

Can seasonal variation in fen water chemistry influence the reliability of vegetation-environment analyses?

Může sezónní variabilita v chemickém složení slatiništní vody ovlivnit spolehlivost vegetačně-stanovištních analýz?

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Temporal variation in fen water chemistry was studied in the Western Carpathian flysch zone (Czech Republic and Slovakia). Ten sites representing particular spring-fen types (tufa-forming fens, rich fens, spring-fen meadows, rich *Sphagnum*-fens, poor *Sphagnum*-fens) were studied. Water chemistry was determined three times a year (spring, summer, autumn) for 3 years. Water pH and conductivity were the most stable of the measured variables. Na⁺, K⁺, Ca²⁺ and SO₄²⁻ were also relatively stable. In contrast, N-NO₃⁻, Cl⁻, Fe, PO₄³⁻ and redox-potential temporally varied. These fluctuating, unstable variables explained very little or insignificant amounts of the variation in plant species data in our study area, possibly because of their instability. Further, seasonal variation in physical-chemical properties of the water confounded associations with vegetation types when data from different seasons was used. The significance of the differences among vegetation types (between-subject effect in RM ANOVA) distinctly changed among seasons for temperature and Si, N-NO₃ and Cl⁻ concentrations and to a slight degree, for Fe, Mg and water redox-potential. The differences in Ca, Na and SO₄²⁻ concentrations, pH and conductivity were highly significant in all three seasons. The first axis of the PCA of the chemical variables reflects the gradient from mineral-poor to mineral-rich fens in all the analyses, i.e. spring, summer and autumn. The separation of the sites along this axis is clearest in the ordination of the autumnal data. Major vegetation types were separated in PCA even when data from all three seasons were pooled. There is no major-nutrient that is characteristic of meadow-species rich and more productive fen habitats, even when repeated water samples are analyzed.

Key words: anion and cation concentration, bog, central Europe, fen meadow, mire, nutrient availability, seasonal variation, spring, Western Carpathians, wetlands

Introduction

There is a long tradition of exploring the relationships between vegetation composition and water chemistry in springs and mires in the Northern hemisphere. The methods used for minimizing variation caused by fluctuations in ion concentrations in water differ. Ion concentrations in water can be determined once at dozens of sites and then correlated with the vegetation or the occurrence of selected plant species at those sites (e.g. Persson 1962, Wassen et al. 1990, Kooijman & Hedenäs 1991, Gerdol 1995, Bootsma & Wassen 1996, Hedenäs & Kooijman 1996, Anderson & Davis 1997, Hájek et al. 2002). A less common way to investigate differences in water chemistry of major mire types is repeated sampling of a small number of sites (e.g. Malmer 1963, Bertram 1988, Gerdol 1990, Proctor 1994,

Vitt et al. 1995, Baumann 1996, Rybníček 1997, Bragazza et al. 1998, Bragazza & Gerdol 1999, 2002). Both approaches have disadvantages, which are sources of errors: an overestimate of the more stable ions in the former versus limited number of replications in the latter. Studies of seasonal variation in poor fens and ombrotrophic bogs revealed a high temporal variation in water chemistry. Surprisingly, there are few publications on temporal variation in water chemistry along the entire gradient from rich fens to bogs (Vitt et al. 1995, Tahvanainen et al. 2003). Financial limits usually prevent repeated sampling at a large number of sites. Spatial patterns in water chemistry, based on one sample from each site, can be detected when a broad vegetation gradient and a sufficient number of sites are analysed. However, it is not clear how the ion concentrations compare with those measured at other sites and times.

Our investigation of water chemistry and spring fen biota in the Western Carpathian flysch zone detected the same acidity-alkalinity gradient (Bridgham et al. 1996) found in many European and North-American regions (Hájek et al. 2002, Horsák & Hájek 2003, Pouličková et al. 2003). Although this gradient is often implicitly considered to be related to nutrient availability, there is a lack of coincidence between these items in many studies (Vitt et al. 1995, Wheeler & Proctor 2000, Bragazza & Gerdol 2002). Previously we found a strong correlation between the acidity-alkalinity gradient and concentrations of calcium and magnesium and a poor correlation between this gradient and major nutrients (N, P, K) (Hájek et al. 2002). The second main gradient of species-data variation was not fully related to the measured factors, but only indicated by an increasing number of nutrient-demanding meadow species. However, we found no patterns, either in soil nutrient content or in dissolved major nutrients (N, P, K), along this fen-meadow gradient in the water chemistry determined at a particular time (Hájek et al. 2002). The question is whether a single sample of mire water per site is sufficient for evaluating nutrient availability along major environmental gradients in fens. This study therefore aims at assessing the reliability of single water samples compared to repeated samples when characterizing fen habitats. We focused on (i) quantifying the relative temporal stability or instability of water chemistry in Western Carpathians spring fens, (ii) comparing seasonal patterns in water chemistry among fens distributed along the acidity-alkalinity gradient, and (iii) testing the differences in seasonal water chemistry among major fen-vegetation types.

Methods

A multidimensional view of the water chemistry of the fens is presented in terms of geographical distribution (various aquifer chemistry types, climatically different areas) and method of data processing. Water chemistry is generally supposed to have a crucial impact on the composition of fen vegetation. Unconstrained ordination of variation in water chemistry gives scores that express overall water chemistry, and reflect ion interactions and their antagonistic or synergistic influence on spring biota. An overlap in the scores of sites with similar vegetation may suggest that differences in water chemistry (i) cannot explain the differences in vegetation (overlap of data from one sampling season) or (ii) can explain these differences, but data collected at various times are not comparable (score overlap in ordination of all samples).

Study area and sites

The study area is the border region between the Czech and Slovak Republics in the Western Carpathians with bedrock of alternating claystone and sandstone (see detailed description and map in Hájek et al. 2002). The geographical coordinates and characteristics of the fens are given in Table 1.

Ten sites were chosen as representative of (i) each vegetation type (phytosociological associations *Carici flavae-Cratoneuretum*, *Valeriano-Caricetum flavae*, *Cirsietum rivularis*, *Sphagno warnstorffii-Eriophoretum latifolii* and *Carici echinatae-Sphagnetum* – for details see Hájek 1998, Hájek & Háberová 2001, Hájek & Hájková 2002 and Tables 1 and 2), (ii) each geographical area with a specific climate, altitude and species pool (the Bílé Karpaty Mts, the Javorníky Mts, the Hostýnsko-Vsetínské Mts, the Turzovská Mts and the Moravian-Silesian Beskydy Mts) and (iii) each type of flysch bedrock with a specific aquifer chemical composition (for details see Hájek et al. 2002). The spring fens were further selected to be easily accessible by car so that water samples could be quickly transferred to the laboratory and to minimize the time between the first and last sample taken. Only sites that were likely to persist relatively unchanged during the research period were considered. The resulting list was small so no random selection was necessary.

Vegetation composition

Vegetation was recorded at the beginning of the research (1999) by phytosociological relevés using 16 m² plots (Westhoff & van den Maarel 1973) and the nine-degree Braun-Blanquet cover scale modified by van den Maarel (1979). All relevés used in this paper are the same as those utilized in a more detailed study of vegetation-water chemistry relationships in the study area (Hájek et al. 2002). Nomenclature follows Kubát et al. (2002) for vascular plants, Frey et al. (1995) for bryophytes and Valachovič (2001) for syntaxa.

Water sampling and analysis

Water samples were collected from permanent plots (shallow pits), which were located in the surroundings of the major stream or headspring at each locality. The shallow pits were always re-exposed and water was pumped-out of them and allowed to refill before sampling. The contact of sampled springwater with air was short. Water conductivity, pH and redox-potential were measured in situ using portable instruments (CM 101 and PH 119, Snail Instruments). The readings were standardized to 20 °C (pH, conductivity) and Ag/AgCl reference electrode (redox-potential). Conductivity caused by hydrogen ions was subtracted (Sjörs 1952). Afterwards, water was placed in plastic bottles using a syringe. Preservatives were added to divided samples: for metallic elements, 0.5 ml of 65% HNO₃ per 100 ml of sample; for anions, 3 ml of chloroform per 1000 ml. All plots were sampled from 1999 to 2001, three times a year (April, July and October).

Since most water samples were turbid due to colloidal suspensions, filtration or centrifugation (4000 turns per minute, 10 minutes) was necessary. The concentrations of sulphates, phosphates, nitrates, ammonium ions, and chlorides were determined by DR 2000 spectrophotometry following colour reactions with certificated HACH-reagents. Metallic and semimetallic cation (Ca²⁺, Mg²⁺, Si, K⁺, Na⁺ and Fe) concentrations were determined using a GBC AVANTA atomic absorption spectrometer (Antanasopulos 1994).

Table 1. – Geographical position and characteristics of the sites. See text for delimitation of site groups. Longitude and latitude were measured using the GPS system (WGS 84). The first DCA-axis (DCA1) is interpreted as the poor-rich gradient, which coincides with the composition of the aquifer. Site 8 has an outlying position on the second axis as it has few fen species and a high cover of dominants. Herb layer biomass was recorded at the end of June. Abbreviations: Siles = Silesian unit of the Magura-flysch bedrock; Rača = Rača unit of the Magura-flysch bedrock; BK = Bílé Karpaty unit of the Magura-flysch bedrock; BMF = brown moss fen; C.d. = *Caricion davallianae*.

Site no.	Site group	Site name	Geological unit	Altitude	Longitude	Latitude	Vegetation		Herb layer biomass	Vegetation type
							DCA1	DCA2		
1	I	Obidová A	Siles	730	18°31'24"	49°31'03"	1.57	2.03	low (134 g/m ³)	rich <i>Sphagnum</i> -fen
2	I	Obidová B	Siles	733	18°31'24"	49°31'02"	0.89	2.07	medium (377 g/m ³)	poor <i>Sphagnum</i> -fen
3	I	Bělý Kríž	Siles	910	18°32'47"	49°29'55"	0.32	2.35	low (234 g/m ³)	poor <i>Sphagnum</i> -fen
4	I	Jančíkovci	Siles	800	18°33'22"	49°29'26"	0.00	2.23	low (54 g/m ³)	poor <i>Sphagnum</i> -fen
5	II	Kelčov	Rača	650	18°28'47"	49°24'03"	2.97	2.01	low (222 g/m ³)	peat-forming BMF (C.d.)
6	II	Brodské	Rača	528	18°10'30"	49°21'59"	2.56	2.25	low (121 g/m ³)	peat-forming BMF (<i>Calthion</i>)
7	II	Jasenka	Rača	514	18°01'25"	49°22'41"	3.30	2.05	low (179 g/m ³)	tufa-forming BMF (C.d.)
8	III	V. Klobouky	BK	380	18°01'24"	49°06'47"	4.15	0.00	high (874 g/m ³)	tufa-forming BMF (<i>Calthion</i>)
9	III	Mechnáč	BK	636	17°47'53"	48°56'34"	3.36	2.37	low (286 g/m ³)	tufa-forming BMF (C.d.)
10	III	Hrnčárky	BK	440	17°40'34"	48°54'30"	4.01	2.67	low (120 g/m ³)	tufa-forming BMF (C.d.)

Table 2. – The species which dominate the areas surrounding the sample points. Data are from phytosociological relevés (16 m²).

Site no.	Bryophyte dominants	Vascular plants dominants
1	<i>Sphagnum contortum</i> , <i>S. warnstorffii</i> , <i>Bryum pseudotriquetrum</i> , <i>Campylium stellatum</i>	<i>Carex nigra</i> , <i>C. panicea</i> , <i>C. echinata</i> , <i>C. demissa</i> , <i>Eriophorum angustifolium</i>
2	<i>Sphagnum flexuosum</i>	<i>Carex echinata</i> , <i>Viola palustris</i> , <i>Crepis paludosa</i> , <i>Equisetum fluviatile</i> , <i>Lysimachia vulgaris</i>
3	<i>Sphagnum palustre</i> , <i>S. papillosum</i> , <i>S. fallax</i>	<i>Carex echinata</i> , <i>C. nigra</i> , <i>Nardus stricta</i> , <i>Equisetum sylvaticum</i> , <i>Eriophorum angustifolium</i> , <i>Drosera rotundifolia</i>
4	<i>Sphagnum palustre</i> , <i>S. papillosum</i> , <i>S. fallax</i> , <i>Polytrichum commune</i>	<i>Nardus stricta</i> , <i>Carex nigra</i> , <i>Drosera rotundifolia</i>
5	<i>Drepanocladus cossonii</i> , <i>Campylium stellatum</i> , <i>Bryum pseudotriquetrum</i>	<i>Carex panicea</i> , <i>Eriophorum latifolium</i> , <i>Epipactis palustris</i> , <i>Valeriana simplicifolia</i>
6	<i>Aulacomnium palustre</i> , <i>Homalothecium nitens</i> , <i>Climacium dendroides</i>	<i>Carex nigra</i> , <i>C. panicea</i> , <i>Eriophorum angustifolium</i> , <i>E. latifolium</i>
7	<i>Cratoneuron commutatum</i> , <i>Campylium stellatum</i> , <i>Bryum pseudotriquetrum</i> , <i>Fissidens adianthoides</i>	<i>Carex panicea</i> , <i>C. flacca</i> , <i>C. nigra</i> , <i>Eriophorum latifolium</i> , <i>E. angustifolium</i>
8	<i>Calliergonella cuspidata</i> , <i>Cratoneuron commutatum</i>	<i>Equisetum telmateia</i> , <i>Valeriana simplicifolia</i> , <i>Carex paniculata</i>
9	<i>Campylium stellatum</i> , <i>Calliergonella cuspidata</i> , <i>Cratoneuron commutatum</i>	<i>Eriophorum latifolium</i> , <i>E. angustifolium</i> , <i>Carex flacca</i>
10	<i>Cratoneuron commutatum</i> , <i>Campylium stellatum</i> , <i>Bryum pseudotriquetrum</i> , <i>Calliergonella cuspidata</i>	<i>Equisetum telmateia</i> , <i>Eriophorum angustifolium</i> , <i>Valeriana dioica</i> , <i>Carex panicea</i> , <i>C. flacca</i>

These methods are the standard ones used in analysis of water, wastewater and drinking water (APHA, USEPA).

Statistical analyses

The Kolmogorov-Smirnov test confirmed the normal distribution of all measured variables, with the exception of redox-potential values, the distribution of which was uniform. We therefore assumed variance distributions to be homogeneous (homoscedasticity; Sokal & Rohlf 1995) and no transformations were made.

Temporal variation (TV) of each component of water chemistry was quantified and standardized using the following steps: (1) The arithmetic mean and standard deviation was calculated for all 9 values of each chemical variable, separately for each locality; (2) The coefficient of variation (CV) was calculated for each locality and each variable; (3) The CVs from all ten localities were averaged for each variable and expressed as a percentage. Further, the CV was calculated for each period and each chemical variable. This was used as a measure of spatial variation among sites.

Localities were divided into three groups (Table 1). Classification criteria were the site score on the first DCA axis and the geological unit (aquifer composition). Using data for all the seasons, the significance of the differences between spring, summer and autumn and three site groups were tested using repeated measures ANOVA with between-subject factors. The differences between the three site groups were also tested by three separate tests of between-subject effect in an univariate general linear model. The water physical-chemical variables were dependent, within-subject variables; site group was an independent, between-subject variable and year was a categorical co-variable in all these tests. F-values and significance levels of these four independent tests were compared.

Chemical variables were also compared between localities with the same calcium concentration and bedrock, but with different vegetation, using the parametric t-test. Three pairs of sites, always from one meadow-species rich fen and one meadow-species poor fen, were compared in three independent tests. SPSS software was used for these one-dimensional statistical processes.

The CANOCO 4.0 package (ter Braak & Šmilauer 1998) was used for ordination analyses. First, four water-chemistry data matrices were prepared (rows: samples, columns: values of water chemistry variables): all samples together ($n = 90$), all vernal samples ($n = 30$), all summer samples ($n = 30$) and all autumnal samples ($n = 30$). These were separately subjected to partial principal components analysis (PCA), where inter-annual variation was eliminated using three categorical co-variables (years 1999, 2000 and 2001) and where the values of each environmental variable were standardized to mean 0 and variance 1. Site (sample) scores based purely on overall water chemistry were obtained for all four PCA-axes in each analysis. Data on sampling season were a posteriori shown as environmental variables in the PCA-scatter of all samples together, but the presented pattern in water chemistry data was extracted from all the variation.

Vegetation relevés were subjected to two ordination analyses: (1) indirect gradient analysis (using detrended correspondence analysis, DCA) and (2) three separate constrained ordinations (using canonical correspondence analysis, CCA), where PCA-site scores of spring, summer and autumn water-chemistry data were constraining variables. The species data set remained the same in all three CCAs. Percentage variances explained

by canonical axes (Økland 1995) were compared and a Monte Carlo test (ter Braak & Šmilauer 1998) of significance of all canonical axes was performed in each CCA.

Primary data from single determinations of water chemistry and vegetation composition for the study area ($n = 70$, for details see Hájek et al. 2002) were utilized to relate the power of each variable to explain the variation in species composition to its temporal variation at the ten reference sites. Percentage variance in species data explained by each chemical variable was calculated for this enlarged data set using the single-variable CCAs.

Results

Univariate comparisons

Water pH and conductivity were the most stable variables at the ten selected spring fens (Fig. 1). Monovalent cations (Na^+ , K^+), calcium and sulphates were also relatively stable. In contrast, nitrates, chlorides, iron, phosphates and water redox-potential showed the highest temporal variation. These fluctuating variables explained very little and insignificant amounts of the variation in plant species data in the 70 fens throughout the study area, when water chemistry was determined only once in August (Fig. 1). Relatively unstable magnesium and ammonium explained a high amount of the variation and relatively stable potassium and sulphates explained rather little.

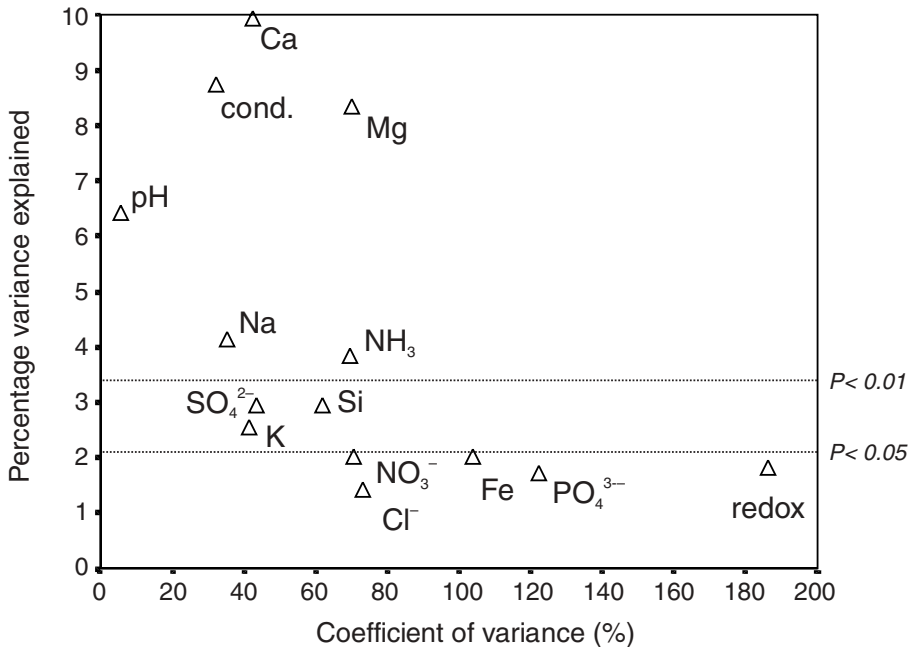


Fig. 1. – The ability of water chemistry variables to explain variation in species composition, plotted against their temporal variation found at the ten reference sites. The x-axis represents the coefficients of variation, the y-axis the percentage of variance explained by each of the variables (single determinations in summer) in a single-variable CCAs of plant species data from 70 sites in the study area. The dotted lines indicate the significance levels of the Monte-Carlo test of the canonical axis.

Only the concentration of sodium, nitrates, water redox-potential and temperature fluctuated significantly among seasons (Table 3). Nevertheless, the seasonal variation in water physical-chemical properties causes the statistical comparison of the means of several variables of the vegetation types to give different results when data from different seasons are used. However, this was verified only for temperature and Si, N-NO₃ and Cl⁻ concentrations and to a lesser degree, for Fe, Mg and water redox-potential (Table 4). The differences in Ca, Na and SO₄²⁻ concentrations, pH and conductivity was highly significant in all three seasons.

Overall summer and autumnal water chemistry explained more of the variation in species data (47.8% and 45.4%) than spring water chemistry (37.3%), when separated canonical correspondence analyses with a single variable was used. It can be explained mainly by the low values for redox-potential and iron concentration, which only differed slightly in the three major site groups in spring (Table 4).

We did not find significant differences in the major nutrient concentrations in the water of the *Calthion* and *Caricion davallianae* sites. The species-poor, high-producing tufa-forming spring fen in which wet-meadow species were prevalent over rich fen species (*Calthion* dominated by *Equisetum telmateia*, *Valeriana simplicifolia* and *Carex paniculata*, site 8) had a higher nitrate concentration than the low-producing, typical tufa-forming spring fen (*Caricion davallianae*), which had the same concentration of bases (Table 5). Other differences in major nutrient concentrations were not significant. The peat-forming low-producing fen meadow with a high number of nutrient-demanding species (*Cirsietum rivularis eriophoretosum latifoliae*, site 6) did not significantly differ in any major nutrient from site 7, which had a typical *Caricion davallianae* rich fen vegetation and a comparable concentration of major metallic cations (Table 5). Different results were obtained when a species-poor *Sphagnum*-fen with *Calthion* vegetation in the herb layer was compared with a typical poorly productive and species-rich *Sphagnum*-fen (sites 2 and 1). They differed significantly in ammonium and potassium concentrations (Table 5).

Multivariate site comparison

The order of sites along the first two PCA axes was similar in all three seasons (not shown in this paper). The site differentiation along the first axis (base saturation) is best in autumn, when *Sphagnum*-sites are clearly differentiated in the following order: 4–3–1. Site 2, dominated by *Sphagnum flexuosum*, *Crepis paludosa* and *Lysimachia vulgaris*, is differentiated along the second axis that correlates with the concentration of ammonium (Fig. 2). This accords well with vegetation differences in the *Sphagnum*-rich sites (see DCA site scores in Table 1 and dominants in Table 2). High autumnal variation in Ca²⁺ and pH between sites (Table 4) is also associated to this pattern. Sites 5 and 10 are well differentiated from all the others in the three seasons (see also Fig. 3), whereas rich fens at sites 6–9 always have overlapping site scores along the first axis. However, they are differentiated along the second axis by high iron and potassium concentrations at site 7 and a high nitrate concentration at site 9 (high-producing *Calthion*).

PCA ordination of the water-chemistry results (spring + summer + autumn, Fig. 3) suggests that the comparison of data recorded at different times has some ecological relevance, especially for the three major vegetation groups. The fine differences between related pairs of sites (3 and 4, 6 and 7), indicated by separate analyses, are obscured in this analysis.

Table 3. – Mean values of the environmental variables (ion concentrations in mg/l) and their standard deviations (in parentheses) for the spring fens. Characteristics, dominant species and classification of these fens are presented in Tables 1 and 2.

Variable	1	2	3	4	5	6	7	8	9	10
Ca	10.76 (5.47)	8.10 (5.91)	6.85 (3.44)	4.14 (3.02)	55.09 (19.44)	83.33 (16.88)	106.64 (41.27)	207.75 (73.24)	78.42 (6.30)	191.23 (77.23)
Mg	2.15 (1.63)	1.46 (1.70)	0.82 (0.66)	0.76 (0.69)	4.22 (3.25)	9.70 (5.14)	7.32 (3.82)	4.63 (2.70)	12.23 (5.68)	13.85 (6.39)
Fe	24.78 (29.59)	11.53 (11.08)	3.68 (3.48)	7.19 (7.39)	64.77 (85.73)	18.75 (24.22)	79.34 (89.29)	5.99 (5.17)	3.58 (3.50)	10.97 (7.16)
K	1.88 (1.49)	4.60 (2.06)	1.16 (0.77)	0.94 (0.34)	1.91 (0.73)	2.79 (0.77)	3.33 (1.42)	2.76 (1.29)	1.21 (0.24)	2.32 (0.33)
Na	4.18 (1.61)	1.91 (0.94)	1.55 (0.97)	1.39 (0.96)	12.89 (3.56)	15.65 (1.84)	18.82 (2.76)	9.64 (1.87)	5.00 (1.23)	16.96 (5.64)
Si	4.84 (2.71)	4.26 (5.41)	3.38 (2.15)	2.65 (1.26)	7.17 (2.42)	9.42 (6.34)	10.93 (6.29)	5.88 (2.30)	7.32 (3.62)	8.64 (6.54)
SO ₄ ²⁻	19.33 (12.74)	18.33 (10.30)	20.78 (8.45)	16.67 (3.35)	9.00 (8.03)	35.11 (12.31)	12.78 (11.65)	49.44 (8.80)	60.22 (3.67)	72.67 (10.7)
PO ₄ ³⁻	0.37 (0.70)	0.22 (0.13)	0.11 (0.08)	0.13 (0.14)	0.27 (0.52)	0.20 (0.15)	0.13 (0.07)	0.29 (0.41)	0.18 (0.31)	0.20 (0.32)
N-NO ₃ ⁻	0.73 (0.67)	1.16 (0.83)	0.44 (0.30)	0.37 (0.33)	0.32 (0.28)	0.20 (0.13)	0.24 (0.21)	1.71 (1.02)	4.74 (0.90)	0.36 (0.24)
N-NH ₃	1.75 (0.82)	2.89 (1.32)	1.43 (0.59)	1.39 (0.64)	1.88 (1.96)	0.98 (0.42)	2.64 (4.88)	0.94 (0.52)	0.63 (0.43)	1.34 (0.82)
Cl ⁻	3.62 (2.62)	3.86 (2.81)	1.64 (1.13)	2.04 (2.05)	2.54 (2.31)	2.11 (2.00)	5.83 (3.09)	6.80 (5.61)	3.79 (2.04)	44.10 (19.4)
pH	6.10 (0.48)	5.53 (0.62)	4.56 (0.21)	4.12 (0.26)	6.99 (0.33)	7.08 (0.17)	7.26 (0.15)	7.62 (0.45)	7.54 (0.35)	7.47 (0.33)
Conductivity (µS/cm)	74.33 (34.78)	47.89 (25.25)	43.44 (18.93)	25.67 (14.61)	273.22 (92.34)	428.11 (57.30)	496.78 (80.01)	471.00 (63.46)	444.44 (84.27)	661.56 (63.94)
Water redox-potential (mV)	56.33 (160.83)	38.67 (188.36)	225.89 (60.88)	235.22 (71.67)	42.33 (113.43)	-134.11 (129.74)	-35.33 (117.63)	91.98 (41.58)	108.67 (93.21)	63.94 (87.12)
Temperature (°C)	10.6 (5.6)	10.7 (5.6)	9.9 (5.6)	10.6 (5.5)	12.4 (6.9)	12.1 (4.8)	12.6 (4.8)	12.6 (3.0)	10.2 (2.8)	13.7 (3.5)

Table 4. – Statistical evaluation of the variation in water chemistry. The differences in water chemistry in spring, summer and autumn were tested using the within-subject effect in a repeated measures RM ANOVA, with year as a covariable. The differences in water chemistry of the site groups (major spring fen types characterized in Table 1) were tested by (a) the between-subject effect in the repeated measures (RM) ANOVA (with year as a covariable) pooling the data from all the seasons, and (b) between-subject effect in three separate univariate general linear models with the year as a covariable, separately for each season. Variables are ordered according to seasonal variation (expressed by the coefficient of variation CV, see Fig. 1). **** $P < 0.001$, *** $P < 0.01$, ** $P < 0.05$, ns – not significant

Variable	Variation among seasons			Variation among three site groups				Maximum values found in site group
	Maximum variation among sites (max. CV)	Maximum mean values (all sites)	F-value and significance of the test of within-subject effect	F-value and significance of the tests of between-subject effect			Autumn (n = 30)	
				RM ANOVA all data (n = 30)	Spring (n = 30)	Summer (n = 30)		
pH	autumn	summer	ns	61.3***	96.3***	32.5***	35.9***	III
conductivity	spring	summer	ns	91.6***	73.7***	90.5***	56.5***	III
Na	autumn	autumn	4.9*	36.3***	35.3***	42***	42.6***	II
K	autumn	autumn	ns	ns	ns	ns	n.s	II
Ca	autumn	autumn	ns	36.7***	22.8***	31.0***	26.7***	III
SO ₄ ²⁻	summer	spring	ns	57.8***	55.1***	46.5***	22.8***	III
Si	spring	autumn	ns	15.9***	3.9*	11.2***	ns	II
N-NH ₃	spring	summer	ns	ns	ns	ns	n.s	I
Mg	summer	spring	ns	14.0***	16.3***	10.3***	9.8**	III
N-NO ₃ ⁻	autumn	spring	3.5*	8.3**	11.4***	5.0*	6.8**	III
Cl ⁻	summer	autumn	ns	5.1*	5.4*	ns	5.3*	III
Fe	summer	summer	ns	4.5*	3.6*	5.6**	6.5**	II
PO ₄ ³⁻	spring	summer	ns	ns	ns	ns	n.s	III
Redox-potential	summer	spring	5.5**	9.3**	3.8*	8.1**	6.1**	I
Temperature	spring	summer	21.1***	5.6**	11.5***	6.4**	ns	I

Table 5. – Comparison of the chemistry of water between sites with the same concentration of calcium and bedrock, but with different vegetation cover. Sites 2, 6 and 8 are “meadow sites” (M) and harbour abundant meadow species typical of the *Molinietalia* order. Sites 1, 7 and 10 are typical poorly productive fens dominated by fen species (“fen site”, F). The ordering of the variables corresponds to that in Table 4. Significance of t-tests (n = 18) is presented; ns = not significant. Sites in which higher values were found are indicated (F, M).

	Silesian unit sites 1, 2		Rača unit sites 6, 7		Bílé Karpaty unit sites 8, 10	
	Higher values	P	Higher values	P	Higher values	P
pH	F	0.048	M	0.033	–	ns
conductivity	–	ns	–	ns	F	< 0.0001
Na	F	0.003	F	0.012	F	0.004
K	M	0.006	–	ns	–	ns
Ca	–	ns	–	ns	–	ns
SO ₄ ²⁻	–	ns	M	0.001	F	< 0.0001
Si	–	ns	–	ns	–	ns
N-NH ₃	M	0.045	–	ns	–	ns
Mg	–	ns	–	ns	F	0.001
N-NO ₃ ⁻	–	ns	–	ns	M	0.001
Cl ⁻	–	ns	F	0.009	F	< 0.0001
Fe	–	ns	–	ns	–	ns
PO ₄ ³⁻	–	ns	–	ns	–	ns
Redox-potential	–	ns	–	ns	–	ns
Temperature	–	ns	–	ns	–	ns

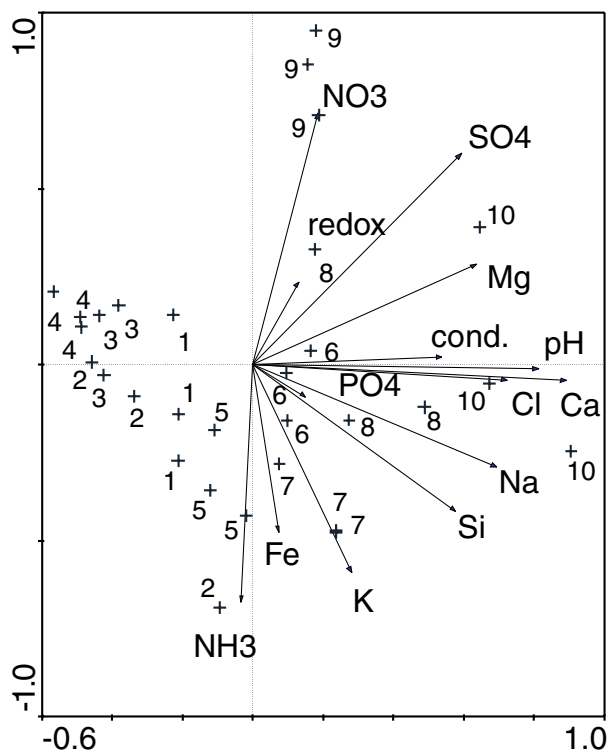


Fig. 2. – The PCA of water chemistry variables based on autumnal samples. Sites are labelled according to the numbers presented in Table 1. Only the first two axes are shown. Percentage variance explained by axes: 1st axis 32.4%; 2nd axis 19.1%. cond. = conductivity.

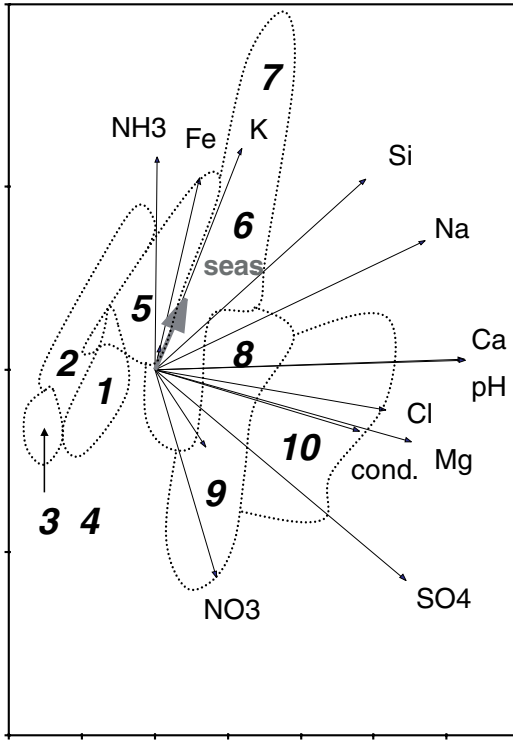


Fig. 3. – The PCA of water chemistry variables based on samples taken in all three seasons. The samples from the same locality are bordered by a dashed line. If the samples from two localities overlap, all the samples are bordered by one line. In such cases, the locality number is that of the area where the majority of samples were collected. The thick arrow (seas.) indicates changes in ion concentration during a year (from spring to autumn) and was a posteriori plotted onto the chart. Percentage variance explained by axes: 1st axis 31.9%; 2nd axis 16.7%. cond. = conductivity.

Discussion

The information value of water chemistry determined once at each site is greatly reduced by the high temporal variation in ion concentrations; this is more so for ombrotrophic bogs (Malmer 1962, Proctor 1994, Rybníček 1997) than spring fens. Our results show that the bivalent cations (Ca^{2+} , Mg^{2+}), pH and conductivity can be used to characterize the acid-alkaline gradient, from extremely rich to extremely poor fen vegetation, even when only a single water sample is analysed. Of these, pH and conductivity are the most easily obtained, can explain a large part of the variation in vegetation (Sjörs 1952, Malmer 1963, 1986, Vitt et al. 1995, Hájek & Hájková 2002) and are relatively highly temporally stable along the entire poor-rich gradient (Fig. 1, Malmer 1962, Bertram 1988, Proctor 1994, Vitt et al. 1995). There is no linear relation between sodium and potassium and the main vegetation gradient, but their high concentration in peat-forming (non-petrifying) spring fens is also stable. This differs from their variable concentration in the water of ombrotrophic or oceanic bogs, where the sodium and potassium concentrations in mire water are associated with precipitation chemistry (Malmer et al. 1992, Proctor 1992, 1994, Bragazza et al. 1998).

Iron concentration and redox-potential fluctuate in time and, therefore, a single determination may not be adequate for finding relationships with species composition (Fig. 2). Their impact on the distribution pattern of species, however, can be comparable to or higher than that of elements that explain little of the variation although highly stable (K^+ , SO_4^{2-} or Si, in our case). Iron, especially, can strongly influence the biotic components of wetland

ecosystems because of its high toxicity (Snowden & Wheeler 1993, Vuori 1995) or its deficiency in calcareous soils (Zohlen & Tyler 2000); its effect is often underestimated as its concentration varies. Nevertheless, it is significantly positively or negatively correlated with bryophyte and mollusc species richness, as shown by a previous study based on single determination of water chemistry (Hájková & Hájek 2003, Horsák & Hájek 2003). Further, a significant difference in single determinations of water iron concentration of samples from tufa-forming (*Carici flavae-Cratoneuretum*) and peat-forming rich fen vegetation (*Valeriano-Caricetum flavae*) was found in the same study area (Hájek et al. 2002). It is often reported that iron is one of the most unstable water chemistry components and reaches its maximum concentration in summer (Fig. 1, Table 4, see also Malmer 1962, Proctor 1994, Vitt et al. 1995). The high fluctuation in iron concentration is causally associated with changes in redox-potential and with the concentration of dissolved organic matter (Malmer 1962, Proctor 1994) as well as with microbial activity (Olivie-Lauquet et al. 2001).

Other studies in central Europe indicated that nutrient availability is not dependent on the acidity-alkalinity gradient (Waughmann 1980, Bragazza & Gerdol 2002, Hájek et al. 2002). Water potassium is weakly correlated with water pH and calcium concentrations in some studies (Hájek et al. 2002, Bragazza & Gerdol 2002). However, our study of reference fens did not reveal a relationship with the poor-rich gradient (Table 4).

Sites with the same base-status, bedrock, and similar water regimes, but with different participation of meadow species, did not differ markedly in the concentration of important nutrients. No element that can be used to categorize a fen meadow and typical fen sites was found in any of our data sets. Vegetation in the isolated fens we studied is nutrient-limited. In such conditions, plants may take up all the available nutrients when their concentrations increase. This may be why an increased nutrient input was not detected in soil water.

In conclusion, late summer or early autumn is best to obtain representative values for the concentrations of major elements in spring fens (see also Tahvanainen et al. 2003). Spring is an unsuitable time for determining iron and silicon concentrations and water redox-potential. Calcium, conductivity and pH are associated with variation in vegetation and can be used to categorize major fen vegetation types at the landscape level, even if measured just once and at different times. The concentrations of available nitrogen and phosphorus need to be determined on several occasions.

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Souhrn

Článek hodnotí sezónní variabilitu v chemickém složení vod na prameništích slatiništích Západních Karpat. Rovněž posuzuje, jak tato variabilita může ovlivnit výsledky studií o vztahu slatiništní vegetace a chemismu vody, pokud jsou k dispozici pouze jednorázově naměřené hodnoty. Bylo vybráno 10 referenčních lokalit, které reprezentovaly různé minerotrofní mokřadní typy (pěnovcová prameniště, vápňitá slatiniště, prameništní louky, různě bohatá společenstva s rašeliníky). Voda byla odebírána třikrát ročně (na jaře, v létě a na podzim) po dobu 3 let. Nejstabilnějšími měřeními proměnnými byly pH a konduktivita, dosti stálou koncentraci vykazovaly i ionty sodíku, draslíku,

vápníku a sírany. Velká časová variabilita byla naopak zaznamenána v případě dusičnanů, chloridů, celkového železa, fosforečnanů a redox-potenciálu vody. Tyto variabilní proměnné rovněž vysvětlují jen velmi málo z druhové variability slatiníšť v území. To může být způsobeno právě jejich nestabilitou. Statistické srovnání koncentrací jednotlivých iontů a fyzikálně-chemických vlastností vody mezi různými vegetačními typy přineslo rozdílné výsledky při použití jamích, letních a podzemních hodnot v případě teploty a koncentrací křemíku, dusičnanů a chloridů; v menší míře též v případě redox-potenciálu vody a koncentrací železa a hořčiku. Naopak, rozdíly v koncentracích vápníku, sodíku a síranů, stejně jako rozdíly v pH a konduktivitě vody byly velmi průkazné ve všech obdobích. Analýza hlavních komponent ukázala, že ve všech třech obdobích je hlavním gradientem v chemických datech gradient od minerálně chudých, kyselých slatiníšť k minerálně bohatým, alkalickým typům. Nejvýrazněji byly jednotlivé lokality a jednotlivé vegetační typy diferencovány při analýze dat z podzemních vzorků vody. Hlavní gradient a diferenciaci hlavních vegetačních typů byly patrné i v případě, že byla analyzována data ze všech tří ročních období současně. Rovněž byly srovnány koncentrace jednotlivých iontů mezi dvojicemi lokalit, které se nacházejí na stejném geologickém podloží a jsou syceny vodou o stejné koncentraci vápníku, ale hostí rozdílné vegetační typy. Opakované analýzy vody ukázaly, že druhově chudé rašeliníště s dominujícím *Sphagnum flexuosum* v mechovém patře a s vysokou pokryvností druhů svazu *Calthion* v bylinném patře mělo oproti polydominantní ostrícovomechové vegetaci zvýšenou koncentraci amoniakálního dusíku a draslíku ve vodě. Druhově chudé vysokoproduktivní společenstvo svazu *Calthion*, vyvinuté na pěnovcovém prameništi, mělo ve vodě průkazně vyšší koncentraci dusičnanů než nízkoproduktivní ostrícovomechové společenstvo pěnovcového prameniště (*Caricion davallianae*). V ostatních případech se žádný průkazný rozdíl v koncentraci živin ve vodě neprojevil.

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