HEAVY METAL DEPOSITION IN POLISH NATIONAL PARKS – CHANGES DURING TEN YEARS

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(Received June 28, 1989; revised November 10, 1989)

Abstract. Biomonitoring studies of heavy metals (Cd, Cr, Ni, Pb, Cu, Zn, Fe, Mn) and other elements (Mg, Na, K, Ca) were done in all Polish national parks in 1976 and again in 1986. Two moss species (Pleurozium schreberi and Hylocomium splendens) were used to estimate the concentrations of these elements, mainly derived from atmospheric deposition. Significant differences were found between particular parks in the concentration of heavy metals and nutrients, the lowest concentration being recorded in the mosses from the parks in northern and eastern Poland, the higher ones in the southern parks. Significant differences in the content of elements were also observed between the green and brown parts of mosses, between moss species and between years of sampling.

1. Introduction

Mosses are very precise and sensitive bioindicators of heavy metal deposition in the environment (Tyler, 1971, 1972; Maschke, 1981; Grodzińska, 1982). They are used for long-term ecological monitoring in many countries – in Scandinavia (Rühling and Tyler, 1971, 1973, 1974; Pakarinen and Tolonen, 1976; Pilegaard *et al.*, 1979; Gydesen *et al.*, 1983; Rühling *et al.*, 1987), in Western Germany (Thomas and Hermann, 1980; Hermann, 1976) and in Poland (Grodzińska, 1978; Berbeka and Godzik, 1982; Godzik, 1988).

The aim of this paper is to present the levels of heavy metal contamination of Polish national parks in 1986 using mosses and to compare the results with those of 1976 (Grodzińska, 1978).

2. Material and Methods

The mosses Pleurozium schreberi (Brid.) Mittl. and Hylocomium splendens (Hedw.) B.S.G. were collected in 14 national parks in Poland in the autumn of 1986 (Figure 1, Table I). In each park the material was sampled both in central and peripheral areas in the same plots as in 1976. Unwashed mosses were separated into green and brown parts. The green parts usually represented 2 yr increments whereas the brown parts were older (2 to 5 yr). Samples were dried at 85 °C, and wet digested in 4:1 mixture of concentrated nitric and perchloric acids. Cadmium, Cr, Ni, Pb, Cu, Zn, Fe, Mn, and Mg, Ca, K, and Na were determined using a Varian Techtron 1000 atomic absorption spectrophotometer. Detailed procedure of sampling and chemical analysis can be found in Grodzińska (1978).

Water, Air, and Soil Pollution **49**: 409–419, 1990.

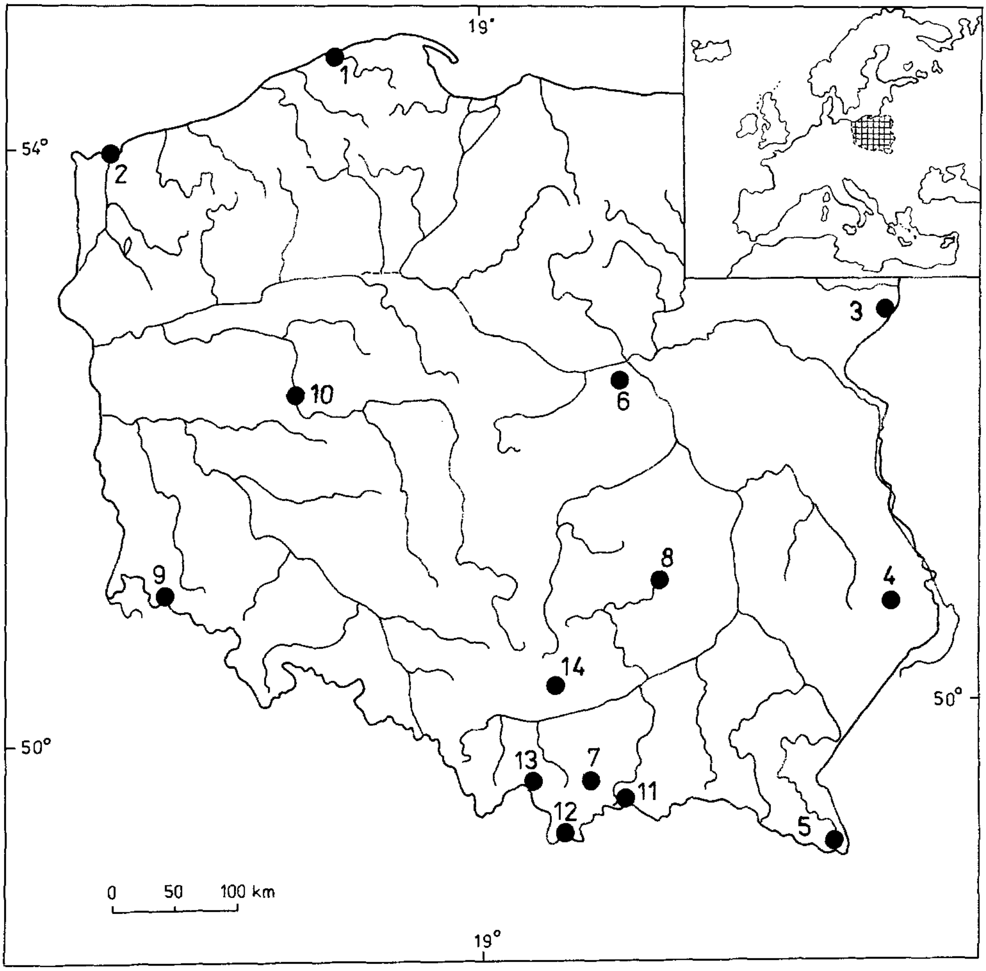

Fig. 1. The location of Polish national parks. (1) Słowiński, (2) Woliński, (3) Białowieża, (4) Roztocze, (5) Bieszczady, (6) Kampinos, (7) Gorce, (8) Świętokrzyski, (9) Karkonosze, (10) Wielkopolski, (11) Pieniny, (12) Tatry, (13) Babia Góra, (14) Ojców.

3. Results

3.1. Heavy metal concentration in mosses

Pleurozium schreberi and Hylocomium splendens accumulated Cd, Cu, Zn and Fe in similar amounts and showed significant differences in accumulation levels of Cr, Ni, and Pb (Table II). Pleurozium schreberi accumulated more of these three elements per dry weight unit than Hylocomium.

Significant statistical differences were found in the concentrations of heavy metals between younger (green) and older (brown) parts of both moss species (Table II).

Significant differences were found in the metal accumulation by mosses between

TABLE I

General characterization of Polish national parks

Name of park	Altitude above sea level (m)	Annual sum of precipitation (mm)	Area (ha)
Słowiński NP.	0 - 56	619	18247
Woliński NP.	0 - 115	581	4844
Wielkopolski NP.	55 - 132	501	5198
Kampinos NP.	60 - 106	500	35482
Białowieża NP.	147 - 170	585	5317
Roztocze NP.	300 - 390	710	6843
Świętokrzyski NP.	260 - 611	560 - 660	5897
Ojców NP.	305 - 478	791	1592
Karkonosze NP.	410 - 1605	1158	5562
Babia Góra NP.	800 - 1725	960 - 1400	1741
Tatry NP.	800 - 2499	1112 - 1810	21164
Gorce NP.	600 - 1310	900 - 1220	5945
Pieniny NP.	420 - 982	805	2328
Bieszczady NP.	630 - 1346	1035	5587

the national parks of Poland (Table II, Figure 2). The highest variations between parks were observed in Pb, Fe and Mn (5 times), smaller in Ni. The concentration of most metals was highest in the mosses from Tatry, Babia Góra and Ojców NP, while the lowest concentrations were measured in mosses from Słowiński, Woliński, Białowieża and Roztocze NP (Figure 2). In the first group of parks the concentration of Cd in Pleurozium ranged from 1.3 to 1.9 $\mu g\ g^{-1}$, in the second group it was from 0.4 to 0.78 $\mu g\ g^{-1}$. The concentrations of Cr were, respectively, 8.1 to 8.7 and 2.7 to 3.6, Ni 4.0 to 7.1 and 2.3 to 3.1, Pb 68 to 101 and 22 to 39, Zn 100 to 136 and 36 to 64, Fe 2110 to 3098 and 657 to 930 $\mu g\ g^{-1}$ (Figure 2). The largest amount of Cu was found in the mosses from the Karkonosze and the Wielkopolski NP, that of Mn from Wielkopolski and Bieszczady NP (Figure 2).

In order to evaluate the general degree of metal contamination of all parks a pollution index was used (Figure 3). It represents the mean standarized contents of 6 elements in mosses (Cd, Ni, Cr, Cu, Pb, Zn). According to this index the parks were classified as relatively clean, moderately contaminated and heavily contaminated (Table III, Figure 3). The first category represents the maritime parks and parks from Eastern Poland (Słowiński, Woliński, Białowieża, Roztocze, Bieszczady), where the index ranged from -0.50 to -0.23. Parks located in the lowlands (Kampinos, Wielkopolski) and some parks in the mountains (Gorce, Świętokrzyski, Karkonosze, Pieniny) were considered moderately contaminated with the index ranging from -0.14 to 0.22. Heavily cotaminated were some parks in Western Carpathians (Tatry, Babia Góra) and in the highland (Ojców) with the index of 0.37 to 0.57 (Table III, Figure 3).

The degree of contamination of parks by the respective heavy metals was also estimated. The parks were arranged in order of increasing concentrations in the

TABLE II

Statistical analysis of the differences in metal concentrations between Pleurozium (P) and Hylocomium (H)

Element	F values and level of significance								
	Species		Parts of mosses (green/brown)		Central and peripheral zones of parks		Parks		Years
	1976	1986	1976	1986	1976	1986	1976	1986	
Cd	131.68[b]	4.40	3.63 P	8.56 P[a]	3.30 P	0.01 P	144.80 P[b]	3.72 P[a]	5.73 P[a]
			0.08 H	9.58 H[a]				2.04 H	
Ni	1.26	6.25	48.93 P[b]	43.81 P[c]	18.17 P[b]	6.87 P[a]	33.51 P[b]	5.33 P[b]	2.93 P
			19.99 H[b]	22.16 H[b]		0.35 H		2.75 H	
Cr	0.81	7.36[a]	35.56 P[b]	37.21 P[c]	31.91 P[b]	1.88 P	27.72 P[b]	2.15 P	5.59 P[a]
			10.96 H[b]	22.94 H[b]				1.02 H	
Cu	166.60[b]	1.35	17.87 P[b]	0.75 P	49.70 P[b]	2.58 P	61.55 P[b]	2.51 P	5.14 P[a]
			13.31 H[b]	4.48 H		0.12 H		1.56 H	
Pb	9.89[a]	8.58[a]	14.41 P[b]	41.90 P[c]	101.98 P[b]	0.18 P	200.77 P[b]	1.88 P	9.64 P[b]
			45.04 H[b]	54.23 H[c]		0.09 H		5.24 H[a]	
Zn	8.67[a]	1.29	3.98 P	43.23 P[c]	202.49 P[b]	0.45 P	384.96 P[b]	3.95 P[a]	9.37 P[a]
			6.48 H[a]	14.48 H[b]		1.18 H		1.83 H	
Fe	7.37[a]	1.04	38.93 P[b]	56.15 P[c]	46.00 P[b]	2.89 P	62.00 P[b]	4.48 P[a]	1.95 P
			41.15 H[b]	8.20 H[a]		0.38 H		0.73 H	
Mn	5.75	0.94	0.75 P	9.06 P[a]	19.74 P[b]	93.70 P[c]	43.57 P[b]	77.30 P[c]	11.40 P[b]
			0.28 H	8.82 H[a]		2.33 H		13.20 H[b]	
Mg	–	0.75	13.60 P[b]	2.05 P	135.00 P[b]	0.04 P	13.90 P[b]	0.83 P	0.36 P
			3.79 H	0.01 H[a]		4.08 H		1.25 H[b]	
Na	–	0.89	170.00 P[b]	0.85 P	394.00 P[b]	0.01 P	837.00 P[b]	8.53 P[b]	13.09 P[b]
			4.60 H[a]	5.73 H[a]		1.27 H		1.07 H	
K	–	0.41	44.00 P[b]	6.71 P[a]	0.99 P	0.14 P	38.00 P[b]	6.57 P[b]	1.73 P
			6.06 H[a]	8.39 H[a]		0.74 H		4.12 H	
Ca	–	0.72	7.20 P[a]	4.56 P	423.00 P[b]	2.56 P	210.00 P[b]	0.78 P	4.14 P
			0.19 H	1.75 H		0.25 H		0.40 H[a]	

[a] $P < 0.05$.
[b] $P < 0.01$.
[c] $P < 0.001$.

mosses. Using Duncan's test of multiple intervals, groups of parks were distinguished which differed statistically in heavy metal content of mosses.

These groups differ significantly in the content of Mn, and not so well of Cd, Pb, Zn, and Cu. The Ojców, Tatry and Babia Góra NP still represent the most heavily contaminated parks, while the Słowiński, Woliński, Białowieża and Roztocze NP belonged to the relatively clean ones. A specificity in the contamination of parks was found. The Karkonosze and Wielkopolski NP were greatly polluted by Cu, and Gorce NP by Ni and Fe.

The concentration of metals was higher in mosses collected from the peripheral zones of parks, but these differences (excl. Ni) were not significant statistically (Table II).

3.2. Other metals

Other metal (Na, K, Ca, Mg) concentrations of the mosses was also determined. Concentrations of Na, Ca and K were different ($p<0.01$) between the particular parks (Table II).

The concentration of Na ranged from 42 to 208 ($\overline{X}$ = 100) μg g^{-1}. The highest content of this element was found in the two maritime parks (Słowiński, Woliński). The K content of mosses ranged from 807 to 2972 ($\overline{X}$ = 1700) μg g^{-1}. In northern and eastern Poland the concentration of this element was lower (about 1000 μg g^{-1}), in the southern part of the country it was 2.5 times higher. The mean concentration of Mg in mosses was about 1000 μg g^{-1}. The mosses from parks located in the mountain showed the highest content of this element. The Ca content of mosses in most parks ranged from 1000 to 2000 μg g^{-1}. Only in samples from calcareous areas (Tatry, Pieniny, Ojców) the values were higher (3000 to 7000 μg g^{-1}) (Table IV).

Differences in concentration between central and peripheral park areas, as well as between species, were not statistically significant (Table II).

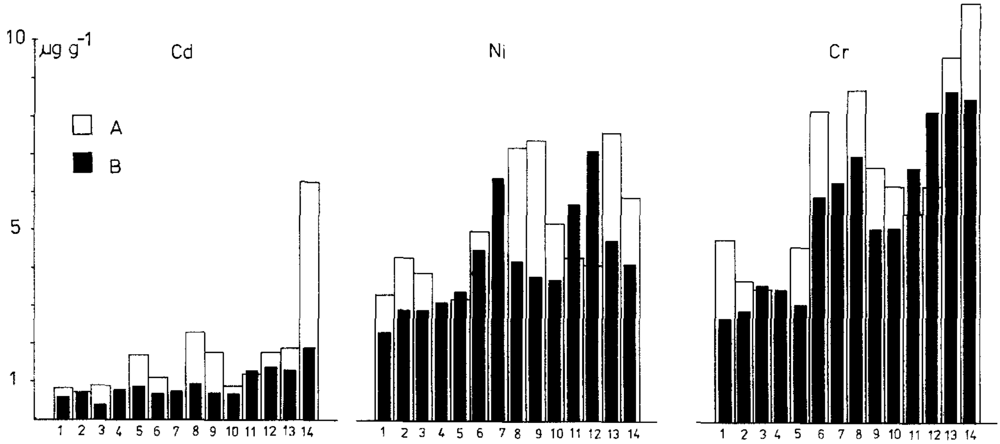

Fig. 2.

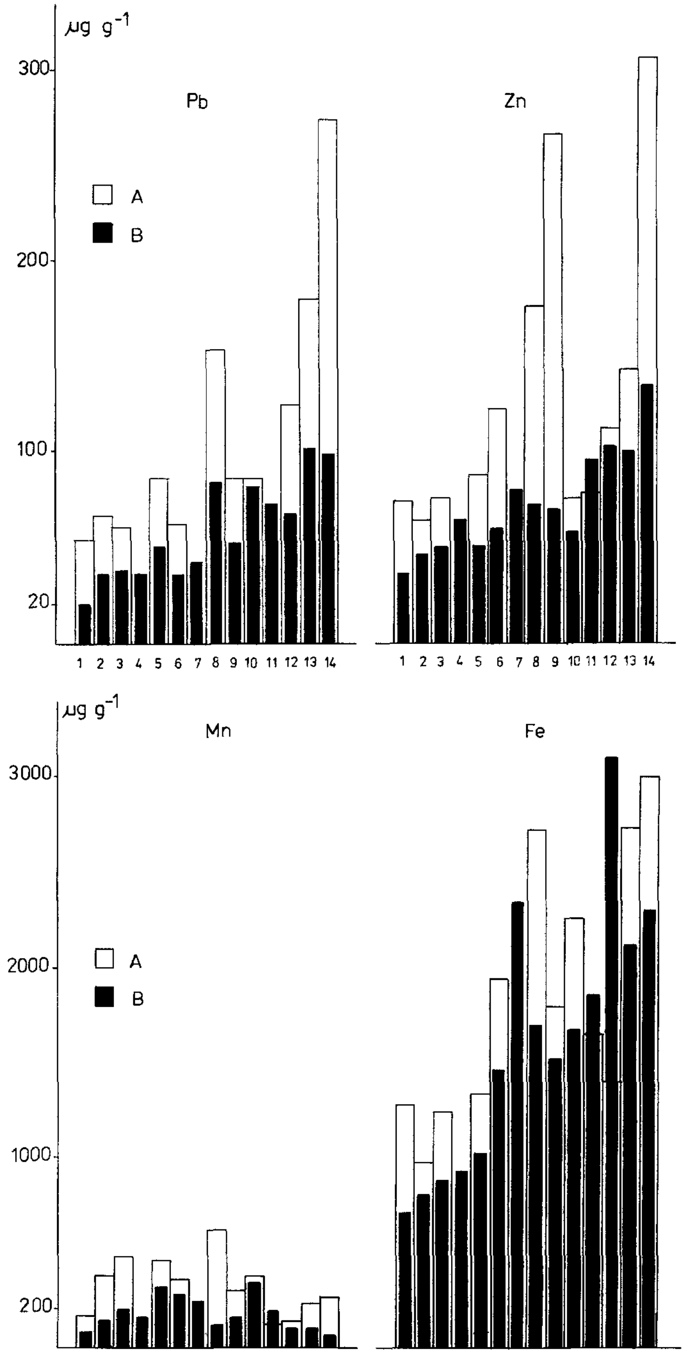

Fig. 2. Cd, Ni, Cr, Pb, Zn, Mn, Fe ($\mu g\ g^{-1}$ d.w.) concentrations in Pleurozium schreberi in Polish national parks. the mean content of metals in green and brown parts of mosses are indicated for both the central and peripheral areas of the parks. (A) 1976, (B) 1986. Parks: see Figure 1.

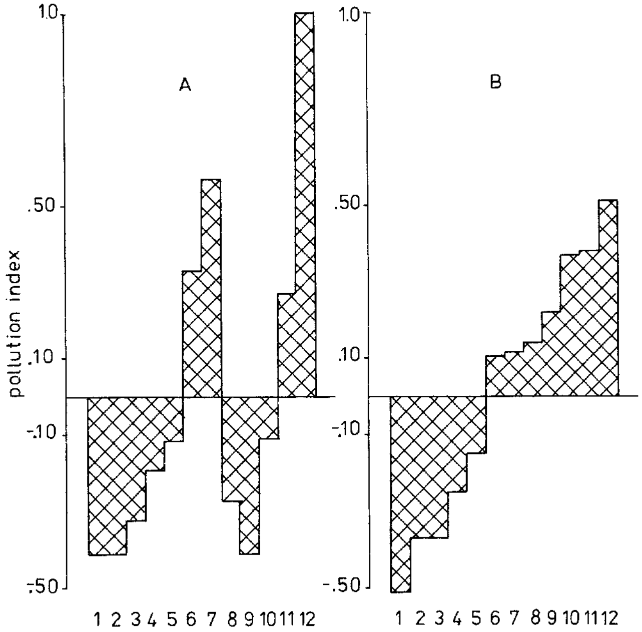

Fig. 3. Pollution index values for 12 Polish national parks defined as a sum of standarized contents of heavy metals in mosses. (A) 1976, (B) 1986. Parks: (1) Słowiński, (2) Woliński, (3) Białowieża, (4) Bieszczady, (5) Kampinos, (6) Świętokrzyski, (7) Karkonosze, (8) Wielkopolski, (9) Pieniny, (10) Tatry, (11) Babia Góra, (12) Ojców. Standarized values (y_{ij}) of i-heavy metal in j-national park is obtained from formula:

$$y_{ij} = \frac{x_{ij} - \bar{x}_i}{\bar{x}_i},$$

where y_{ij} is the content of i-heavy metal in j-national park; $\bar{x}_i$-mean content of i-heavy metal in all parks. Pollution index of j-national park (S_j) is defined according to:

$$S_j = \sum_{i=1}^{\sigma} y_{ij}.$$

TABLE III

Heavy metal concentration (μg g^{-1} d.w.) in Pleurozium schreberi from 3 groups of Polish national parks. Mean concentration of metals in green and brown parts of mosses from central and peripheral areas of parks

Group of parks	Cd	Cr	Ni	Pb	Zn	Fe
relatively clean[a]	0.69	3.16	2.92	37.0	50.0	864
moderately contaminated[b]	0.83	6.00	4.70	62.1	73.4	1756
heavily contaminated[c]	1.54	8.46	5.30	89.4	113.0	2505

[a] Słowiński, Woliński, Białowieża, Roztocze, Bieszczady.
[b] Wielkopolski, Kampinos, Świętokrzyski, Pieniny, Gorce, Karkonosze.
[c] Babia Góra, Tatry, Ojców.

TABLE IV

Concentration of some elements (μg g^{-1} d.w.) in Pleurozium schreberi from Polish national parks The mean content of elements in green and brown parts of mosses are indicated for both the centra and peripheral areas of the parks

Park	Mg		Ca		K		Na	
	1976	1986	1976	1986	1976	1986	1976	1986
Słowiński	913	365	2386	417	3647	807	299	208
Woliński	800	724	2453	994	3826	1032	461	148
Białowieża	1193	854	3203	1513	4705	924	183	68
Roztocze	–	822	–	3099	–	1015	–	70
Bieszczady	1158	1107	4064	3244	6298	847	97	42
Kampinos	1109	996	2991	1590	3900	2140	245	108
Gorce	–	2784	–	3932	–	2451	–	88
Świętokrzyski	1019	595	5931	1914	7518	2097	191	87
Karkonosze	1121	928	3974	2142	7779	2982	359	74
Wielkopolski	977	859	2766	3130	4215	1319	169	89
Pieniny	764	1670	2505	3050	7350	1467	134	77
Tatry	966	3156	3535	7276	6281	1835	120	54
Babia Góra	807	991	2131	2452	6218	2058	150	83
Ojców	993	1034	3471	3050	7486	2758	187	99

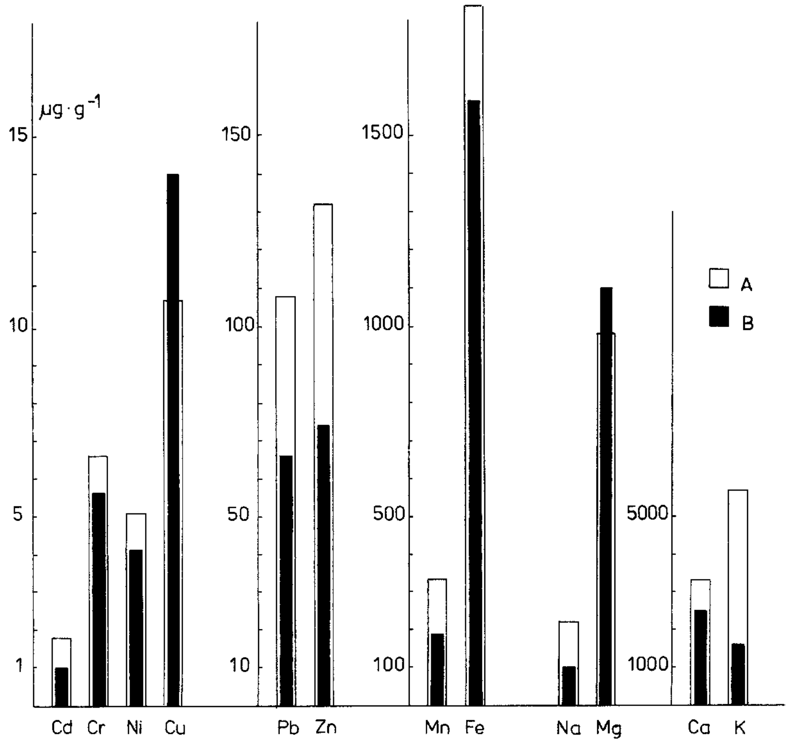

Fig. 4. Changes in metal concentrations in mosses of Polish national parks over 10 yr (A) 1976, (B) 1986.

3.3. Changes in the Contamination of Mosses with Heavy Metals over the Decade 1976–1986

The concentration of heavy metals in Pleurozium schreberi and Hylocomium splendens samples in 12 Polish national parks in 1976 and 1986 was compared and differences over the last 10 yr were found. The concentration of Cd, Pb, Zn and Mn was about 50% lower that of Ni, Cr and Fe about 20 to 30% lower in 1986 than in 1976 (Figure 4). The differences (excl. Ni, Fe) were statistically significant (Table II).

The changes in the contamination of mosses with heavy metals were, however, different in particular parks. In parks heavily contaminated 10 yr ago (Ojców, Karkonosze, Świętokrzyski NP) heavy metal concentrations had decreased in 1986. In the parks moderately and slightly contaminated in 1976 (e.g., Bieszczady, Kampinos, Białowieża) the concentration of heavy metals was only slightly lower or unchanged in 1986. In two parks lying in the mountains (Pieniny, Tatry) and also in the Wielkopolski NP the contamination of mosses increased considerably (Figure 4).

The differences in the levels of metals between mosses in the central and border part of national parks were also determined (Table II). The metals occurred always in higher concentration in mosses sampled in the border areas of parks. The differences were statistically significant for all metals (except Cd) in 1976, while in 1986 they were significant for Ni and Mn only (Table II).

Highly significant differences were also found in the concentration of heavy metals between the younger (green) and older (brown) parts of mosses. These differences were most distinct in 1986.

Słowiński NP – the least contaminated park in 1976 and 1986 was used as the 'background' for Poland. Woliński, Białowieża, Bieszczady, and Kampinos NP were about 1.5 times and Ojców NP 3 times more contaminated than the Słowiński NP. Other parks were 1.5 to 2 times more contaminated in 1976, 2 to 3 times in 1986 than the 'back ground'.

The concentration of Na and K in mosses was always lower in 1986 than in 1976, while the Mg and Ca content was in some parks lower and in others higher. The difference was statistically significant in the case of Na only (Table II, Figure 4).

4. Discussion

The contamination of national parks with heavy metals determined by means of mosses corresponds to the distribution of industrial emission in Poland (Leszczycki, 1971; Kassenberg and Rolewicz, 1985; Kassenberg and Marek, 1986). At present among the most polluted are Ojców, Babia Góra, Tatry and Pieniny NP. They are under the emissions from the largest Cracow-Silesian Industrial Region. Moderately contaminated (e.g. Wielkopolski, Kampinos NP) are quite distant from industrial regions, but lie close to the large cities (Poznań Warszawa). The relatively clean national parks (Słowiński, Białowieża, Roztocze, Bieszczady) lie in that part of the country which is least industrialized.

During the last 10 yr the concentration of heavy metals in mosses decreased distinctly in Ojców, Świętokrzyski and Karkonosze NP, while in the Kampinos, Bieszczady and Białowieża only slightly. The contamination of mosses in the mountain parks (Pieniny, Tatry, Babia Góra) and in the Wielkopolski NP increased considerably. The deposition of metallurgical dusts in Poland in 1976 was 173 000 t (0.6 t km^{-2}), in the period of 1980–1984 about 140 000 t (0.4 t km^{-2}), in 1985 and 1980 it reached 170 000 t (0.7 t km^{-2}) (Statistical Yearbook GUS, 1977–1987). The decrease of metallurgical dustfall was most pronounced in the large industrial regions and in adjacent areas. In central and southern Poland this change was much smaller (Statistical Yearbook GUS, 1977–1987). Changes in the contamination of national parks with heavy metals recorded with the mosses correlate with changes in the dust emissions in the period of 1976–1986 in Poland. The mountain parks (Pieniny, Tatry, Babia Góra) are exceptions, however. They are located at the southern border of Poland where they are exposed to additional emissions from Czechoslovakia.

A decrease in the concentration of heavy metals, especially Cd, Pb, in the mosses of Northern Europe over the period of 1968–1985 was also reported from Scandinavia (Gydesen *et al.*, 1983; Rühling and Tyler, 1984; Rühling *et al.*, 1987). These authors also cite data concerning the decrease in the emissions of metallic dusts in various countries of Western and Central Europe. A trend of decrease in the emissions of industrial dusts was the most pronounced in our country in early 1980's due to a recession in the heavy industry. Mosses showed this trend very precisely because they contain dusts deposited during the last 3 or 4 yr.

The differences in the contamination of mosses by heavy metals between particular parks were much more distinct 10 yr ago than at present. This can be explained by the establishment of new local emission sources of dusts in Central and Northern Poland.

The differences in the heavy metal contamination of mosses between central and border parts of parks decreased in 1986 in comparison with 1976. It showed that the whole areas of parks are under the pressure of emissions. The functioning of the ecosystems of these parks is at present at greater risk.

The present increase in the concentration of metals between green (younger) and brown (older) parts of mosses can be explained by the decrease of dust deposition in the early eighties (now brown parts of mosses) and greater dustfall in the mid-eighties (now green parts). The mosses in all Polish national parks are seriously contaminated by heavy metals in comparison with the mosses in Scandinavia (Rühling *et al.*, 1987). Mosses from Polish national parks contained in 1976, 5 to 6 times more Cd and Cr than mosses in northern part of Scandinavia, and about 4 times more Pb and 2 times more Ni and Zn. In 1986 the concentration of these elements was in mosses from Polish national parks 2 to 3 times higher than in Northern Scandinavia. When the cleanest parks in Poland are compared with the areas in

Northern Scandinavia, the accumulation of Pb and Cd 10 yr ago was 4 to 10 times higher and Ni, Cr and Zn 2 to 3 times higher. The present accumulation of all heavy metals was about 2 times higher in this group of parks in comparison with far north. Mosses of heavily contaminated Polish national parks contained 3 to 4 times more Cd, Cr, Pb, and Zn than mosses in Southern Sweden 10 yr ago and 4 times more of these metals at present. It showed that the decreasing of dust emissions in Poland during the last 10 yr was less efficient than in Sweden.

This study has shown that Polish national parks are under the stress of dust emissions containing high amounts of heavy metals.

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