

Original Research

# Multielement Concentration in Mosses in the Forest Influenced by Industrial Emissions (Niepołomice Forest, S Poland) at the End of the 20<sup>th</sup> Century

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## Abstract

Terrestrial moss (*Pleurozium schreberi*) was used as a biomonitor in multielement studies aimed to estimate the present level of contamination of the Niepołomice Forest environment (S Poland), influenced by industrial emissions since the 1950s. The concentrations of 33 elements (life essential – Na, Mg, Al, Cl, Ca, V, Mn, Fe, Ni, Cu, Zn, Br, Mo, Rb, Cr, As, Se; non-essential elements strongly toxic – Cd, Pb; others – Sc, Sr, Ag, Cs, Ba, La, Tb, Hf, Ta, W, Au, Th, U, Sm) were determined. The results of this study showed that at the end of the 20<sup>th</sup> century the Niepołomice Forest was an area with average load of industrial emissions in comparison with mean European values. Various sources of elements (long-range and local emissions, crustal/soil dust, vegetation), which influenced their contents in moss, were discussed. It was found that local emissions and crustal/soil dust were the main sources of elements in *P. schreberi* in the studied area.

**Keywords:** biomonitors, bioindicators, *Pleurozium schreberi*, multielement analysis, Southern Poland

## Introduction

Morphological and physiological properties of mosses on the one hand and the wide geographical distribution of many species and their occurrence in both “clean” and industrial areas on the other make these organisms very useful for assessing the state of the environment permanently changed by human activity [1].

Mosses accumulate in their tissues many chemical substances occurring in the atmosphere. They are particularly efficient accumulators of heavy metals [1-5]. Due to these properties they are used in passive and active, spatial and temporal monitoring in many international, national and local programs. In the European monitoring

program called “Heavy metal deposition in Europe – UNECE ICP Vegetation Project,” [6] two moss species, *Pleurozium schreberi* and *Hylocomium splendens*, were used as indicator species. The content of 10 elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) was reported.

At present the concentrations of many elements, until recently observed but at minimal amounts, are increasing in the environment. To these belong: platinum group, actinide series and lanthanides, or rare earth elements. The lanthanides consist of a group of fifteen homologous metals together with scandium and yttrium. In contrast to what this name suggests, they are not rare at all and lanthanides can be found in most environmental media. However, their soluble concentrations are strongly limited by the low solubility products of lanthanides with carbonate and phosphate. The increasing industrial uses of lanthanides are accom-

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panied by increasing emissions, which mainly end up in the atmospheric deposition. At least in part, they originate from industrial emissions [7]. Thus the determination of their concentration in mosses as indicator species deserves serious attention. Reimann et al. [8, 9] recommend multi-element analysis for assessing the state of the environment under human impact because only this analysis ensures that the original cycling and fate of chemical elements in the terrestrial environment will be understood.

Since the mid 20th century Niepołomice Forest, situated in the southern, highly industrialized part of Poland (Fig. 1), is experiencing the impact of industrial emissions changing with time. They were increasing until the mid 1970s and then decreased [10, 11].

The aim of this study was to determine concentrations of many elements (toxic, life essential and others of unknown significance for living organisms) in *Pleurozium schreberi*, an indicator moss species and, on the basis of these analyses, to assess the present state of contamination of the Niepołomice Forest environment.

## Material and Methods

### Study Area

Niepołomice Forest is a large forest complex (110 km<sup>2</sup>) in southern Poland (49°59' – 50°07'N, 20°13' – 20°28'E), 10-30 km from the urban-industrial agglomeration of Kraków and of about 70 km from the highly industrialized Silesian region (Fig. 1).

### Material

The moss samples (*Pleurozium schreberi*) were collected in Niepołomice Forest in 1998. They originated from 68 sampling sites, regularly distributed in the southern, pine-oak (*Pinus sylvestris*, *Quercus robur*) part of the



Fig. 1. Location of the study area in Poland and sampling sites of moss (*Pleurozium schreberi*) in the Niepołomice Forest.

Forest (Fig. 1). All samples were collected at least 300 m from main roads and human settlements and at least 100 m from smaller roads crossing the forest. Each sample consisted of 5–10 sub-samples which formed one mixed sample. Only green parts of mosses, representing 3-year growth, were used for analyses.

### Chemical Methods

Unwashed moss samples were cleaned from needles, leaves and soil particles, air-dried and again dried at 105°C. For spectrophotometric analyses (AAS – Varian 20BQ) a 2.5 g dry weight (d.wt) sample was used. Samples were mineralized in 35 ml mixture of concentrated HNO<sub>3</sub> and HClO<sub>4</sub> acids, in the proportion 4:1. The obtained solution was evaporated to about 1 ml and next diluted with deionized water to a volume of 25 ml. In this solution 8 elements (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were determined. The concentrations of these elements were determined also in the standard reference material (SRM 1575). Analyses using the AAS method were carried out in the laboratory of the Department of Ecology of the Institute of Botany PAS in Kraków.

For neutron activation analyses, moss samples of about 0.3 g d.wt were heat-sealed in polyethylene foil bags for short-term irradiation and packed in aluminium cups for long-term irradiation. A long irradiation of 100 hr in Ch1 was used to determine Ag, As, Au, Ba, Br, Cs, Hf, La, Mo, Rb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, W and a short irradiation of 2 min in Ch 2 – to determine Al, Ca, Cl, Mg, Mn, Na, V [12]. Neutron activation analyses were performed in the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna (Russia).

### Statistical Analysis

Descriptive statistics and multivariate statistics were applied using standard software STATISTICA.6. Uncorrelated data describing the chemistry of mosses obtained using factor analysis with the principal components method (PCA) for factor extraction. Extracted factors with eigenvalues >1 were varimax rotated. Prior to analysis, data (element concentrations) deviating from normal distribution were transformed using natural logarithms.

## Results

The 33 analyzed elements were divided, following Markert [7], into three groups: life essential elements, non-essential elements - strongly toxic to living organisms and elements of unknown significance for living organisms. The group of life essentials were represented in this study by 17 elements. Of these, 13 (Na, Mg, Al, Cl, Ca, V, Mn, Fe, Ni, Cu, Zn, Br, Mo) are important for all

living organisms, one (Rb) only for plants, and three (Cr, As, Se) only for animals and humans. The second group, non-essential - strongly toxic elements, was represented by two elements (Cd and Pb) and the third group, by 14 elements (Sc, Sr, Ag, Cs, Ba, La, Tb, Hf, Ta, W, Au, Th, U and Sm).

The concentrations of all the above-mentioned elements (mean, median, maximum and minimum values) are listed in Table 1. The range of concentrations of some elements was very wide in mosses from the Niepołomice Forest. The biggest (more than 20-fold difference) was shown by Au, Ag and Ni, and over 10-fold by Sr, Tb, Hf, Cs and Se. Differences between the minimum and maximum concentrations of most elements were generally 3- to 6-fold (Table 1).

The results showed spatial variability of the concentrations of elements in mosses from Niepołomice Forest. However, there was no uniform and distinct pattern of the distribution of elements in the area. In the case of some elements (Fe, Cr) the highest concentrations were found in mosses from the western part of the forest (Fig. 2). The highest concentrations of Pb and V were determined in moss samples from the proximity of roads crossing the forest (Fig. 3), while the maximal values of Cl and U were found in mosses growing in the vicinity of a military base located in the forest (Fig. 4).

Table 2 shows the results of PC analysis. Eight factors (F1 - F8) accounted for 72% of total variability. In factor F1 (15% of total variability) the most significant were Th, Sc and Hf. Factor F2 (14% of total variability) included Cr, Zn, Pb and Cd. Factor F3 (11% of total variability) assembled Mo, Sm, U and La, and factor F4 (10% of total variability) were represented by Cs, Se and Rb. In the next factors F5-F8 the most significant were Ca, Cl, Mg, Au, Ag and Ni.

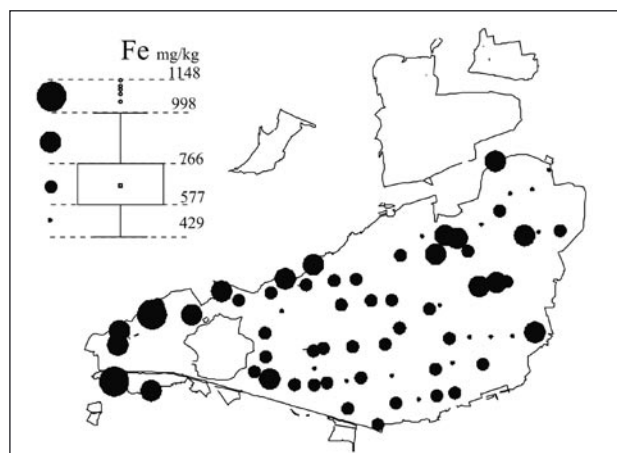


Fig. 2. Iron (Fe) concentration ( $\text{mg kg}^{-1}$ ) in *Pleurozium schreberi* in Niepołomice Forest. The boxplot – based class concentration is represented as follows: the first – the smallest dot minimum/lower whisker to 25<sup>th</sup> percentile; the second dot to 75<sup>th</sup> percentile; the third dot to upper whisker; the fourth-the largest dot to maximum.

### Discussion

Niepołomice Forest is now characterized by an average load of industrial emissions, as shown by a comparison of the concentrations of elements in mosses collected in the forest with those from strongly industrialized and relatively “clean” areas (Table 3).

The mosses from the forest accumulated 4-5 times less La, W and Pb and over twice less V, Zn, Cd, Tb, Ta, Au and Th than mosses from the industrial region (Silesia), and at the same time 8 times more (as much) Cd, 5 times more Cs and over twice more Fe, Cr, Mo, Rb, Au and Ag than mosses from the northern, non-industrialized part of Poland. A comparison between the concentrations

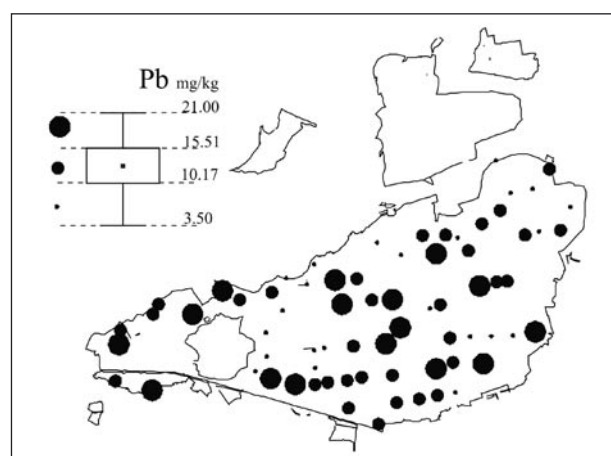


Fig. 3. Lead (Pb) concentration ( $\text{mg kg}^{-1}$ ) in *Pleurozium schreberi* in Niepołomice Forest. The boxplot – based class concentrations is represented as follows: the first – the smallest dot minimum/lower whisker to 25<sup>th</sup> percentile; the second dot to 75<sup>th</sup> percentile; the third dot to upper whisker.

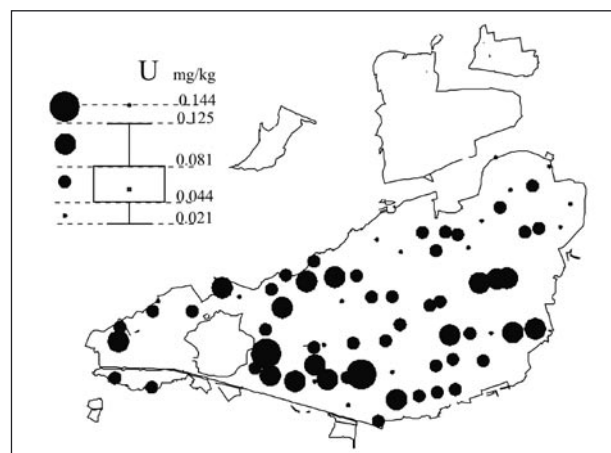


Fig. 4. Uranium (U) concentration ( $\text{mg kg}^{-1}$ ) in *Pleurozium schreberi* in Niepołomice Forest. The boxplot – based class concentrations is represented as follows: the first – the smallest dot minimum/lower whisker to 25<sup>th</sup> percentile; the second dot to 75<sup>th</sup> percentile; the third dot to upper whisker; the fourth - the largest dot to maximum.

Table 1. Element concentrations (mg kg<sup>-1</sup>) in moss (*Pleurozium schreberi*) in Niepołomice Forest.

Element	Average	Median	Minimum	Maximum
Essential elements for living organisms				
Na	214	211	116	376
Mg	1041	1015	376	1996
Al	550	531	199	1196
Cl	356	304	143	1067
Ca	2790	2724	1588	5778
V	1.60	1.56	0.69	2.86
Mn	172	164	52	467
Fe	705	665	429	1148
Ni	1.89	1.75	0.30	6.05
Cu	8.74	8.55	5.25	12.48
Zn	63	60	38	108
Br	1.53	1.44	0.81	2.71
Mo	0.37	0.34	0.14	0.98
Essential elements for plants only				
Rb	51	48	17	95
Essential elements for animals (including man) only				
Cr	2.48	2.36	0.96	4.57
As	0.42	0.38	0.15	0.94
Se	0.40	0.38	0.10	1.02
Non-essential elements – strongly toxic				
Cd	0.73	0.72	0.37	1.07
Pb	12.69	12.83	3.50	21.00
Other elements				
Sc	0.12	0.11	0.08	0.27
Sr	8.64	7.61	1.50	21.21
Ag	0.077	0.063	0.020	0.448
Cs	1.09	1.06	0.23	2.80
Ba	22.53	20.57	8.78	49.29
La	0.52	0.51	0.19	1.12
Sm	0.069	0.066	0.025	0.169
Tb	0.008	0.008	0.002	0.023
Hf	0.121	0.108	0.031	0.441
Ta	0.016	0.014	0.006	0.038
W	0.133	0.119	0.049	0.362
Au	0.011	0.008	0.002	0.054
Th	0.103	0.090	0.057	0.214
U	0.063	0.057	0.021	0.144

Table 2. Results of factor analysis after varimax rotation of element concentrations in moss (*Pleurozium schreberi*) in Niepołomice Forest.

Factors	1	2	3	4	5	6	7	8
% of variance	15	14	11	10	8	5	5	4
Na	0.26	-0.04	0.54	0.33	0.22	0.35	-0.06	0.28
Mg	0.09	0.09	-0.03	-0.04	<b>0.89</b>	0.12	-0.02	-0.05
Al	0.47	0.45	0.18	-0.14	-0.07	0.27	0.13	0.28
Cl	-0.18	0.07	0.11	0.07	<b>0.85</b>	-0.06	0.02	0.10
Ca	0.33	0.09	-0.03	-0.11	<b>0.78</b>	0.04	0.01	-0.12
V	0.27	0.19	0.22	-0.19	0.27	-0.30	0.17	0.49
Mn	0.03	0.44	-0.10	-0.19	0.39	0.24	-0.31	-0.13
Fe	0.27	0.69	0.13	-0.18	0.08	0.24	0.13	-0.09
Ni	0.16	0.08	0.15	0.00	-0.17	-0.02	-0.22	<b>0.76</b>
Cu	0.01	0.58	0.1	0.54	0.10	0.36	0.02	0.10
Zn	0.14	<b>0.78</b>	0.02	0.12	0.09	0.05	0.17	0.20
Br	0.24	0.41	0.49	0.29	0.25	0.32	0.04	0.23
Mo	0.06	0.13	<b>0.82</b>	0.01	-0.19	-0.04	-0.01	-0.11
Rb	0.27	0.02	0.05	<b>0.78</b>	-0.03	0.10	-0.19	-0.22
Cr	0.28	<b>0.79</b>	0.23	0.05	0.13	0.15	-0.17	-0.03
As	0.32	0.18	0.31	0.43	0.03	0.32	0.12	0.28
Se	0.35	0.21	-0.06	<b>0.73</b>	-0.01	-0.06	0.10	-0.09
Cd	0.19	<b>0.71</b>	-0.03	0.37	0.07	0.04	-0.14	-0.03
Pb	-0.09	<b>0.78</b>	0.24	0.05	0.04	-0.25	-0.07	0.08
Sc	<b>0.79</b>	0.28	0.30	0.12	0.04	0.05	0.14	0.11
Sr	0.58	0.23	-0.16	0.29	-0.01	-0.14	-0.50	0.02
Ag	-0.08	-0.04	-0.09	-0.02	-0.01	0.19	<b>-0.74</b>	0.13
Cs	-0.15	-0.02	0.06	<b>0.88</b>	-0.12	-0.12	0.03	0.14
Ba	0.69	0.09	0.18	0.08	0.17	-0.15	-0.29	-0.08
La	0.53	0.18	<b>0.71</b>	0.02	0.09	0.10	0.06	0.15
Sm	0.31	0.21	<b>0.80</b>	0.05	0.01	0.04	-0.04	0.06
Tb	0.49	0.39	0.21	0.11	-0.10	-0.09	0.02	0.22
Hf	<b>0.73</b>	-0.07	0.02	0.13	0.18	0.25	0.14	0.23
Ta	0.69	0.31	0.24	0.01	0.06	0.08	-0.06	0.09
W	0.23	0.33	0.33	0.31	-0.06	0.39	0.25	0.01
Au	-0.02	0.14	0.05	-0.05	0.10	<b>0.75</b>	-0.24	-0.11
Th	<b>0.86</b>	0.04	0.28	0.15	-0.03	-0.01	0.11	-0.01
U	0.13	0.02	<b>0.76</b>	-0.05	0.12	-0.01	0.21	0.21

of elements in mosses from the forest and data reported from several sites in Norway [13] showed that the concentrations of Fe, W, Cr, Th, Ta, Hf and La in moss from Niepołomice Forest were 2-5 times higher than those reported for southern Norway, also affected by low in-

dustrial emissions; the concentrations of the rest of the elements are similar.

The low industrial emissions affecting Niepołomice Forest were confirmed by concentrations of heavy metals and other elements by mosses, as well as tree dam-

Table 3. Comparison of element concentrations (median, mg kg<sup>-1</sup>) in moss (*Pleurozium schreberi*) from various regions (Poland, Norway); NF – Niepołomice Forest; SK – southern Poland, Silesia Industrial Region; CR – northern Poland, non-industrialized region; S – southern Norway, Ualand; C – central Norway, Kärvant; N – northern Norway, Jergul.

Element	Poland			Norway [13]		
	NF	SK	CR	S	C	N
Essential elements for living organisms						
Na	211	198	117	.	.	.
Mg	1015	802	1685	1800	1500	1400
Al	531	1036	538	.	.	.
Cl	304	182	176	.	.	.
Ca	2724	2843	2333	3100	2900	3000
V	1.56	4.04	1.76	0.82	0.77	0.67
Mn	164	84	169	190	160	270
Fe	665	971	279	350	170	160
Ni	1.75	.	.	1.4	0.43	1.7
Cu	8.55	9.97	4.65	8.1	2.4	3.3
Zn	60	168	35	64	26	40
Br	1.44	1.17	1.35	.	.	.
Mo	0.34	0.26	0.15	0.26	0.042	0.038
Essential elements for plants only						
Rb	48	29	16	8.5	12	15
Essential elements for animals (including man) only						
Cr	2.36	3.36	0.79	0.92	0.32	0.25
As	0.38	0.37	0.21	0.26	0.07	0.11
Se	0.38	0.45	0.20	0.85	0.24	0.24
Non-essential elements - strongly toxic						
Cd	0.72	1.90	0.09	0.43	0.077	0.070
Pb	12.83	55	8.9	19	2.3	2.0
Other elements						
Sc	0.11	0.18	0.09	.	.	.
Sr	7.61	9.99	7.01	15	11	7.8
Ag	0.063	0.09	0.03	.	.	.
Cs	1.06	0.99	0.19	0.19	0.39	0.15
Ba	20.57	21.39	13.6	28	22	21
La	0.51	3.02	0.41	0.28	0.15	0.25
Tb	0.066	0.02	0.01	.	.	.
Hf	0.008	0.13	0.11	0.021	0.0077	0.0077
Ta	0.108	0.02	0.01	0.005	0.0013	0.0013
W	0.014	0.64	0.07	0.028	0.0038	0.018
Au	0.119	0.004	0.003	.	.	.
Th	0.008	0.18	0.09	0.045	0.016	0.016
U	0.090	0.10	0.05	0.029	0.011	0.0075
Sm	0.057	.	.	0.039	0.013	0.012

age degree [14], species composition of lichens and a degree of damage to their thalli [15], and composition of soil fauna [16, 17].

In contrast to the 1970s and 1980s, the metal concentrations in mosses from Niepołomice Forest did not show clear gradient depending on a distance from emission sources [18, 19]. The absence of these differences was caused by much lower dust and gas emissions than in previous study periods [10, 11]. On the other hand, the effect of local emission sources (roads crossing the Forest, military base), previously masked by high emissions from more distant areas, has increased.

To identify in different areas the probable sources of elements for mosses, PC analysis is often used [5, 13, 20-23]. The results of PC analysis for 33 elements in mosses from the forest is not unequivocal. It is probably caused by the overlapping of effects of long-distance (Silesian and Kraków agglomerations) and local emissions (military base inside the forest, traffic on roads crossing the forest) in such small areas as Niepołomice Forest. Nevertheless, one may conclude that the main sources of elements accumulated by these plants are soil dust (F1) and industrial contaminants (F2, F3). Some elements may originate from both these sources. The concentrations of W, Th, Ta, Hf and La connected usually with crust/soil dust, are much higher in mosses from Niepołomice Forest those in mosses from "clean" areas. It seems, therefore, that in addition to natural soil dust, contamination may also be the source of these elements. The other source of elements for mosses in Niepołomice Forest is vegetation (F4, F5). However, the high concentrations of Rb, Cs and Se (elements that are easily washed out from plants) may originate additionally from soil dust.

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