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Spatial variation of mire surface water chemistry and vegetation in northeastern Finland

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Surface water chemistry of two mires was studied in an area with siliceous bedrock and consequently dilute fen waters. Range of variation from moderately rich fen to ombrotrophic bog vegetation was found. Rich fen vegetation was found in Ca concentrations similar to bogs and poor fens, found in many other studies. The poor–rich gradient was related most distinctly to pH, alkalinity, conductivity and the concentrations of Mg and Na. Contrary to the vertical isolation theory of development from fen to bog, in our study the poor–rich gradient was found in an inverse vertical sequence. In the case of weakly buffered waters, downstream spatial succession of water chemistry, including accumulation of organic acidity, is suggested to play a part in the development of the poor–rich gradient. The variation of Al, Fe, Mn and S was found to form a partly independent chemical gradient, related to surface water flow from a podzolic catchment.

Keywords: bryophytes, ecohydrology, organic acidity, pH, poor–rich gradient

Introduction

In the Scandinavian tradition, mires are generally divided into three major categories in the poor–rich gradient: ombrotrophic bogs, poor-fens and rich-fens, on the basis of vegetation (Sjörs 1983, Malmer 1986, Rydin *et al*. 1999). Witting (1947, 1949) was the first to find differences in pH and cation concentrations in surfaces waters between the poor–rich categories. Taking a more continuum-oriented view, Sjörs (1950) related the poor–rich gradient to the pH and conductivity of surface water. Thereafter, the water chemistry of the poor–rich gradient has been studied in numerous studies (reviewed by Malmer 1986, Gorham *et al*. 1987, Shotyk 1988). Detailed descriptive studies concerning the circumboreal zone have been made especially in different parts of North America. In Finland the terms ombrotrophic, oligotrophic, mesotrophic and eutrophic have been used for the same vegetation gradient (for review *see* Ruuhijärvi 1983). The importance of water chemistry to the 'trophic' gradient has been known for long, *see* e.g. Kivinen (1935). More detailed studies on mire water chemistry, concerning the mineral water limit, were conducted by Tolonen (1974) and Tolonen and Hosiaisluoma (1978).

The relationship between pH and total electrolyte content in mire waters is non-linear. In the pH range from 4 to 6, there is usually only a slight increase in conductivity, but above pH 6 conductivity may increase sharply (Sjörs 1950, Newbould & Gorham 1956, Havas 1962). The same relationship has been defined more specifically between pH and Ca concentration in several studies (Gorham 1956, Gorham *et al*. 1987, Mullen *et al*. 2000, Wheeler & Proctor 2000). The extremes of the relationship are very consistent, as in most cases, low pH is, in practice, impossible in extremely high Ca concentrations, and high Ca concentrations are very unlikely when pH is extremely low. However, high pH is possible even in very low Ca concentrations when, for example, there is substitutive Mg alkalinity or simply not enough acids.

In northern Sweden, the pH ranges of the poor–rich categories are comparable to southern Sweden and broadly so in comparison to the British and North American studies, while the electrolyte ranges have more overlap and are often distinctly lower in northern Sweden (Sjörs 1950, Malmer 1962, Sjörs 1983, Rydin *et al*. 1999). The low electrolyte concentrations in minerogenous mire waters are related to the siliceous, poorly weathering bedrock that is common to the Fennoscandian shield, both in northern Sweden and in Finland. If calcium concentration *per se* was a primary factor in the poor–rich gradient, rich fen vegetation would not be expected at low calcium availability. So far there are no detailed studies of surface water chemistry, in the case of rich fen vegetation occurrence at low Ca availability, in Fennoscandia. Furthermore, dilute fen waters are potentially influenced by organic acidity developed by mire vegetation and peat. Most of the studies concerning dissolved organic carbon in mire waters have concentrated on ombrotrophic bogs and little is known of dissolved organic carbon in fen waters.

In this study two mire basins in northeastern Finland, together representing a wide poor–rich vegetation gradient from a bog to a moderately rich fen, are explored for their vegetation and surface water chemistry. Both mires are on drainage areas typical of the region, with poorly weathering siliceous bedrock, highly podzolised soils and, consequently, ground waters characteristic of the area. The water chemistry is analysed on a broad analytical basis to enable ionic balance assessment and description of the different directions of variation in water chemistry. Dissolved organic carbon is measured in addition to inorganic elements, and the organic acidity is approached with ionic balance calculations. The main questions are: (1) Which chemical variables are related to the poor–rich vegetation gradient? (2) What is the role of organic acidity along the gradient? (3)What other directions of variation are found in water chemistry?

Material and methods

Study area

Two mire basins, Härkösuo and Joutensuo (HS and JS hereafter), in the Friendship Nature Reserve in Kuhmo, northeastern Finland, were selected as the study areas. HS (64°12´N, 30°26´E, altitude 240 m) is a soligenous sloping fen (0.171 km^2) with substantial ground water influence and very diverse vegetation. JS (64°13´N, 30°18´E, altitude 270 m) is a small (0.319 km^2) aapa-fen typical of the area, with its margins sloping towards the centre. The study area is situated on the Archaean Karelian province of the Fennoscandian shield, and the bedrock is formed of granite and gneiss (Luukkonen 1992). The study area is situated in the middle boreal climatic-phytogeographical zone (Tuhkanen 1984) and in the southern aapa-mire region (Ruuhijärvi 1988). Mire vegetation types in the area have been described in detail by Ruuhijärvi (1960). The mean annual rainfall is 600 mm and the mean annual temperature 1.2 °C. The meteorological conditions during the field work were representative for the area. The precipitation chemistry is typified by the following long term mean concentrations (mg l^{-1}): pH 4.6, Cl^- 0.25, NO_3^- 0.23, SO_4^{2-} 1.86, NH_4^+ 0.20, Fe 0.017, Ca 0.17, K 0.14, Mg 0.04, Mn 0.002, Na 0.17, Pb 0.002, Zn 0.003 (Kulmala *et al.* 1998) and Al 0.013, Si 0.030 (pers. obs. of T. Tahvanainen, $n = 3$). The ground water chemistry in the catchment of HS is typified by the following mean concentrations (mg l^{-1}), measured from five samples taken from open springs on the mire margin: pH 6.5, conductivity 38 μS cm^{-1}, Cl^- 0.79, SO_4^{2-} 1.61, Al 0.056, Ca 2.68, Fe 0.068, K 0.57, Mg 1.34, Mn 0.002, Na 2.71, Si 5.79 and Zn 0.002 (T. Tahvanainen pers. obs.).

Sampling methods

Systematic grids of water sampling sites were constructed on the mires. In HS the frequency of the grid was 50 metres and in JS 100 metres. Sometimes shorter distances were allowed on the mire margins. There were 84 water sampling sites in HS and 40 in JS. Vegetation was analysed for presence/absence of species within approximately 50 m^2 at the water sampling sites. In HS vegetation was also analysed from 0.25-m^2 plots at 278 sites, selected by random sampling within squares of the grid. The gross scale vegetation patterns, indicating the poor–rich gradient in vegetation, were defined on the basis of the vegetation plot data, aerial photographs and notes from field surveys. Special emphasis was placed on the bryophyte species of wet surfaces. Thus, the vegetation patterns described should not be considered as limited communities but as spatial zones that can be described by general poor–rich categories, especially as indicated by bryophyte species. References to the poor–rich status of species were taken mainly from Sjörs (1950), Eurola *et al.* (1995) and Rydin *et al.* (1999). The nomenclature follows Hämet-Ahti *et al.* (1998) for vascular plants and Söderström and Hedenäs (1998) for bryophytes.

The total cover of species of three poor–rich indicator groups of bryophyte species in HS were counted for the vegetation plots. The poor–rich indicator species groups were:

1. Intermediately or moderately rich fen Bryidae species: *Bryum weigelii*, *Calliergonella cuspidata*, *Campylium stellatum*, *Cinclidium stygium*, *Dicranum bonjeanii*, *Helodium blandowii*, *Hylocomium umbratum*, *Loeskypnum badium*, *Paludella squarrosa*, *Philonotis fontana*, *Plagiomnium ellipticum*, *Pseudocalliergon trifarium*, *Rhizomnium magnifolium*, *R. pseudopunctatum*, *Scorpidium revolvens*, *S. scorpioides*, *Tomentypnum nitens*, *Warnstorfia exannulata* and *W. sarmentosa*.
2. Extremely poor fen or bog *Sphagnum* species (excluding hummock species): *Sphagnum annulatum*, *S. balticum*, *S. jensenii*, *S. lindbergii* and *S. majus*.
3. Indifferent hummock *Sphagnum* species: *Sphagnum angustifolium*, *S. fuscum* and *S. russowii*.

A special sampling well was used for obtaining comparable water samples from different types of mire surfaces. A well consisted of a water chamber and a sampling tube. The water chamber was a two litre plastic bottle. The diameter of the bottle was 12 cm and the height 25 cm. The bottle was densely perforated with 3 mm holes in a 15 cm high area. The sampling tube was a plastic pipe (PVC), that fitted tightly into the mouth of the bottle. The pipe was pressed to the bottom of the bottle, so that the water from the bottom of the well, with any sedimented particulate matter, would come out first when a water sample was taken. A plug blocked the sampling tube.

When installing a sampling well, the water table depth was measured and a peat core was taken so that the bottom of the hole was approx. 20 cm below the water table. The sampling well was placed in the hole. A piece of the peat core, the size of the water chamber, was removed and the rest of the core was placed carefully back into the hole, surrounding the water sampling tube. The corer was made of a steel cylinder, 12 cm in diameter.

The first water samples attained from the sampling wells were often turbid and very difficult to filter. After emptying the wells of the first disturbed waters, the samples were always clear, regardless of the colour and there was very little particulate matter in the samples. All sampling wells were emptied on at least two occasions prior to the sampling. Water samples were collected from the sampling wells with an electric water pump. Approximately 500 ml of the water was first discarded, after which a sample was taken in a 500 ml plastic bottle. The water samples were then placed in styrofoam boxes with ice-bottle coolers and transported to the laboratory for further handling within four hours. Aeration of samples was carefully avoided. Sampling for chemical analyses was done on 4–5 Aug. 1998 in HS and on the 11 Aug. 1998 in JS.

Chemical analyses

Water samples were analysed for pH, conductivity, alkalinity, dissolved organic carbon (DOC), total nitrogen, NH_4^+, $NO_2^- + NO_3^-$, Cl^-, SO_4^{2-} and several elements (Al, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si and Zn). pH was measured with a Beckman ΦISFET 110 pH meter and a Beckman Φ smart ISFET micro probe pH electrode. Two point calibration with 4.00 and 7.00 pH standards was used. Conductivity and pH were measured in the laboratory within six hours from collection. Temperature corrections for conductivity and pH were made to a reference temperature of 25 °C and conductivity was corrected for protons using equivalent conductivity of 349.6 μS cm^{-1} per meq H$^+$ l^{-1} (25 °C) (Miller *et al.* 1998). Alkalinity was measured from unfiltered samples by potentiometric titration (pH 4.5–4.2), with a Mettler Toledo DL70 ES titrator, after two to five days of storage. Alkalinity was extrapolated to zero proton concentration. Water samples for elemental and DOC analyses were filtered through 0.45 μm membrane filters (Schleicher & Schuell, ME 25/21 ST) and those for analyses of anions, N, NH_4^+ and $NO_2^- + NO_3^-$ with paper filters (Macherey-Nagel, MN 640d). Samples for DOC, the nitrogen species and anions were stored frozen (–20 °C). DOC was analysed after five to six months with a Shimadzu TOC-5000 analyser. Total nitrogen was analysed spectrophotometrically with an automatic Skalar Sun Plus analyser. Cl^- and SO_4^- were analysed by ion chromatography, after one month of storage, with an automatic FIAstar 5020 analyser. NH_4^{2+} was measured by a spectrophotometric indophenol blue method (Hitachi U-2000 spectrophotometer) and $NO_2^- + NO_3^-$ was analysed spectrophotometrically with an automatic Skalar Sun Plus analyser. Samples for elemental analyses were treated with HNO_3 (1:100) and stored in a refrigerator (+5 °C) until analysed six moths later by ICP-emissionspectroscopy.

Two samples of purified water were taken and treated among other samples and analysed for elements. The following mean concentrations of elements were found: Al < 0.01, B < 0.003, Ca 0.03, Cr < 0.001, Cu 0.005, Fe 0.003, K 0.02, Mg 0.008, Mn < 0.001, Na 0.08, P < 0.016, Pb < 0.01, S < 0.025, Si 0.02, Zn 0.007 (all concentrations are mg l^{-1}). There was probably some leaching of Cu and Zn from the brass water chamber of the pump used for sampling.

Ionic balance calculations

Anion deficit (AD^-) was calculated as follows (in equivalent electrical charges):

$$AD^- = (Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+ + H^+) - (Cl^- + SO_4^{2-} + ALK^-), \quad (1)$$

where ALK^- is the sum of weak anions (mainly HCO_3^- and weak organic acids). As alkalinity can be defined as the sum of weak anions minus proton concentration, ALK^- was calculated as the sum of proton concentration and alkalinity. Negative alkalinity was treated as zero. Some negative alkalinities rose to slightly positive with the addition of protons. In these cases, a positive value of ALK^- was used only if pH was above 4.4. Since ALK^- is included in the anions, AD^- represents mainly the strong organic anions. Organic anion (OA^-) was also calculated from DOC and pH according to the dissociation behaviour of organic acids following Oliver *et al.* (1983).

Statistical analysis

After the descriptions of the vegetation zones, water samples from sites located within a particular zone were taken for comparison in Tukey's test (SPSS 10.1), to test for significant differences in water chemistry between the different vegetation zones. Only the sites that were located clearly within the spatial zone in question and with representative vegetation were taken for the analysis.

Principal components analysis (PCA) was applied to the chemical data of HS. All other variables but pH were log-transformed ($\log_{10}[x + 1]$) to approximate normal distributions. Some undetectably low concentrations of Al, Mn and Pb were given arbitrary values below the detection limits. Other variables used had always values above the detection limits. Cu and Zn were excluded because of high concentrations in the purified water samples. The correlation option was selected for the cross-products matrix. The broken-stick eigenvalue (Jackson 1993) was used to assess significance of axes. The PCA was performed with PC-ORD 4.09.

The water chemistry variables and the scores of the three first PCA-axes of HS were taken for spatial interpolation in Vertical Mapper 2.5. The interpolation method used was inverse distance weighting. The options used were an exponent of 4 and a search distance of 150 m. The interpolated raster maps were then changed to contour maps with 10 or 11 even contour intervals. The high exponent value used strongly emphasises the influence of the closest observations.

The total cover of the indicator species groups of bryophytes were mapped by ordinary kriging interpolation (Vertical Mapper 2.5). The options used were coincident point distance 0.0012, average value for coincident point aggregation, and the maximum number of points used for interpolation was 10. The difference of the total covers of the intermediately and moderately rich fen Bryidae and the bog and poor fen *Sphagnum* species, was used as a 'poor–rich indicator index' and compared with interpolated water chemical variables with correlation coefficients. The interpolation method used here was inverse distance weighting. Only the four nearest water samples were used. Only sites with positive cover of either species group were included, excluding most of the hummock samples. The objective of this analysis is the comparison of relative importance of different chemical variables to the poor–rich gradient. Pearson and Spearman correlation coefficients gave very similar results. Only Pearson correlations are reported.

Results

Vegetation zonation

Härkösuo

Five gross vegetation zones were defined in HS (Fig. 1).

1. The forested moderately rich fen zone, in the SW part of the mire, has abundant ground water input from open springs on the mire margin and diffuse updwelling throughout the zone. There is a sparse canopy cover of *Pinus sylvestris* and *Picea abies* and scattered *Betula pubescens*. In the mire margin intermediate surfaces with high bryophyte cover are found with characteristic species such as *Bryum weigelii*, *Calliergonella cuspidata*, *Helodium blandowii*, *Paludella squarrosa*, *Philonotis fontana*, *Plagiomnium ellipticum*, *Rhizomnium magnifolium*, *Sphagnum teres*, *Carex dioica*, *Epilobium palustre*, *Filipendula ulmaria*, *Pedicularis sceptrum-carolinum*, *Salix phylicifolia* and *Solidago virgaurea*. Towards the centre, low intermediate and hummock surfaces

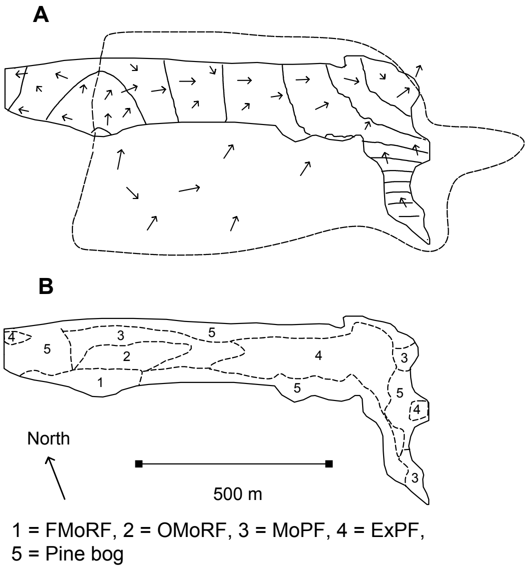

Fig. 1. Description of Härkösuo mire. — **A**: Contour gradient (interval 70 cm) and catchment (broken line). The arrows indicate the directions of surface water flow. — **B**: Vegetation zones. For abbreviations *see* Table 1.

with e.g. *Aulacomnium palustre*, *Sphagnum angustifolium*, *S. fuscum*, *S. warnstorfii*, *Tomentypnum nitens*, *Carex dioica*, *C. lasiocarpa*, *Empetrum nigrum*, *Molinia caerulea* and *Juniperus communis* become typical and alternate with wetter surfaces, where characteristic species are e.g. *Aneura pinguis*, *Campylium stellatum*, *Cinclidium stygium*, *Loeskypnum badium*, *Lophozia rutheana*, *Scorpidium revolvens*, *Equisetum fluviatile*, *Eriophorum latifolium* and *Trichophorum alpinum*.

2. The open moderately rich fen is mostly open, with a few pines on the hummocks. The zone follows the forested moderately rich fen zone in the direction of the slope and water flow, and it is patterned with *Sphagnum* dominated strings and intervening Amblystegiaceae dominated flarks. The flarks are rather poor in species and partly have bare mud bottoms with free water. Typical species of the flarks are *Pseudocalliergon trifarium*, *Scorpidium scorpioides*, *Warnstorfia sarmentosa*, *Carex rostrata*, *Drosera longifolia* and *Equisetum fluviatile*. On intermediate surfaces characteristic species are *Dicranum bonjeanii*, *Loeskypnum badium*, *S. contortum*, *S. papillosum*, *S. subfulvum*, *S. warnstorfii*, *Carex lasiocarpa*, *Selaginella selaginoides*, *Tofieldia pusilla* and often very dense *Trichophorum alpinum*. The hummock surfaces are characterised by *Sphagnum fuscum*, *S. subfulvum*, *S. warnstorfii*, *Betula nana*, *Calluna vulgaris*, *Carex pauciflora*, *Empetrum nigrum*, *Juniperus communis*, and *Molinia caerulea*.
3. The next zone is a narrow moderately poor fen zone, surrounding most of the open moderately rich fen zone. *Scorpidium* is completely absent and replaced by *Sphagnum annulatum*, *S. majus*, *S. platyphyllum* and *Warnstorfia procera*. Typical vascular plants of the wet and intermediate surfaces are *Andromeda polifolia*, *Carex limosa*, *C. rostrata*, *Drosera rotundifolia* and *Rhynchospora alba*. On intermediate surfaces *Sphagnum annulatum*, *S. papillosum* and *S. subsecundum* are the most characteristic bryophyte species. The hummocks show little signs of minerotrophy and are similar to those in the pine bog zones (below). In the eastern and south-eastern marginal parts of HS, there are small moderately poor fen areas as indicated by e.g. *Sphagnum riparium*, *S. subsecundum*, *S. aongstroemii* and *Menyanthes trifoliata*.
4. The extremely poor fen zone shows little indications of minerotrophy in vegetation. Flarks are in general rich in *Sphagnum* species and typical species are *S. annulatum*, *S. angustifolium*, *S. balticum*, *S. fallax*, *S. flexuosum*, *S. jensenii*, *S. lindbergii*, *S. majus*, *S. papillosum*, *Warnstorfia fluitans*, *Andromeda polifolia*, *Carex limosa*, *C. rostrata* and *Scheuchzeria palustris*. *Sphagnum angustifolium*, *S. magellanicum*, *Eriophorum vaginatum* and *Trichophorum cespitosum* are typically found on intermediate surfaces. The hummocks are similar to those in pine bog zones (below). Although there are frequent signs of weak minerotrophy, this zone is distinctly dominated by species typical to ombrotrophic bogs.
5. Most of the narrow mire margin zones in HS are pine bogs, while in the southern mire margins and scatteredly in the northernmost

mire margins there are also spruce dominated forested poor fen areas. There are also small areas of pine bog vegetation in more central parts of HS at both western and eastern ends of the basin. Typical species are *Dicranum bergeri*, *Polytrichum strictum*, *Sphagnum angustifolium*, *S. fuscum*, *S. magellanicum*, *C. pauciflora*, *Chamaedaphne calyculata*, *Empetrum nigrum*, *Eriophorum vaginatum*, *Ledum palustre*, *Rubus chamaemorus*, *Vaccinium uliginosum* and *V. vitis-ideae*. *Sphagnum fuscum* and *Polytrichum strictum* are most typical in the northern and north-western mire margins and in central pine bog areas, while *Polytrichum commune* and *Sphagnum russowii* are more characteristic to the southern mire margins.

Joutensuo

In JS there was far less variation in vegetation than in HS. Three vegetation zones could be distinguished in this context.

1. The extremely poor fen is located in the central part of the basin and is surrounded by bog vegetation. There is no tree cover, the surface peat is very loose and small open pools are found. Species richness is low and single species stands of *Sphagnum papillosum* and *S. pulchrum* are typical. Other typical species are *Sphagnum lindbergii*, *S. platyphyllum*, *Carex rostrata* and *Menyanthes trifoliata*.
2. Open bogs are found around the central poor fen zone. The vegetation is essentially ombrotrophic bog vegetation. *Sphagnum balticum*, *S. jensenii*, *S. majus*, *Carex limosa* and *Scheuchzeria palustris* are the most typical species. Sometimes *Sphagnum fallax* is found among the bog species. In western and northern parts *Sphagnum compactum*, *S. papillosum* and *Eriophorum vaginatum* are also abundant.
3. Mire margins are *Sphagnum fuscum* pine bogs similar to those described for HS. The pine bog zones are more extensive than in HS and largely ombrotrophic.

Spatial variation in surface water chemistry

The range of variation in surface water chemistry was fairly wide e.g. in pH (3.78–6.52) and DOC (1.2–79.3 mg l^{-1}), while the range of variation was rather more limited e.g. in Ca (0.20–4.91 mg l^{-1}) and Mg (0.08–2.43 mg l^{-1}) (Table 1). Concentrations were always below the detection limits in B (< 3 μg l^{-1}), Cd (< 1μg l^{-1}), Mo (< 8 μg l^{-1}) and Ni (< 5 μg l^{-1}). Concentrations above the detection limits were only found from a few samples in Cr (1–4 μg l^{-1}) and P (16–40 μg l^{-1}) irrespective of the vegetation zones.

The forested moderately rich fen zone had the highest mean pH, conductivity, alkalinity and concentrations of several ground water influence indicating elements such as Ca, Mg, Na, K and Si, while the mean concentrations of DOC, Cu, Fe and Zn were the lowest (Table 1). The water chemistry of the open moderately rich fen zone is typified by a moderately high mean pH and DOC concentration. The mean concentration of Si was the highest and that of $NO_2^- + NO_3^-$ was the lowest in the open moderately rich fen zone. The moderately poor fen zone of HS had intermediate mean pH, alkalinity around zero and a high mean concentration of DOC. The main cation concentrations were clearly lower than in the moderately rich fen zones. The extremely poor fen zone of HS had very low and comparably constant pH, no alkalinity, and a very high mean concentration of DOC. The main cation concentrations were very low, while the concentrations of Si were still remarkably high.

The extremely poor fen zone of JS had a low mean pH and no alkalinity. The DOC concentrations were of intermediate range. Conductivity and the mean concentrations of e.g. Ca, Mg and Na were low. The bog zone of JS had the lowest mean pH with little variation, and the lowest concentrations of ground water indicating elements as Ca, Mg, Na and Si, while the concentrations were high for DOC, N, Cu and Zn (Table 1).

Significant differences ($p < 0.05$) between the six poor–rich vegetation zones were found most often in Tukey’s test for pH, conductivity, alkalinity, DOC, Ca, Mg and Na (Table 1). Differences were non-significant between the

Table 1. Means and standard deviations (in parentheses) of water chemistry for representative groups of samples in Härkösuo (HS) and Joutensuo (JS). Abbreviations: FmoRF = forested moderately rich fen, OMoRF = open moderately rich fen, MoPF = moderately poor fen, ExPF = extremely poor fen, PCA 2 group = samples with extreme scores in the second axis of PCA of water chemistry, Obog = open bog. The letters below the mean values indicate significant differences between sites in Tukey's test ($p < 0.05$).

Variable	HS FMoRF (a)	HS OMoRF (b)	HS MoPF (c)	HS ExPF (d)	HS PCA2 group (e)	JS ExPF (f)	JS Obog (g)
pH	6.07 (0.43)	5.43 (0.16)	4.75 (0.44)	4.26 (0.08)	4.20 (0.18)	4.37 (0.11)	3.97 (0.11)
	b,c,d,e,f,g	a,c,d,e,f,g	a,b,d,e,g	a,b,c	a,b,c	a,b,g	a,b,c,f
Alkalinity (μeq l^{-1})	295 (133)	198 (73)	19 (29)	0	0	0	0
	c,d,e,f,g	c,d,e,f,g	a,b	a,b	a,b	a,b	a,b
DOC (mg l^{-1})	12.4 (6.4)	24.9 (5.1)	36.8 (12.7)	45.3 (8.9)	56.6 (6.5)	27.6 (3.3)	41.3 (11.2)
	c,d,e,f,g	d,e,g	a,e	a,b,f	a,b,c,f,g	a,d,e,g	a,b,e,f
N (mg l^{-1})	2.0 (0.8)	2.2 (1.0)	2.6 (1.0)	2.0 (0.6)	2.6 (0.5)	2.3 (0.6)	3.1 (0.7)
	–	–	–	–	–	–	–
NH$_4^+$ (mg l^{-1})	1.26 (0.68)	1.35 (0.64)	1.33 (0.30)	1.42 (0.69)	1.26 (0.34)	1.16 (0.40)	1.25 (0.39)
	–	–	–	–	–	–	–
NO$_2^-$ + NO$_3^-$ (μg l^{-1})	5 (4)	2 (1)	5 (2)	3 (1)	4 (2)	5 (2)	4 (2)
	b	a	–	–	–	–	–
Cl$^-$ (mg l^{-1})	0.77 (0.20)	0.52 (0.20)	0.65 (0.26)	0.65 (0.18)	0.91 (0.28)	0.57 (0.24)	0.41 (0.23)
	–	–	–	–	g	–	e
SO$_4^{2-}$ (mg l^{-1})	0.80 (0.75)	0.27 (0.18)	0.24 (0.18)	0.27 (0.07)	0.49 (0.25)	0.35 (0.08)	0.30 (0.07)
	c,d	–	a	a	–	–	–
Al (mg l^{-1})	0.05 (0.06)	0.08 (0.13)	0.10 (0.07)	0.23 (0.12)	0.60 (0.24)	0.08 (0.04)	0.09 (0.12)
	e	e	e	e	a,b,c,d,f,g	e	e
Ca (mg l^{-1})	2.88 (1.28)	2.41 (0.72)	1.47 (0.50)	1.05 (0.42)	1.60 (0.17)	1.06 (0.28)	0.64 (0.25)
	c,d,e,f,g	d,f,g	a	a,b	a	a,b	a,b
Cu (μg l^{-1})	8 (4)	10 (4)	17 (7)	23 (6)	28 (4)	19 (4)	29 (9)
	d,e,g	d,e,g	g	a,b	a,b	–	a,b,c
Fe (mg l^{-1})	0.08 (0.06)	0.45 (0.87)	0.59 (0.58)	0.89 (0.68)	2.65 (1.96)	0.41 (0.20)	0.30 (0.39)
	e	e	e	e	a,b,c,d,f,g	e	e
K (mg l^{-1})	0.45 (0.11)	0.32 (0.10)	0.26 (0.25)	0.17 (0.12)	0.42 (0.17)	0.25 (0.15)	0.16 (0.10)
	d,g	–	–	a,e	d,g	–	a,e
Mg (mg l^{-1})	1.39 (0.63)	1.29 (0.31)	0.52 (0.17)	0.35 (0.10)	0.55 (0.12)	0.25 (0.06)	0.15 (0.08)
	c,d,e,f,g	c,d,e,f,g	a,b	a,b	a,b	a,b	a,b
Mn (μg l^{-1})	8 (7)	6 (7)	11 (8)	16 (10)	26 (7)	10 (6)	8 (8)
	e	e	e	–	a,b,c,f,g	e	e
Na (mg l^{-1})	2.62 (0.79)	2.37 (0.44)	1.53 (0.23)	1.24 (0.22)	1.67 (0.40)	1.15 (0.52)	0.99 (0.36)
	c,d,e,f,g	c,d,f,g	a,b	a,b	a	a,b	a,b
Pb (μg l^{-1})	19 (3)	33 (14)	50 (21)	29 (13)	48 (16)	30 (13)	30 (13)
	–	–	–	–	–	–	–
S (mg l^{-1})	0.32 (0.20)	0.31 (0.14)	0.29 (0.08)	0.32 (0.06)	0.54 (0.08)	0.35 (0.14)	0.37 (0.08)
	e	e	e	e	a,b,c,d	–	–
Si (mg l^{-1})	4.41 (1.15)	4.66 (1.26)	3.21 (1.45)	3.46 (1.68)	3.98 (1.74)	2.39 (1.55)	1.11 (0.71)
	g	g	–	g	g	–	a,b,d,e
Zn (μg l^{-1})	12 (7)	22 (10)	25 (10)	28 (5)	38 (9)	29 (6)	48 (17)
	e,f,g	g	g	g	a	a,g	a,b,c,d,f
Conductivity (μS cm^{-1})	35.0 (12.7)	29.1 (5.8)	16.4 (3.7)	13.3 (2.6)	16.1 (4.3)	8.5 (2.2)	2.1 (2.5)
	c,d,e,f,g	c,d,e,f,g	a,b,g	a,b,g	a,b,g	a,b	a,b,c,d,e
AD$^-$ (μeq l^{-1})	165 (65)*	242 (69)	265 (77)	277 (67)	339 (32)	234 (44)	277 (49)
OA$^-$ (μeq l^{-1})	130 (38)*	244 (89)	252 (74)	271 (49)	329 (35)	172 (17)	216 (49)
n	7	6	6	8	6	8	8

* = one outlier eliminated

poor–rich groups in Cl$^-$, NH$_4^+$, Al, Fe, K, Mn, Pb and S.

In the PCA of the surface water chemistry in HS (Table 2), the three first PCA-axes had eigenvalues greater than the broken-stick eigenvalues, indicating that the axes contained more information than expected by chance. The strongest eigenvector scores in the first PCA-axis were found for pH, conductivity, Na, Mg and Ca. In the second axis the strongest eigenvector scores were found for Fe, Al, S and Mn. For the third axis the scores were highest for N, SO$_4^{2-}$ and NH$_4^+$. A group of six samples with extreme scores in the second PCA-axis were taken to comparison with the poor–rich groups. They had clearly higher mean concentrations of Al (0.60 mg l^{-1}) and Fe (2.65 mg l^{-1}) than any of the other groups. Also mean DOC, Mn and S were higher than in most of the poor–rich groups (Table 1).

The first PCA-axis and variables connected to it showed a clear spatial pattern closely connected with the pattern of the poor–rich vegetation zones (Figs. 1 and 2). The scores were lowest in the forested moderately rich fen zone, intermediate in the open moderately rich fen zone and the moderately poor fen zones, and highest in the mire margin pine bogs and in the extremely poor fen zone. In the same sequence there is a highly regular drop in pH, alkalinity, conductivity, Ca, Mg, Na and a simultaneous increase in DOC. Some trace metal concentrations (Cu, Pb, Si, Zn) reflect the same pattern as DOC, though less distinctly. The second PCA-axis shows a spatial pattern clearly separate from that of the first axis (Fig. 2). The scores are lowest in the south-eastern mire margin area and highest on the northern and northwestern mire margin and in the moderately rich fen zones. The third PCA-axis shows a highly irregular spatial pattern in the whole basin scale. However, it

Table 2. Eigenvalues, broken stick eigenvalues and eigenvector scores for the first three axis of PCA on water chemistry data of Härkösuo.

Axis	1	2	3
Eigenvalue	5.01	3.60	2.05
Broken stick	3.50	2.50	2.00
pH	–0.40	0.12	0.08
Na	–0.39	–0.07	–0.10
Conductivity	–0.38	–0.09	–0.02
Mg	–0.38	0.02	–0.06
Ca	–0.36	–0.06	–0.11
DOC	0.29	–0.24	–0.18
Si	–0.27	–0.21	–0.06
K	–0.19	–0.05	–0.21
SO$_4^{2-}$	–0.16	–0.12	0.40
Pb	0.16	–0.13	–0.27
Cl$^-$	–0.11	–0.27	–0.12
Al	0.08	–0.44	0.11
Fe	0.06	–0.49	0.01
NH$_4^+$	–0.05	–0.13	–0.37
NO$_2^-$ + NO$_3^-$	–0.04	–0.07	0.26
S	–0.03	–0.40	0.09
N	0.01	–0.02	–0.62
Mn	0.01	–0.37	0.17

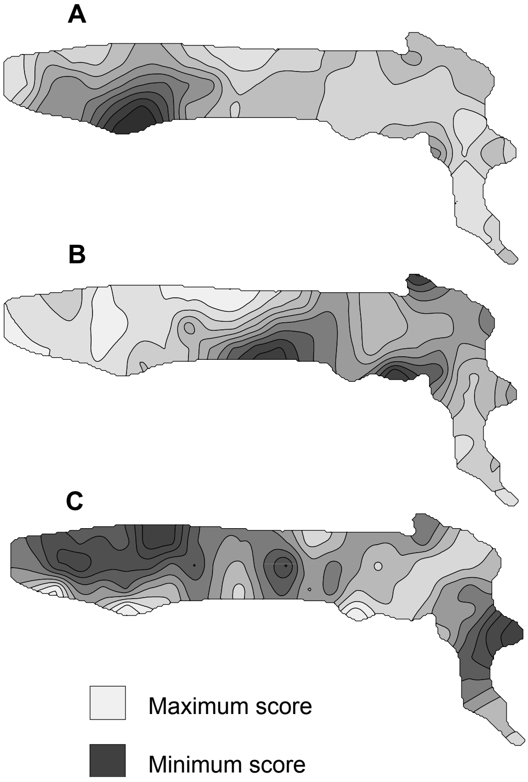

Fig. 2. Spatial patterns of sample scores of the PCA of water chemistry. — **A**: First axis. — **B**: Second axis. — **C**: Third axis.

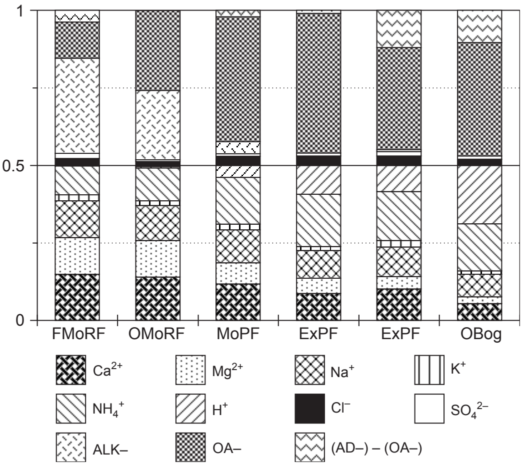

Fig. 3. Mean proportions of equivalent charges of ions, relative to the sum of ions, in surface water of six vegetation zones. For abbreviations *see* Table 1.

clearly separates the forested and the open moderately rich fen zones (Figs. 1 and 2).

Ionic balance of surface water

Considering the proportions of anions, weak anion (ALK^-) and anion deficit (AD^-) were dominant in all observations while Cl^- and SO_4^{2-} were of minor importance (Fig. 3). ALK^- was present in the moderately rich and moderately poor fen zones in HS, but represented a dominant proportion of anions only in the forested moderately rich fen zone. AD^- was the dominant anion in all poor fen and bog zones. In the open moderately rich fen zone, ALK^- and AD^- were almost equal in importance.

As regards cations, there was rarely a single dominant cation in any of the described zones (Fig. 3). In the moderately rich fen zones Ca^{2+}, Mg^{2+} and Na^+ were usually of fairly equal importance, with proportions between 0.20 and 0.30. In the poor fen and bog zones Mg^{2+} and Ca^{2+} were clearly more depleted in proportions compared to Na^+. The moderately poor fen of HS was intermediate to the open moderately rich fen zone and the extremely poor fen zones, in ionic proportions. The moderately poor fen of HS and the extremely poor fen of JS were very similar in their proportional ionic balance. The open bog of JS had the highest proportion of H^+ and the lowest proportions of Ca^{2+} and Mg^{2+} in the cation sum. NH_4^+ represented a considerably high proportion of cations in all zones. The mean proportion of NH_4^+ in the moderately rich fens was lower than that in the poor fen and bog zones.

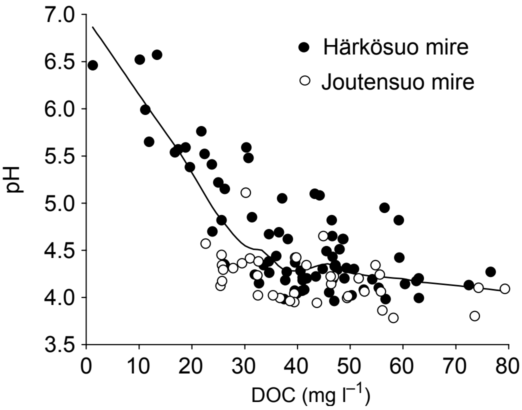

Fig. 4. The relationship between pH and DOC concentration in surface water. The line represents the fit of Loess regression.

Anion deficit (AD^-) was sometimes higher than OA^- in JS and in the forested moderately rich fen zone of HS. In the rest of the data, the estimates of AD^- and OA^- were very close to each other (Table 1). After eliminating five outliers, the relationship between AD^- and OA^- was rather well defined ($r^2 = 0.70$, $p < 0.001$).

Relationships between pH and surface water components

Most of the chemical variables were correlated with pH to some extent. Exceptions were the concentrations of N, $NO_2^- + NO_3^-$, NH_4^+, Cl^-, Fe, Mn, Pb and S, that were very variable in relation to pH. Fairly high correlations (Pearson) were found between pH and conductivity ($r = 0.79$), Mg ($r = 0.72$), Na ($r = 0.67$), DOC ($r = 0.64$), Cu ($r = 0.60$), Ca ($r = 0.57$), and Zn ($r = 0.57$) (all with $p < 0.001$). Clearly weaker correlations were found between pH and Si ($r = 0.44$), SO_4^{2-} ($r = 0.30$), K ($r = 0.30$), and Al ($r = 0.26$) (all with $p < 0.05$). The sum of equivalent Ca, Mg, K and Na correlated strongly with pH ($r = 0.73$,

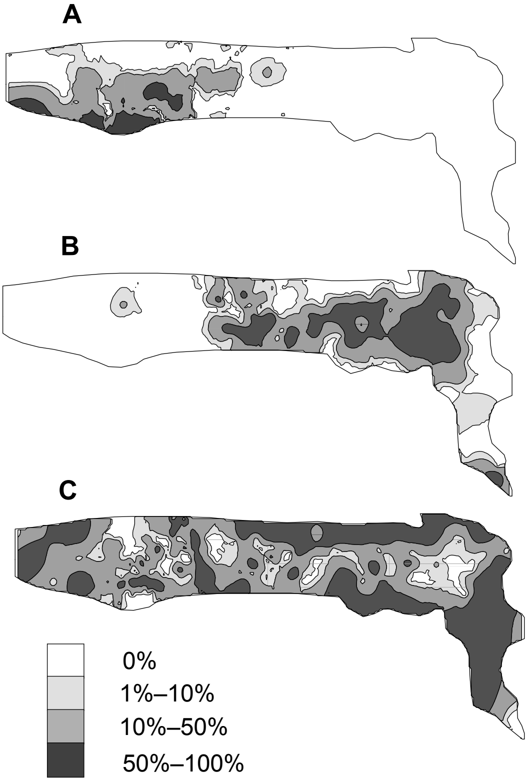

Fig. 5. The total covers of ecological groups of bryophyte species in Härkösuo mire. — **A**: Intermediately and moderately rich fen Bryidae. — **B**: Bog and extremely poor fen flark *Sphagnum* sp. — **C**: Indifferent hummock *Sphagnum* sp.

$p < 0.001$). The relationships between pH and other variables were essentially linear, with most notable exception of DOC. The relationship between pH and DOC appears as a negative linear correlation in the DOC range from 0 to approximately 40 mg l^{-1}, where pH decreases, from around 6.5 to between 4.0 and 4.5, after which there is no further consistent decrease in pH with increasing DOC concentration. When DOC is below 20 mg l^{-1} pH is always above 5.3 (Fig. 4).

AD^- correlates with DOC ($r = 0.64$, $p < 0.001$) and pH ($r = -0.54$, $p < 0.001$). There were very strong correlations between pH and the proportions of AD^- ($r = -0.92$, $p < 0.001$) and ALK^- ($r = 0.92$, $p < 0.001$) in the ionic balance. On the other hand, there were very weak correlations between pH and the proportions of Cl^- ($r = -0.02$, ns) and SO_4^{2-} ($r = 0.21$, $p < 0.05$).

The correlations between pH and the proportions of Mg^{2+}, Na^+ and Ca^{2+} in the cation sum were significant ($r = 0.70$, 0.55 and 0.39 respectively, $p < 0.001$), while there were no significant correlations between pH and the proportions of K^+ or NH_4^+ ($r = 0.18$ and -0.16 respectively, ns).

Pattern and correlations of bryophyte cover

The spatial patterns of the total covers of the two bryophyte species groups, indicating the poor–rich gradient had little overlap (Fig. 5). The correlations between the difference of the poor and rich indicator covers and the water chemical variables indicated significant relationships between water chemistry and the poor–rich gradient (Table 3). The strongest correlations were found for pH, Mg, conductivity, Na and DOC. Clearly weaker correlations were found for Ca, Al, Fe and K. Only weak correlations were found for SO_4^-, S, Si and N, while NH_4^+, $NO_2^- + NO_3^-$ and Cl^- did not correlate significantly with the poor–rich indicator index.

Table 3. Pearson correlation co-efficients between the poor–rich indicator index (difference of cover of rich and poor indicating species groups) and interpolated chemical variables in Härkösuo.

Chemical variable	Correlation	
	r	*p*
pH	0.82	< 0.01
Mg	0.75	< 0.01
Conductivity	0.75	< 0.01
Na	0.70	< 0.01
DOC	–0.69	< 0.01
Al	–0.62	< 0.01
Ca	0.60	< 0.01
Fe	–0.53	< 0.01
K	0.44	< 0.01
SO_4^{2-}	0.27	< 0.01
S	–0.23	0.01
Si	0.20	0.01
Pb	–0.18	0.05
N	0.17	0.04
NH_4^+	0.04	0.59
$NO_2^- + NO_3^-$	0.02	0.77
Cl^-	–0.01	0.86
n = 148		

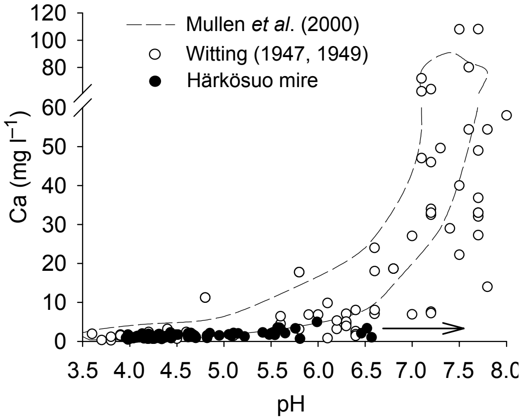

Fig. 6. The relationship between pH and Ca concentration in mire surface water in the present study, in Swedish mires (Witting 1947, 1949) and in North American mires (Mullen *et al.* (2000). The arrow points out the maximum pH of aerated samples in the present study sites.

Discussion

Water chemistry along the poor–rich gradient

The vegetation in the study areas indicated a wide poor–rich gradient from bog to moderately rich fen. As was expected, pH, alkalinity, conductivity and concentrations of major mineral cations and DOC in the surface water were clearly connected with the poor–rich gradient in vegetation. The pH and conductivity values of the moderately rich fen zones of HS were comparable to those found by Sjörs (1950) for transitional (moderately) rich fens. Especially the concentrations of Ca, however, were extremely low, compared to those described for poor–rich gradients in most other areas, and are situated at the lowest borders of the Ca gradient in relation to pH, found for mire waters (Witting 1947, 1949, Gorham 1956, Tolonen & Hosiaisluoma 1978, Glaser *et al.* 1981, Gorham *et al.* 1987, Malmer *et al.* 1992, Vitt *et al.* 1995, Mullen *et al.* 2000, Wheeler & Proctor 2000) (Fig. 6). Sjörs (1950) introduced the vegetation type of intermediate fens in northern Sweden, which have high pH but low electrolyte concentrations. In moderately rich fen zones of HS, however, there were several critical species listed by Sjörs (1950) as 'rich fen proper' indicators, and more are found in the list of moderately rich fen indicators in Rydin *et al.* (1999).

Calcium concentration is here taken for more detailed comparison, since it has been subjected to special attention in studies of mire water chemistry after the work of Witting (1949), until recently (Mullen *et al.* 2000, Wheeler & Proctor 2000). One of the moderately rich fen indicator species, particularly characteristic of the open moderately rich fen zone in HS, is *Scorpidium scorpioides*. It has been studied rather a lot, and references to Ca concentrations of water in its habitats are frequent. Most frequently it has been connected with extremely high Ca concentrations (20–100 mg l^{-1}) (Witting 1947, 1949, Borysławski 1978, Karlin & Bliss 1984, Glaser *et al.* 1990, Kooijman & Hedenäs 1991, Kooijman 1993, Mullen *et al.* 2000). However, some records of low Ca concentrations are found as well. Sjörs (1948) reported a Ca concentration of 2.0 mg l^{-1} from one *S. scorpioides* site in central Sweden. Witting (1949) found rather low Ca concentrations (2.6–7.0 mg l^{-1}) from seven *S. scorpioides* habitats in Härjedalen and Jämtland, middle Sweden. In northern Britain, Gorham and Pearsall (1956) reported Ca concentrations of 3.2 and 7.5 mg l^{-1} from two *S. scorpioides* habitats. In the present study, the mean Ca concentration of the open moderately rich fen zone, throughout a *S. scorpioides* habitat, was 2.41 mg l^{-1}, and the lowest concentration of *S. scorpioides* dominated sites was only 1.8 mg l^{-1}. This short review shows that the Ca range of *S. scorpioides* is extremely wide and it does not require particularly high Ca levels. In the same light, it also seems unlikely that any of the rich fen species found in HS are primarily dependent on high Ca levels, as such were not found. The common association of these species with high Ca levels is probably a coincidence with more influential factors, such as high pH and high total mineral alkalinity.

Instead of Ca, the highest of the correlations of single cations with the poor–rich indicator index was found for Mg. Furthermore, pH correlated most strongly with Mg, both in concentrations and in proportions of ionic budget. The proportions of Ca, Mg and Na of the sum of cations were closely equal and they all were important as sources of mineral alkalinity and the maintenance of high pH. The total equivalent sum of charges of Ca, Mg, Na and K in the moderately rich fen zones in HS was between 270 and 630 μeq l^{-1}, that should represent the lowest levels found for moderately rich fens. In northeastern Fennoscandia, with very sparse occurrence of lime rich soils in general, Ca evidently does not have as determinant role in the poor–rich gradient of mire vegetation, as it has in some other regions. Alkalinity and pH are probably more important to moderately rich fen vegetation than any single cation concentration. Mg, Na and K may also compensate lack of Ca in some bryophytes (Bell & Lodge 1963, Brown 1982). In extremely rich fens, high Ca levels *per se* are possibly of more importance.

The poor–rich gradient *sensu* Du Rietz is a vegetation gradient. It has been related to variation in water chemistry (Witting 1947, 1949, Sjörs 1950), and the terms 'rich' and 'poor' have, thereafter, often been used to refer to the ionic strength of water. It has been proposed by several authors (Bridgham *et al.* 1996, Mullen *et al.* 2000, Wheeler & Proctor 2000), that the poor–rich gradient should be recognised, not by vegetation alone, but by a combination of vegetation and water chemistry data. This approach presupposes that the relationship between vegetation and water chemistry along the gradient is unidimensional. Mullen *et al.* (2000) and Wheeler and Proctor (2000) underline the importance of covariation of pH and calcium along the poor–rich gradient. It is evident, however, that under the geological conditions of northeastern Fennoscandia, the variation of pH, and consequently the poor–rich gradient, is not strictly bound to variation of calcium. For example, with only one exception, the Ca concentrations in the moderately rich fen sites in the current data were lower than mean concentrations of ombrotrophic sites in Alberta, Canada (Vitt *et al.* 1995). Therefore, Ca concentrations should not be used for determination of the poor–rich gradient.

Downstream development of acidity and the poor–rich gradient

Many different factors influence the complex acid–base balance in mire waters, including hydrology, bedrock and soil quality and weathering rate, nutrient uptake by plants, cation and anion exchange, decomposition, redox reactions and atmospheric deposition (for a review, *see* Shotyk 1988). Hemond (1980) showed by means of a hydrogeochemical mass balance analysis that ombrotrophic bog water acidity is maintained by organic acids and that the role of mineral acidity or cation exchange by *Sphagnum* is of minor importance for the acidity of bog water. The cation exchange of *Sphagnum* is, nevertheless, an important primary source of acidity in many cases (Clymo 1987, Vitt 2000), while in other cases atmospheric deposition acidifies mire waters (Gorham *et al.* 1987, Proctor & Maltby 1998, Gunnarsson *et al.* 2000). Gorham (1956) showed that while pH of acidic bog waters did not change after bubbling with nitrogen, pH of fen waters increased, indicating the acidifying effect of CO_2 in fen waters. As the water samples in the current study were obtained from sampling wells instead of open water surfaces and kept unaerated, the pH values are often lower than in equilibrium with air. Sampling wells provide, however, more comparable samples than open water surfaces. For example, on a 40 metre long transect in the open moderately rich fen zone of HS, pH values ranging from 4.94 to 7.96 were measured from open water surfaces, while in samples obtained from sampling wells pH ranged from 5.01 to 5.31 (T. Tahvanainen & T. Tuomaala, unpubl.).

The development of surface water acidity in ombrotrophic bogs involves vertical isolation from minerogenous water flow. In some cases there is a dramatic shift from high to low pH in transects from minerogenous to ombrogenous sites (Gorham & Janssens 1992) and in vertical peat pore water profiles (Steinmann & Shotyk 1997). As a consequence, the mechanism has been found to cause a universal phenomenon of bimodality of the frequency distribution of mire water pH (Gorham *et al.* 1987, Gorham & Janssens 1992). The bimodality theory was recently criticised by Økland *et al.* (2001), and it may not be applicable in Fennoscandia, where calcareous rocks are rare and poor fens are the commonest mire types (e.g. Sjörs 1983).

In the case of HS, vertical isolation is not the primary reason for the development and maintenance of acidity in the extremely poor fen zone, as it is situated at a clearly lower altitude than the rich fen zones and the minerogenic water input. Topography and field observations show that water flow takes place from the moderately rich fen zones to the moderately and extremely poor fen zones, and additional evidence of minerotrophy may be found in water chemistry. For example, the extremely poor fen zone of HS had clearly higher mean pH, conductivity and Si concentration than the open bog zone of JS, which is apparently more dependent on precipitation. Si is a good indicator of minerogenic water in this case, as the contrast in its concentrations between the minerogenic water and precipitation is most pronounced.

Depletion of several elements, most notably of Ca and Mg, in surface water in the direction of the water flow is known from several studies (Malmer 1962, Vitt *et al*. 1975, Vitt & Bayley 1984). Glaser *et al*. (1990) named three mechanisms that could cause spatial change in water chemistry: dilution with rain water, active assimilation of cations by living plants and passive cation exchange. In addition, the accumulation of DOC, in the course of the water flow, should have an impact on the water as well. Glaser *et al*. (1981) used light absorbance (320 nm) as a measure of organic content and discussed its relation to the rate of water flow: stagnant waters are more coloured than mobile waters, indicating that DOC has an accumulative property. As the minerogenic water in the case of HS is very dilute in all mineral contents, it is very susceptible to changes caused by DOC accumulation and cation exchange by living plants and peat. These factors cause the development of a spatial gradient in water chemistry through spatial succession, without vertical isolation from minerogenic water. Vitt (2000) hypothesised that organic acidity has greater influence on acidity in stagnant bog waters and that cation exchange has more significant influence in downstream development of acidity of more mobile waters. However, in HS the downstream development of acidity includes the accumulation of DOC. In the case of dilute fen waters, rich water flow rate is essential for maintenance of sufficiently high mineral cation concentrations and alkalinity for rich fen vegetation. In other words, it prevents depletion of cations and accumulation of organic acidity in surface water, and neutralises the peat.

The total acidity of organic acids in various natural fresh waters, including bog waters, is known to be around 10 μeq per mg DOC and the average pK_a values are around 4.5 (Oliver *et al*. 1983). Organic anion (OA^-) was calculated for the samples according to Oliver *et al*. (1983) and compared to the anion deficit (AD^-) from the ionic balance calculations. In general the correspondence was good ($r^2 = 0.70$), indicating that the dissociation of organic acids was predictable with pH. In some cases AD^- gave slightly higher estimates than OA^-, however. A possible explanation is a cumulative error from errors in each ionic concentrations used for calculation of AD^-. On the other hand, it is possible that in cases where AD^- exceeded OA^-, part of the cations were in non-ionic form, complexed with DOC. This is supported by the extremely low conductivity values in JS, that are clearly lower than expected from specific conductivities of mineral ions, if they were supposed to exist totally in ionic forms. Determinations of both elemental and ionic concentrations of major ions would be needed to examine the ionic balance in more detail.

The relationship between pH and DOC was rather well-defined in the current data. Organic acids acidify mire water and there is a negative relationship between pH and DOC until pH is around 4 and DOC around 40 mg l^{-1}, after which there is no consistent decrease in pH with increasing DOC concentrations (up to 80 mg l^{-1}). This result, as such, quite possibly only applies to the present study area and comparable sites in northeastern Fennoscandia. Concentrations and controls of DOC in different mire types and climates are fairly unknown and more attention should be paid to organic chemistry of mire waters. As DOC is potentially influenced by climate change (Freeman *et al*. 2001), it may have a role in ecological changes of mire-ecosystems.

Chemical variation independent of the poor–rich gradient

The concentrations of Al, Fe, Mn and S had the highest eigenvector scores for the second

PCA-axis and for the third PCA-axis the highest eigenvector scores were found for N, NH_4^+, $NO_2^- + NO_3^-$, and SO_4^{2-}. These two directions of chemical variation were partly independent of the poor–rich related chemical variation. The variation of Al, Fe and Mn is partly related to pH, as the solubility of these metals is regulated in part by pH. However, only a weak negative correlation was found between pH and Al.

The first and second PCA-axes of water chemistry were very similar to those found by Mullen *et al.* (2000) for 135 widely ranging samples from different parts of North America. In their analysis the same three metal concentrations (Al, Fe, Mn) formed the second axis, which distinguished only one areal group of samples, while all the other six areal groups were rather uniformly distributed along the axis, indicating that the gradient took place within different areas. In the case of HS, the soil in the drainage area is podzolized, and thus Al, Fe and Mn are easily leached in the acidic soil surface water. Because the concentrations of Al, Fe and Mn are very low both in the ground water and in precipitation, their gradient should indicate the influence of surface water flow from mineral land (*see* Malmer 1962, Damman 1995). It must be remembered, though, that these elements are sensitive to redox conditions and are affected by water table fluctuation and aeration (Damman 1978). In some cases atmospheric dry deposition causes elevated concentrations of Al and Fe in bog waters (Urban *et al.* 1987).

The spatial map of the second PCA-axis scores showed a pattern of gradual zonation clearly separate from that of the first axis. The lowest scores for the second PCA-axis (highest metal concentrations) were found on the southern mire margin and at one site on the northern mire margin. These sites seem to be connected with surface water flow from the minearal land. Most of the drainage area of HS is to the south (240% in relation to the mire basin area), where there is a relatively high hillside with approximately 40 m difference in altitude within 500 m from the mire margin. By contrast, to the north of the basin, the drainage area is very small (20% in relation to the mire basin area). Consequently, the surface water flow from mineral land may be significant especially to the southern mire margin. In JS the spatial pattern could not be studied similarly, since the sampling was too sparse. Marginal sites had, in general, higher concentrations of Al and Fe than the more central sites.

The influence of minerogenic surface water could be related to the ‘margin-expanse’ gradient in vegetation (Sjörs 1948, Malmer 1962) or ‘forested swamp — open mire’ gradient as named by Økland *et al.* (2001). In forested wetlands, in northeastern Ontario, Jeglum and He (1995) found the first axis in a CCA to be related to peat depth and concentrations of Al, Fe and Cu in peat. The vegetational variation along the axis was typical to a margin-expanse gradient. The ecological factors affecting the margin-expanse gradient have remained unclear until recently (Wheeler & Proctor 2000, Økland *et al.* 2001) and it is also unclear whether the potential variation of Al, Fe and Mn along the gradient would have influence on vegetation. However, given the well-known potential for toxic effects of high Al and Mn levels, especially when connected to low Ca availability, their variation along the margin-expanse gradient may be significant to some plant species. According to Small (1972), bog plants should selectively exclude Al and Mn. The variation of Al and Fe was also connected to the poor–rich gradient in HS. In JS, at ombrotrophic bog and extremely poor fen sites, the levels of Al and Fe were very low, however, and thus there is no strict connection with the poor–rich gradient and these concentrations.

The partial independence of the availability of many essential nutrients in water, in relation to the poor–rich gradient, is known from several studies (Vitt *et al.* 1995, Bridgham *et al.* 1996, Wheeler & Proctor 2000), and it becomes apparent from the current results as well. The variation of the nitrogen species was essentially independent of the poor–rich gradient. An interesting contrast in these concentrations was found between the forested and the open moderately rich fen zones as indicated by the spatial pattern of the third PCA-axis and the significant differences in concentrations of $NO_2^- + NO_3^-$ and SO_4^{2-}. The concentrations of P were usually below the detection limit but single concentrations above it appeared at all zones. Furthermore, the concentrations of K showed only little relation to the poor–rich gradient. The NH_4^+ concentrations found were very high. Increasing concentrations of NH_4^+ with depth (Vitt *et al*. 1995, Steinmann & Shotyk 1997), as well as higher concentrations in sampling wells compared to open pools (Vitt & Bayley 1984) have been found in other studies, which could explain the relatively high concentrations found in this study.

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