Concentrations of heavy metals in aquatic bryophytes used for biomonitoring in rhyolite and trachybasalt areas: a case study with *Platyhypnidium rusciforme* from the Sudety Mountains

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The elemental composition of the aquatic bryophyte *Platyhypnidium rusciforme* (Neck.) Fleisch. growing in streams embedded in trachybasalts (melaphyrs) and rhyolites (porphyrs) in the Polish and Czech Republic part of the Sudety Mts. was studied. Water from trachybasalt streams contained significantly higher concentrations of Ni as compared with water from rhyolite streams. Plants from rhyolite areas contained significantly higher levels of Mg and significantly lower levels of Co and Ni as compared with those from trachybasalt areas. The molar ratio of calcium and magnesium (Ca:Mg) in water (1.0–1.6 in trachybasalt streams and 0.5–1.8 in rhyolite streams) in some of the streams was different from the values presented in the literature. The Ca:Mg ratio in the plants was within the range of values calculated for serpentinite for plants in rhyolite streams, and higher than this range for plants in all trachybasalt streams. Concentrations of microelements in the plants were greater than the background values; however, there were no morphological aberrations in the plants. The relationships between all the variables concerning the chemical composition of mosses from the two areas were tested with the principal component analysis (PCA).

Keywords: bioaccumulation, bioindication, heavy metals, *Platyhypnidium rusciforme*

INTRODUCTION

Aquatic bryophytes are primary producers and provide habitats for a variety of organisms in freshwater ecosystems (Lopez & Carballeira 1993). The widespread occurrence of these plants and their ability to accumulate metals has led to their use in environmental monitoring programs (Claveri & Mouvet 1995). Despite their relative tolerance for a wide variety of ecological conditions, the development of aquatic bryophytes and their geographical distribution is limited mainly to water bodies in cold and temperate climatic zones (Glime & Vitt 1984, Claveri & Mouvet 1995, Carter & Porter 1997). Aquatic mosses can be used in active monitoring (transplanted plants), and passive monitoring (autochthonous species) programs (Claveri & Mouvet 1995, Claveri *et al.* 1995, Mersch & Reichard 1998, Sawidis *et al.* 1999, Vanderpoorten 1999). The use of bryophytes permits the evaluation of both overall environmental quality of a given water body (on the basis of degree of stress; Lopez *et al.* 1997), and environmental concentrations of particular contaminants (from tissue analyses). The latter application is favoured because many aquatic bryophytes have a high pollution tolerance and capacity for bioconcentration (Lopez *et al.* 1994). In addition mosses integrate changes in concentrations of metals through time, thus providing a biologically-weighted average. The superiority of bryophytes for this purpose as compared with other water ecosystem components such as fish, higher plants and sediments was demonstrated in a recent study of heavy metal pollution, organometallic pollution, and in radioecology (Beaugelin-Seiller *et al.* 1995).

Knowledge of the influence of a chemical composition of different types of rocks on the background concentration of elements in bryophytes can be very useful. The objective of this paper was to investigate the chemical characteristics of the aquatic bryophyte *Platyhypnidium rusciforme* (Neck.) Fleisch. collected in streams embedded in trachybasalts (basic melaphyrs) and rhyolites (acid porphyrs). The results are compared with the chemistry of both types of stream waters in the Polish and Czech Republic part of the Sudety Mts. Trachybasalts are basic igneous rocks (Ryka & Maliszewska 1991) and rhyolites are acidic rocks of volcanic origin and both usually contain elevated levels of their own specific heavy metals (Kabata-Pendias & Pendias 1993, Vavřin & Frýda 1996) forming special conditions for plant growth.

MATERIAL AND METHODS

In Lower Silesia, rhyolites and trachybasalts are present among other rock types in the western part of the Intra-Sudetic Depression (Walbrzyskie Mts. & Krucze Mts.) and in the central part of the Kaczawa Mts. In this area, trachybasalts and rhyolites were formed during Late Carboniferous–Early Permian volcanisms, and represent two extremes with respect to mineralogy and chemistry (Dziedzic *et al.* 1979). In the Intra-Sudetic Depression, samples of water and bryophytes were collected from 11 sites (Fig. 1). The sampling sites were selected so that the streams upwards to their source were embedded either in trachybasalts or in rhyolites (Fig. 1).

At each sampling site, one stream water sample and five samples of the aquatic bryophyte *Platyhypnidium rusciforme* were collected. Sampling was conducted three times in late spring and early summer. The sampling resulted in a total of three streamwater samples and fifteen samples of *Platyhypnidium rusciforme* per site.

Prior to analysis the water samples were filtered through a Whatman glass microfibre filter (GF/C). The following parameters were measured in the water samples: pH (potentiometrically), phosphate (colorimetrically with molybdate blue), Ca and K (atomic emission spectrophotometry), Mg (atomic absorption spectrophotometry). The microelements Ni, Cr, Co, V, Ba, Sr, Fe, Zn, Mn, Pb, Cd and Cu were measured with Simultaneous Sequential Inductively Coupled Plasma Emission Spectrophotometry (Spectro Analytical Instruments) against standards (BDH Chemicals Ltd, reagent grade) and blanks (distilled water). Hg was measured after reduction with tin chloride with cold-vapour atomic absorption spectrophotometry.

After collection, bryophytes were rinsed thoroughly in the field with streamwater and in the laboratory with distilled water, and dried at 60 °C. Plant material (200 mg) was digested with nitric acid and hydrogen peroxide at 95 °C until the digest became clear. After dilution to a total of 10 ml, the digestate was analysed for Ca, K, Mg, P, Ni,
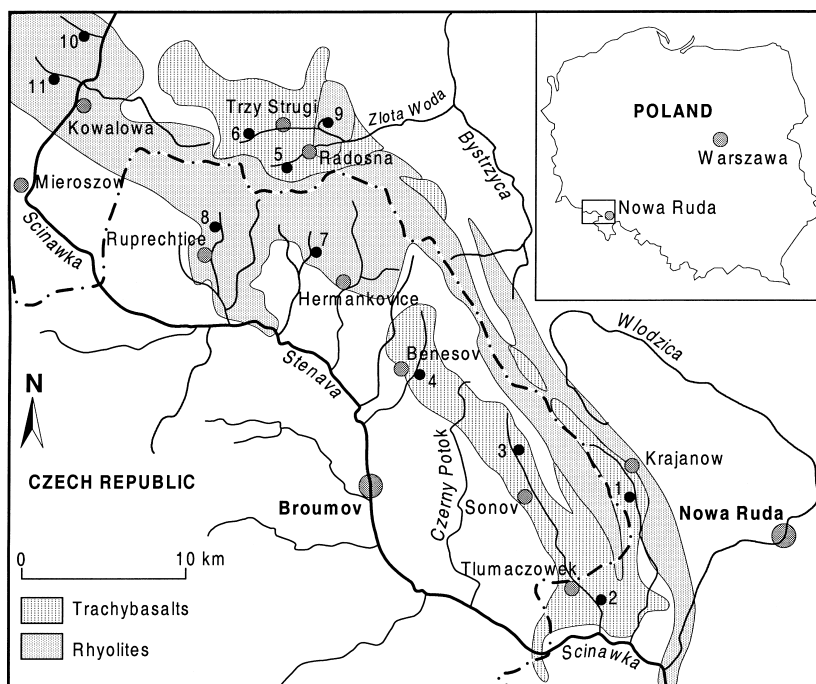
Fig. 1. Location of the sampling sites.

Cr, Co, V, Ba, Sr, Fe, Zn, Mn, Pb, Cd, Cu and the non volatile part of Hg, with the same procedures as described for the water samples. Standards and blanks were prepared in 0.5 M nitric acid. All analyses were done in duplicate.

The recovery efficiencies of the above procedures as compared with those of an interlaboratory study on digesting and analysing reference material appeared to be 100%.

The structure of relationships between all the variables concerning the chemical composition of mosses from the two areas were analysed with PCA.

The variability of results of the chemical analyses of water was tested with ANOVA (Grimm & Reckanagel 1985). The χ^2-test was used to compare the observed data with the normal distribution (Żuk 1989). Summary statistics, including means and standard deviations, were calculated for plant data. Significance of differences between the mean contents of elements in water and bryophytes collected in streams embedded in rhyolites and trachybasalt rocks was tested with the *t*-test (Parker 1983).

The weighted sum of square roots of relative concentrations of cations in plant leaves was calculated with Czarnowski's method (Czarnowski 1977) according to the equation:

$$\sum c_i \sqrt{P_i}$$

where c_i is a coefficient (a value expressing the influence of cation i on concentration of other cations in leaves) and P_i is the weight percentage of cation i of the sum of all cations; the values of c_i calculated by Czarnowski (1977) are: Ca = 1.000, K = 0.701, Na = 0.530, Mg = 0.342, Mn = 0.227, Cu = 0.049, Fe = 0.001 and Al = 0.279.

RESULTS AND DISCUSSION

Water

The composition of elements in water samples from streams in the trachybasalt and rhyolite areas are summarized in Tables 1 and 2. Concentrations of Ni were significantly higher ($t = 2.27$, $p = 0.05$) and concentrations of Co pointed towards higher values ($t = 2.16$, $p = 0.06$) in the trachybasalt streams as compared with the rhyolite streams, which is in accordance with investigations done by geologists in the same area (M. Awdankiewicz pers. comm.). Water in streams flowing through trachybasalt and rhyolite areas all contained Hg below the detection limit (0.001 µg l⁻¹).

According to water quality classes set by the

Polish Government (summarized in Kozłowski 1991) all the streams belong to the first class of water purity; concentrations of phosphates (sampling sites 2 and 4) and Zn (all sites) were, however, higher.

Concentrations of microelements in water of the various streams (Table 2) were compared with the background (control) values reported by Dojlido 1987, Kozłowski 1991, Kabata-Pendias and Pendias 1993, and Samecka-Cymerman and Kem-

Table 1. pH and mean concentrations (mg l^{-1}) of macroelements in stream water from trachybasalt and rhyolite areas and significance of the difference. * significant at $p < 0.05$.

Site	pH	PO_4	K	Ca	Mg	Fe
Trachybasalts						
1	6.6	0.068	5.2	15.2	5.8	0.022
2	7.0	0.24	4.0	51.3	22.4	0.008
3	6.3	0.065	4.4	21.6	13.1	0.008
4	6.2	0.25	3.6	16.8	7.8	0.002
5	6.2	0.11	3.8	15.2	7.9	0.008
6	7.4	0.14	2.0	18.4	10.9	0.009
Rhyolites						
7	6.4	0.04	5.0	8.2	9.2	0.003
8	6.7	0.09	4.4	16.7	9.9	0.007
9	6.7	0.16	2.4	20.8	9.2	0.009
10	6.8	0.14	3.8	23.3	7.9	0.007
11	6.6	0.12	5.1	20.0	7.8	0.005
$F_{0.05}$	5.5*	12*	67*	21 326*	8 029*	5.3*
mean ± SD trachybasalt	6.5 ± 0.5	0.15 ± 0.08	3.8 ± 1.1	23.1 ± 14	11.3 ± 6	0.009 ± 0.007
mean ± SD rhyolite	6.6 ± 0.1	0.11 ± 0.05	4.1 ± 1.1	17.8 ± 6	8.8 ± 0.9	0.006 ± 0.002
t	−0.10	0.85	−0.47	0.78	0.92	1.05
p	0.92	0.42	0.65	0.45	0.38	0.32

Table 2. Mean concentration (μg l^{-1}) of microelements in stream water from trachybasalt and rhyolite areas and significance of the difference. * significant at $p < 0.05$.

Site	Ni	Cr	Co	V	Ba	Sr	Zn	Mn	Pb	Cd	Cu
Trachybasalts											
1	9.5	< 3.0	7.2	11.0	54	50	125	30.8	7.4	0.49	4.7
2	8.3	< 3.0	8.1	7.9	76	219	275	5.2	5.3	0.42	< 3.4
3	8.6	< 3.0	5.9	< 5.3	42	90	222	10.3	< 1.5	0.34	< 3.4
4	6.2	< 3.0	4.1	< 5.3	29	29	81	3.8	< 1.5	0.24	< 3.4
5	10.5	4.0	7.1	< 5.3	23	63	156	10.2	2.8	0.38	4.6
6	11.5	4.4	7.2	5.4	204	159	323	21.3	6.6	0.58	< 3.4
Rhyolites											
7	5.0	< 3.0	6.8	<5.3	22	57	181	4.5	2.0	0.41	< 3.43
8	6.3	< 3.0	3.8	<5.3	23	138	177	7.3	4.6	0.27	< 3.43
9	7.6	3.4	4.8	<5.3	95	114	207	7.9	8.1	0.59	5.01
10	6.3	3.9	4.9	<5.3	143	40	146	5.8	4.6	0.57	< 3.43
11	8.8	3.3	4.2	6.2	20	63	193	6.9	4.2	0.55	3.80
$F_{0.05}$	24*	7.3*	46*	6.3*	32 145*	43 519*	8 842*	951*	688*	42*	5.9*
mean ± SD[1]	9.1 ± 1.8	3.4 ± 0.6	6.6 ± 1.4	6.7 ± 1.4	71 ± 68	101 ± 73	197 ± 93	13.6 ± 10	4.2 ± 2.6	0.41 ± 0.1	3.8 ± 0.06
mean ± SD[2]	6.8 ± 1.5	3.3 ± 0.4	4.9 ± 1.1	5.5 ± 0.4	60 ± 56	82 ± 41	181 ± 23	6.5 ± 1.4	4.7 ± 2.2	0.48 ± 0.14	3.8 ± 0.7
t	2.27	0.19	2.16	1.15	0.29	0.52	0.38	1.50	−0.35	−0.91	0.05
p	0.05	0.85	0.06	0.28	0.78	0.62	0.71	0.17	0.73	0.39	0.96

[1] trachybasalt
[2] rhyolite

pers 1994. Concentrations of Ni, Cd and Zn in water were higher than background values in both the trachybasalt area (Ni: $t = 8.14$, $p < 0.001$; Zn: $t = 4.68$, p < 0.001; Cd: $t = 4.31$, $p < 0.01$) and the rhyolite area (Ni: $t = 6.49$, $p < 0.001$; Zn: $t = 17.55$, $p < 0.001$; Cd: $t = 5.06$, $p < 0.001$).

Ca concentrations in water from trachybasalt and rhyolite streams (except for sampling site 7) were higher than the average of 15 mg l^{-1} given by Bowen (1979).

The background molar ratio of Ca:Mg is usually from 1.2 to 2.4 (Dojlido 1987). This ratio characterized water of trachybasalt streams 1, 2 and 4 and all rhyolite streams except for sites 7 and 8, where the relation between these two elements was 0.54 and 1.02 respectively.

Ranges of concentrations of the elements in trachybasalts and rhyolites are given in Table 3. According to Ryka and Rygiel (1987), and Kabata-Pendias and Pendias (1993), concentrations of Co, Cu, V and Ni are higher in basic trachybasalts than in acidic rhyolites. However, acidic rhyolite rocks contain more Ba and Pb as compared with basic trachybasalts.

Moss

No major differences in the average element composition in the plants between the two areas could be found. However, the concentration of Mg was significantly higher ($t = -4.03$, $p = 0.003$), and the concentrations of Ni and Co ($t = 2.29$, $p = 0.047$ for Ni, and $t = 2.28$, $p = 0.048$ for Co) were significantly lower in the plants from the rhyolite areas. Since there are similar differences in the concentrations of the above elements in trachybasalts and rhyolites (M. Awdankiewicz pers. comm.), it may be concluded that the concentrations of Ni and Co in mosses reflect the chemical composition of rocks on which they grow. Mg

might point to the same conclusion, although the concentrations of Mg in the stream water of both areas were not significantly different.

Concentrations of microelements in the examined plants were, in general, higher than those in aquatic bryophytes from the monitoring site in an area remote from sources of industrial contamination (Table 4; Wiersma *et al.* 1990, Kabata-Pendias & Pendias 1993).

Concentrations of Hg up to about 0.5–1 mg kg^{-1} d.w. can be considered as the natural background values in aquatic bryophytes collected in the nonpolluted parts of the Sudety Mts. (Samecka-Cymerman & Kempers 1995). The Hg contents in the bryophytes we examined were lower than 1 mg kg^{-1} d.w. We saw no evidence of aberrations in the morphology of the plants.

The Ca:Mg molar ratios in the plants from the trachybasalt and rhyolite areas were 1.58–4.73, and 1.03–1.58, respectively. In most of the plants from the trachybasalt area, this ratio was higher than that calculated for the plants growing on serpentine: 0.36–1.58 (Angelone *et al.* 1993) and 1.15–1.70 (Samecka-Cymerman & Kempers 1994) and for the plants from amphibolite areas: 0.42–2.36 (Samecka-Cymerman & Kempers 1996). In the plants from sites 1, 2 and 6 the Ca:Mg ratio was greater than that calculated for the plants from greenstone areas: 0.85–3.64 (Samecka-Cymerman & Kempers 1996). The Ca:Mg ratio in the plants from the rhyolite area is within the above mentioned ranges in all the examined populations. According to Ryka and Rygiel (1987) the Ca:Mg ratio ranges from 0.18 to 2.0 in trachybasalts and from 0.3 to 6.06 in rhyolites.

Principal component analysis (PCA) was used to reduce variables influencing the chemical composition of plants.

In the first part of the statistical analysis we calculated the regression lines of the significantly correlated variables and we calculated factor load-

Table 3. Concentration of elements in trachybasalts (T) and rhyolites (R) in the investigated region, (Ryka & Rygiel 1987).

	g/kg rock						mg/kg rock							
Fe	Mg	Ca	K	P	Ba	Sr	V	Cr	Mn	Co	Ni	Cu	Pb	Zn
T 24–85	5–57	8–74	5–65	1.2–8	0.3–0.8	0.1–0.75	< 5–100	< 2–7	200–2300	< 5–25	< 3–20	13–60	5–25	80–120
R 5–50	1–18	1–20	40–83	0.2–0.8	0.4–1.3	0.02–0.1	< 5–25	< 2–6	160–1300	< 5–10	< 3–9	8–12	20–50	40–60

Table 4. Concentrations of microelements (mg kg⁻¹ d.w. ± SD, $n = 15$) in *Platyhypnidium rusciforme* from trachybasalt and rhyolite streams.

| Site	Ni	Cr	Co	V	Ba	Sr	Zn	Mn	Pb	Cd	Cu	Hg
Trachybasalts												
1	40.7 ± 1.3	4.6 ± 0.1	6.8 ± 0.2	10.5 ± 0.5	16.5 ± 0.7	18.7 ± 0.7	581 ± 9.6	545 ± 8.9	23.0 ± 0.5	1.6 ± 0.1	9.4 ± 0.2	0.42 ± 0.07
2	23.0 ± 0.5	7.2 ± 0.2	15.8 ± 0.6	19.1 ± 0.7	45.5 ± 1.6	49.3 ± 1.7	899 ± 11	2 210 ± 11	5.3 ± 0.6	2.1 ± 0.1	14.2 ± 0.5	0.74 ± 0.09
3	13.1 ± 0.1	1.8 ± 0.1	6.9 ± 0.1	3.0 ± 0.2	45.2 ± 1.8	19.1 ± 0.8	578 ± 8.5	145 ± 3.2	30.2 ± 0.4	0.9 ± 0.07	3.1 ± 0.1	0.51 ± 0.06
4	14.5 ± 0.7	10.1 ± 0.4	7.6 ± 0.3	13.9 ± 0.6	110 ± 4.3	41.2 ± 1.5	903 ± 9.1	363 ± 4.1	37.1 ± 2.1	2.7 ± 0.1	24.0 ± 0.8	0.71 ± 0.10
5	12.7 ± 0.03	0.4 ± 0.05	5.7 ± 0.2	0.4 ± 0.1	9.7 ± 0.4	6.4 ± 0.2	153 ± 4.1	27 ± 1.2	22.6 ± 0.1	0.3 ± 0.01	0.9 ± 0.04	0.13 ± 0.02
6	16.0 ± 0.2	2.8 ± 0.1	5.9 ± 0.2	0.6 ± 0.06	275 ± 5.9	32.9 ± 1.9	797 ± 7.9	542 ± 4.3	25.4 ± 0.6	1.6 ± 0.1	6.0 ± 0.2	0.69 ± 0.09
x̄ ± SD	23.0 ± 10.8	4.5 ± 1.5	8.12 ± 3.8	7.9 ± 3.2	83.6 ± 41	27.9 ± 6.5	652 ± 116	639 ± 326	23.9 + 4.3	1.5 ± 0.3	9.6 ± 3.5	0.53 ± 0.10
Rhyolites												
7	9.0 ± 0.8	1.5 ± 0.1	4.9 ± 0.6	22.2 ± 0.1	168 ± 0.6	19.7 ± 0.3	330 ± 3.2	153 ± 1.6	76.0 ± 1.2	17.0 ± 0.3	30.2 ± 0.9	0.29 ± 0.03
8	10.8 ± 0.3	4.4 ± 0.2	5.1 ± 0.4	8.1 ± 0.7	145 ± 4.6	25.3 ± 1.1	951 ± 12	1 300 ± 12	23.9 ± 0.8	2.7 ± 0.1	9.2 ± 0.3	0.84 ± 0.12
9	12.7 ± 0.4	2.5 ± 0.1	4.5 ± 0.3	7.1 ± 0.4	32.5 ± 1.2	37.1 ± 1.7	749 ± 8.3	2 220 ± 10	12.4 ± 0.4	2.4 ± 0.1	4.3 ± 0.1	0.64 ± 0.08
10	3.1 ± 0.1	2.3 ± 0.1	3.6 ± 0.1	4.2 ± 0.2	416 ± 6.2	22.7 ± 0.9	843 ± 9.0	404 ± 3.6	18.2 ± 0.8	1.2 ± 0.1	7.2 ± 0.3	0.74 ± 0.12
11	5.6 ± 0.5	0.7 ± 0.06	1.8 ± 0.1	1.1 ± 0.1	59.0 ± 0.4	10.5 ± 0.3	232 ± 4.6	133 ± 2.5	2.3 ± 0.1	0.2 ± 0.01	8.2 ± 0.2	0.20 ± 0.05
x̄ ± SD	8.24 ± 3.9	2.3 ± 0.6	3.98 ± 1.3	8.5 ± 3.6	164 ± 68	23.1 ± 4.3	621 ± 143	842 ± 403	26.6 ± 12.9	4.7 ± 3.1	11.8 ± 4.7	0.54 ± 0.13
t	2.29	1.28	2.28	-0.13	-0.97	0.59	0.17	-0.40	-0.21	-1.12	-0.39	-0.06
p	0.047	0.23	0.048	0.90	0.36	0.57	0.87	0.70	0.84	0.29	0.71	0.96
Background concentrations from Wiersma (1990) and Kabata-Pendias (1993)												
	< 7.6	< 0.9	< 1.5	3.1	34	17	25–150	1 400	7.7	2.9	8.2	
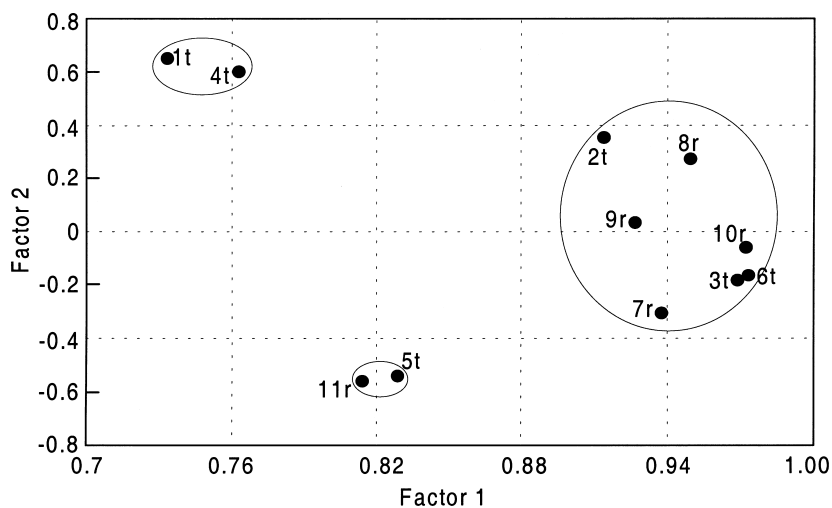
Fig. 2. Factor loadings (unrotated). Extraction: principal components (r = rhyolites and t = trachybasalts). The axes represent the first two factors of the PCA analysis.

ings by the PCA's analysis.

The first factor explained 79.8%, and the second factor only 15.9%, of the total variance, so differentiation between sampling sites is characterized mostly by the first factor. Three groups of sampling sites may be distinguished (Fig. 2). Sites 1 and 4 (trachybasalts, first group) were characterized by the highest contents of Fe and P in plants, site 1 by the highest level of Ni and site 4 the highest level of Cr and a similar level of Ca (average in relation to all the examined populations) in plants. The second group (sites 5 and 11) was characterized by the lowest levels of Ni, Cr, V, Ba, Sr, Zn, Mn, Hg, Co and P (site 5), the highest level of potassium (site 11) and the lowest levels of Pb, Cd and Co (site 11) in plants. Both sites (5 and 11) characterized similar levelss of Cr and Cd in plants.

In the second part of calculations we transposed the data and established the main factors. Table 5 includes loadings of the first three factors. The first factor is related to the concentrations of Ni, Sr, Pb, Cu, Hg, Ca and Mg in plants, the second factor is related to Cr, Cd and P in plants and the third factor is related to Zn in plants.

In the present study, the following inverse relationships between elements in streamwater and in *Platyhypnidium rusciforme* were found: Ca in water and Pb in plants ($R^2 = 0.83$, $p = 0.032$), Ca in water and Cd in plants ($R^2 = 0.86$, $p = 0.021$), and Ca in water and Cu in plants ($R^2 = 0.94$, $p = 0.019$) from rhyolites areas; and Ca in water and Pb in plants ($R^2 = 0.81$, $p = 0.049$), and Pb in wa-

ter and Mg in plants ($R^2 = 0.88$, $p = 0.038$) from the trachybasalt areas. How inverse relationships between elements in water and plants affect the relationships of elements within plants needs further investigation. Plants may counteract metal toxicity by maintaining high levels of Ca (Johnston & Proctor 1977, Angelone *et al.* 1993). A similar protective role has been shown for Mg (Samecka-Cymerman 1994). Excess accumulation of one element results in a reduced uptake of (an)other element(s) because the capacity of a plant to absorb mineral salts is finite (Brooks 1972). As an example Brooks (1972) presented inverse relationships for Ca and Ni, for Ca and Co and for

Table 5. Factor loadings (unrotated). Extraction: Principal components (loadings higher than 0.700 are shown).

Variables	Factor 1	Factor 2	Factor 3
Ni	0.785		
Cr		–0.800	
Sr	–0.777		
Zn			0.800
Pb	0.863		
Cd		–0.910	
Cu	0.904		
Hg	–0.837		
P		–0.804	
Ca	–0.770		
Mg	0.879		
% of total variance	35.087	24.921	11.802

Mg and Ni in plants from serpentine soils.

Czarnowski (1977) hypothesized that the concentration of a cation in plant leaves is a function of the concentrations of other cations. Thus, in order to obtain the cationic equilibrium in plant leaves, one should compare the relative concentrations, i.e. concentrations of individual cations versus the sum of concentrations of all the cations in leaves, or at least the sum of the quantitatively dominant cations. Czarnowski (1977) stated that the weighted sum of square roots of relative concentrations of cations in plant leaves is constant for a given species (*see* Materials and methods). For most plants in temperate regions this weighted sum is about 12.5 (Czarnowski 1977). In this investigation, the values calculated with Czarnowski's method varied in *Platyhypnidium rusciforme* from 10.7 (site 1) to 12.3 (sites 5 and 6) (Table 6). *Platyhypnidium rusciforme* from sites 1 and 4, with the lowest values of the weighted sum, contained the highest levels of Fe and the highest concentrations of Ni (site 1) and Cr (site 4) and one of the highest concentrations of V, Sr, Zn, Pb, Cd and Cu (site 4; Table 4). As Czarnowski (1977) calculated, the coefficient c_i for Fe as very low, we suggest that the concentrations of microelements other than Fe also had an effect on the weighted sum of the plants we studied.

According to Markert and Wtorova (1992), metal accumulation seems to be directly associated with an exclusion of Mg and Ca. Our investigation identified a similar trend, on the basis of negative correlations between these elements and various heavy metals. However, no depletion of K was noted in the mosses investigated by Markert and Wtorova (1992), suggesting that K in these plants fulfils important metabolic functions. *Platyhypnidium rusciforme* from site 4 (containing one of the highest concentrations of heavy metals) contained relatively high levels of K. The value of the weighted sum found in *Platyhypnidium rusciforme* from sites 5 and 6 was 12.3, quite similar to that given by Czarnowski (1977). Plants from site 5 contained, with the exception of Pb, the lowest concentrations of all the examined microelements.

CONCLUSIONS

1. Water in streams embedded in trachybasalts (melaphyrs) and rhyolites (porphyrs) contained higher levels of Zn.
2. Water from trachybasalt streams contained

Table 6. Concentration of macroelements (g kg^{-1} d.w. ± SD, n = 15) in *Platyhypnidium rusciforme* from trachybasalt and rhyolite streams and significance of the difference. Cz = Czarnowski values (= weighted sum of relative concentrations, *see* Material and methods).

Site	P	K	Ca	Mg	Fe	Cz
Trachybasalts						
1	2.7 ± 0.3	5.4 ± 1.1	12.0 ± 1.1	1.9 ± 0.1	9.1 ± 0.6	10.7
2	2.5 ± 0.3	4.4 ± 0.5	15.4 ± 1.1	2.0 ± 0.1	4.9 ± 0.3	11.8
3	1.2 ± 0.1	5.2 ± 0.6	11.2 ± 0.9	3.9 ± 0.2	1.5 ± 0.1	12.2
4	2.8 ± 0.2	7.9 ± 1.1	10.0 ± 0.8	3.9 ± 0.2	7.6 ± 0.5	10.9
5	1.2 ± 0.1	5.8 ± 0.5	11.2 ± 0.7	2.9 ± 0.2	2.2 ± 0.1	12.3
6	2.3 ± 0.2	5.0 ± 0.4	14.2 ± 0.9	2.0 ± 0.1	2.0 ± 0.1	12.3
mean ± SD	2.1 ± 0.7	5.6 ± 1.2	12.3 ± 2.0	2.8 ± 0.9	4.6 ± 3.2	
Rhyolites						
7	2.0 ± 0.1	6.1 ± 0.4	8.4 ± 0.4	5.1 ± 0.3	1.6 ± 0.1	12.0
8	1.5 ± 0.1	3.6 ± 0.2	10.4 ± 0.6	4.0 ± 0.2	3.0 ± 0.2	11.6
9	1.3 ± 0.1	3.8 ± 0.2	13.6 ± 1.0	6.3 ± 0.4	2.1 ± 0.1	11.8
10	2.0 ± 0.1	2.9 ± 0.2	10.4 ± 0.8	4.4 ± 0.4	1.4 ± 0.1	11.9
11	2.0 ± 0.1	9.8 ± 1.1	12.0 ± 1.0	5.3 ± 0.5	2.1 ± 0.1	12.1
mean ± SD	1.8 ± 0.3	5.2 ± 2.8	11.0 ± 1.9	5.0 ± 0.9	2.0 ± 0.6	
t	1.00	0.30	1.13	−4.03	1.71	
p	0.34	0.77	0.29	0.003	0.12	

significantly higher concentrations of Ni ($t = 2.27$, $p = 0.05$) as compared with water from rhyolite streams.

3. Concentrations of microelements in the aquatic bryophyte *Platyhypnidium rusciforme* were higher than the background values, but there were no morphological aberrations in the plants.

4. The Ca:Mg ratio in the plants of rhyolite streams was within the range of values calculated for plants growing on serpentinite, and higher than the range for plants in all trachybasalt streams.

5. Plants from rhyolite areas contained significantly higher ($t = -4.03$, $p = 0.003$) levels of Mg and significantly lower levels of Ni ($t = 2.29$, $p = 0.047$) and Co ($t = 2.28$, $p = 0.048$) as compared with the plants from trachybasalt areas.

REFERENCES

Angelone, M., Vaselli, O., Bini, C. & Coradossi, N. 1993: Pedogeochemical evolution and trace elements availability to plants in ophiolitic soils. — *Sci. Total Env.* 129: 291–309.

Beaugelin-Seiller, K., Baudin, J. P. & Casellas, C. 1995: Experimental study of the effects of various factors on the uptake of ^{60}Co by freshwater mosses. — *Arch. Env. Contam. Toxicol.* 28: 125–133.

Bowen, H. J. M. 1979: *Environmental chemistry of the elements*. — Acad. Press, New York. 382 pp.

Brooks, R. R. 1972: *Geobotany and biogeochemistry in mineral exploration*. — Harper & Row, New York. 290 pp.

Carter, L. F. & Porter, S. D. 1997: Trace element accumulation by *Hygrohypnum ochraceum* in the upper Rio Grande Basin, Colorado and New Mexico, USA. — *Env. Toxicol. Chem.* 16: 2521–2528.

Claveri, B. & Mouvet, C. 1995: Temperature effects on copper uptake and CO_2 assimilation by the aquatic moss *Rhynchostegium riparioides*. — *Arch. Env. Contam. Toxicol.* 28: 314–320.

Claveri, B., Guerold, F. & Pihan, J. C. 1995: Use of transplanted mosses and autochthonous liverworts to monitor trace metals in acidic and non-acidic headwater streams (Vosges mountains, France). — *Sci. Total Env.* 175: 235–244.

Czarnowski, M. S. 1977: Równowaga kationowa w liściach roślin lądowych [Cationic equilibrium in leaves of terrestrial plants]. — *Archiwum Ochrony Środowiska* 2: 49–59. [In Polish with English summary].

Dojlido, J. 1987: *Chemia wody*. — Arkady, Warszawa. 352 pp.

Dziedzic, K., Kozłowski, S., Majerowicz, A. & Sawicki, L. 1979: *Surowce mineralne Dolnego Śląska*. — Ossoli-neum, Wrocław. 510 pp.

Glime, J. M. & Vitt, D. H. 1984: The physiological adaptations of aquatic musci. — *Lindbergia* 10: 41–52.

Grimm, H. & Reckanagel, R. D. 1985: *Grundkurs Biostatistic*. — VEB G. Fisher Verlag, Jena. 156 pp.

Johnston, W. & Proctor, J. 1977: Metal concentration in plants and soils from two British serpentine sites. — *Plant Soil* 46: 275–278.

Kabata-Pendias, A. & Pendias, H. 1993: *Biogeochemia pierwiastków śladowych*. — PWN, Warszawa. 363 pp.

Kozłowski, S. 1991: *Gospodarka a środowisko przyrodnicze*. PWN, Warszawa. 290 pp.

Lopez, J. & Carballeira, A. 1993: Interspecific differences in metal bioaccumulation and plant-water concentration rates in five aquatic bryophytes. — *Hydrobiologia* 263: 95–107.

Lopez, J., Retuerto, R. & Carballeira, A. 1997: D665/D665a index vs frequencies as indicators of bryophyte response to physicochemical gradients. — *Ecology* 78: 261–271.

Lopez, J., Vazquez, M. D. & Carballeira, A. 1994: Stress responses and metal exchange kinetics following transplant of the aquatic moss *Fontinalis antipyretica*. — *Freshw. Biol.* 32: 185–198.

Markert, B. & Wtorova, W. 1992: Inorganic chemical investigations in the Forest Biosphere Reserve near Kalinin. Part 3. Comparison of the multielement budget with a forest ecosystem in Germany — aspects of rejection indication and accumulation of chemical elements. — *Vegetatio* 98: 43–58.

Mersch, J. & Reichard, M. 1998: In situ investigation of trace metal availability in industrial effluents using transplanted aquatic mosses. — *Arch. Env. Contam. Toxicol.* 34: 336–342.

Parker, R. E. 1983: *Introductory statistics for biology*. — Edward Arnold Publishers Ltd., London. 163 pp.

Ryka, W. & Maliszewska, A. 1991: *Słownik petrograficzny*. — Wydawnictwo Geologiczne, Warszawa. 415 pp.

Ryka, W. & Rygiel, W. 1987: *Katalog analiz chemicznych akał i minerałów Polski*. — Prace Instytutu Geologicznego CXXIII, Wydawnictwo Geologiczne Warszawa. 371 pp.

Samecka-Cymerman, A. & Kempers, A. J. 1994: Macro- and microelements in bryophytes from serpentinite and greenstone streams. — *Polish Arch. Hydrobiol.* 41: 431–449.

Samecka-Cymerman, A. & Kempers, A. J. 1995: Preliminary investigations into the bioaccumulation of mercury by the liverwort *Scapania undulata* L.(Dum). — *Ecotoxicol. Env. Safety* 31: 57–61.

Samecka-Cymerman, A. & Kempers, A. J. 1996: Elemental composition of aquatic bryophytes from amphibolite areas. — *Polish Arch. Hydrobiol.* 43: 323–334.

Sawidis, T., Heinrich, G. & Chettri, M. K. 1999: Cesium-137 monitoring using mosses from Macedonia, N. Greece. — *Water, Air, Soil Poll.* 110: 171–179.

Vanderpoorten, A. 1999: Aquatic bryophytes for a spatio-temporal monitoring of the water pollution of the rivers Meuse and Sambre (Belgium). — *Env. Poll.* 104: 401–410.

Vavřin, I. & Frýda, J. 1996: Mineralizace Cu-Ag-Hg v mela-fyru ze Studence u Jilemnice (Podkrkonoší) [Cu-Ag-Hg mineralization in melaphyrs from Sudetic near Jilemnice (foothills of the Giant Mts, Czech Republic)]. — *Czech Geol. Soc.* 41: 33–39. [In Czech with English summary].

Wiersma, B. G. B, Bruns, D. A., Boelcke, C., Whitworth, C. & McAnulty, L. 1990: Elemental composition of mosses from a remote nothofagus forest site in Southern Chile. — *Chemosphere* 20: 569–583.

Żuk, B. 1989: *Biometria stosowana.* — PWN, Warszawa. 425 pp.