

Atmospheric deposition and mass balance of major and trace elements in two oceanic peat bog profiles, northern Scotland and the Shetland Islands

William Shotyk *

Geological Institute, University of Berne, Baltzerstr. 1, CH-3012 Berne, Switzerland

Received 31 July 1996; accepted 5 December 1996

Abstract

A mass balance was performed on the major (Si, Al, Fe, Na, K, Mg, Ca) and some trace elements (Rb, Sr, Cl, Br, S) in peat cores from two oceanic blanket bogs in northern Scotland: Loch Laxford (LL) is 15 km east of the open ocean in the extreme northwest of the Scottish mainland; Fleck's Loch (FL) is on the small (15 km²) island of Foula, 50 km west of the 'mainland' of Shetland. The supply of these elements to the peats can be explained in terms of two main atmospheric sources: mineral aerosols from weathering of crustal rocks, and sea salt spray. The average Al/Sc and Fe/Sc ratios of the peats at both sites are comparable to the corresponding ratios in soil-derived aerosols suggesting that crustal inputs account for essentially all of the Al and Fe in the profiles. The Si/Sc ratios of the peats from LL again correspond with the value for soil-derived aerosols, but at FL there is an excess of Si in the uppermost part of the profile mainly because of quartz from sources immediately around the bog. In contrast to Al, Fe, Si, the concentrations of Na, Mg, Ca, and Sr in the peats exceed the corresponding ratios in soil-derived aerosols by 5 to 30 times, reflecting the importance of marine aerosols for these elements.

The conservative behaviour of Cl[−] allows the concentration of this species in the pore waters to be used as a quantitative indicator of the relative importance of sea salt inputs to the two bogs. In contrast, the concentrations of other important pore water species (SO₄^{2−}, Br[−], Na⁺, K⁺, Mg²⁺, and Ca²⁺) do not simply reflect their concentrations in rainwater because of biological transformations (S, Br, K), ion exchange (Na, K, Mg, Ca), and possibly mineral dissolution (Na, Mg, Ca).

The average pore water Cl[−] concentrations at FL (97.0 ± 15.2 mg/l) show that marine inputs are 4 times greater than at LL (24.0 ± 2.6 mg/l). The concentrations of other major and trace elements in the rainwater supplied to the bogs were calculated using the known abundances of the elements in seawater, and normalizing to the pore water Cl[−] concentrations at the two sites. These estimated rainwater compositions were then combined with rainfall data to calculate the annual inputs to the bogs. The peat core inventory of major and trace elements (corrected for crustal contributions) was compared with these inputs to determine the percentage of each element retained in the peat profiles. These findings indicate that 91.5 to 99.9% of the major elements (Cl, Na, Mg, K, Ca) and trace elements (Br, Sr, Rb) supplied to the bogs by rainwater are not retained

* Tel.: +41 31 631-8770; Fax: +41 31 631-4843; E-mail: shotyk@geo.unibe.ch

by the peat. Thus, none of these elements in the solid phase (peat) can be used as a quantitative measure of sea salt inputs to the bogs.

Keywords: Blanket bogs; Peat chemistry; Pore water chemistry; Geochemical mass balance; Crustal aerosols; Marine aerosols

1. Introduction

Peat cores taken from European bogs have been used in a number of studies to try to reconstruct present and past rates of atmospheric metal deposition (Glooschenko, 1986; Glooschenko et al., 1986; Livett, 1988). Most of the cores have been taken in central Europe where present rates of anthropogenic atmospheric metal deposition are high compared to the natural metal fluxes (Shotyk et al., 1996). In these kinds of studies, metal inputs from human activity must be clearly separated from natural sources of metals to the bogs (Shotyk, 1996a). In central Europe, by far the most important natural source of metals to the peats is soil dust derived from crustal weathering (Shotyk, 1995). For comparison with central European records it would be helpful to have reliable data from remote sites to determine the range in present-day metal deposition rates across the continent. However, with the exception of limited studies undertaken in northern Norway (Hvatum et al., 1983; Njåstad et al., 1987; Steinnes and Njåstad, 1995), there have been few cores taken from peat bogs in such locations. There are many suitable sampling sites in the Shetland and Orkney Islands and in northern Scotland. However, depending on the proximity to the sea, marine spray may introduce large quantities of dissolved salts to such bogs (Gorham and Cragg, 1960; Vitt et al., 1990; Malmer et al., 1992) and this could contribute significantly to the natural supply of trace metals to the peats. To successfully use peat cores from remote maritime bogs to determine rates of anthropogenic metal deposition, the atmospheric metal fluxes must be corrected for inputs from both soil dust and sea salt spray.

In order to be able to quantify inputs of metals derived from marine sources, the sea salt inputs to the bogs must be known. While there are several possible ways to do this, it is desirable to have a geochemical parameter, either in the peats or in the

corresponding pore waters, which could be easily and routinely analyzed and would provide a reliable measure of sea salt inputs to oceanic bogs. It is well known that Cl^- in rainwater is derived primarily from marine aerosols, especially in coastal areas (Gorham, 1955; Berner and Berner, 1987). In addition, Cl^- behaves conservatively in natural waters (Livingstone, 1963) including sediment pore waters (Lord and Church, 1983; Casey and Lasaga, 1987; Hines et al., 1989). The Cl^- concentrations in rain over the oceans averages 10–15 mg/l, but over land the concentration drops rapidly within 10–20 km of the coast. In the continental U.S., by 600 km inland the concentration is a fairly constant 0.15–0.20 mg/l (Berner and Berner, 1987). As expected, many ecological studies which have included chemical analyses of bog surface waters have found the same trend in Cl^- concentration with increasing distance from the coast (Webb, 1947; Ogden, 1982; Gorham et al., 1985; Comeau and Bellamy, 1986). Some of the published Cl^- concentrations in bog surface waters are listed in Table 1, given in order of increasing proximity to the sea. Of particular importance is extent to which the Cl^- concentrations in surface waters can change over relatively small distances: on the west coast of British Columbia, Canada, for example, the cation and anion concentrations in bog surface waters decreased 10-fold over a narrow zone from the islands to the mainland (Vitt et al., 1990).

The main purpose of this report is to determine which, if any, of the major and trace elements in the peats and pore waters can be used to quantify sea salt inputs to two oceanic blanket bogs. This is done using Cl^- as an index of sea spray, assuming that (1) Cl^- in the rain water supplied to the bogs is derived exclusively from marine aerosols, and (2) that Cl^- behaves conservatively in the surface waters and pore waters. Using Cl^- to construct a geochemical mass balance of atmospheric inputs, it is found that 91.5 to 99.9% of the major and trace elements supplied by marine aerosols are not retained by the

Table 1
Chloride concentrations in bog surface waters from continental and maritime locations

Region	Average chloride (mg/l)	Reference
<i>Continental sites</i>		
Southern, Poland	0.2–0.3	Tolpa and Gorham (1961)
Minnesota, USA	0.7 ± 0.8	Verry (1975)
NW Ontario, Canada	0.55 ± 0.42	Vitt and Bayley (1984)
Central Ontario, Canada	0.16–0.18	Blancher and McNicol (1987)
<i>Maritime sites (listed in order of increasing proximity to the sea)</i>		
SW Finland	1.1–1.2	Tolonen et al. (1979)
N England	2.2–6.5	Gorham (1956)
NW Scotland	18.3 (12 km)	Pearsall (1956)
	29.6 (3 km)	
W British Columbia, Canada	23.4	Malmer et al. (1992)
Yell, Shetland	33.4	Shotyk (unpubl. data)
W Ireland	33.6	Shotyk (unpubl. data)
Falkland Islands	72.2	Gorham and Cragg (1960)

peat in these bogs. As a consequence, the concentrations of these elements in the solid phase (peats) cannot be used to quantify sea salt inputs to the bogs.

2. Materials and methods

2.1. Location of sites

The approximate locations of the two sites are shown in Fig. 1. The blanket bog at Loch Laxford (LL) is approximately 15 km from the open ocean near Laxford Bridge in Sutherland (approximately 58°22'N, 5°00'W). The site where the core was taken is essentially a very small blanket bog approximately 150 m in diameter. Confined on all sides by outcrops of Lewisian gneiss, shallow pools of open water are abundant on the surface of the bog. At an elevation of approximately 30 m asl, this bog is bordered to the south by a block of Lewisian gneiss up to 60 m high; to the north, the site overlooks a larger blanket bog (up to 750 m long) at an elevation of 10 m; far beyond this lies Laxford Bay and Loch Laxford, both of which can be seen off in the distance. The bog is approximately 500 m from the road to the north and 250 m from the road to the south.

Loch o' da Fleck (FL) is a blanket bog on the Island of Foula. Foula (60°09'N, 2°06'W) is approximately 50 km west of the main island ('Mainland')

of Shetland. The island is 3 km wide and 5 km long, with a population in 1994 of 36. The bog has developed in a hanging valley, approximately 1 km east of the Atlantic Ocean, on Devonian Old Red

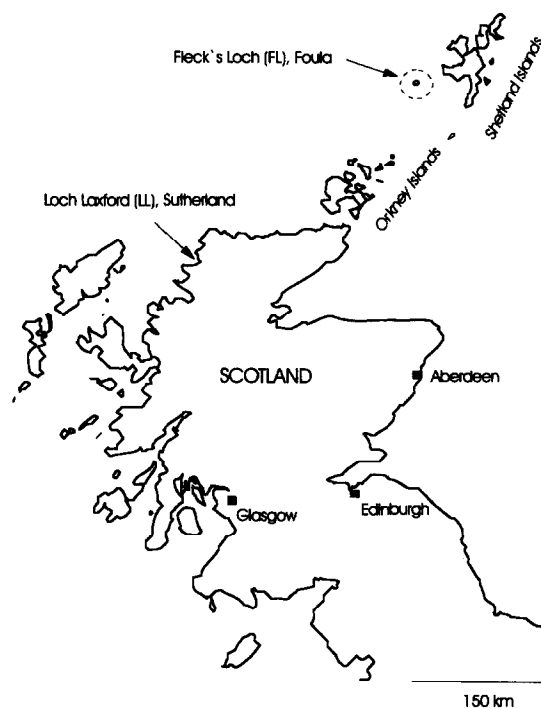


Fig. 1. Map showing the approximate location of the two sampling sites on the Scottish mainland (Loch Laxford, Sutherland) and on the Shetland Islands (Fleck's Loch, Island of Foula).

Sandstone. The valley is flanked to the north by the North Bank (210 m asl), to the west by The Kame (376 m asl), and to the south by The Sneug (418 m asl). In this sense the site is somewhat protected from direct inputs of sea salt spray in that the bog is at the valley bottom (approximately 170 m asl) and is exposed only to the east. The bog itself is approximately 500 m long and up to 275 m wide, with the surface where the core was taken perhaps 2 to 3 m higher than the edges of the bog. The pronounced dome shape of this bog, however, does not necessarily mean that FL is a raised bog in the traditional sense of a 'Hochmoor'. In fact, the morphology of the bog today may have less to do with climate, and more to do with erosion: the perimeter of the bog is extensively eroded, with some bare peat banks, deep gulleys, and small streams which frequently arise out from and disappear into the thick blanket peat. The convex morphology of this bog combined with the well decomposed peats and the extensive erosion features surrounding the bog suggest little, if any, penetration of the middle of the bog (where the peat core was taken) by surface runoff.

The climate at the two sites is similar (Lindsay et al., 1988). The average annual temperature is approximately 8°C at LL and 7.5°C at FL, and rainfall averages 1000 to 1500 mm per year. The average number of rain days (24-h period in which at least 0.25 mm precipitation is recorded) is 250 or more. From September to April the excess of precipitation over evapotranspiration is approximately 200 mm in both areas.

2.2. Present vegetation and peat stratigraphy

The dominant plant species at each of the sites are given elsewhere (Shotyk, 1996a). The stratigraphy at LL is dominated by *Sphagnum–Eriophorum* peat from the surface to 140 cm, varying in degree of decomposition on the von Post scale (Clymo, 1983; Hobbs, 1986; Landva et al., 1986) from H3 to H6. From 140 cm to 180 cm the peat is a very well decomposed (H8) mixture of *Sphagnum* and sedges. Between 180 and 230 cm the peats appear to be made up mainly of sedge remains, varying from H4 (160 to 200 cm) to H9 (200 to 230 cm). From 230 cm to 390 cm the peat is very well decomposed (H9 to H10) with some small pieces of wood bark; no remains of *Eriophorum* were found below 345 cm.

The stratigraphy of the peat bog at FL has been described by Lewis (1911), Hawksworth (1970), and Barkham et al. (1981). The first 150 cm of the profile consists of *Sphagnum–Eriophorum* peat, poorly decomposed (H3) within the first 40 cm, and well decomposed (H7) below. Descending from 150 cm there is a horizon approximately 20 cm thick consisting of *Juniperus*; from 170 to 350 cm the profile consists of well decomposed woody, *Sphagnum–Trichophorum* peat (Barkham et al., 1981).

With respect to the cores which were analyzed for the present study, their stratigraphy is summarized in Table 2. Both of these sections of the peat cores appear to represent the 'ombrotrophic' section of these bogs meaning that the inorganic fraction of the peats was supplied exclusively by atmospheric deposition, and that the peat cores were never influenced by surrounding groundwaters or mineral soil water (Shotyk, 1988, 1995). This interpretation follows from the thickness of the peat profiles and their botanical composition (typical blanket bog flora), the very high degree of humification (and therefore low hydraulic conductivity) of the deeper peat layers, and the low ash contents (LL). In addition, the bog at FL is strongly convex as noted above. Moreover, the Ca/Mg molar ratios of the peat samples show very little change with depth in either core, averaging 0.55 ± 0.08 in the FL core and 0.82 ± 0.12 in LL

Table 2
Simplified stratigraphy of the 1-m core from the two bogs

Depth (cm)	Peat type ^a	Humification (von Post) ^b
<i>Fleck's Loch</i>		
0–8	S9ER1	3
8–38	S7ER3	3
38–102	S8ER2	7
<i>Loch Laxford</i>		
0–9	S0	3
9–25	S9ER1	3
25–39	S8ER2	5
39–65	S7ER3	4
65–100	S8ER2	6

^a S9ER1 refers to peat which is estimated to contain approximately 90% by volume *Sphagnum* peat and 10% *Eriophorum*; S0 is pure *Sphagnum* peat, and so on.

^b The von Post 10-point humification scale is described in more detail elsewhere (Clymo, 1983; Hobbs, 1986; Landva et al., 1986; Shotyk, 1988).

profile ($n = 34$ in each case). The molar ratio of Ca/Mg in peat profiles is sometimes compared with rainwater and groundwater values to distinguish ombrotrophic from minerotrophic peats (Shotykh, 1996a). With respect to the peat cores from FL and LL, these values are not only uniform with depth, they are well below the corresponding ratios for the host rocks which are 2.3 for Devonian Old Red Sandstone (Pettijohn et al., 1987, p. 151) and 1.9 for Laxfordian Lewisian gneiss (Craig, 1983, p. 29), respectively. While the Ca/Mg molar ratios of the peats from these cores exceed the seawater (and therefore also local rainwater) ratio of 1:5, they are consistent with the preferential removal from rainwater of Ca^{2+} versus Mg^{2+} by ion exchange (Shotykh, 1996a). Thus, the Ca/Mg ratios of the peats from FL and LL are consistent with an ombrotrophic interpretation of the cores, and provide no evidence of any chemical influence by the rocks surrounding the bogs.

The deepest peat sample from each of these approx. 100-cm cores was age dated using ^{14}C . The preparation, processing, and age dating was carried out by the Radiocarbon Laboratory of the Physics Institute of the University of Berne. The following radiocarbon ages were obtained: sample 7d34 at LL (96–99 cm), 1420 ± 30 years BP (B-6460); sample 6a34 at FL (93–96 cm), 1170 ± 30 years BP (B-6461).

2.3. Sample collection, preparation, and analysis

2.3.1. Peats

Using a Wardenaar peat profile sampler (Wardenaar, 1987), peat cores approximately $100 \times 10 \times 10$ cm were removed from each bog (on 28.9.91 from FL and on 2.10.91 from LL), packaged and prepared as described earlier for peat cores from Switzerland (Shotykh, 1996b). Major elements (Al, Si, Ti, Fe, Na, K, Mg, Ca, Cl) were analyzed using conventional wavelength-dispersive X-ray fluorescence spectrometry, whereas Rb, Sr, and Br were measured using the EMMA XRF miniprobe (Cheburkin and Shotykh, 1996). Scandium was measured using instrumental neutron activation analysis (ACTLABS, Ancaster, Ontario).

2.3.2. Rainwater

Fifteen rain events on the Island of Foula were sampled between December 1994 and October 1996.

These samples were kept refrigerated until they could be analyzed at the University of Berne for selected anions (Cl^- and SO_4^{2-}) and cations (Na^+ and Mg^{2+}) using ion chromatography (Steinmann and Shotykh, 1995). Unfortunately, the area around Loch Laxford is largely uninhabited, and it was not possible to have rainwater samples collected at that site.

2.3.3. Surface and pore waters

Collection of surface and pore waters from bogs has been described elsewhere (Shotykh and Steinmann, 1994). Anions (Cl^- , Br^- , SO_4^{2-}) and cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were measured using chemically suppressed ion chromatography with conductivity detection (Shotykh, 1993a,b). Each of the samples was analyzed at least twice. The average coefficients of variation (%) for a set of pore waters analyzed in duplicate were Cl^- 0.7, Br^- 1.7, SO_4^{2-} 0.6, Na^+ 2.9, K^+ 13.3, Mg^{2+} 1.8, Ca^{2+} 8.7 ($n = 28$).

3. Results

3.1. Bulk density, ash content, and sulphur

The age dates of the deepest sample from each core allow the net rates of peat accumulation to be calculated simply by integrating the dry bulk density of each sample over the entire core: this yields annual organic matter accumulation rates of 90.4 g/m^2 at FL and 62.6 g/m^2 at LL. The dry bulk densities of the peat cores range from 0.04 to 0.16 g/cm^3 at FL and from 0.04 to 0.14 g/cm^3 at LL (Fig. 2). On average, the bulk densities are about 17% higher at FL compared to LL, despite the faster net rate of peat accumulation at FL. The increase in density with depth seen in the uppermost part of each core reflects the transition from living plant material, through dead plant material, to poorly decomposed peat. At FL, the deeper parts of the core are more dense, reflecting the higher degree of decomposition of these peats.

The average ash content at FL (6.9%) is more than 3 times higher than at LL (2.2%). A part of this difference can be attributed to the two very pronounced peaks in ash content at FL: 23% ash at approximately 20 cm and 13% at 95 cm (Fig. 2).

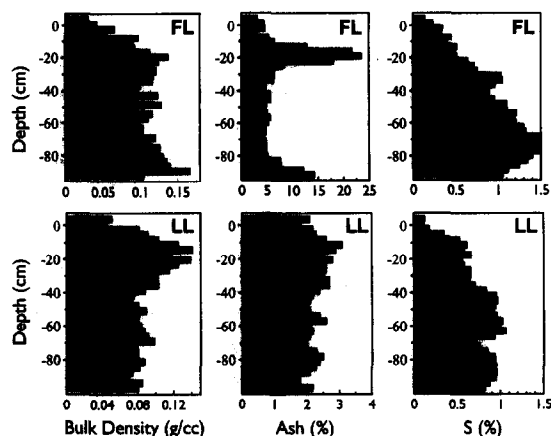


Fig. 2. Bulk density, ash, and sulphur concentrations in the peat cores from Fleck's Loch (FL) and Loch Laxford (LL).

Even if these peaks in the ash profile at FL were subtracted, however, the average ash contents of the FL peats would still be twice those at LL. Integrated over the entire length of each core, the average annual rates of accumulation of inorganic matter (ash) are 2.21 g/m^2 at FL compared with 0.48 g/m^2 at LL.

The sulphur concentrations increase with depth from approximately 0.1% to more than 1% (Fig. 2). The maximum concentrations at FL are somewhat higher than the maximum concentrations at LL. These S concentrations are generally a factor of 10 times

greater than typical values for continental ombrotrophic peats (Steinmann and Shotyk, 1997).

3.2. Average chemical composition of the peats

A summary of the average chemical composition of the two profiles is given in Table 3. In general, the Al, Fe, and Sc concentrations at FL are approximately twice those of LL, and Si about 4 times higher. The ash fraction of peats generally is derived mainly from atmospheric inputs of pedogenic dust (Feustel and Byers, 1930; Chapman, 1964; Gorham and Tilton, 1978), but volcanic ash may also be important (Persson, 1971; Dugmore, 1989; Zoltai, 1989; Froggatt and Rogers, 1990; Newnham et al., 1995) at some sites.

In contrast to Al, Fe, Si and Sc, the Cl, Br, Ca and Sr concentrations in the two profiles are not significantly different. The Mg concentrations at FL on average are 50% greater than at LL, Na is approximately 2 times greater, and K more than 3 times greater (Table 3).

3.3. Continental versus marine sources of major elements to the peats

The two most important natural sources of atmospheric aerosols are mineral dust from soils and sea salt from the oceans, with average annual global emissions on the order of 2×10^9 and $1 \times 10^9 \text{ T/a}$,

Table 3

Average chemical composition of the peats ($\pm 1 \text{ S.D.}$) at the two sites ($\mu\text{g/g}$ except where noted)

	Fleck's Loch	Loch Laxford
Ash (%)	6.9 ± 4.8	2.2 ± 0.3
Si (%)	0.669 ± 0.660	0.159 ± 0.083
Al (%)	0.163 ± 0.083	0.070 ± 0.018
Fe (%)	0.079 ± 0.029	0.042 ± 0.010
S (%)	0.907 ± 0.399	0.712 ± 0.253
Cl	1280 ± 121	1341 ± 268
Br	271 ± 118	266 ± 93
Na	1140 ± 130	540 ± 110
K	590 ± 450	170 ± 200
Mg	2960 ± 380	2020 ± 210
Ca	2690 ± 460	2720 ± 460
Rb	2.7 ± 1.9	1.2 ± 0.7
Sr	54.8 ± 8.5	41.2 ± 7.5
Sc	0.37 ± 0.16	0.20 ± 0.07

Table 4

Average element/Sc mass ratios in the two peat bog profiles, and in soil-derived aerosols

	Aerosol ^a	FL	(FL/ aerosol)	LL	(LL/ aerosol)
Si/Sc	8420	16320	(1.9)	8880	(1.1)
Al/Sc	4280	4400	(1.0)	3740	(0.9)
Fe/Sc	2620	2430	(0.9)	2410	(0.9)
Na/Sc	430	3690	(8.6)	3290	(7.6)
K/Sc ^b	930	1320	(1.4)	560	(0.6)
Mg/Sc	1250	9810	(7.9)	11970	(9.6)
Ca/Sc	1580	8580	(5.5)	15600	(9.9)
Rb/Sc	4.5	7.2	(1.6)	6.7	(1.5)
Sr/Sc	7.3	174	(23.8)	226	(31.0)

^a From L. Schütz (pers. commun., 1995).

^b K/Sc ratios of the first 10 cm of the peat cores were not considered because of extensive enrichment by biological cycling.

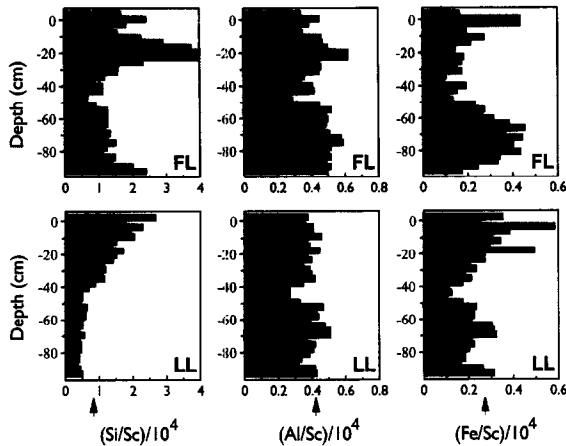


Fig. 3. Si/Sc, Al/Sc, and Fe/Sc ratios of the peats (divided by 10,000). The average ratios for soil-derived aerosols $< 16 \mu\text{m}$ (from L. Schütz, pers. commun., 1995) are indicated by the arrows.

respectively (Schütz, 1989). To estimate how much of each of these elements has been supplied by lithogenic aerosols versus sea salt spray, their concentrations have been normalized to Sc, a conservative metal which is often used as a reference element in soil-derived aerosols (Schütz, 1989; Shotyk, 1996a,b). The average Al/Sc ratios of the peats at

both sites agree to within 15% of the corresponding average ratios in soil-derived aerosols (Table 4). In other words, soil-derived inputs from crustal weathering can account for essentially all of the Al in both profiles. With respect to Fe, the average Fe/Sc ratios of the peats agree to within 10% of the soil-derived aerosol value, but the profiles exhibit more variation in Fe/Sc than in Al/Sc (Fig. 3).

The average Si/Sc ratios of the peats from LL correspond to within 5% of the value for crustal aerosols, but the profile shows that the Si/Sc ratio varies by a factor of about 5 times within the profile, with values much higher in the surface and subsurface peats compared to deeper layers (Fig. 3). The higher Si/Sc ratios in surface layers and their progressive decrease with depth may be due to recent increases in atmospheric deposition of opaline phytoliths from agricultural plants, plus biological cycling of Si at the surface of the bog (Steinmann and Shotyk, 1997). In the deeper layers at LL, the Si/Sc ratio is generally about one-half that of the typical crustal aerosol value. At FL, the average Si/Sc ratio is almost twice that of the crustal aerosol, but the profile shows that the excess of Si is especially pronounced in a zone from approximately 10 to 30 cm (Fig. 3). This peak, with Si/Sc ratios exceeding

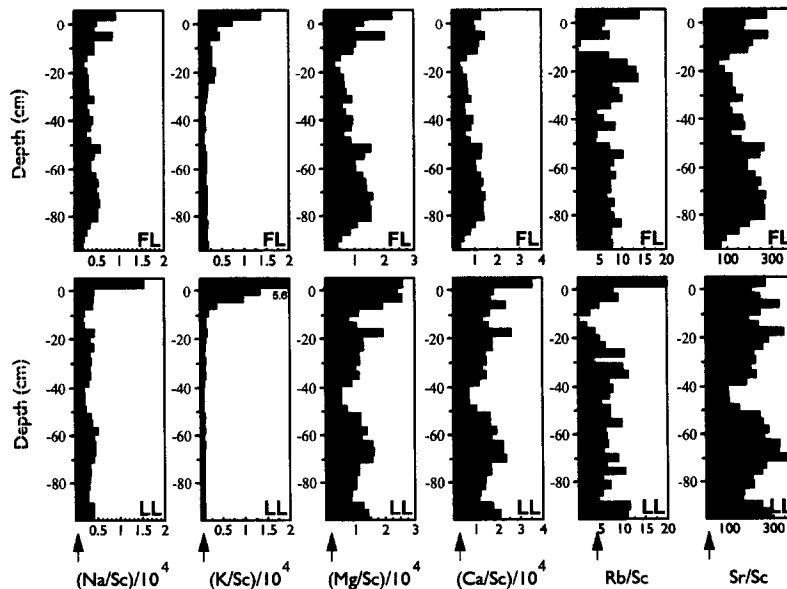


Fig. 4. Na/Sc, K/Sc, Mg/Sc and Ca/Sc ratios of the peats (divided by 10,000), and the Rb/Sc and Sr/Sc ratios of the peats. The average ratios for soil-derived aerosols $< 16 \mu\text{m}$ (L. Schütz, pers. commun., 1995) are indicated by the arrows.

the soil-derived aerosol value by 5 times, corresponds to the pronounced peak in ash shown in Fig. 2. As noted later, the mineral fraction at this depth contains abundant quartz, and this probably accounts for most of the excess Si.

In contrast to the elements described above, the Na/Sc, Mg/Sc, and Ca/Sc ratios in the peat bog profiles exceed the corresponding ratios in crustal aerosols by 5 to 10 times (Table 4). With respect to Sr, the Sr/Sc ratios exceed the value for crustal aerosols by 20 to 30 times or more, indicating that other sources of Sr are much more important. The variation in metal/Sc ratios with depth through the profiles is shown in Fig. 4. Except for surface layers where K is strongly recycled by the living plants, much of the K and Rb in the peat profiles can be explained by crustal inputs. In contrast, the Na/Sc, Mg/Sc, Ca/Sc and Sr/Sc ratios of the profiles are much higher than in the soil-derived aerosol (Fig. 4). The most likely additional source of these elements to the bogs is the sea, suggesting that marine aerosols supply almost 90% of the Na, Mg, and Ca, and more than 95% of the Sr.

3.4. Chemical indicators of sea spray inputs

3.4.1. Rainwater

The average concentration of Cl^- in fifteen rain events sampled on the Island of Foula from December 1994 to October 1996 was 61.4 mg/l (range 6.2–305.5).

3.4.2. Surface waters

At the time of sample collection, the surface waters at FL contained 3.7 times as much Na^+ and 3.4 times as much Cl^- as the waters at LL. With respect to the other major element species, they were more abundant in the surface pools at FL by factors ranging from 1.6 to 2.7 times (Table 5). While the Na/Cl molar ratios in the surface waters are within 11% of the seawater ratio, the metal/Cl ratios for K, Mg, and Ca are generally different from the corresponding ratio in seawater. For example, at LL, the molar ratios K/Cl, Mg/Cl, and Ca/Cl were substantially greater than the corresponding seawater ratios (K 2.6, Mg 1.3, and Ca 1.8 times greater, respectively). Assuming that Cl^- is conservative (Livingstone, 1963), K^+ , Mg^{2+} , and Ca^{2+} appear to

Table 5

Chemical composition (± 1 S.D.) of surface waters at the two sites (mg/l) and the ratio of the concentrations (FL/LL)

	FL (mg/l)	LL (mg/l)	FL/LL
pH	4.82	4.46	
Cl^-	85.8 ± 0.2	25.0 ± 0.4	3.4
Br^-	0.30 ± 0.0	0.13 ± 0.0	2.3
SO_4^{2-}	13.4 ± 0.1	4.4 ± 0.0	3.0
Na^+	54.3 ± 1.5	14.5 ± 0.4	3.7
K^+	2.3 ± 0.3	1.4 ± 0.1	1.6
Mg^{2+}	5.1 ± 0.2	2.1 ± 0.1	2.4
Ca^{2+}	2.4 ± 0.3	0.9 ± 0.0	2.7

be affected by other processes following their supply to the bogs by sea spray.

3.4.3. Peats and pore waters

Cl and Br. The Cl concentrations in the solid phase show a similar range at the two sites (Fig. 5). On average, the Cl concentrations in the two peat cores are not significantly different (Table 3). In contrast, the pore waters reveal a large difference between the two bogs: Cl^- concentrations range from 80 to 120 mg/l at FL, versus 20 to 30 mg/l at LL (Fig. 5 and Table 6). Because the concentrations of Cl in the peats are the same at the two sites, decomposition of the solid phase and the consequent release of Cl^- to solution is an unlikely explanation for the differences in Cl^- concentrations in the pore waters. Assuming that (1) Cl^- in the rain water supplied to the bogs is derived exclusively from

Table 6

Average chemical composition (± 1 S.D.) of pore waters at the two sites (mg/l except where noted) and the ratio of the concentrations (FL/LL)

	Fleck's Loch	Loch Laxford	FL/LL
pH	4.89	4.80	
DOC	85.1 ± 27.4	49.4 ± 10.1	
Cl^-	97.0 ± 15.2	24.0 ± 2.6	3.9
Br^-	0.7 ± 0.3	0.9 ± 0.4	0.8
Na^+	61.8 ± 9.4	11.5 ± 1.3	5.4
K^+	1.5 ± 1.5	0.7 ± 0.4	2.1
Mg^{2+}	5.5 ± 1.7	0.5 ± 0.3	10.5
Ca^{2+}	2.3 ± 0.7	0.4 ± 0.3	5.7
Si	1.19	1.22	1.0
Al	0.279	0.025	11.1
Fe	0.228	0.032	7.1

marine aerosols, and (2) that Cl^- behaves conservatively in the pore waters, it follows that the average concentrations of pore water Cl^- (97.0 ± 15.2 mg/l at FL compared with 24.0 ± 2.6 mg/l at LL) indicate that the supply of inorganic solids from sea spray is 4 times greater at FL compared to LL.

The range in concentrations of Br in the peats are also similar at the two sites (Fig. 5). On average, the Br concentrations in the two peat cores are not significantly different (Table 3). Thus, the difference in sea spray inputs to the two bogs revealed by the pore water Cl^- concentrations is not reflected in the Br content of the peats. In contrast to the large differences in pore water Cl^- concentrations between the two sites, the Br^- concentrations in the pore waters are similar (Table 6). Thus, the Br^- concentrations in the pore waters also do not indicate any differences in sea spray inputs to the two bogs.

Na and K. With respect to the peats, the Na concentration profiles are similar in shape but the average Na concentration at FL is about twice that of LL (Fig. 6 and Table 3). In contrast, the pore waters at FL contain about 5 times more Na^+ than at LL (Table 6). The lack of correspondence between the Na concentrations in the pore fluids and in the peats suggests that the Na^+ concentrations in the solutions

are not controlled by a simple chemical equilibrium with the peats, and some other source of Na^+ is needed to explain the much higher pore water Na^+ concentrations at FL.

The K concentrations in the peats at FL (Fig. 6) more or less reflect the distribution of ash (Fig. 2). For example, the pronounced peaks in K concentrations at depths of approximately 20 cm and 95 cm correspond to the peaks in ash content at the same depths. Despite the elevated concentration of K at 20 cm, however, the pore water concentrations of K show no response (Fig. 6). At both sites, the K concentrations in the living plant layer are elevated out of proportion with the ash content (Fig. 6), reflecting strong biological uptake (Damman, 1978). The effect of plant uptake is clearly seen in the pore water K^+ concentrations at both sites (Fig. 6). In the uppermost part of the cores and including the waters expressed from living plants, the K/Cl molar ratio exceeds the seawater values by 5 to 6 times at each site. Below the plant rooting zone, the K/Cl ratios are fairly constant with depth and are well below seawater values.

Mg and Ca. The Mg concentrations in the peats on average are approximately 50% greater at FL versus LL (Table 3). At both sites the Mg concentra-

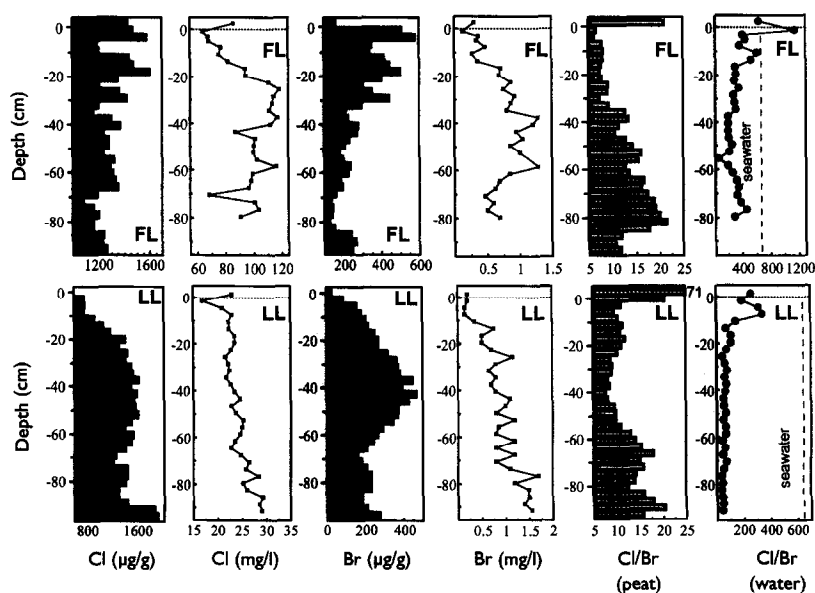


Fig. 5. Cl and Br concentrations in the peats ($\mu\text{g/g}$) and pore waters (mg/l), and the Cl/Br molar ratio in the peats and pore waters.

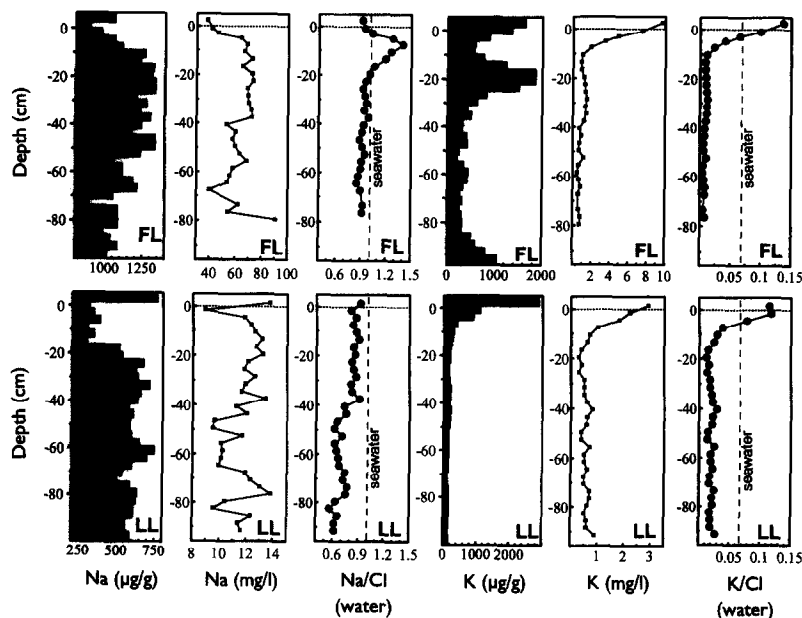


Fig. 6. Na concentrations in the peats ($\mu\text{g/g}$) and pore waters (mg/l), and the Na/Cl molar ratios in the pore waters; K concentrations in the peats ($\mu\text{g/g}$) and pore waters (mg/l), and the K/Cl molar ratios in the pore waters.

tions in the pore waters decrease significantly with depth (Fig. 7). Like Na and K, the average differences in pore water Mg concentrations between the

two sites do not correspond with the differences in Cl^- concentrations. In fact, the average pore water Mg^{2+} concentrations are about 10 times greater at

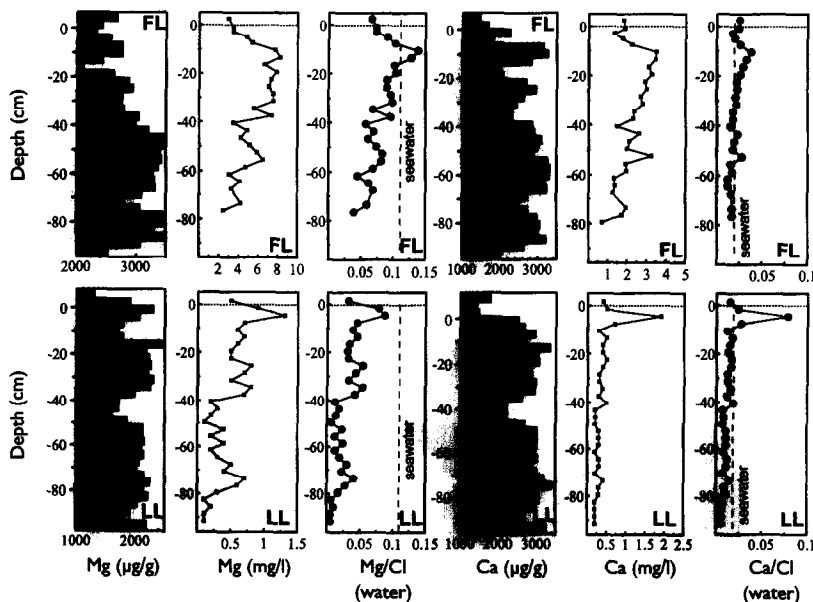


Fig. 7. Mg concentrations in the peats ($\mu\text{g/g}$) and pore waters (mg/l), and the Mg/Cl molar ratios in the pore waters; Ca concentrations in the peats ($\mu\text{g/g}$) and pore waters (mg/l), and the Ca/Cl molar ratios in the pore waters.

FL than at LL compared to a four-fold difference in Cl^- (Table 6). Relative to the Mg/Cl ratio of seawater, most of the pore waters are depleted in Mg^{2+} . At FL, the Mg/Cl ratio is up to 60% lower than the seawater value, and LL up to 95% lower. One exception is the zone from 10 to 20 cm below the surface at FL which is enriched in Mg relative to the seawater Mg/Cl ratio; this enrichment is comparable to the Na^+ enrichment described earlier and may be due to active dissolution of mineral matter.

The average Ca concentrations in the peats are not significantly different between the two sites (Table 3). Again, the average differences in pore water Ca^{2+} concentrations between the two sites do not correspond with the differences in Cl^- concentrations (Table 6). In the pore waters, Ca^{2+} generally decreases in concentration with depth, as is true of Mg^{2+} (Fig. 7). At FL, however, only the pore waters deeper than approx. 60 cm are depleted in Ca compared to Ca/Cl in seawater. In fact, the zone 10 to 20 cm below the surface is enriched in Ca^{2+} relative to the Ca/Cl ratio of seawater, as is true of Na^+ and Mg^{2+} at the same depth; once again, this appears to be due to mineral dissolution of the ash-rich layer. At LL, effectively all of the porewaters below 10 cm are depleted in Ca, relative to Ca/Cl in seawater.

3.5. Geochemical mass balance on major and trace elements

Using the Cl^- concentrations in the pore waters as an indication of the differences in sea spray inputs, a mass balance was constructed for the major (Cl, Na, Mg, Ca, K) and some trace elements (Br and Sr) as follows. First, the concentrations of inorganic solids in the rainwater supplied to the bogs were calculated using the known abundances of the elements in seawater (Berner and Berner, 1987), and normalizing them to the average pore water Cl^- concentrations at the two sites. Studies of precipitation chemistry in coastal areas of Scandinavia have used this approach to calculate Na, K, Mg, and Ca concentrations in rainwater and the results agreed to within a few percent of the measured values (Skartveit, 1981; Foltescu et al., 1994). The calculated rainwater composition was then combined with rainfall data (assuming 1500 mm per year at both sites) to estimate annual sea salt inputs to the bogs.

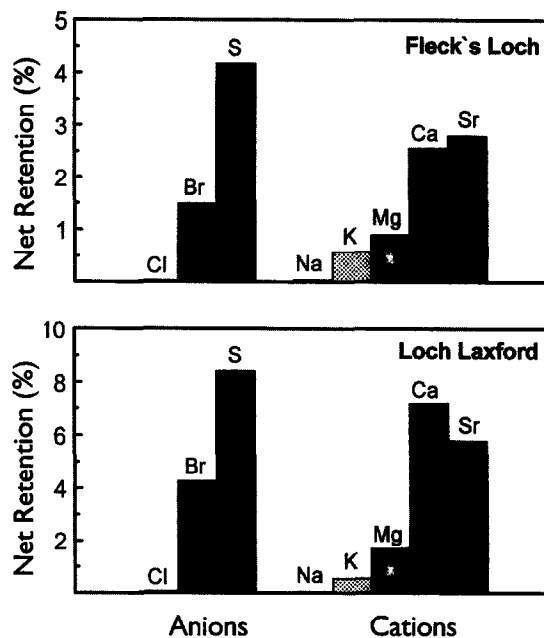


Fig. 8. Summary of the geochemical mass balance for the two peat cores showing net retention expressed as the percentage of rainwater supply.

Given the known volume, dry bulk density, and elemental concentrations of each peat slice, the mass of each element stored in any given segment of the core can be calculated. These storage terms were then corrected for crustal inputs using the measured Sc concentrations and the element/Sc ratios for soil-derived aerosols (Table 4); this yields the storage term due exclusively to precipitation. Using the age dates for the last sample in each core, these data can be summed over the entire core to allow net retention to be calculated for each element in the approx. 1 m peat columns. These calculations indicate that 91.5 to 99.9% of the major elements (Cl, Na, Mg, K, Ca) and trace elements (Br and Sr) supplied to the bogs by rainwater are not retained by the peat (Fig. 8).

4. Discussion

4.1. Quantitative geochemical indicators of sea spray inputs

4.1.1. Peats

The average ratio of metal concentrations at FL versus LL is approximately 2:1 for Na, 1.5:1 for

Mg, and 1:1 for Ca (Table 3). With respect to Cl, Br, and S, there is no significant difference between the two sites (Table 3). Thus, the concentrations of these major elements in the solid phase (peat) provide no consistent indication of the different degree of sea spray influence. The mass balance calculations indicate that 91.5 to 99.9% of the major elements (Cl, Na, Mg, K, Ca) and trace elements (Br and Sr) supplied to the bogs by rainwater are not retained by the peat (Fig. 8). Thus, none of these elements in the solid phase (peat) can be used as a quantitative measure of sea salt inputs to the bogs.

The order of the net retention of cations at FL (Fig. 8) is:

$$\text{Sr}(2.80) \approx \text{Ca}(2.56) > \text{Mg}(0.90)$$

$$> \text{K}(0.58) \gg \text{Na}(0.04)$$

with the percentage of the total rainwater input retained by peat given in brackets. This sequence is consistent with the lyotropic series of cation exchange which reveals the preferential retention of large, divalent metals compared to small, monovalent ones (Helfferich, 1962). The order of net cation retention in the peats is consistent with the hypothesis that cation exchange is the dominant mechanism of metal removal from precipitation. Also, these results agree in a general way with the observation that the exchangeable cation pool in peats from blanket bogs is dominated by Mg^{2+} and Ca^{2+} (Gore and Allen, 1956; Boatman, 1957, 1961).

If cation exchange dominates metal removal from rainwater, and if peat generally is an efficient cation exchanger (Puustjärvi, 1958), why is the net retention of these cations so low? The annual inputs of these metals to the bog at FL can be expressed in meq/100 cm^2 per year: 36.3 Na, 8.23 Mg, 1.59 Ca, 0.79 K, 0.01 Sr. Thus, the sum of cation inputs is approximately 46.9 meq/100 cm^2 per year. Assuming the peat has a cation exchange capacity of 1 eq/kg (Puustjärvi, 1958), the average annual rate of peat accumulation (90.4 g/ m^2 at FL) indicates that only 0.90 meq of cation exchange capacity is added per 100 cm^2 per year. Even if H^+ as an exchangeable cation is ignored, the annual input of cations (46.9 meq/100 cm^2) exceeds the annual supply of new cation exchange capacity (0.9 meq/100 cm^2) by more than 50 times. Thus, the supply of cations to

the bogs exceeds by a large margin the ability of the peat to retain them.

4.1.2. Surface waters

The surface waters at FL contain 3 to 4 times more Cl^- , Na^+ , Ca^{2+} , and SO_4^{2-} than the surface waters at LL (Table 5). Although this may provide an indication of the relative difference in sea salt inputs, such data must be interpreted with caution because ionic concentrations in surface pools are known to depend on local weather conditions at the time of sample collection. For example, the concentrations of major ions in bog pools may be as much as 3 to 4 times higher in dry compared to wet periods (Gorham, 1956). Could a part of the difference in ionic concentrations in the surface waters be due simply to evaporative concentration of the surface waters at FL (which were collected on a clear day), or dilution of the surface water samples at LL (collected on a rainy day)? While very wet or dry weather may significantly affect ionic concentrations in surface waters at inland or continental sites (Gorham, 1956), the bogs at FL and LL receive very high amounts of rainfall evenly distributed throughout the year: with an annual average of 250 rain days at both sites, the probability of an extremely dry period having caused the relatively high ionic concentrations in surface pools at FL seems unlikely. Given the frequency and relatively high concentrations of dissolved salts in the rainfall, the concentration of Cl^- in the surface waters at FL and LL could perhaps be used as a rough guide to marine inputs. However, the average concentration of Cl^- in the pore waters is probably a more reliable indicator because the composition of these waters is less dependent on changes in local weather conditions at the time of sample collection.

4.1.3. Pore waters

Cl^- and Br^- . On average, the concentrations of Cl^- in the pore waters (Table 6) are not significantly different from the average Cl^- concentration in the surface waters (Table 5) at both sites. However, the average concentrations of Cl^- in the pore waters (97.0 ± 15.2 mg/l) and surface waters (85.8 mg/l) at FL clearly exceed the rainwater average (61.4 mg/l based on fifteen events over two years). The higher concentrations of Cl^- in the pore waters and

surface waters probably reflect the additional inputs to the bog of dry deposition and fog. According to Hultberg and Grennfelt (1992), in coastal areas dry deposition of Na and Cl from marine aerosols can exceed precipitation fluxes. Similarly, in his studies of short-term mass balance in blanket bogs from Newfoundland, Price (1994) found that dry deposition of Na supplied more than two-thirds the Na of wet deposition. Moreover, fog events studied over a two-month period provided the bogs with twice as much Na as did rain during the same period. The concentrations of Cl^- in the pore waters, therefore, represent the sum of the fluxes from precipitation, dry deposition, and fog.

The concentrations of Cl^- in the pore waters are independent of the Cl concentrations in the peats (Fig. 5). In general then, this species is not added to or removed from the pore waters by the peat in significant amounts. In other words, Cl^- is conservative. The average concentrations of Cl^- in the pore waters are 4 times higher at FL compared with LL, and this can be taken as a quantitative measure of the sea salt inputs to the two bogs.

In contrast to the four-fold difference in average Cl^- concentrations in the two sets of pore waters, the average Br^- concentrations are not significantly different (Table 6). Unlike Cl^- which is conservative, Br^- is not. Whereas the Cl/Br molar ratio in seawater is approximately 650, the average molar ratio of Cl/Br in the pore waters is only 324 at FL and 84 at LL. In the living plant layers, the molar ratio of Cl/Br (Fig. 5) ranges from 20 (FL) to 70 (LL), revealing a strong preference for Br^- over Cl^- by the plants. In fact, the average Cl/Br molar ratio in the peats at both sites is only 12 (Table 3), with values as low as 6 to 7 found in the peat core at FL (Fig. 5). The mass balance summarized in Fig. 8 is therefore consistent with these findings in that the percentage of the Br input retained by the bogs is 50 to 60 times greater than that of Cl. Despite this difference, net retention of Br^- inputs is still very low: only 1.5% at FL and 4.3% at LL.

Na^+ and K^+ . If the pore waters at FL contain 4 times as much Cl^- as LL, why do they contain 5 times as much Na^+ ? The molar ratio Na/Cl in the pore waters shows that the pore waters in the first 20 cm of the core at FL are enriched in Na, relative to seawater (Fig. 6). Thus, there must be a significant

source of Na^+ in addition to sea spray. This Na^+ enrichment may be due to dissolution of the ash layer shown in Fig. 2. Support for this interpretation is found in the concentrations of total dissolved Al in the pore waters at FL: Al averages 0.28 mg/l (Table 6), but the pore waters from 18 to 21 cm contained 0.59 mg/l. Below this zone of Na and Al enrichment, the Na/Cl ratios in the pore waters at FL are comparable to seawater. In the deeper sections of both cores the Na/Cl molar ratio is less than the seawater value, indicating active removal of Na^+ ; the concentrations of Na^+ in the pore waters, therefore, do not provide a direct measure of the extent of sea salt inputs to either bog.

Compared to seawater, K/Cl is also significantly higher in the uppermost part of each pore water profile (Fig. 6). The characteristic enrichment of K in the biologically active surface layers of peat bogs is the result of uptake and recycling of K by the living plants (Feustel and Byers, 1930; Damman, 1978). Below the biologically active layer (uppermost 10 to 15 cm), the K^+ concentrations in the pore waters at FL are only twice those of LL. The molar ratio K/Cl reveals a depletion of K^+ relative to Cl^- throughout most of the FL core (Fig. 6), possibly because of ion exchange. Given the influence of biological cycling and ion exchange, the K^+ concentrations in the pore waters also do not directly reflect differences in marine salt supply to the two bogs.

Mg^{2+} and Ca^{2+} . The average pore water concentrations of Mg^{2+} and Ca^{2+} are higher at FL versus LL, but the differences are not consistent: Mg^{2+} is 11 times greater versus 6 times for Ca^{2+} (Table 6). The molar ratios Mg/Cl and Ca/Cl are also enriched in the uppermost part of the FL core, relative to the seawater value, by 40% and 100%, respectively (Fig. 7). The peaks in these enrichments are found at the same depth as the Na^+ , suggesting that the enrichments may have a common source. With increasing depth, the Mg/Cl and Ca/Cl molar ratios illustrate the strong depletion of both of these cations with respect to the seawater ratio. At LL, for example, up to 95% of the Mg^{2+} and up to 30% of the Ca^{2+} has been removed from the pore waters, probably by ion exchange. Similar trends in Mg/Cl and Ca/Cl with depth have been found in the pore waters of continental bogs (Shotyk and Steinmann, 1994). Because of the exchange of Mg^{2+} and Ca^{2+}

by the solid phase, the concentrations of Mg^{2+} and Ca^{2+} in the pore waters do not in any simple way reflect differences in the sea spray inputs to the two bogs.

4.2. Aerosols derived from crustal weathering

Volcanic ash has been found in a number of peat cores from northern Scotland and the Shetland Islands (Dugmore, 1989; Blackford et al., 1992; Dugmore and Newton, 1992; Dugmore et al., 1992), arising mainly from various Icelandic events. To evaluate the possibility that volcanic ash might have caused the pronounced peak in ash content at 20 cm in the FL core (Fig. 2), a frozen, replicate core was sectioned and examined. In the replicate core at a similar depth, some large grey inclusions (up to 7 mm in diameter) were found (Fig. 9). This material was analyzed using the SEM which indicated that the grey fragments were clusters of individual silicate minerals consisting predominately of mica, feldspar, and quartz ranging in size up to approximately 70 μm or more, with most grains much smaller than this. Some of these grains were weathered, but most of them appeared quite fresh. An XRD trace confirmed the presence of mica (biotite and muscovite), feldspar (orthoclase and albite), and quartz. The mineralogy of this sample (typical of granitic rocks), therefore, argues against an Icelandic source (which would be expected to be basaltic). No glassy volcanic debris such as the material reported by Dugmore (1989) and Dugmore et al. (1992) could be found with the SEM. There are several factors which argue strongly in favour of a local source for this pronounced peak in ash content: the distance of the site from the Scottish mainland, the relatively large size of some of the mineral grains, and the comparatively high Si/Al ratio.

First, compared to Loch Laxford on the Scottish mainland, the bog at Fleck's Loch is in an extremely maritime setting (Fig. 1), yet FL on average contains more than 3 times as much mineral matter. It seems unlikely, therefore, that long-range transport of mineral matter from the continents could result in higher rates of aerosol deposition (and, therefore, greater concentrations of mineral matter in the peats) at FL compared to LL.

Second, SEM analyses of the grains which constitute the inclusion of mineral matter shown in Fig. 9



Fig. 9. Cross-section through a replicate core (6b) from Fleck's Loch, Foula. This slice (1 cm thick) was taken from a depth of 19 cm and contains large inclusions (up to 7 mm across) of grey mineral material. The presence of this material explains the pronounced peak in ash content in the FL core (Fig. 2). SEM analyses revealed a predominance of mica, feldspar, and quartz ranging in size up to approximately 70 μm , with most grains much smaller than this. An XRD trace confirmed the presence of mica (biotite and muscovite), feldspar (orthoclase and albite), and quartz.

reveal a bimodal distribution of grain sizes: particle numbers are clearly dominated by grains $\leq 2 \mu\text{m}$, but particle mass appears by far to be dominated by abundant grains in the range 30 to 50 μm , with some grains as large as 70 μm or more. This bimodal distribution of grain sizes is characteristic of mineral aerosols during episodes of moderate to heavy dust loadings (Patterson and Gillette, 1977). It is well known, however, that mineral particles $\geq 10 \mu\text{m}$ in the air are rapidly removed near their source by gravitational sedimentation and scavenging (Schütz, 1980, 1989; Colbeck, 1995). While particles on the

order of 100 μm may be suspended for short periods during desert sandstorms, these are seldom transported in excess of 100 km (Greeley and Iversen, 1985). In contrast, long-range transport (i.e. > 1000 km) is restricted to aerosols with diameters < 10 μm (Schütz, 1980; Schütz and Rahn, 1982), with most particles in the range 0.1–5 μm (Colbeck, 1995). For example, in the background aerosol at the Jungfraujoch (3450 m asl in the Swiss Alps), the distribution of particles by volume is dominated by those with an average diameter of 0.3 μm (Schwikowski et al., 1995). In contrast, a recent Saharan dust event recorded at the same site revealed an average diameter of only 2 μm (Schwikowski et al., 1995). Given that Saharan mineral aerosols account for approximately one-half of the dust cycle in the Northern Hemisphere (Pacyna, 1995), a local source is certainly needed to explain the occurrence of comparatively large mineral particles in the peats at FL. In addition to the large size of many of the mineral grains at FL, some of them are strongly elongate with ratios of $d_{\text{max}}/d_{\text{min}}$ in the range 2.3–2.9. In contrast to the fine (< 2 μm), spheroidal aerosols capable of long-range transport, the elongation of many of the larger mineral grains found in the FL sample indicate a local source (Colbeck, 1995).

Finally, the background Si/Al ratio at FL (2.4 ± 0.2) is more than twice that of LL (1.0 ± 0.2). Measurements of atmospheric aerosols during soil erosion events show that grains in the range 10 to 100 μm are dominated by quartz and feldspars (relatively high Si/Al), with the fraction of < 10 μm dominated by clays (relatively low Si/Al). During transport, there is a continuous winnowing effect with clay minerals becoming increasingly important and quartz and feldspars progressively less so (Glaccum and Prospero, 1980). The comparatively high Si/Al ratios in the peats at FL (Fig. 10), therefore, could be explained in terms of the predominance of relatively large quartz and feldspar grains derived from the physical and chemical weathering of the local sandstone outcrops. The size of some of these particles and their abundance at a depth of 20 cm (Fig. 2), however, could not be explained without strong winds: both marine and mineral aerosol mass concentrations increase exponentially with wind speed (Blanchard and Woodcock, 1980; Schütz,

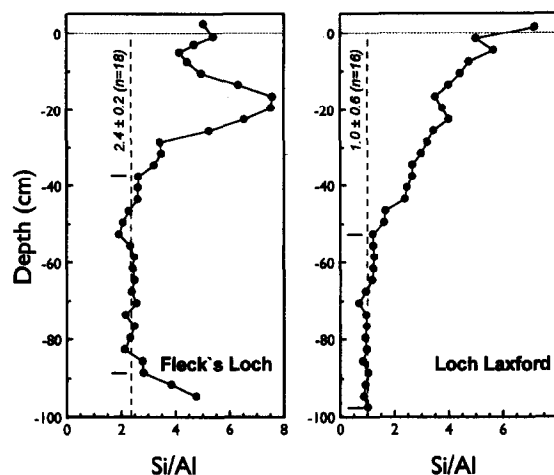


Fig. 10. Si/Al of the peats in the two cores from FL and LL.

1989). Intense storms are characteristic of Shetland, with an average of 44 gale force events (wind speeds exceeding 62 km/h) per year (Meteorological Office, 1979), and maximum recorded wind speeds of up to 285 km/h (Schei and Morberg, 1988).

5. Summary and conclusions

The major elements supplied to these two maritime peat bogs arise from two main atmospheric sources: soil-derived aerosols from weathering of crustal rocks, and sea salt spray. Crustal inputs account for essentially all of the Al and Fe in the profiles, and most of the Si. At FL the Si/Sc ratio indicates an excess of Si, but in the upper layers of the profile this is mainly because of quartz derived from the surrounding hills, possibly reflecting local events such as violent storms. Sea salt inputs account for 90 to 95% of the Na, Mg, Ca, and Sr, and effectively all of the Cl, Br, and S.

Pore water Cl^- is approximately 4 times greater at FL compared to LL and provides a quantitative indication of the relative importance of sea salt inputs to the two bogs. The concentrations of other important pore water species (SO_4^{2-} , Br^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) do not reflect their supply from rainwater in any simple way because of biological transformations (S, Br, K), ion exchange (Mg, Ca), and possibly mineral dissolution (Na, Mg, and Ca at FL).

A mass balance suggests that 91.5 to 99.9% of the major elements (Cl, Na, Mg, K, Ca) and trace elements (Br, Sr, Rb) supplied to the bogs by rainwater are not retained by the peat. Thus, none of these elements in the solid phase (peat) can be used as a quantitative measure of sea salt inputs to the bogs.

Acknowledgements

Financial support from the Canton of Berne (SEVA Lottofonds) and the Swiss National Science Foundation (Grants 21-30207.90, 20-36371.92, and 20-42273.94), is sincerely appreciated. Richard Lindsay suggested the study sites, enthusiastically helped with every aspect of the field work, and provided the lists of plant species. Philipp Steinmann prepared the samples and measured the ash contents, and together with Dominik Weiss and Steve Burns, provided helpful comments on a draft version of the manuscript. Andrij Cheburkin provided the expert XRF analyses. Thanks to Karl Ramseyer for the XRD analyses and to Fred Zweili for the SEM/EDAX analyses of the mineral material from FL. The rainwater samples on the Island of Foula were kindly collected by Isabel Holbourn. Special thanks to Lothar Schütz for sharing his data on the chemical composition of mineral aerosols, and to Liv Schei for sharing her insight into the climate of Shetland. The text was further improved with the helpful comments of Sandra Neuzil, Tapani Sallantausta, and one anonymous reviewer.

References

- Barkham, J.P., Gear, S., Hawksworth, D.L. and Messenger, K.G., 1981. Foula, Shetland, Volume 2. The Flora of Foula. Brathay Centre for Exploration and Field Studies, Old Brathay, Ambleside, Cumbria, 71 pp.
- Berner, E.K. and Berner, R.A., 1987. The Global Water Cycle. Geochemistry and Environment. Prentice-Hall, Englewood Cliffs, N.J.
- Blackford, J.J., Edwards, K.J., Dugmore, A.J., Cook, G.T. and Buckland, P.C., 1992. Icelandic volcanic ash and the mid-Holocene Scots pine (*Pinus sylvestris*) pollen decline in northern Scotland. *Holocene*, 2(3): 260–265.
- Blanchard, D.C. and Woodcock, A.H., 1980. The production, concentration, and vertical distribution of the sea-salt aerosol. *Ann. N.Y. Acad. Sci.*, 338: 330–347.
- Blancher, P.J. and McNicol, D.K., 1987. Peatland water chemistry in central Ontario in relation to acid deposition. *Water Air Soil Pollut.*, 35: 217–232.
- Boatman, D.J., 1957. An ecological study of two areas of blanket bog on the Galway-Mayo peninsula, Ireland. *Proc. R. Ir. Acad. Sect., B* 59: 29–42.
- Boatman, D.J., 1961. Vegetation and peat characteristics of blanket bogs in County Kerry. *J. Ecol.*, 49: 507–517.
- Casey, W.H. and Lasaga, A.C., 1987. Modeling solute transport and sulfate reduction in marsh sediments. *Geochim. Cosmochim. Acta*, 51: 1109–1120.
- Chapman, S.B., 1964. The ecology of Coom Rigg Moss, Northumberland, II. The chemistry of peat profiles and the development of the bog system. *J. Ecol.*, 52: 315–321.
- Cheburkin, A.K. and Shotyk, W., 1996. An Energy-dispersive Miniprobe Multielement Analyzer (EMMA) for direct analysis of Pb and other trace elements in peats. *Fresenius J. Anal. Chem.*, 354: 688–691.
- Clymo, R.S., 1983. Peat. In: A.J.P. Gore (Editor), *Mires: Swamp, Bog, Fen, and Moor, A. General Studies*. Elsevier, Amsterdam, pp. 159–224.
- Colbeck, I., 1995. Particle emission from outdoor and indoor sources. In: T. Kouimtzis and C. Samara (Editors), *Airborne Particulate Matter. The Handbook of Environmental Chemistry*, Vol. 4, Part D. Springer-Verlag, Berlin, pp. 2–33.
- Comeau, P.L. and Bellamy, D.J., 1986. An ecological interpretation of the chemistry of mire waters from selected sites in eastern Canada. *Can. J. Bot.*, 64: 2576–2581.
- Craig, G.Y., 1983. *Geology of Scotland*. Scottish Academic Press, Edinburgh.
- Damman, A.W.H., 1978. Distribution and movement of elements in ombrotrophic peat bogs. *Oikos*, 30: 480–495.
- Dugmore, A.J., 1989. Icelandic volcanic ash in Scotland. *Scott. Geogr. Mag.*, 105: 168–172.
- Dugmore, A.J. and Newton, A.J., 1992. Thin tephra layers in peat revealed by X-radiography. *J. Archaeol. Sci.*, 19: 163–170.
- Dugmore, A.J., Newton, A.J., Sugden, D.E. and Larsen, G., 1992. Geochemical stability of fine-grained silicic Holocene tephra in Iceland and Scotland. *J. Quat. Sci.*, 7: 173–183.
- Feustel, I.C. and Byers, H.G., 1930. The physical and chemical characteristics of certain American peat profiles. *U.S.D.A. Tech. Bull.*, 214, 26 pp.
- Foltescu, V.L., Isakson, J., Selin, E. and Stikans, M., 1994. Measured fluxes of sulphur, chlorine and some anthropogenic metals to the Swedish west coast. *Atmos. Environ.*, 28: 2639–2649.
- Froggatt, P.C. and Rogers, G.M., 1990. Tephrostratigraphy of high-altitude peat bogs along the axial ranges, North Island, New Zealand. *N.Z. J. Geol. Geophys.*, 33: 111–124.
- Glaccum, R.A. and Prospero, J.M., 1980. Saharan aerosols over the tropical North Atlantic—mineralogy. *Mar. Geol.*, 37: 295–321.
- Glooschenko, W.A., 1986. Monitoring the atmospheric deposition of metals by use of bog vegetation and peat profiles. In: J.O. Nriagu and D.I. Davidson (Editors), *Toxic Metals in the Atmosphere*. John Wiley and Sons, New York, pp. 508–533.
- Glooschenko, W.A., Holloway, L. and Arafat, N., 1986. The use

- of mires in monitoring the atmospheric deposition of heavy metals. *Aquat. Bot.*, 25: 179–190.
- Gore, A.J.P. and Allen, S.E., 1956. Measurement of exchangeable and total cation content for H^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and iron, in high level blanket peat. *Oikos*, 7: 48–55.
- Gorham, E., 1955. On the acidity and salinity of rain. *Geochim. Cosmochim. Acta*, 7: 231–239.
- Gorham, E., 1956. On the chemical composition of some waters from the Moor House Nature Reserve. *J. Ecol.*, 44: 375–382.
- Gorham, E. and Cragg, J.B., 1960. The chemical composition of some bog waters from the Falkland Islands. *J. Ecol.*, 48: 175–181.
- Gorham, E. and Tilton, D.L., 1978. The mineral content of *Sphagnum fuscum* as affected by human settlement. *Can. J. Bot.*, 56: 2755–2759.
- Gorham, E., Eisenreich, S.J., Ford, J. and Santelmann, M.V., 1985. The chemistry of bog waters. In: W. Stumm (Editor), *Chemical Process in Lakes*. John Wiley and Sons, New York, pp. 339–363.
- Greeley, R. and Iversen, J.D., 1985. *Wind as a Geological Process on Earth, Mars, Venus, and Titan*. Cambridge University Press, Cambridge.
- Hawthornthwaite, D.L., 1970. Studies on the peat deposits of the Island of Foula, Shetland. *Trans. Proc. R. Soc. Edinburgh*, XL, Part V, pp. 576–591.
- Helferich, F., 1962. *Ion Exchange*. McGraw-Hill, New York, 624 pp.
- Hines, M.E., Knollmeyer, S.L. and Tugel, J.B., 1989. Sulfate reduction and other sedimentary biogeochemistry in a northern New England salt marsh. *Limnol. Oceanogr.*, 34: 578–590.
- Hobbs, N.B., 1986. Mire morphology and the properties and behaviour of some British and foreign peats. *Q. J. Eng. Geol. London*, 19: 7–20.
- Hultberg, H. and Grennfelt, G., 1992. Sulphur and seasalt deposition as reflected by throughfall and runoff chemistry in forested catchments. *Environ. Pollut.*, 75: 215–222.
- Hvatum, O., Bolviken, E. and Steinnes, E., 1983. Heavy metals in Norwegian ombrotrophic bogs. *Ecol. Bull. (Stockholm)*, 35: 351–356.
- Landva, A.O., Korpijaakko, E.O. and Pheaney, P.E., 1986. Notes on the original von Post peat and peatland classification system. In: *Proceedings, Advances in Peatlands Engineering*. National Research Council Canada, Ottawa, August 25, 26, 1986, pp. 17–29.
- Lewis, F.J., 1911. The plant remains in the Scottish peat mosses. IV. The Scottish Highlands and Shetland, with an appendix on the Icelandic peat deposits. *Trans. R. Soc. Edinburgh*, 47: 793–833.
- Lindsay, R.A., Charman, D.J., Everingham, F., O'Reilly, R.M., Palmer, M.A., Rowe, T.A. and Stroud, D.A., 1988. *The Flow Country. The Peatlands of Caithness and Sutherland*. Nature Conservancy Council, Peterborough, 174 pp.
- Livett, E.A., 1988. Geochemical monitoring of atmospheric heavy metal pollution: theory and applications. In: M. Begon, A.H. Fitter, E.D. Ford and A. Macfadyen (Editors), *Advances in Ecological Research*, Vol. 18. Academic Press, New York, pp. 65–175.
- Livingstone, D.A., 1963. Chemical composition of rivers and lakes. In: *Data of Geochemistry*, 6th ed. U.S. Geol. Surv. Prof. Pap., 440-G, 64 pp.
- Lord, C.J. and Church, T.M., 1983. The geochemistry of salt marshes: sedimentary ion diffusion, sulfate reduction, and pyritization. *Geochim. Cosmochim. Acta*, 47: 1381–1391.
- Malmer, N., Horton, D.G. and Vitt, D.H., 1992. Element concentrations in mosses and surface waters of western Canadian mires relative to precipitation chemistry and hydrology. *Ecography*, 15: 114–128.
- Meteorological Office, 1979. *Scotland's Climate in Facts and Figures*. Meteorological Office, Met.O.924, Edinburgh, 21 pp.
- Newnham, R.M., de Lange, P.J. and Lowe, D.J., 1995. Holocene vegetation, climate and history of a raised bog complex, northern New Zealand based on palynology, plant macrofossils and tephrochronology. *Holocene*, 5(3): 267–282.
- Njåstad, O., Næumann, R. and Steinnes, E., 1987. Variations in atmospheric trace element deposition studied by INAA of peat cores from ombrotrophic bogs. *J. Radioanal. Nucl. Chem. Articles*, 114: 69–74.
- Ogden, J.G., 1982. Seasonal mass balance of major ions in three small watersheds in a maritime environment. *Water Air Soil Pollut.*, 17: 119–130.
- Pacyna, J.F., 1995. Sources, particle size distribution and transport of aerosols. In: T. Kouimtzis and C. Samara (Editors), *Airborne Particulate Matter. The Handbook of Environmental Chemistry*, Vol. 4, Part D. Springer-Verlag, Berlin, pp. 69–97.
- Patterson, E.M. and Gillette, D.A., 1977. Commonalities in measured size distributions for aerosols having a soil-derived component. *J. Geophys. Res.*, 82: 2074–2082.
- Pearsall, W.H., 1956. Two blanket-bogs in Sutherland. *J. Ecol.*, 44: 493–516.
- Persson, C., 1971. Tephrochronological investigation of peat deposits in Scandinavia and on the Faroe Islands. *Sver. Geol. Unders.*, 65: 3–34.
- Pettijohn, F.J., Potter, P.E. and Siever, R., 1987. *Sand and Sandstone*. Springer Verlag, Berlin.
- Price, J.S., 1994. Sources and sinks of sea salt in a Newfoundland blanket bog. *Hydrol. Processes*, 8: 167–177.
- Puustjärvi, V., 1958. On the base status of peat soils. *Acta Agric. Scand.*, 7: 190–223.
- Schei, L.K. and Morberg, G., 1988. *The Shetland Story*. B.T. Batsford, London.
- Schütz, L., 1980. Long range transport of desert dust with special emphasis on the Sahara. *Ann. N.Y. Acad. Sci.*, 338: 515–532.
- Schütz, L., 1989. Atmospheric mineral dust-properties and source markers. In: M. Leinen and M. Sarnthein (Editors), *Paleoclimatology and Paleometeorology: Modern and Past Patterns of Global Atmospheric Transport*. NATO ASI Series C: Mathematical and Physical Sciences, Vol. 282. Kluwer Academic Publishers, Dordrecht, pp. 359–383.
- Schütz, L. and Rahn, K.A., 1982. Trace-element concentrations in erodible soils. *Atmos. Environ.*, 16: 171–176.
- Schwikowski, M., Seibert, P., Baltensperger, U. and Gäggeler, H.W., 1995. A study of an outstanding Saharan dust event at the high-alpine site Jungfraujoch, Switzerland. *Atmos. Environ.*, 29: 1829–1842.

- Shotyk, W., 1988. Review of the inorganic geochemistry of peats and peatland waters. *Earth Sci. Rev.*, 25: 95–176.
- Shotyk, W., 1993a. Ion chromatography of organic-rich natural waters from peatlands, 1. Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and oxalate. *J. Chromatogr.*, 640: 309–316.
- Shotyk, W., 1993b. Ion chromatography of organic-rich natural waters from peatlands, 2. Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} . *J. Chromatogr.*, 640: 317–322.
- Shotyk, W., 1995. Peat bog archives of atmospheric Pb deposition. Habilitation thesis, Geological Institute, University of Berne.
- Shotyk, W., 1996a. Peat bog archives of atmospheric metal deposition: geochemical assessment of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environ. Rev.*, 4: 149–183.
- Shotyk, W., 1996b. Natural and anthropogenic enrichments of As, Cu, Pb, Sb, and Zn in rainwater-dominated versus groundwater-dominated peat bog profiles, Jura Mountains, Switzerland. *Water Air Soil Pollut.*, 90: 375–405.
- Shotyk, W. and Steinmann, P., 1994. Pore water indicators of rainwater-dominated and groundwater-dominated peat bog profiles, Jura Mountains, Switzerland. *Chem. Geol.*, 116: 137–146.
- Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A. and Kramers, J.D., 1996. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in a peat bog profile, Jura Mountains, Switzerland. *Earth Planet. Sci. Lett.*, 145: E1–E7.
- Skartveit, A., 1981. Relationships between precipitation chemistry, hydrology, and runoff acidity. *Nor. Hydrol.*, 1981: 65–80.
- Steinmann, P. and Shotyk, W., 1995. Ion chromatography of organic-rich natural waters from peatlands, 3. Improvements for measuring anions and cations. *J. Chromatogr.*, A706: 281–286.
- Steinmann, P. and Shotyk, W., 1997. The geochemistry of major elements in peats from two contrasting *Sphagnum* bogs, Jura Mountains, Switzerland. *Chem. Geol.*, 138: 25–53.
- Steinnes, E. and Njåstad, O., 1995. Ombrotrophic peat bogs as monitors of trends in atmospheric deposition of pollutants: role of neutron activation analysis in studies of peat samples. *J. Radioanal. Nucl. Chem. Articles*, 192: 205–213.
- Tolonen, K., Raikamo, E., Lahti, T. and Viista, J., 1979. Siikaneva mire complex. Excursion guide, International Symposium on Classification of Peat and Peatlands, Hyytiälä, Finland, September 1979. International Peat Society, Helsinki, 26 pp.
- Tolpa, S. and Gorham, E., 1961. The ionic composition of waters from three Polish bogs. *J. Ecol.*, 49: 127–133.
- Verry, E.S., 1975. Streamflow chemistry and nutrient yields from upland-peatland watersheds in Minnesota. *Ecology*, 56: 1149–1157.
- Vitt, D.H. and Bayley, S., 1984. The vegetation and water chemistry of four oligotrophic basin mires in northwestern Ontario. *Can. J. Bot.*, 62: 1485–1500.
- Vitt, D.H., Horton, D.G., Slack, N.G. and 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.
- Wardenaar, E.C.P., 1987. A new hand tool for cutting peat profiles. *Can. J. Bot.*, 65: 1772–1773.
- Webb, D.A., 1947. Notes on the acidity, chloride content, and other chemical features of some Irish fresh waters. *Sci. Proc. R. Dublin Soc.*, 24: 215–228.
- Zoltai, S.C., 1989. Late Quaternary volcanic ash in the peatlands of central Alberta. *Can. J. Earth Sci.*, 26: 207–214.