUCZOWE: *Pleurozium schreberi*, *Hylocomium splendens*, *Hypnum cupressiforme*, metale ciężkie, równowaga kationowa, bioindykacja, skażenie środowiska.