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Geochemical Background of Selected Trace Elements in Mosses *Pleurozium schreberi* (Brid.) Mitt. and *Hylocomium splendens* (Hedw.) B.S.G. from Wigierski National Park

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Abstract

This article presents the results of study of the moss species *Pleurozium schreberi* and *Hylocomium splendens* from Wigierski National Park (northeastern Poland). To assess the geochemical background of selected trace elements (Al, Ba, Fe, Hg, Mn, Pb, Ti and Zn) in these moss species collected at 12 investigation sites in Wigierski National Park, a formula: mean ± 2 standard deviations and a statistical method defined as iterative 2σ-technique was used. Of these elements, Al and Fe background concentrations are distinctly diverse in the two species examined. Both *P. schreberi* and *H. splendens* shows spatial and inter-species variation in concentrations of elements. The bedrock lithology and soil taxonomy seem to have a great influence on geochemical background values.

Keywords: mosses, plant bioindicators, geochemical background, Wigierski National Park

Introduction

The moss species *Pleurozium schreberi* (Brid.) Mitt. and *Hylocomium splendens* (Hedw.) B.S.G. are widely used for assessing environment quality (mostly based on trace element levels). These species have successfully been applied to monitor pollution sources in Poland and throughout Europe since 1970s [1–4]. Of the features of a good bioindicator, these two species show a wide occurrence in most of the coniferous forests, forming dense, tangled mats. Numerous data derived from different studies give a unique opportunity to draw a comparison, taking into account the methods of sample collection, preparation and analysis.

One of the most crucial issues in biomonitoring studies is to distinguish anthropogenic input (pollution) from natural (geogenic and/or biogenic) concentrations of elements in plant tissues (background). Many studies involving geochemical background of trace elements in mosses have usually been conducted in selected control (unpolluted) areas serving as a reference level for comparison with samples influenced by anthropogenic activity. This approach is often criticized for subjective decision criteria of selecting unpolluted areas that differ in their geology, soil taxonomy, and plant communities, for background assessment.

The methods of background evaluation can be divided into (1) direct, (2) indirect and (3) integrated [5]. The direct (geochemical) ones are based on the analysis of samples recognized as not anthropogenically influenced. The samples may be collected from herbaria, ice-cores, overbank sediments, and from relatively pristine sites. In these studies, the background concentrations are usually presented as mean or median values.

The indirect (statistical) methods encompass different techniques, *i.e.* regression analysis (partial least squares regression analysis) [6], fractal method [7], probability plots [8] and techniques used to eliminate the outliers that

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are considered to be anthropogenically influenced thus creating more normal distribution [9].

Integrated methods of geochemical background evaluation combine both direct and indirect approach. However, the prerequisite for this is that the samples should be collected in pristine areas (*e.g.* national parks, forest ecosystems), restricting purposely the range of obtained data that are subjected to statistical analysis.

The principal objective of this article is to present the geochemical background values evaluated with an integrated method for Al, Ba, Fe, Hg, Mn, Pb, Ti and Zn in two moss species – *P. schreberi* and *H. splendens* collected in Wigierski National Park.

Experimental Procedures

A total number of 11 *P. schreberi* and 7 *H. splendens* samples were collected in 12 sites located in Wigierski National Park in June of 2003. The plant communities within the sites examined represent the fresh mixed coniferous forests – *Peucedano-Pinetum* (site 9) and *Serratulo-Pinetum* (remaining sites) [10]. The sampling design is presented in Fig. 1. During sample collection and preparation, precautions were taken to reduce the possibility of contamination. Moss samples were collected in double paper bags, dried at ambient temperature to avoid decay and developing fungi. After drying at ambient temperature the samples were placed in teflon beakers, rinsed briefly with deionized water, and dried. As a result, outer contamination (pollen, soil particles, cobweb, dead insects, *etc.*) was removed. In most studies, moss samples are not washed because it may lead to removing intracellular soluble elements. However, the surface contamination (geogenic particulates) may greatly influence the results, as shown by Mäkinen in 1994 (cited from [11]). After air-drying, the plant samples were pulverized using a Retsch's blender. The fraction that passed a 0.5-mm sieve was digested with nitric acid (1:1) in a closed microwave system (MDS 81, CEM Corp.).

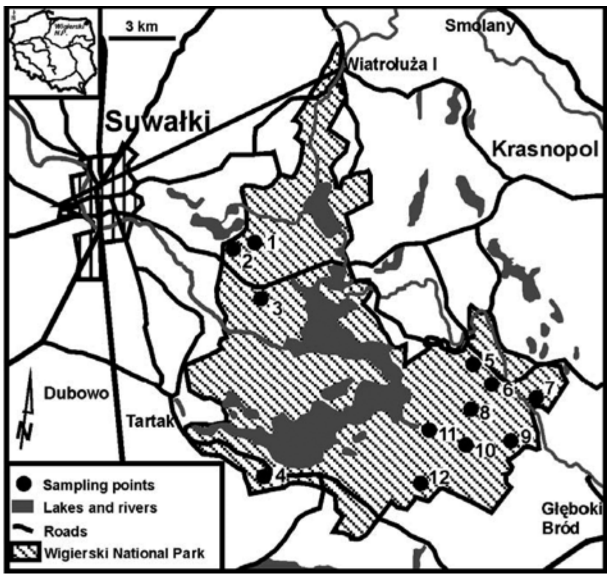

Fig. 1. Location of investigation sites.

Sample preparation and chemical analyses were performed according to methods and techniques used for plants in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw. In order to ensure the quality of results, routine replicate analyses were made, and international standards (Pine Needles 1575, Forrest Litter IPE 858, Tomato Leaves 1573a) were used. For the purpose of this study the samples were analyzed for 7 elements (Al, Ba, Fe, Mn, Pb, Ti, Zn) using inductively coupled plasma-atomic emission spectrometry (ICP-AES; spectrometer Jobin-Yvon model JY 70 PLUS with vertical plasma), and by flame atomic absorption spectrometry (FAAS; spectrometer PU 9100 X UNICAM). In addition, mercury was determined using atomic absorption spectroscopy (AAS; Altec amalgam analyzer AMA 254).

A statistical approach was applied to evaluate geochemical background concentrations [5]. The iterative 2σ-technique is based on the assumption that in the background samples data sets show a normal distribution. First, mean and standard deviation are calculated for the original results. The values that lie outside the range of mean ± 2 standard deviations are omitted and the new mean and standard deviation are calculated. This procedure is repeated until no value is beyond the range: mean ± 2 standard deviations. As described by Matschullat and others [9], this technique constructs an approximated normal distribution around the mode value of the original data set.

Results

The concentrations of selected trace elements in *P. schreberi* and *H. splendens* of Wigierski National Park are presented in Table 1. The element concentration ranges in both species are: 260–717 mg·kg^{-1} Al, 9–37 mg·kg^{-1} Ba, 194–795 mg·kg^{-1} Fe, 53–123 μg·kg^{-1} Hg, 122–837 mg·kg^{-1} Mn, <5–11 mg·kg^{-1} Pb, 2–13 mg·kg^{-1} Ti and 33–54 mg·kg^{-1} Zn.

Most of the elements show a close to normal distribution with a very small tendency to right skewness. Of the elements discussed, only for Ba, Fe and Mn in *P. schreberi* samples the outliers were recorded and eliminated using iterative 2σ-technique. As for the remaining elements, a formula: "mean ± 2 standard deviations" was used for geochemical background calculation. The upper limits of geochemical background (presented in detail with means and standard deviations in Table 2) for the selected trace elements in the moss species examined are as follows:

- 565 mg·kg^{-1} Al, 31 mg·kg^{-1} Ba, 527 mg·kg^{-1} Fe, 123 μg·kg^{-1} Hg, 693 mg·kg^{-1} Mn, 12 mg·kg^{-1} Pb, 10 mg·kg^{-1} Ti and 59 mg·kg^{-1} Zn in *P. schreberi*,
- 824 mg·kg^{-1} Al, 32 mg·kg^{-1} Ba, 918 mg·kg^{-1} Fe, 137 μg·kg^{-1} Hg, 693 mg·kg^{-1} Mn, 12 mg·kg^{-1} Pb, 13 mg·kg^{-1} Ti and 61 mg·kg^{-1} Zn in *H. splendens*.

Discussion

The moss species *P. schreberi* and *H. splendens* of Wigierski National Park show both spatial and interspecies variation in concentrations of elements. Due to the small number of *H. splendens* samples, the concentrations of Al, Fe and Ti are more scattered. There is a lesser diversity in accumulation of elements between *P. schreberi* and *H. splendens* of the same investigation site than between each of these species from different sites (Table 1). This evidence suggests that the main source of these elements in the moss is soil dust and mineral particles [12]. The differences in background concentrations are noted only for Fe and Al in both moss species, with a higher tendency of *H. splendens* to accumulate these metals, *i.e.* Fe (43%) and Al (31%). The background concentrations of the remaining elements either are the same or closely matched.

Of the elements discussed, the strongest positive correlation was recorded in *H. splendens* between the following element pairs: Al and Fe ($R^2 = 0.84$), Hg and Pb ($R^2 = 0.77$), Fe and Ti ($R^2 = 0.74$), Al and Hg ($R^2 = 0.71$). The species *P. schreberi* reveals a somewhat weaker positive correlation between Al and Fe ($R^2 = 0.69$), Fe and Ti ($R^2 = 0.63$), Ba and Mn ($R^2 = 0.61$) as well as Hg and Ti ($R^2 = 0.61$). All these correlations are statistically significant at 0.05 confidence level. It is interesting to note that in both species Fe correlates with Al and Ti. These interrelationships may be linked to a similar source of the element. Ti replaces Fe and Al in biotites, augites and other Fe- and Al-bearing minerals that are common in postglacial deposits, especially in tills and erratic boulders. The soils of Wigierski National Park also show distinct abundance in

Table 1. Concentrations of elements (in dry weight) in *Pleurozium schreberi* and *Hylocomium splendens* at 12 investigation sites of Wigierski National Park (WNP) and at three investigation sites in south-central Alaska.

Site number	Moss species	Al	Ba	Fe	Hg	Mn	Pb	Ti	Zn
		mg·kg^{-1}			µg·kg^{-1}	mg·kg^{-1}			
WNP1.	*P. schreberi*	315	23	353	95	454	6	4	52
WNP2.	*P. schreberi*	325	25	392	88	481	11	6	52
WNP3.	*H. splendens*	697	28	795	120	236	10	13	40
WNP4.	*P. schreberi*	315	20	325	71	311	5	4	45
WNP5.	*P. schreberi*	277	14	341	59	148	5	5	36
	H. splendens	376	9	525	53	122	5	8	33
WNP6.	*P. schreberi*	526	18	629	102	179	9	10	48
	H. splendens	717	18	712	117	221	8	6	54
WNP7.	*P. schreberi*	570	21	526	85	641	8	5	40
WNP8.	*P. schreberi*	373	37	490	123	837	10	10	54
	H. splendens	368	23	257	95	661	9	2	50
WNP9.	*P. schreberi*	398	14	392	69	450	6	4	50
	H. splendens	474	15	365	76	456	7	2	52
WNP10.	*P. schreberi*	412	21	396	58	353	7	4	40
WNP11.	*P. schreberi*	364	12	324	67	124	<5	3	36
	H. splendens	302	14	260	67	138	<5	4	37
WNP12.	*P. schreberi*	349	30	385	93	439	7	5	51
	H. splendens	260	23	194	70	319	5	2	47
Alaska1.	*P. schreberi*	1269	16	1289	134	1188	<5	40	28
	H. splendens	1170	17	1279	101	1356	<5	48	24
Alaska2.	*P. schreberi*	514	58	700	176	772	<5	27	41
	H. splendens	551	48	557	163	389	<5	22	27
Alaska3.	*P. schreberi*	316	52	304	98	892	<5	7	46

For sampling locations in Wigierski National Park, see Figure 1

Ti with geometric mean values varying from 10 mg·kg^{-1} in the organic horizon-Ol to 130 mg·kg^{-1} in the eluvial horizon-E [13]. The main source of Mn and Ba in mosses is leaching from living or dead plant material. This is also evidenced by high bioaccumulation of Mn in Scots pine (*Pinus sylvestris* L.) needles, varying from 90 to 1028 mg·kg^{-1}, and Ba from 1 to 14 mg·kg^{-1} [13]. Hg, Pb and Zn come primarily from the long-range atmospheric transport of pollutants [14].

Despite many studies on the trace element contents in *P. schreberi* and *H. splendens*, only Matschullat and others [9] calculated the geochemical background concentrations with iterative 2σ-technique receiving, for example, 4.4 mg·kg^{-1} for Pb. However, it should be stressed that these results were obtained from a large number of mixed moss samples (*P. schreberi* and *H. splendens*) coming from the Kola Peninsula. Compared to central Europe, the rock formations and soils of this area are depleted in Pb. The other geochemical background concentrations of trace elements for *P. schreberi* and *H. splendens* represent original datasets derived from relatively unpolluted areas. An example of such an approach is the study that also encompassed northeastern Poland [2]. The results obtained were presented as mean values that correspond only to Al in the present study. It should be stressed, that the calculated background concentrations are usually higher as compared to those obtained with direct methods. The slight variation in the background levels for mosses presented by many authors (Table 3) may be due to different methods of sample preparation and analysis, as well as different geologic, geomorphologic, edaphic, hydrologic and climatic factors.

The influence of geologic setting on the moss chemistry is also confirmed by investigations carried out in south-central Alaska (Table 1). The results obtained showed distinct variations in the concentrations of elements induced primarily by diverse geologic setting. In the south-central coastal area of Alaska, glacial and other deposits associated with heavily glaciated alpine mountains are prevalent [15]. This is evidenced by a lesser diversity of element concentrations between *H. splendens* and *P. schreberi* at the same investigation sites than between the same moss species of different sites. Of these two species, *P. schreberi* is highlighted by the widest concentration ranges of Al (316 – 1269 mg·kg^{-1}), Fe (304 – 1289 mg·kg^{-1}) and Ti (7 – 40 mg·kg^{-1}) (Table 3). *H. splendens* of site 1 reveals the element contents that fall in the range recorded by Severson and others in the Kenai Peninsula [16]. It is interesting to note that the levels of Hg are higher in the Alaskan than in the northeastern Poland mosses (Table 1). This seems to be linked to more severe climatic factors that prevail in Alaska. In contrast, the higher annual temperatures and longer periods of insolation in Poland may favor the formation of volatile forms of mercury that escapes to the atmosphere [17]. Moreover, *P. schreberi* tends to accumulate more Hg and presumably Pb and Zn

Table 2. Mean, standard deviation values, and geochemical background concentrations for trace elements in *Pleurozium schreberi* and *Hylocomium splendens* of Wigierski National Park.

Species/number of samples	Element/unit	Mean	Standard deviation	Geochemical background
P. schreberi (n = 11)	Al (mg·kg^{-1})	384	90	565
	Ba (mg·kg^{-1})	21	7	31
	Fe (mg·kg^{-1})	414	96	527
	Hg (μg·kg^{-1})	83	20	123
	Mn (mg·kg^{-1})	401	215	693
	Pb (mg·kg^{-1})	7	2	12
	Ti (mg·kg^{-1})	5	2	10
	Zn (mg·kg^{-1})	46	7	59
H. splendens (n = 7)	Al (mg·kg^{-1})	456	184	824
	Ba (mg·kg^{-1})	19	6	32
	Fe (mg·kg^{-1})	444	238	918
	Hg (μg·kg^{-1})	85	26	137
	Mn (mg·kg^{-1})	308	193	693
	Pb (mg·kg^{-1})	7	3	12
	Ti (mg·kg^{-1})	5	4	13
	Zn (mg·kg^{-1})	45	8	61

than *H. splendens*. Because these metals belong primarily to airborne toxicants, *P. schreberi* seems to be a better bioindicator of air pollution.

Conclusions

The following conclusions can be drawn from the data obtained:

1. The differences in background concentrations occur only for Fe and Al in both moss species, with a higher tendency of *H. splendens* to accumulate these metals The mosses examined show both spatial and interspecies variation in concentrations of elements. In general, *H. splendens* tended to be more enriched in the elements determined than *P. schreberi*.
2. The background values of Al, Ba, Fe, Hg, Mn, Pb, Ti and Zn in *P. schreberi* and *H. splendens* presented by many authors using direct method are similar to those derived from the present study. The minor variations in background concentrations may be due to different methods of sample preparation and analysis, as well as different geologic, geomorphologic, edaphic, hydrologic and climatic factors of the study area.
3. The greatest diversity in concentration of elements occurs between the same moss species growing at different sites. In contrast, both *P. schreberi* and *H. splendens* usually reveals similar element levels at a specific site.
4. Of the element examined, Fe shows a more distinct correlation with Al and Ti in moss species, reflecting mineralogy and chemistry of postglacial deposits and related soils of Wigierski National Park.

Considering this, in relatively pristine areas with a subordinate anthropogenic imprint, the geologic setting leaves its distinct mark on the chemistry of mosses. This fact should be taken into account when interpreting the geochemical background concentrations of elements in mosses.

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Table 3. Background concentrations (mean or range values) of selected elements in *Pleurozium schreberi* and *Hylocomium splendens* compiled from different authors.

Element/unit	*P. schreberi*	*H. splendens*	Analytical method/sample digestion	Country/Reference
Al ($mg \cdot kg^{-1}$)	590 171	- -	AAS/ HNO_3+$HClO_4$ ICP-AES/HNO_3	Poland [2] Sweden [18]
Ba ($mg \cdot kg^{-1}$)	13–40 14 15.2	15–40 - -	ICP-MS/HNO_3 AAS/ HNO_3+$HClO_4$ ICP-AES/HNO_3	Norway [12] Poland [2] Sweden [18]
Fe ($mg \cdot kg^{-1}$)	150–1500 298 138	310–2400 - -	ICP-MS/HNO_3 AAS/ HNO_3+$HClO_4$ ICP-AES/HNO_3	Norway [12] Poland [2] Sweden [18]
Hg ($\mu g \cdot kg^{-1}$)	51	-	ICP-MS/HNO_3	Sweden [18]
Mn ($mg \cdot kg^{-1}$)	81–650 189 289	110–390 -	ICP-MS/HNO_3 AAS/ HNO_3+$HClO_4$ ICP-AES/HNO_3	Norway [12] Poland [2] Sweden [18]
Pb ($mg \cdot kg^{-1}$)	1.7–24 18 4.2	1.4–24 - -	ICP-MS/HNO_3 AAS/ HNO_3+$HClO_4$ ICP-MS/HNO_3	Norway [12] Poland [2] Sweden [18]
Ti ($mg \cdot kg^{-1}$)	8.5	-	ICP-MS/HNO_3	Sweden [18]
Zn ($mg \cdot kg^{-1}$)	26–64 37 32.3	23–100 - -	ICP-MS/HNO_3 AAS/ HNO_3+$HClO_4$ ICP-MS/HNO_3	Norway [12] Poland [2] Sweden [18]

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