# Seasonal variation of water chemical gradients in three boreal fens

# Teemu Tahvanainen<sup>1</sup>, Tapani Sallantaus<sup>2</sup> & Raimo Heikkilä<sup>3</sup>

- <sup>1)</sup> Department of Biology, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland (e-mail: teemu.tahvanainen@joensuu.fi)
- <sup>2)</sup> Pirkanmaa Regional Environment Centre, P.O. Box 297, FIN-33101 Tampere, Finland (e-mail: tapani.sallantaus@ymparisto.fi)
- <sup>3)</sup> Friendship Park Research Centre, Kainuu Regional Environment Centre, Lentiirantie 342, FIN-88900 Kuhmo, Finland (e-mail: raimo.heikkila@ymparisto.fi)

Received 5 May 2003, revised version received 6 June 2003, accepted 10 June 2003

Tahvanainen, T., Sallantaus, T. & Heikkilä, R. 2003: Seasonal variation of water chemical gradients in three boreal fens. — *Ann. Bot. Fennici* 40: 345–355.

Surface water chemistry was monitored in three fens through one growing season by weekly sampling in the southern aapa mire zone, middle boreal Finland. The fens included a soligenous moderately rich fen, a soligenous extremely poor fen, and a topogenous extremely poor fen. The chemical variables most clearly related to the poor–rich gradient were pH, alkalinity, Ca, Mg, and Na concentrations. The soligenous and topogenous extremely poor fens differed in DOC, Al, Fe, Si, and S concentrations. The main chemical gradients were related to the season. In early summer (June to July) the chemical gradients were variable and weakly definable. In late summer (August to September) the gradients were more stable and separated the three fens clearly. Late summer is suggested optimal for comparable sampling of surface water in boreal fens.

Key words: aapa mire, ecology, poor-rich gradient, wetlands

# Introduction

Surface water chemistry is of fundamental importance to mire vegetation. Important aspects of variation in mire water chemistry include: variation related to the degree of ombrogenous *vs.* minerogenous influence (Tolonen & Hosiais-luoma 1978, Damman 1995), variation along the gradient from poor to rich vegetation types (Witting 1947, 1949, Sjörs 1950, Vitt *et al.* 1995, Sjörs & Gunnarsson 2002, Tahvanainen *et al.* 2002), climate-dependent geographical variation (Vitt *et al.* 1990, Malmer *et al.* 1992,

Slack & Hallingbäck 1992, Damman 1995), vertical variation in peat pore waters (Vitt *et al.* 1995, Steinmann & Shotyk 1997), variation in capillary water along the microtopographical gradient (Kivinen 1932, Bellamy & Rieley 1967, Tahvanainen & Tuomaala 2003), seasonal variation (reviewed below), diurnal variation (Tahvanainen & Tuomaala 2003), and long-term trends (Gunnarsson *et al.* 2000, 2002).

Frequently, in studies concerning water chemistry along the poor-rich gradient, considerable overlap has been found between different categories (*see* Sjörs 1950, Sjörs & Gunnarsson 2002). Although the overlap is evident and ecologically interpretable in some cases, a part of it is due to the fact that most data sets have been based on sampling in single occasions. Seasonal and short-term variation may cause considerable overlap in time. Further overlap is caused by methodological problems in water sampling (Tahvanainen & Tuomaala 2003). Analyses of seasonal variation of water chemistry during the growing season using comparably sampled data sets are important for the evaluation of comparability and representativeness of single sampling occasions, as well as for assessing the seasonal availability of nutrients in surface water.

Although the chemistry of mire waters and its relationship with vegetation has been studied extensively, there are few published studies concerning seasonal variation. Most of the work on seasonal variation of mire water chemistry has concentrated on ombrogenous bogs (Boatman et al. 1975, Damman 1988, Bragazza 1993, Proctor 1994, Bragazza et al. 1998) and only a few studies have included minerogenous fens (Malmer 1962b, Proctor 1995, Vitt et al. 1995). In most cases, sampling has been conducted at monthly or longer intervals. An extensive survey of seasonal variation of water chemistry across the poor-rich vegetation gradient was conducted by Vitt et al. (1995) in central Alberta, continental western Canada. It is, however, very difficult to say to which extent the seasonal patterns found by Vitt et al. (1995) apply to climatically and geologically different regions. The north-eastern part of Fennoscandia is characterised by Archaic siliceous bedrock in contrast to the study area of Vitt et al. (1995), where calcareous Cretaceous deposits of sandstones and shales are prevailing. The water chemical gradients of mires differ between these regions, as a consequence of the differences in mineral composition and weathering rates of bedrock and soil minerals. In some cases, moderately rich fen waters in north-eastern Finland (Tahvanainen et al. 2002) have lower Ca concentrations than bog waters in central Alberta (Vitt et al. 1995), for example. Comparable data sets of seasonal variation from climatically and geologically different areas are needed to better understand the patterns of water chemistry in mires.

Furthermore, there is a lack of knowledge on seasonal variation of water chemistry as related to other ecohydrological variation than the poor-rich gradient. Minerogenous (geogenous) fens can be divided into soligenous and topogenous hydrological types. Soligenous mires have an inclined water table and are influenced by unidirectional water flow, while topogenous mires have more stagnant water and are formed on depressions in the landscape.

We conducted weekly monitoring of surface water chemistry in three fens through one growing season in north-eastern Finland. Our objective is to reveal the seasonal patterns in water chemistry in relation to the poor-rich gradient and soligenous vs. topogenous hydrology, in the siliceous region of north-eastern Fennoscandia. We also aim to find optimal timing for representative sampling during the growing season.

# Material and methods

# Study area

The study area is situated within the Nature Reserve Friendship Park in Kuhmo, north-eastern Finland (64°12 N, 30° 26 E, elevation 240 m above sea level). The study area is located within the middle boreal climatic-phytogeographical zone and in the southern aapa mire region. The mean annual rainfall is 600 mm and the mean annual temperature +1.2 °C. The bedrock in the study area consists of Archaic siliceous migmatites, granites, and gneisses. The upland soils are mostly unsorted moraines and they are strongly podzolised.

Three different fen areas in two separate mire basins Härkösuo and Joutensuo (HS and JS hereafter) were selected as the study sites. Two sampling sites were established at each fen. HS is a long (1 km) and narrow (100–150 m) soligenous sloping fen. JS is a topogenous aapa-fen (0.32 km<sup>2</sup>) with minerotrophic centre and mostly ombrotrophic margins. Spatial variation of water chemistry and vegetation in the study areas are reported in a previous study (Tahvanainen *et al.* 2002), and only short descriptions of vegetation are given here. Plant nomenclature follows Söderström and Hedenäs (1998) for bryophytes and Hämet-Ahti *et al.* (1998) for vascular plants.

# Site descriptions

#### Site 1: Moderately rich fen

The two sampling sites were located in a patterned, central part of an open moderately rich fen in HS. The fen receives minerogenous waters as surface flow from a spring-influenced fen in the mire margin and partly as more diffuse updwelling flow of ground water through peat. The wet surfaces range from mud-bottoms, covered with open water, to flarks with pure stands of Scorpidium scorpioides and scattered Pseudocalliergon trifarium. Characteristic species of the intermediate surfaces are Campylium stellatum, Loeskypnum badium, and Cinclidium stygium. In low hummocks (10-15 cm) Sphagnum warnstorfii and S. subfulvum are abundant, and high hummocks (15-30 cm) are S. fuscum dominated. Typical vascular plants of the wet microsites are Drosera longifolia, Carex limosa, C. rostrata, and Rhynchospora alba. In intermediate surfaces and low hummocks, species like Carex lasiocarpa, Selaginella selaginoides, Tofieldia pusilla, and Trichophorum alpinum are found. In higher hummocks, typical bog dwarf shrub vegetation is dominating. Both of the sampling sites were located in wet Scorpidium scorpioides flark surfaces, with partly open mud-bottoms.

### Site 2: Soligenous extremely poor fen

Two sampling sites were located in *Sphagnum*dominated flarks in an extremely poor fen in HS, 500 metres apart from the moderately rich fen sites. Minerogenous waters flow through this zone as surface flow from upper fen areas and from adjacent mineral land. Thus, the fen is hydrologically soligenous and margin-influenced. Most of the surfaces are flarks with abundant *Sphagnum balticum*, *S. fallax*, *S. flexuosum*, *S. jensenii*, *S. majus*, and *S. papillosum*. The vascular plant flora consists mainly of sparse *Andromeda polifolia*, *Carex limosa*, *C. rostrata*, *Eriophorum vaginatum*, and *Scheuchzeria palustris*.

## Site 3: Topogenous extremely poor aapa-fen

In JS, the two surveillance sites were situated in an extremely poor fen, in the centre of the mire. JS is a typical topogenous aapa fen where surface water flow is relatively weak. The other site was a relatively deep (about 3 m) open pool, from which water samples were taken directly, and the other one was a sampling well site at an adjacent Sphagnum pulchrum carpet. This fen area is irregularly patterned with open pools. Mostly flark and intermediate surfaces are found. Typical species are Sphagnum fallax, S. jensenii, S. majus, S. lindbergii, S. papillosum, and S. pulchrum. Vascular plant species are few but more abundant than in the extremely poor fen of HS. Most frequent species include Andromeda polifolia, Carex rostrata, Eriophorum vaginatum, and Vaccinium oxycoccos.

# Sampling and water analyses

Precipitation was monitored with a rain gauge, which was located 5 km from HS and 6 km from JS. Water table level (WTL) was measured, in relation to reference poles, from perforated PCV pipes, 20 mm in diameter. The measurements were adjusted to the mean water table depth (WTD), i.e. the depth of the water table in relation to the bryophyte capitula. WTD is usually less variable than WTL, because bryophytes and surface peat are buoyant to varying degrees. Only WTL was monitored routinely.

Water samples were taken weekly between 11 June and 31 September 1999, with the exception of a two week interval between 10 July and 22 July. Water samples were obtained from sampling wells installed the previous year. Chemical analyses were performed for pH, dissolved organic carbon (DOC),  $SO_4^{2-}$ , Cl<sup>-</sup>, and for total concentrations of 19 elements, of which Al, Ca, Cu, Fe, K, Mg, Mn, Na, N, S, and Zn had always concentrations above the detection limits. Occasionally also B, Cr, P, and Pb had concentrations



Fig. 1. Hydrological observations during the 1999 growing season. — A: Daily precipitation. — B: Weekly water table level measurements. HS = Härkösuo, JS = Joutensuo.

above the detection limits. The methods of water sampling, sample treatment and analyses were similar to those in Tahvanainen *et al.* (2002), with the following amendments: pH was measured immediately in the field; DOC samples were stored in -20 °C and analysed in November 1999; total N, SO<sub>4</sub><sup>2–</sup>, and Cl<sup>-</sup> samples were stored for three to four days at +4 °C in the dark before weekly analyses; samples for elemental analyses in February 2000.

# Statistical analysis

The effects of mire site (moderately rich fen, extremely poor fen of HS, extremely poor fen of

JS), sampling time (week) and their interaction (site  $\times$  week) on water chemistry were tested by repeated measures ANOVA (SPSS 10.1). Only variables with concentrations above the detection limits at all sites were tested. Cu and Zn were excluded because of considerably high concentrations in control samples of purified water (Tahvanainen et al. 2002). Centred, standardised principal component analysis was applied to logtransformed data to unravel common patterns of variation in water chemistry (PC-ORD 4.09). Log-transformation  $(\log_{10}[x + 1])$  was used to approximate normal distributions and applied to all variables except pH to preserve the correlation structure between the variables. The first week's data were excluded from the statistical analyses because the results were outlying in many cases and possibly disparate because the wells were not emptied prior to sampling. There were also some data on pH and DOC missing from the first week.

# Results

# Weather and water table level

The monthly precipitation values from June to September were: 31, 78, 38 and 28 mm (Fig. 1). In the closest national weather station, the monthly precipitation values from May to September were: 19, 24, 65, 61 and 15 mm, and the monthly mean temperatures were 4.5, 17.3, 16.1, 11.8, and 9.8 °C, respectively (Finnish Meteorological Institute 2000). June 1999 was warmer than average, but otherwise the meteorological conditions were 'unexceptional' and representative of the area. Weather observations did not have general correlations with the measured chemical variables or WTL (Fig. 1).

There were no seasonal trends in the variation of the WTL (Fig. 1). Fluctuation was more considerable in the extremely poor fen sites of HS than in the two other fens. In the two moderately rich fen sites in HS, the ranges of fluctuation of the WTL were only 2.0 and 5.0 cm. In the two extremely poor fen sites in HS, WTL was more variable, having ranges of 9.5 and 7.0 cm. In the extremely poor fen of JS, WTL was surveyed from the sampling well site only, at which the range of WTL fluctuation was only 4.5 cm during the study period.

#### The main water chemical gradients

The first and second PCA-axes had eigenvalues greater than the broken stick eigenvalues (i.e. higher eigenvalues than expected by chance) and together they explained 68% of the variation (Table 1). The third axis explained only 11% of the variation and was clearly less interpretable. The first axis represented the variation of the main cations (Mg, Ca, Na, K) and pH, and separated the moderately rich fen sites from the extremely poor fen sites (Table 1 and Fig. 2). The second axis separated the extremely poor fen of JS (Fig. 2). The highest eigenvector scores in the second axis were found for DOC, Fe, Si, Al and S (Table 1).

All of the three first PCA-axes were related to the season (Fig. 2). Along the first axis, the early summer scores of the moderately rich fen sites were close to the scores of the extremely poor fen sites. There was a linear trend in the scores of the moderately rich fen sites till the end of July, after which the scores settled at relatively constant levels, clearly separate from the

 Table 1. Summary of principal components analysis of water chemistry.

Axis	1	2	3
Eigenvalue	5.88	3.67	1.52
Broken stick	3.25	2.25	1.75
Cum. % explained	42	68	79
Na	-0.39	0.13	-0.02
Mg	-0.38	0.08	-0.10
Ca	-0.38	0.10	-0.18
pН	-0.33	-0.16	0.20
K	-0.31	0.21	0.17
SO42-	-0.27	-0.11	-0.28
N	-0.24	0.19	0.40
Al	0.22	0.39	0.21
Fe	0.22	0.41	0.08
DOC	0.21	0.41	0.03
Si	-0.17	0.41	0.08
Mn	0.16	0.14	-0.65
S	-0.16	0.35	-0.41
CI-	-0.07	0.22	-0.04



**Fig. 2.** Variation of the main water chemical gradients during the 1999 growing season, as indicated by the seasonal patterns of sample scores in principal component analysis of water chemistry variables. **A**: First PCA axis. **B**: Second PCA axis. **C**: Third PCA axis. *See* Fig. 1 for explanations of symbols.

extremely poor fen sites. The extremely poor fen sites moved only slightly, though continuously, towards smaller scores (higher cation concentrations), during the summer. On the second axis, the three fens were partly over-lapping in June and July, while in August and September, the two extremely poor fens were clearly separated. The three fens were over-lapping throughout the season on the third PCA-axis and all sites had a general decreasing trend.

# Seasonal patterns of individual surface water chemistry variables

Considerable seasonal variation was found in water chemistry at all sites. Most of the seasonal variation took place in early summer, whereas in late summer water chemistry was more stable. Means of water chemical variables during the late summer steady phase (August and September) are given in Table 2. Repeated measure ANOVAs of water chemistry showed significant effects (p < 0.05) of the "site" factor, representing the three fens, for pH, DOC, Ca, Mg, Na, S, and Si. Significant effects of the "week" factor, representing the different sampling occasions, were found for pH, N, Cl, Al, Ca, K, Mg, Mn, Na, and S. The interaction of "site" and "week" was significant only for DOC, Fe, Ca, and Mg.

There were no seasonal trends in pH (Fig. 3). Small, notably synchronic fluctuations

were found at both sites in HS, while more considerable fluctuation was found in JS. Also DOC levels were fairly constant in time, except at site 2 in the extremely poor fen of HS (Fig. 3).

In the moderately rich fen, concentrations of Ca, Mg, Mn, and Na had minimum values in early summer, sometimes preceded by higher values, followed by increases to nearly constant levels in August and September (Fig. 3). Similar but less distinct patterns were found in the extremely poor fens. Concentrations of K were more variable than of other main cations (Fig. 3). In the moderately rich fen, the pattern of K resembled that of other cations. In the extremely poor fens, K levels were suppressed in the middle of summer.

The concentrations of Al and Fe showed a distinct seasonal pattern at Site 1 in the extremely poor fen of HS: there was a gradual rise to maximum levels in August, followed by gradual decrease towards the end of the season. Concentrations of Fe were slightly elevated during June and July in the extremely poor fen of JS (Site 2). The three fens had overlapping concentrations of Cl<sup>-</sup> throughout the monitoring period and all sites had a continuous increasing trend (Fig. 3). Concentrations of total N had

**Table 2.** Means and standard errors (in parentheses) of alkalinity (meq  $l^{-1}$ ), pH, and elemental or ionic concentrations (mg  $l^{-1}$ ) in surface water in the three fens during August and September.

Chemical variable	Härkösuo mire		Joutensuo mire	
	Moderately rich fen	Extremely poor fen	Extremely poor fen	
Alkalinity	0.256 (0.015)	0 (0)	0 (0)	
рН	5.49 (0.05)	4.02 (0.04)	4.46 (0.07)	
DOC	20.6 (0.8)	42.6 (1.2)	21.1 (0.5)	
Ν	0.92 (0.04)	0.67 (0.03)	0.50 (0.05)	
CI-	0.99 (0.05)	0.97 (0.06)	1.08 (0.07)	
SO42-	0.49 (0.04)	0.29 (0.02)	0.34 (0.03)	
AI	0.020 (0.002)	0.229 (0.029)	0.032 (0.003)	
Са	2.21 (0.08)	0.72 (0.04)	0.49 (0.04)	
Cu	0.016 (0.003)	0.056 (0.003)	0.037 (0.020)	
Fe	0.10 (0.01)	0.76 (0.08)	0.24 (0.01)	
К	0.51 (0.03)	0.27 (0.04)	0.21 (0.02)	
Mg	1.20 (0.03)	0.25 (0.01)	0.15 (0.02)	
Mn	0.004 (0.000)	0.011 (0.001)	0.009 (0.001)	
Na	2.80 (0.05)	1.36 (0.06)	1.18 (0.04)	
S	0.42 (0.01)	0.43 (0.01)	0.31 (0.01)	
Si	5.56 (0.44)	5.51 (0.25)	0.40 (0.03)	
Zn	0.041 (0.002)	0.098 (0.006)	0.038 (0.006)	

n = 18 for each fen, including nine weekly samples from two sites.

very little seasonal variation, apart from some high peak concentrations (Fig. 3). Si was almost invariable in late summer at all sites, while in the moderately rich fen, there were lower levels in early summer (Fig. 3). Concentrations of S and SO<sup>2-</sup> had rather unclear seasonal patterns and occasional peak concentrations (Fig. 3). The concentrations of P were usually below the detection limit (0.016 mg l-1) but some concentrations above it were found at all sites (data not shown). In the moderately rich fen, detectable P concentrations were found mainly in September (up to 0.020 mg  $l^{-1}$ ), while in the extremely poor fen of HS, they were more common throughout the season (up to 0.037 mg  $l^{-1}$ ). In the extremely poor fen of JS, only one detectable P concentration was found from the open pool, against seven at the sampling well site (up to  $0.064 \text{ mg } l^{-1}$ ).

Differences in water chemistry between the sampling well and open pool samples were in general very small in the extremely poor fen of JS. Most notably, the well samples had higher pH than the open pool (Fig. 3). In early summer, the concentrations of Fe and Si were slightly higher in the sampling well than in the open pool (Fig. 3). In late summer, the concentration of  $SO_4^{2-}$ , Al, Ca, Mg, Mn, and P tended to be slightly higher in the open pool than in the sampling well (Fig. 3).

# Discussion

The geological conditions in the current study area are typical of middle boreal north-eastern Fennoscandia, with poorly weathering siliceous bedrock, podzolised mineral ground soils, and ground waters very low in most mineral concentrations. Also precipitation in the area is characterised by extremely low ionic concentrations. Consequently, mire water chemistry is characterised by low concentrations of mineral elements, especially of Ca, as compared to other regions (Tahvanainen *et al.* 2002).

# Patterns across ecohydrological gradients

The first two PCA-axes of water chemistry were very similar to those found for a data set covering

the whole mire basin of HS (Tahvanainen et al. 2002). The first axis, related to the main cation concentrations (Mg, Ca, Na, K) and pH, was connected to the poor-rich gradient in vegetation, as it separated the moderately rich fen from the two extremely poor fens. Several studies have indicated a water chemical gradient partly independent of the poor-rich gradient, related to concentrations of Al, Fe, Mn, S, and Si (Malmer 1962a, Mullen et al. 2000, Tahvanainen et al. 2002). High concentrations of these elements are connected to input of soil surface water from podzolised mineral land (Malmer 1962a, Damman 1995, Bragazza & Gerdol 2002, Tahvanainen et al. 2002). This 'mineral soil water gradient' reappeared in the second PCA-axis, which separated the extremely poor fens of HS and JS in the current data. The spatial variation and dynamics of these water chemical gradients are discussed in detail by Tahvanainen et al. (2002).

The concentrations of the main cations (Ca, Mg, and Na) in the extremely poor fens were extremely low throughout the growing season. In fact, their concentrations did not give clear evidence of minerogenic water source, when compared to ombrogenous mire water in the area (Tahvanainen et al. 2002). Instead, in the soligenous extremely poor fen of HS, the concentrations of Al, Fe, and Si gave clear indications of a strong minerogenic influence. In this fen, concentrations of DOC were very high and pH was buffered to 4.0 by organic acids. The acidic conditions develop in this fen in a down-stream successive gradient, through cation exchange and accumulation of DOC (Tahvanainen et al. 2002). In the topogenous extremely poor fen of JS, on the other hand, there were no clear indications of a minerogenous water source in elemental concentrations. The DOC concentrations were however comparably low, similar to the moderately rich fen, and pH was only weakly buffered by organic acids. Thus, the two extremely poor fens studied had differences in water chemistry in comparison to bog waters, but these effects were different between the two fens. The results of Tolonen and Hosiaisluoma (1978) also showed that in some cases extremely poor fens differed from bogs by having higher pH, while in other cases the concentrations of Ca, Mg, and Fe, in particular, separated fens from bogs.



Fig. 3. Variation of individual water chemical variables during the 1999 growing season. See Fig. 1 for explanations of symbols. (Continues on next page).

#### Seasonal patterns in water chemistry

There are few previous records of temporal variation in water chemistry of pristine mires in Finland. Tolonen and Hosiaisluoma (1978) searched for interannual variation of water chemistry in 30 bog and poor fen sites and found significant differences between years only in conductivity and concentrations of total P and Fe. The current data can be compared to results of Tahvanainen *et al.* (2002) from the same study sites in 1998 (data not shown). Slightly lower concentrations in the one-time sampling in 1998 were found for Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca, K, Na, and Si at some sites, than during the same period in the current data sampled in 1999. However, none of the differences were consistently found at all sites and the differences were small in relation to the whole ranges of the chemical gradients. More considerable differences were found only in total N concentrations, which were probably due to the contribution of the comparably high concentrations of  $NH_4^+$  found in 1998 (Tahvanainen *et al.* 2002). Besides  $NH_4^+$ , there was little interannual variation in water chemistry in these fens. Variation of water chemistry during the growing season has not been studied in pristine mires in Finland until the present study.

The seasonal patterns of the PCA-scores showed that the main water chemical gradients were unclear in the early summer and more distinct and stable in the late summer. The con-



Fig. 3. Continued.

centrations of Ca, Mg, and Na had minimums in the beginning of the growing season and rose to higher levels in the middle and late summer. This pattern was especially evident in the moderately rich fen. A similar seasonal pattern was observed by Vitt *et al.* (1995) in central Alberta, western Canada, even though the concentration levels of Ca and Mg were almost ten-fold higher than in the current data. Close resemblance to this pattern in cation concentrations has also been found in bogs in some cases (Vitt *et al.* 1995, Bragazza *et al.* 1998). In bog waters, the pattern reflects mainly evaporative concentration and release from decomposition (Bragazza *et al.* 1998). In minerogenous boreal fens the pattern is amended by the transition from spring snow melt

influence towards a more stable minerogenous hydrology in the late summer. The reappearance of this seasonal pattern at such different concentration levels indicates that the pattern is mediated rather by physicochemical changes than by plant uptake of nutrients. However, also plant growth may contribute to the depletion of cations in water in early summer, as many vascular plants have growth peaks early in the growing season (Lindholm & Vasander 1981, Lindholm 1982, Saarinen 1998). Especially the more variable pattern of K indicates the influence of plant uptake. The concentrations of K remained suppressed longer in the summer, than concentrations of the other cations. The depletion of K in mire water during active growth periods has been observed in many studies (Boatman et al. 1975, Damman 1988, Gerdol 1990, Bragazza 1993, Proctor 1994, 1995, Vitt et al. 1995, Bragazza et al. 1998).

The comparably stable pH in the extremely poor fen of HS was buffered by organic acids, as the DOC concentrations were very high (see Tahvanainen et al. 2002). In the extremely poor fen of JS, the DOC concentrations were lower and pH fluctuated between 4.0 and 5.6. The pH fluctuation could not be explained by variation of DOC, and it was possibly due to fluctuations of CO<sub>2</sub> concentrations. Tahvanainen and Tuomaala (2003) found considerable variation in pH, connected to aeration of samples and diurnal rhythm in fens, reflecting the acidifying effect of CO<sub>2</sub>. In the moderately rich fen, pH did not show the same seasonal pattern as did the main cations and alkalinity, which implies that an effect of seasonal change in CO, following peat temperature may contribute to the pattern of pH. The gradual rise of peat temperature in early summer enhances the release of CO<sub>2</sub> from decomposition and thus increases the CO<sub>2</sub> concentration of water and lowers pH from what would be expected from the increasing alkalinity. Unfortunately, no measurements of CO<sub>2</sub> or aerated sample pH were conducted in this study.

The precipitation observations were probably conducted too distantly to give accurate estimates of precipitation at the study sites. Especially the highest daily precipitation amounts in June and July resulted from thundershowers that are typically very local. Therefore, no clear connections were found between precipitation and fluctuation in water chemistry or WTL. Also, the responses of the WTL to rain can be fairly rapid and undetectable in weekly surveillance. The WTL was most variable in the extremely poor fen of HS. This fen is located in the lower part of a soligenous mire basin and thus all hydrological changes have accumulative effects on its water budget.

#### Representative sampling period

The seasonal patterns in water chemistry give important implications for the comparability and representativeness of water samples in fens. In general, the results show that seasonal variation is predictable and single sampling occasions can be considered representative with certain precautions. The gradients in water chemistry were unclear in early summer and developed towards a more stationary phase in late summer. During this period, weekly fluctuation was very small especially for DOC, SO4<sup>2-</sup>, Ca, Mg, N, Na, Al, Fe, S, and Si. More considerable weekly fluctuation was found for Cl-, K, Mn, and P. Although pH separated the three fens throughout the season, there was considerable fluctuation in the extremely poor fen of JS. In fen waters, pH is greatly influenced by CO<sub>2</sub> (Tahvanainen & Tuomaala 2003), a factor which could not be assessed with the current data. In contrast to the current results, Vitt et al. (1995) found clearly more irregular, fluctuating patterns of Al and Fe. Otherwise their results also indicate comparably stable water chemistry in late summer. For most of the chemical variables representative water samples are most likely acquired in late summer.

# Acknowledgements

We thank Pirjo Appelgren and Mauri Heikkinen for field and laboratory assistance, and Kimmo Tolonen for helpful advice. Håkan Rydin, Urban Gunnarsson, and two anonymous reviewers are thanked for critical comments on earlier versions of the manuscript. The work was financially supported by the Faculty of Science, University of Joensuu, and the Academy of Finland.

# References

- Bellamy, D. J. & Rieley, J. 1967: Some ecological statistics of a "miniature bog". – Oikos 18: 33–40.
- Boatman, D. J., Hulme, P. D. & Tomlinson, R. W. 1975: Monthly determinations of the concentrations of sodium, potassium, magnesium and calcium in the rain and in pools of the Silver Flowe National Nature Reserve. — J. Ecol. 63: 903–912.
- Bragazza, L. 1993: Seasonal changes in water chemistry in a bog on the southern Alps. — Suo 44: 87–92.
- Bragazza, L., Alber, R. & Gerdol, R. 1998: Seasonal chemistry of pore water in hummocks and hollows in a poor mire in the southern Alps (Italy). — *Wetlands* 18: 320–328.
- Bragazza, L. & Gerdol, R. 2002: Are nutrient availability and acidity-alkalinity gradients related in *Sphagnum*-dominated peatlands? – J. Veg. Sci. 13: 473–482.
- Damman, A. W. H. 1988: Spatial and seasonal changes in water chemistry and vegetation in an ombrogenous bog. — In: Verhoeven, J. T. A., Heil, G. W. & Werger, M. J. A. (eds.), Vegetation structure in relation to carbon and nutrient economy: 107–119. Acad. Publ., The Hague.
- Damman, A. W. H. 1995: Major mire vegetation units in relation to the concepts of ombrotrophy and minerotrophy: a worldwide perspective. — *Gunneria* 70: 23–34.
- Finnish Meteorol. Inst. 2000: Meteorological yearbook of Finland 1999. — Finnish Meteorol. Instit., Finland.
- Gerdol, R. 1990: Seasonal variations in the element concentrations in mire water and in Sphagnum mosses on an ombrotrophic bog in the southern Alps. — *Lindbergia* 16: 44–50.
- Gunnarsson, U., Malmer, N. & Rydin, H. 2002: Dynamics or constancy in *Sphagnum* dominated mire ecosystems? A 40-year study. — *Ecography* 25: 685–704.
- Gunnarsson, U., Rydin, H. & Sjörs, H. 2000: Diversity and pH changes after 50 years on the boreal mire Skattlösbergs Stormosse, Central Sweden. – J. Veg. Sci. 11: 277–286.
- Hämet-Ahti, L., Suominen, J., Ulvinen, T. & Uotila, P. (eds.) 1998: *Retkeilykasvio*, 4th ed. — Finnish Mus. Nat. Hist., Bot. Mus., Helsinki.
- Kivinen, E. 1932: Sphagnum-lajien reaktiosta. Maataloustieteellinen Aikakauskirja 4: 91–115.
- Lindholm, T. 1982: Growth dynamics and the effect of frost in Andromeda polifolia on a raised bog. — Ann. Bot. Fennici 19: 193–201.
- Lindholm, T. & Vasander, H. 1981: The effect of summer frost damage on the growth and production of some raised bog dwarf shrubs. — Ann. Bot. Fennici 18: 155–167.
- Malmer, N. 1962a: Studies on the Archaean area of the southwestern Götaland (South Sweden) I. Vegetation and habitat conditions on the Åkhult mire. — Opera Botanica 7(1): 1–322.
- Malmer, N. 1962b: Studies on the Archaean area of the southwestern Götaland (South Sweden) II. Distribution

and seasonal variation in elementary constituents on some mire sites. - *Opera Botanica* 7(2): 1–67.

- Malmer, N., Horton, D. G. & Vitt, D. 1992: Element concentrations in mosses and surface waters of western Canadian mires in relation to precipitation chemistry and hydrology. — *Ecography* 15: 114–128.
- Proctor, M. C. F. 1994: Seasonal and short-term changes in surface-water chemistry on four English ombrogenous bogs. – J. Ecol. 82: 597–610.
- Proctor, M. C. F. 1995: Hydrochemistry of the raised bog and fens at Malharm Tarn National Nature Reserve, Yorkshire, UK. – In: Hughes, J. M. R. & Heathwaite, A. L. (eds.), *Hydrology and hydrochemistry of British wetlands*: 273–289. John Wiley & Sons, Chichester.
- Saarinen, T. 1998: Demography of *Carex rostrata* in a boreal mesotrophic fen: shoot dynamics and biomass development. – *Ann. Bot. Fennici* 35: 203–209.
- Sjörs, H. 1950: On the relation between vegetation and electrolytes in north Swedish mire waters. — *Oikos* 2: 241–258.
- Sjörs, H. & Gunnarsson, U. 2002: Calcium and pH in north and central Swedish mire waters. – J. Ecol. 90: 650–657.
- Slack, N. & Hallingbäck, T. 1992: Community and species responses to environmental gradients in suboceanic mires of the Swedish coast. — Ann. Bot. Fennici 29: 269–293.
- Steinmann, P. & Shotyk, W. 1997: Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two Sphagnum peat bogs, Jura Mountains, Switzerland. — *Geochim. Cosmochim. Acta* 61: 1143–1163.
- Söderström, L. & Hedenäs, L. 1998: Checklista över Sveriges mossor 1998. – Myrinia 8: 58–90.
- Tahvanainen, T., Sallantaus, T., Heikkilä, R. & Tolonen, K. 2002: Spatial variation of mire surface water chemistry and vegetation in north-eastern Finland. — Ann. Bot. Fennici 39: 235–251.
- Tahvanainen, T. & Tuomaala, T. 2003: The reliability of mire water pH measurements — a standard sampling protocol and implications to ecological theory. — *Wetlands* 23. [In press].
- Tolonen, K. & Hosiaisluoma, V. 1978: Chemical properties of surface water in Finnish ombrotrophic mire complexes with special reference to algal growth. — Ann. Bot. Fennici 15: 55–72.
- Vitt, D. H, Bayley, S. E. & Jin, T. L. 1995: Seasonal variation in water chemistry over a bog-rich fen gradient in continental western Canada. — *Can. J. Fish. Aquatic Sci.* 52: 587–606.
- Vitt, D. H., Horton, D. G., Slack, N. S. & Malmer, N. 1990: *Sphagnum*-dominated peatlands of the hyperoceanic British Columbia coast: patterns in surface water chemistry and vegetation. — *Can. J. For. Res.* 20: 696–711.
- Witting, M. 1947: Katjonsbestämmingar i myrvatten. Bot. Notiser 4: 287–304.
- Witting, M. 1949: Kalciumhalten i några Nordsvenska myrvatten. – Svensk Bot. Tidskr. 43: 715–739.