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Heavy metal concentrations in the mosses of the Tatra Mountains (Czecho-Slovakia): Multivariate analysis

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Abstract. The results of chemical analysis on 267 samples of 26 moss species for Pb, Cd, Cu, Zn, Cr, Fe, Mn and Mo have led to their use for principal component analysis. Moss samples were collected throughout the Tatra Mountains (Czecho-Slovakia) from 1986 until 1989. This approach revealed the following important trends:

- Disproportion between increasing concentration of Cr and the other elements. This trend explains 45% of the data variance.
- Increasing Cd and Mn concentrations in tissues of *Plagiomnium affine, Mnium spinosum, Hygrohypnum duriusculum, Sphagnum centrale* and *S.recurvum* between the years 1988 - 1989. This trend accounts for 22% of the variance in the pattern of the heavy metal concentrations in the mosses.
- Increase of Pb in relation to the altitude. This trend summarizes 14 % of the total data variance.

Hygrohypnum duriusculum has appeared as a convenient moss species for Cr, Cd and Mn monitoring, *Plagiomnium affine, Mnium spinosum, Sphagnum centrale* and *Sphagnum recurvum* for Cd and Mn monitoring, *Paraleucobrym longifolium* for Pb and Cd monitoring and *Andreaea nivalis* and *Sphagnum robustum* for Pb monitoring, *Polytrichum commune* and *Polytrichum formosum* for Mo and Mn monitoring.

Key-words: Bryophytes, air pollution, heavy metals

Introduction

Our present knowledge on atmospheric deposition of heavy metals in the Tatra Mountains is prevainlingly based on analysis of precipitation (Chudíková 1988) and air-borne particulates (Rak *et al.* 1982). The distribution pattern of air-borne pollutants is dependent upon certain emissions and meteorological parametres. An attempt was made to predict level concentrations of sulphur dioxide from sources in the vicinity of the Tatra Mountains by incorporation of these factors into a mathematical dispersion model (Rak *et al.* 1982). But the actual deposition or fallout rate on the vegetation cannot be accurately adduced from such formulae (Ratcliffe 1974). Bryophytes are important constituents in the vegetation of the Tatra Mountains, chiefly in the non-forest communities. With regard to their nutritional independence on the soil they are considered to be convenient bioindicators for monitoring of heavy metal deposition. The great exchange capacity, absence of a cuticle and simple organization of the tissues render bryophytes incapable of avoiding heavy metal uptake from deposition (Tyler 1990). The cation exchange capacity (CEC) is related to the concentration of peptic substances in moss tissue. In the literature sources, the different accumulation possibilities are shown in different moss species (Burton 1990; Ratcliffe 1974), retention efficiency of different metal ions is different as well (Tyler 1970). A number of studies have shown the value of using mosses for the determination of heavy metal deposition. Gordon *et al.* (1971) recommend using of *Hypnum cupressiforme* for monitoring of air purity, Briggs (1972) searched Pb concentration in the liverwort *Marchantia polymorpha* in the dependence on distance from motorways. Groet (1976) used *Leucobrym glaucum* for the determination of regional and local variations in the deposition of air-borne heavy metals in the northeastern USA. Gydesen and Rasmussen (1981) , and Pilegaard *et al.* (1979) used the moss *Hypnum cupressiforme* for purposes of monitoring, Särkelä and Nuorteva (1987) used *Pleurozium schreberi.* Gailey and Lloyd (1986) tested the reliability of using the moss *Hypnum cupressiforme* for monitoring purpose. Transplants of moss *Dicranoweisia crispula* have been used in the paper of Pilegaard (1979).

Two main aims of this paper are set:

- To value the essential component changes in the moss tissue in response to changes in environmental conditions;
- To find out the most convenient moss species for the purpose of monitoring at remote localities where instrumental methods would be inappropriate.

Material and Methods

We have analyzed 267 samples of 26 moss species collected throughout the Tatra Mountains from 1986 until 1989. The following moss species were used as bioindicators: *Andreaea nivalis* Hook., *Aulacomnium palustre* (Hedw.) Schwaegr., *Bazzania trilobata* (L.) S. Gray, *Dicranum scoparium* Hedw., *Hygrohypnum duriusculum* (De Not) Jameson, *Hylocomium splendens* (Hedw.) B.S.G., *Leucobryum glaucum* (Hedw.) *Angstr.*, *Mnium spinosum* (Voit.) Schwaegr., *Paraleucobrym longifolium* (Hedw.) Loeske, *Plagiomnium affine* (Bland.) T. Kop., *Pleurozium schreberi* (Brid.) Mitt., *Polytrichum commune* Hedw., *Polytrichum formosum* Hedw., *Polytrichum juniperinum* Hedw., *Polytrichum strictum* Brid., *Ptilidium pulcherrimum* (G. Web.) Vain., *Ptilium crista-castrensis* (Hedw.) De Not., *Rhytidiadelphus triquetrus* (Hedw.) Warnst., *Sanioinia uncinata* (Hedw.) Loeske, *Sphagnum palustre* L., *Sphagnum compactum* DC., *Sphagnum girgensohnii* Russ., *Sphagnum capillifolium* (Ehrh.) Hedw., *Sphagnum quinquefarium* (Lindb.) Warnst., *Sphagnum recurvum* P. Beauv. and *Sphagnum russowii* Warnst.

The majority of samples were collected from fairly open stands, in forest ecosystems the canopy closure ranged from 60 - 90%. All samples were sorted, washed and dried for 24 h at 105°C

Chemical analysis

Elemental analysis (Mn, Cu, Zn, Pb, Cr, Cd, Fe) was carried out in the Laboratory Center of Geological Research in Turčianske Teplice. The rough crushing was carried out on equipment made from titanium steel, eliminating secondary contamination. The fine homogenization was carried out in an agitator. After ashing (450°C, 300 min.), the ash was digested in 20 ml 6 M HCl, the digest was gently evaporated dry. The evaporation residue was dissolved in 40 ml 0.2 M HCl, filtered hot and the filtrates brought to a volume of 100 ml with 0.2 M HCl. The chemical analysis for Mn, Cu, Zn, Pb, Cr and Cd was performed by atomic absorption spectrophotometry (Varian Modell 1475). Deuterium background correction was applied in order to correct broad band absorption. Standards in 1 - 20 mg/kg range were prepared daily. The detection limit, defined as three times the background noise, was 2 mg/l for Mn, 3 mg/l for Cu, 1 mg/l for Zn, 10 mg/l for Pb, 6 mg/l for Cr and 2 mg/l for Cd. The repeatability of the measurements was at least 98% for every element. The conditions of determination were as follows (for Mn, Cu, Zn, Pb, Cr, and Cd respectively): Wavelength (nm)=279.5, 324.8, 213.9, 217.0, 357.9, 228.0; spectral band with (nm)=0.2, 0.5, 1.0, 1.0, 0.2, 0.5; lamp current (mA)=5.0, 4.0, 5.0, 5.0, 7.0, 4.0; atomization temperature 2,125°C. An oxidizing flame was used for the atomization of each metal except chromium, in this case reducing flame was used. Iron was determined using the photometry method with sulphosalicylic acid (device SPECOL 11).

Statistics

The mean values of the metal concentrations in the moss tissues and a number of measurements are compiled in Table 1. Principal component analysis has been used for the analysis of the structure of multivariete observation of heavy metal concentrations *in sensu* Nishida *et al.* (1985). We used a covariance matrix because the eigenvector PC 1 extracted from such a covariance matrix describes relative changes in the increasing characters (Jolicouer 1963a). For example if the proportions of an *ith* variete to a *jth* variete were to remain constant as the content of heavy metals in the moss tissue increases, that is, if the relative increase of the two dimensions is isometric. In our case the hypothesis that the *ith* variete is isometric could thus be expressed as eigenvector=1/sqr (8)=0.35, because we use 8 variables. We used logarithmic transformation of data which tends in itself to make covariance matrix independent from magnitude and scaling (Jolicouer 1963a). Principal components (PCs) are linear combinations of the measured original variables, and so their orientations are defined by the vectors of coefficients (eigenvectors) in those combinations. PCA often reveals relationships in the data that were not previously suspected, thereby allowing for interpretations that would not ordinarily result (Meyer *et al.* 1991). Closely related is the problem of how many PCs should be interpreted. We think that the procedure does not depend on a file of limiting assumptions and we try to explain 95% of data variance (Jolicouer 1963b). Except for species differentiation the individual species were sorted into ecological groups. The difference between ecological groups was identified with one-way analysis of variance (ANOVA) of the component scores (Somers 1986).

Results

The mean concentrations of heavy metals in the moss samples (mg/100g of dry material) collected throughout the Tatra Mountains are compiled in Table 1. Ten different types of ecosystem patterns or ecological groups can be recognized: forest ecosystem (1), subnival ecosystem (2), wet meadows (3), swampy woods (4), epiphytic species (5), species of mountain streams (6), epilitic species (7), species of sandy substratum (8), acid peatery (9) and alpine ecosystem (10). Anomalously high concentrations of several metals were found in samples of endohydric moss *Hygrohypnum duriusculum*, growing in rapidly flowing mountains streams: Mn 250 mg/100g, Pb 38.9 mg/100g (Veľká Studená Valley); Cr 30 mg/100g, Fe 582 mg/100g (Zelené pleso Valley).

Species	1	2	3	4	5	6	7	8	9	10	11	12	13
Number of measurements	16	4	8	4	7	6	14	4	16	12	13	14	16
Ecological unit	1	2	3	4	5	6	1	1	1	1	7	1	1
Pb	6.06	12.29	3.59	2.50	3.98	9.27	4.81	3.14	4.04	3.94	11.70	5.50	2.75
Cd	0.07	0.09	0.07	0.06	0.17	0.18	0.06	0.03	0.11	0.16	0.18	0.06	0.05
Cu	1.76	1.70	1.51	1.39	1.58	1.60	1.80	1.07	2.53	1.67	1.73	1.66	1.30
Zn	8.01	3.00	8.50	7.34	14.99	6.87	0.11	5.75	11.53	12.67	12.51	7.59	4.58
Cr	3.05	0.81	1.29	0.34	1.28	8.06	1.12	0.87	0.61	0.67	1.23	1.97	1.26
Fe	353.15	364.29	210.79	128.74	215.78	233.49	195.50	141.82	148.00	183.32	216.86	242.03	146.09
Mn	22.39	5.65	19.68	11.00	13.47	53.12	16.04	9.97	45.33	22.53	11.93	25.05	9.04
Mo	0.58	0.29	0.93	0.61	0.63	0.55	0.72	0.76	0.38	0.69	0.44	0.56	0.62

Species	14	15	16	17	18	19	20	21	22	23	24	25	26
Number of measurements	13	13	6	8	8	12	8	8	17	13	9	9	9
Ecological unit	1	8	9	5	1	1	4	10	4	1	1	9	4
Pb	5.20	3.61	2.65	2.03	3.27	3.95	2.39	4.89	3.94	3.16	3.76	2.82	4.31
Cd	0.04	0.10	0.07	0.07	0.10	0.07	0.08	0.06	0.07	0.06	0.08	0.19	0.07
Cu	1.61	1.70	1.80	1.46	1.60	1.82	1.30	1.68	1.46	1.57	1.73	1.70	1.68
Zn	6.91	6.53	6.11	8.45	9.03	8.22	7.63	6.59	6.60	7.55	9.16	6.89	7.37
Cr	2.88	0.71	0.55	0.51	2.20	0.86	0.33	0.92	0.53	0.98	0.71	0.64	0.63
Fe	257.18	100.42	96.32	156.72	232.60	152.97	114.00	177.34	124.94	190.96	104.57	94.50	124.32
Mn	13.10	13.80	13.75	7.94	24.82	12.89	28.60	7.20	14.63	18.84	18.00	21.22	11.90
Mo	0.93	0.33	0.34	0.34	0.31	0.55	0.22	0.41	0.51	0.60	0.61	0.61	0.20

Table 1. Concentration mean values (mg/100 g) 1 - *Dicranum scoparium*, 2 - *Andreaea nivalis*, 3 - *Aulacomnium palustre*, 4 - *Bazzania trilobata*, 5 - *Sanioinia uncinata*, 6 - *Hygrohypnum duriusculum*, 7 - *Hyloconium splendens*, 8 - *Leucobryum glaucum*, 9 - *Plagiomnium affine*, 10 - *Mnium spinosum*, 11 - *Paraleucobrym longifolium*, 12 - *Pleurozium schreberi*, 13 - *Polytrichum commune*, 14 - *Polytrichum formosum*, 15 - *Polytrichum juniperinum*, 16 - *Polytrichum strictum*, 17 - *Ptilidium pulcherrimum*, 18 - *Ptilium crista-castrensis*, 19 - *Rhytidiadelphus triquetrus*, 20 - *Sphagnum centrale*, 21 - *Sphagnum compactum*, 22 - *Sphagnum girgensohnii*, 23 - *Sphagnum capillifolium*, 24 - *Sphagnum quinquefarium*, 25 - *Sphagnum recurvum*, 26 - *Sphagnum robustum*. For numbers of ecological units see Results.

Both sampling sites were situated below the mountain cottages.These centres could confound the local paterns of metal deposition. Component weights for eight original variables are shown in Table 2. Principal component scores of the first and second component derived from covariance matrix of metal measurements for all moss species are shown in Fig.1, principal component scores of the first and second component for ecological groups 1 - 10 are shown in Fig. 2. Principal component scores of the first and third component derived from covariance matrix of metal measurements in mosses for all species 1 - 26 are shown in Fig. 3, principal component scores of the first and third component for ecological groups 1 - 10 are shown in Fig. 4.

	PC1	PC2	PC3	PC4	PC5	PC6
Eigen-values	0.739 (45.0)	0.364 (22.2)	0.237 (14.4)	0.129 (7.8)	0.067 (4.1)	0.061 (3.7)
Pb	0.354	-0.124	0.564	0.087	0.447	-0.374
Cd	0.154	0.568	0.470	0.354	-0.444	-0.117
Cu	0.056	0.112	0.096	-0.001	0.146	-0.034
Zn	0.054	0.336	-0.095	0.417	0.170	0.650
Cr	0.797	-0.187	-0.179	-0.192	-0.462	0.121
Fe	0.320	-0.223	0.172	0.089	0.411	0.453
Mn	0.280	0.652	-0.363	-0.368	0.401	-0.201
Mo	0.167	-0.146	-0.500	0.716	0.099	-0.404

Table 2. Component weights for eight original variables. The variance accounted for by each component follow the component number and eigenvalues in parentheses.

Discussion

All component weights in PC 1 show positive values indicating mainly Cr increase on the territory of the High Tatra, on the contrary to Zn and Cu. The concentration of all metals tended to increase, but e. g. the ratio of the increasing trend of Cr versus Cd was 8 : 1.5. In the comparison to the other examined metals the increase of Pb tended to be isometric. We may call the component PC1 as the increasing trend of heavy metals at the territory. We found Cr mainly in the moss *Hygrohypnum duriusculum* and since we did not find any metal in a such high value in the component PC1 we consider this endohydric moss species as conveniet for Cr monitoring. About 45% of the total variance was explained by this first trend. The trend was supported by data in Fig. 2, when the PC scores were divided according to the ecological units. On the contrary, the species belonging to ecological units 4 and 9 (see Table 1) with the lowest trend of Cr increase in their tissues are remarkable (Fig. 2). One-way ANOVA identified significant separation of the group 4 and 9 from other ecological units on principal component 1 (F=10.5, P=0.004). In this applications of PC analysis, the first principal component was acceptable as a „increasing" vector. The second principal component (PC2), indicating a positive correlation between Cd and Mn, may be accepted as a „structure" vector. For this trend the following moss species are responsible: *Plagiomnium affine, Mnium spinosum, Hygrohypnum duriusculum, Sphagnum centrale* and *Sphagnum* recurvum (Fig. 1). The principal component scores derived from covariance matrix for ecological units suggest that this process prevailingly takes place in the wet and water habitats, less frequent in the mesophytic forest ecosystem (Fig. 2). The years of sample collections submitted to the investigation are of particularly importance. The results are shown in the Table 3.

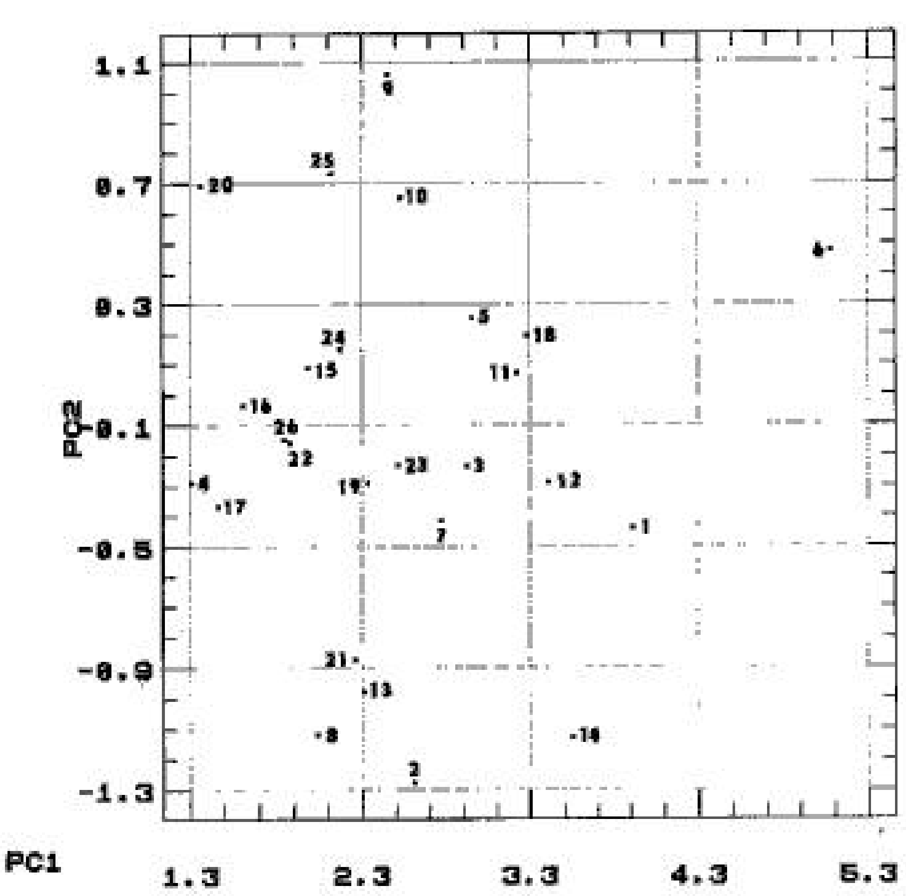

Fig. 1 Principal component scores of the first and second component derived from covariance matrix of metal measurements in mosses. For numbers of species see Table 1.

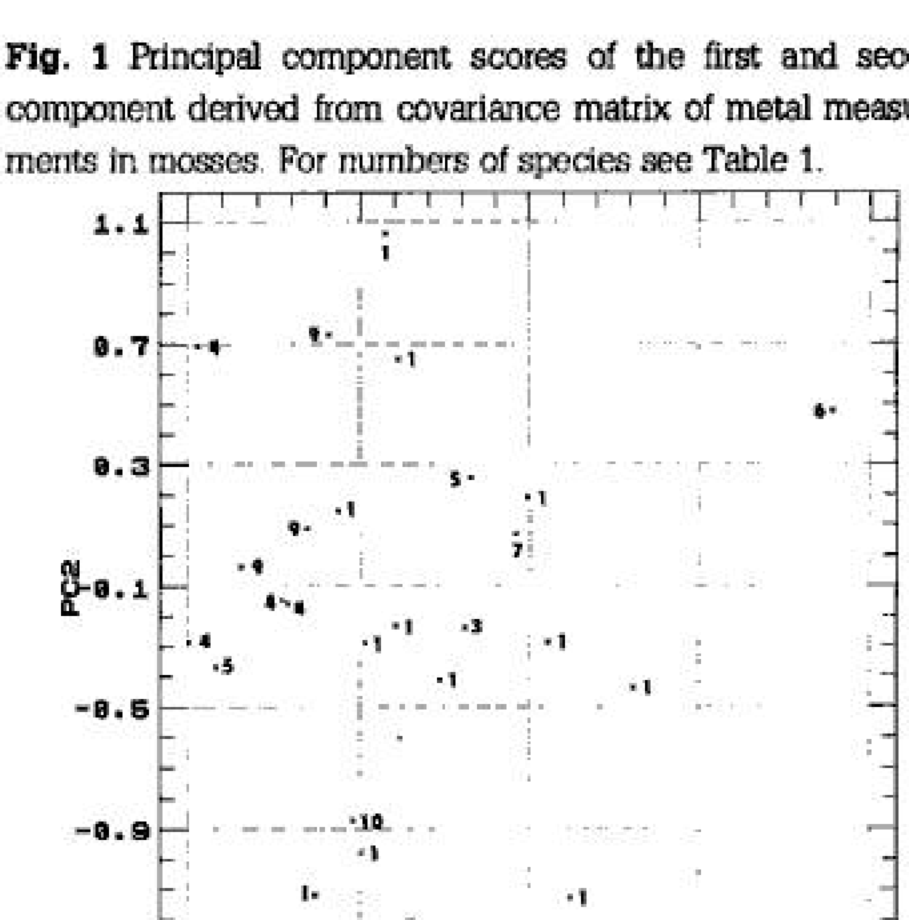

Fig. 2 Principal component scores of the first and second component derived from covariance matrix of metal measurements in mosses for ecological groups 1 - 10. For numbers see Results.

This trend probably correlates to the time factor, because 74.6% of all samples, explaining this phenomenon, were collected in the years 1988-89 (Tab. 3). On the base of this comparison, an event of environmental contamina-

Years	Examined species	Other species
1986 - 1987	25.4	48.7
1988 - 1989	74.6	51.3

Table 3. The comparison of the years of collecting moss samples: *Mnium affine, M. spinosum, Hygrohypnum duriusculum, Sphagnum centrale, S. recurvum* (the part of the total samples in %).

tion with Cd and Mn is clearly shown in the years 1988 - 89 in the Tatra Moutains. Thus, the second important trend (PC2) is increase of Cd and Mn concentrations in tissue of *Plagiomnium affine, Mnium spinosum, Hygrohypnum duriusculum, Sphagnum centrale* and *S. recurvum* during the years 1988 - 1989. About 22% of the total variance is explained by this second trend. We assume that these moss species are suitable for Cd and Mn monitoring. PC3 shows high significance in increasing concentration of Mn and Mo in the forest ecosystem in contrast to increasing concentration of Pb and Cd mainly in the alpine and subnivale region (Fig. 3 and 4). One-way ANOVA identified statistically significant forest - other ecological units separation on PC3 (F=8.3, P=0.008). For increasing concentration of Mn and Mo in the forest ecosystem *Polytrichum commune* and *Polytrichum formosum* are responsible. They have one common feature, nerves with longitudinal lamellae on their ventrale surface. Maybe, this anatomical speciality would work as a Mn and Mo trap. In the general trend of decreasing concentration of Pb and Cd in forest ecosystem, *Paraleucobryum longifolium* and *Sphagnum robustum* (Fig. 2, 3) are exceptions. They have one common feature: the presence of dead hyaline cells in the lamina tissue. Besides the long-distance transmission, the only source of Pb and Cd situated on the territory, is motor traffic. In the form of aerosols, the exhaust pollutants rise up into the higher sites and are regarded as a potential danger for herbivorous animals (*Marmota marmota, Rupicapra rupicapra tatrica*) The third important trend in PC3 is a positive correlation between an increasing concentration of Pb and the altitude. About 14% of the total variance is explained by this third trend. This is supported by the results in Fig. 4, where the PC scores are divided according to the ecological groups. For the highest concentration of Pb, the moss *Andreaea nivalis* is responsible, growing in the subnivale ecosystem. Since in the component PC3 we have not found any moss species except of *Andreaea nivalis, Paraleucobryum longifolium* and *Sphagnum robustum* respectively accumulating Pb in such a high concentration, we consider these moss species as suitable for Pb monitoring. This third principal component may be accepted as a „distribution" vector.

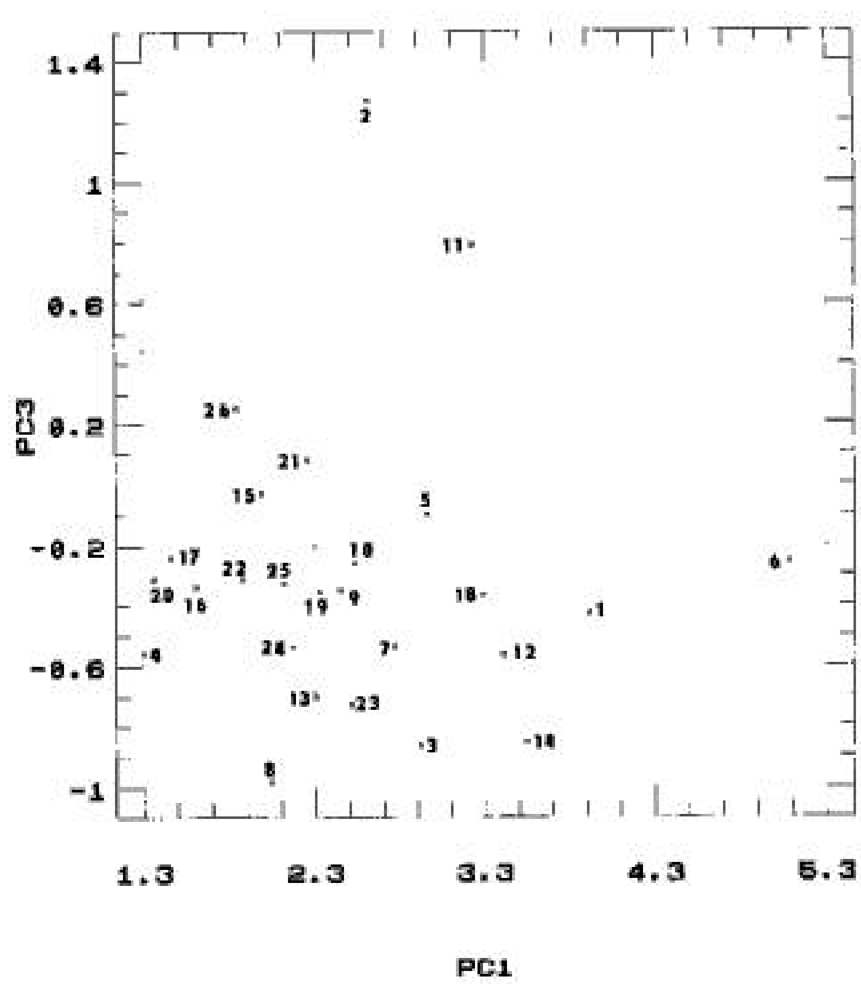

Fig. 3 Principal component scores of the first and third component derived from covariance matrix of metal measurements in mosses. For numbers of species see Table 1.

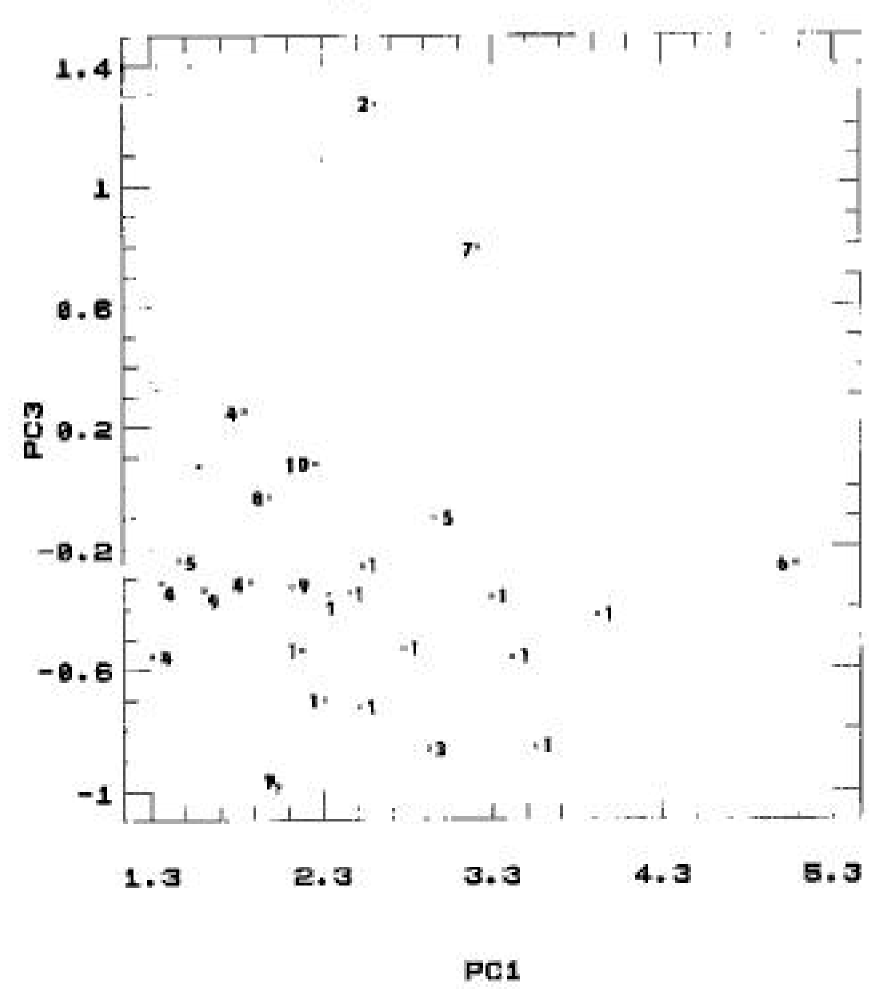

Fig. 4 Principal component scores of the first and third component derived from covariance matrix of metal measurements in mosses for ecological groups 1 - 10. For numbers of groups see Results.

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