JOLANTA BORKOWSKA-BURNECKA*,
DAGMARA MAZUR*, WIESŁAW ŻYRNICKI*

A STUDY OF REE CONCENTRATIONS IN MOSSES FROM VARIOUS LOCATIONS BY THE ICP-AES METHOD

Samples of the terrestrial moss (*Pleurozium schreberi*) collected from different pollutant impact areas (Lower Silesia, Masuria and Rhineland-Palatinate) were analysed. Concentrations of eight lanthanides (La, Ce, Nd, Sm, Eu, Gd, Dy, Ho) and fifteen other elements (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Na, Ni, Mg, Mn, Pb, Sr and Zn) were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES). Correlations between rare earth element (REE) concentrations and contents of the other elements in mosses were analysed. Applicability of mosses to the monitoring of atmospheric deposition of REEs was discussed.

1. INTRODUCTION

Terrestrial mosses have been used to monitor atmospheric deposition of heavy metals since 1968 [1]. Evaluation of environmental pollution by moss analysis is systematically extended [2]–[9]. A great majority of mosses receive most of their nutrients from the atmosphere and have a high capacity for capturing and retaining a variety of contaminants. For the monitoring of heavy metal deposition the feather mosses, i.e. *Hylocomium splendens* and *Plurozium schreberi*, are preferred due to their high capacity for sorption and retention of some metal elements [2].

Rare earth elements (REEs) are recently applied in agriculture as microelement fertilizers and in many industrial fields to production of numerous new materials. This results in large amounts of REEs entering the environment, which fact leads to an increasing attention paid to their accumulation and distribution patterns. Analysis of REE concentrations in soil and soil-grown plants is very useful, e.g., in predicting the plant's uptake of these elements from soil [10]–[12]. Concentrations of lanthanides in plants are extremely variable and different abundance of REE in the plant cannot be

* Wrocław University of Technology, Chemistry Department, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

only attributed to the soil composition [12]. Bioavailability of REEs and their accu-
mulation in plants are studied mainly for different types of cereal crops or edible parts
of other plants [10], [11], [13] and for fern [14], [15]. Low concentration levels of
REEs in plants and biota require a sensitive analytical technique for their determina-
tion. Neutron activation analysis (NAA), inductively coupled plasma atomic emission
and mass spectrometry (ICP-AES and ICP-MS) are frequently applied.

For mosses only La and Ce were determined together with other elements for pre-
paration of two Moss Reference Materials [16]. In our study, the concentrations of
some REEs and 15 other (minor and trace) elements in mosses collected from diffe-
rent pollutant impact areas were determined by ICP-AES. The correlations between
the element concentrations were investigated.

2. MATERIALS AND METHOD

Sampling. Mosses (*Pleurozium schreberi*) were collected during August and Sep-
tember 2001 from three different locations:
- mountain area (Lower Silesia, Poland) – moss 1,
- forest area (Masuria, Poland) – moss 2,
- industrial area (Rhineland-Palatinate, Germany) – moss 3.

At each sampling place several subsamples were taken from the area of about 10 m^2
and then combined to a bulk sample. Only the upper segments and green parts of plants
were analysed. Samples were cleaned to remove the outer particles and dried at 60 °C,
homogenized in an agate mill, sieved and then the fraction of particle size less than
150 μm was subjected to the next steps of a sample preparation procedure.

Sample preparation. Dry ashing combined with ultrasonic leaching of the ash
were applied for preparation of moss samples used in element concentration meas-
urements. 5 g of the moss sample were weighed in a beaker and put into the micro-
wave muffle furnace (MAS 7000 CEM). Heating was performed by increasing the
temperature up to 500 °C. The total ashing time was 4 hours. Six samples were ashed
simultaneously. In the next step, the ash was transferred to a polyethylene centrifuge
tube, 20 cm^3 of diluted HNO_3 (1 M) were added and the tube was placed in the ultra-
sonic bath. After sonication (1 h, 60 °C) the liquid phase was separated by centrifuga-
tion (2500 r.p.m., 20 min) and the solution was transferred to the flask. The solid resi-
due was rinsed with 10 cm^3 of the acid and the liquid phases were combined. The
solution was finally made up to 50 cm^3.

Instrumentation. Concentrations of the elements (with the exception of Na and K)
were measured using sequential ICP spectrometer JY38S. Instrumental parameters are
given in table 1. The concentrations of Na and K were measured using flame emission
spectrometry (Perkin Elmer 1100 spectrometer).

Instrumental parameters

ICP JY 38S spectrometer	
Frequency	40.68 MHz
Monochromator	1 m, Czerny-Terner mounting
Gratings	2400 and 4320 line mm^{-1}
Forward power	1200 W
Nebulizer	concentric in a cyclonic chamber
Plasma argon flow rate	14 dm^3 min^{-1}
Sheath gas flow rate	0.22 dm^3 min^{-1}
Carrier gas flow rate	0.4 dm^3 min^{-1}
Sample uptake rate	1.2 cm^3 min^{-1}

3. RESULTS AND DISCUSSION

Two analytical lines of 12 from among all lanthanides were employed for determination of their concentrations in mosses. The other elements (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Na, Ni, Mn, Pb, Sr and Zn) were measured using the most sensitive lines as in our earlier study [17].

Determination of REEs. In the first step, the instrumental detection limits (DLs) for REEs were determined using 3σ criterion. The line wavelengths and values of DL are given in table 2.

Table 2

Analytical lines and detection limits (DL) for lanthanides

Element	Wavelength (nm)	DL (μg/dm^3)	Element	Wavelength (nm)	DL (μg/dm^3)
La	379.478	16	Gd	310.050	19
	408.672	5		342.247	7
Ce	394.275	72	Tb	350.917	20
	413.765	82		387.417	59
Pr	414.311	50	Dy	353.170	4
	422.535	58		353.602	30
Nd	401.225	25	Ho	339.898	50
	430.358	25		345.600	6
Sm	359,260	22	Er	337.271	30
	442.434	35		369.265	17
Eu	272.778	9	Lu	219.554	18
	381.967	3		261.542	0.4

In the next step, the concentrations of REEs were measured in the mosses. For some lanthanides (Pr, Tb, Er, Lu) their contents were found to be below the detection limits of the method.

Concentrations of REEs in moss samples were determined in a standard way using calibration curves (CC) and by standard additions (SA) method considering possible interelement effects, i.e., influence of easily ionized elements and spectral overlapping. The results are compared in table 3.

Table 3

Concentrations of some lanthanides in mosses obtained by calibration curves (CC) and standard additions (SA) methods, in mg kg^{-1} (dry mass)

Element	Moss 1		Moss 2		Moss 3	
	CC	SA	CC	SA	CC	SA
La	2.50±0.05	**3.49±0.06**	1.32±0.07	**1.73±0.05**	3.91±0.03	**4.70±0.12**
Ce	4.45±0.21	**5.13±0.19**	2.34±0.16	**2.99±0.11**	6.32±0.20	**8.35±0.32**
Nd	2.14±0.08	**3.20±0.09**	1.05±0.08	**1.49±0.03**	3.35±0.08	**4.01±0.14**
Sm	0.44±0.04	**0.73±0.01**	0.44±0.08	**0.286±0.002**	0.85±0.07	**0.929±0.004**
Eu	0.080±0.005	**0.13±0.001**		< 0.09	0.14±0.01	**0.17±0.02**
Gd	0.63±0.03	**0.86±0.01**	0.32±0.03	**0.43±0.01**	1.19±0.03	**1.39±0.01**
Dy	0.24±0.04	**0.371±0.002**		**0.093±0.001**	0.50±0.01	**0.53±0.01**
Ho	0.20±0.02	**0.138±0.005**		< 0.06	0.29±0.10	**0.331±0.002**

Higher values of concentration obtained by the SA method indicate that in the moss analysis, matrix effects play important role and correction of these effects is necessary. Moreover, the standard deviation is usually lower for the standard additions method. Summing up, for such plant materials as mosses the values obtained by the standard additions method are recommended.

Reliability of the method of REE determination was tested for La and Sm in two standard reference materials (tobacco leaves CTA-OTL-1 and CTA-VTL-2). A very good agreement was obtained between results of our measurements and certified data. The concentrations of La and Sm measured in CTA-OTL-1 were 1.36±0.03 mg kg^{-1} and 0.233±0.055 mg kg^{-1}, while the certified values were 1.44±0.16 and 0.229±0.052 mg kg^{-1}, respectively. For CTA-VTL-2 only La content (1.01±0.10 mg kg^{-1}) was reported and our value was found to be 0.96±0.03 mg kg^{-1}.

Other elements. Concentrations of the other metals in mosses were determined by the ICP-AES and the flame AES methods and the results are presented in table 4. For these elements a validation of measurements is given in [17], [18].

Ba, Cd, Cu, K, Na, Pb and Zn occurred in comparable proportions in the samples analysed and showed approximately 2-fold range of variation. For the other elements, the concentration values differed more than 4-fold. The concentrations of trace ele-

ments in the moss growing in the mountain area in the south-west Poland (moss 1) are higher than those obtained for moss collected from the forest, non-industrial area in north-east Poland (moss 2), but lower than those determined for moss collected near industrial region in Germany (moss 3). For comparison, the data reported for mosses in Poland [8] and in Germany [9] are collected in table 4.

Table 4

Concentrations of some major and trace elements in mosses (in mg kg^{-1} dry mass)

Element	Moss 1	Moss 2	Moss 3	Range in Poland [8] (in Germany [9])
Al	2550	1120	7350	
Ba	49	27	56	
Ca	11200	3060	16800	
Cd	0.69	0.66	0.57	0.05–6.29 (0.13–0.87)
Cr	6.2	1.4	8.1	0.2–9.0 (0.5–11.8)
Cu	3.7	6.8	5.6	3.5–650 (4.1–25.5)
Fe	2950	1100	6250	87–5170 (153–6257)
K	7200	4330	6800	
Mg	1300	740	2400	
Mn	100	430	210	
Na	175	140	380	
Ni	10	2.8	12	0.53–4.72 (0.56–16.0)
Pb	19	29	15	4.2–270 (5.1–80.5)
Sr	72	19	43	
Zn	74	102	86	19–208 (23.7–396)

Generally, the values obtained here for Cd, Cr, Cu Fe, Ni, Pb and Zn fall in the usual range of the content of elements in mosses in Poland and Germany. Concentrations of the other trace and minor elements are similar to those observed in other countries [3]–[5].

Correlation between REEs and other elements. To evaluate the existing relations between concentration of REEs and the content of other elements, Pearson coefficients of correlation r were calculated. Very high values of correlation coefficient ($r \geq 0.9$) were obtained for the lanthanides (both for single elements and for the sum of REEs) and for some minor elements, i.e., Al, Ca, Mg and Fe. Concentration of the REEs was found to be also positively correlated with Ba, Cr, Na and Ni content ($r \geq 0.8$). The statistically significant negative correlation coefficients were found between REEs and Cd, Pb ($-0.74 \geq r \geq -0.99$).

4. CONCLUSIONS

For the mosses analysed the concentration levels of eight out of twelve lanthanides under study were found here to be relatively high (above 0.1 mg kg^{-1}) contrary to low

concentrations of REEs reported for plants, particularly for grains and vegetables (ranging from 10^{-4} to 10^{-2} mg kg^{-1}). This indicates that the moss analysis might be useful in monitoring the atmospheric REE deposition. The concentration of REEs obtained was in agreement with the Oddo-Harkins rule and was related to the concentration of the other elements. Concentration ratios of each REE in mosses collected from different growth areas were approximately constant and were in the range of 0.6–0.8 and 0.25–0.4 for moss 1/moss 3 and moss 2/moss 3 ratios, respectively. A similar relationship was observed by WYTTENBACH et al. [11] and FU et al. [12], with the exception of cerium. In our study, no such exception for cerium was observed probably due to atmospheric source of REEs.

For the moss with higher concentrations of the other heavy metals the REE concentrations were also higher than those obtained for the moss with lower content of the heavy metals. High correlation coefficients between REE concentration and Ni (occurring in fuel oil) content in the mosses can be an additional evidence for atmospheric REEs deposition. Being widespread moss might be used as an indicator plant for REE atmospheric deposition. The ICP-AES method was found to be suitable for determination of the majority of lanthanides in mosses.

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BADANIE STĘŻEŃ LANTANOWCÓW W MCHACH Z RÓŻNYCH OBSZARÓW ZA POMOCĄ METODY ATOMOWEJ SPEKTROMETRII EMISYJNEJ PLAZMY INDUKCYJNIE SPRZĘŻONEJ

Analizowano próbki mchu (*Pleurozium schreberi*) zebrane z trzech obszarów o różnym stopniu narażenia na zanieczyszczenia (Dolny Śląsk, Mazury i Nadrenia-Palatynat). W mchach oznaczono zawartość ośmiu lantanowców (La, Ce, Nd, Sm, Eu, Gd, Dy, Ho) oraz piętnastu innych pierwiastków (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr i Zn). Stężenia pierwiastków mierzono metodą atomowej spektrometrii emisyjnej plazmy indukcyjnie sprzężonej (ICP-AES). Analizowano korelacje między stężeniem lantanowców i zawartością pozostałych pierwiastków w próbkach mchu. Omówiono możliwość zastosowania mchów do monitorowania zanieczyszczenia atmosfery lantanowcami.