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Ion chromatography of organic-rich natural waters from peatlands

I. Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-} and oxalate

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ABSTRACT

Organic-rich natural waters from peat bogs in continental (Switzerland) and maritime (Shetland Islands, Scotland) areas were analysed for Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-} and oxalate using ion chromatography. These anions can be determined simultaneously in the surface and pore water samples from the continental bogs using a 250-μl injection loop. Using this loop, the detection limits were *ca.* 5 ng/g for the monovalent anions and SO_4^{2-} and 10 ng/g for HPO_4^{2-} and oxalate. An organics-removal cartridge (Dionex OnGuard P) was used to remove humic materials. These cartridges did not significantly affect the measured concentrations of anions in blind standards. Analyses of deionized water treated with these cartridges are not significantly different from those for untreated deionized water. For the maritime bogs, the relatively high concentrations of Cl^- (more than 100 μg/g in many samples) and SO_4^{2-} (up to 50 μg/g) require two separate determinations for complete analyses. A 10-μl injection loop was used to determine Cl^-, Br^-, and SO_4^{2-}. A 250-μl injection loop was used to measure NO_2^-, NO_3^-, HPO_4^{2-} and oxalate. In each instance a Dionex OnGuard P cartridge was used to remove humic materials. In addition, a chloride-removal cartridge (Dionex OnGuard AG) was used to remove Cl^- when the larger injection loop was used. This cartridge has no significant effect on the measurement of HPO_4^{2-} at concentrations of 20 ng/g. In each of the bog water chromatograms there were usually a number of unknown peaks. These are probably due mainly to organic anions.

INTRODUCTION

The surface waters of "ombrotrophic" (rain-fed) peat bogs are isolated from the influence of groundwaters and mineral soil waters, and are fed only by atmospheric deposition [1]. Consequently, these waters contain relatively low concentrations of inorganic solids, are rich in dissolved organic matter [of the order of 100 mg/l of dissolved organic carbon (DOC)] and are acidic (pH 4). Nitrogen and especially phosphorus are thought to be the most important nutrients limiting plant growth. However, there have been relatively few reports of the concentrations of inorganic anions such as nitrate and phosphate in bog surface and pore waters [2]. The paucity of quantitative information regarding the abundance of such species in these waters may be partly due to the interference of dissolved organic compounds in the spectrophotometric determination of inorganic anions [3].

Accurate measurement of inorganic nutrient anions such as nitrate, phosphate and sulphate could be extremely helpful in ecological peatland studies. Species such as nitrite, nitrate, and sulphate in pore waters are redox indicators and their determination may be useful to describe the oxidation–reduction status of the peatland system [1]. Chloride and bromide in bog waters may be used as indicators of ionic strength or the extent of marine influence. Finally, quantitative analyses of each of the major anionic species are necessary in order to calculate the electrical charge balance of the waters:

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the total organic anionic charge is calculated as the difference between the sums of the total cationic and total inorganic anionic charges.

Traditionally, the quantitative measurement of each of these anionic species required at least as many different analytical methods as the number of species to be determined [4]. Even in a recent study of diagenesis in anaerobic sediments, the analytical methods employed to determine fluoride, chloride, nitrate, phosphate and sulphate included spectrophotometry, gravimetry, turbidity and ion-selective electrode potentiometry [5]. Clearly, the amount of time and labour required in the laboratory increase with the number of analytical methods employed.

One of the principle advantages of ion chromatography (IC) is the simultaneous determination of each of these inorganic anionic species, in addition to some organic species, in a relatively short time, with minimum sample preparation [6, 7]. The results presented here show that IC is convenient for the determination of chloride, bromide, nitrite, nitrate, phosphate, sulphate and oxalate in less than 10 min with acceptable accuracy and precision. Even in chloride-rich pore waters from bogs at maritime sites, the method can be used without modification for determinations of inorganic anions. To illustrate its applicability and reproducibility, examples of the abundance and distribution of some of the major inorganic anionic species in representative continental and maritime bog pore water profiles are presented.

EXPERIMENTAL

Locations of sites

The two continental bogs studied (Etang de la Gruyère and Tourbière des Veaux) are located in the Franches-Montagnes region of the Jura Mountains in the northwestern part of Switzerland. Lochs o' da Fleck is on the Island of Foula, *ca.* 50 km west of the main island (The Mainland) of Shetland in Scotland.

Sampling of surface waters

Water samples were collected from surface pools in clean polypropylene bottles. They were stored in a refrigerator and analysed as soon as possible after collection.

Sampling of peat pore waters

The pore waters were collected as follows. Using a Wardenaar peat profile sampler [8], a peat core *ca.* 100 × 10 × 10 cm was removed from the bog, wrapped in plastic and brought to the laboratory. The fresh core was immediately sliced using a serrated stainless-steel knife into 3-cm slices. The first slice (+3 cm to 0 cm) corresponds to the living plant material on the bog surface and the subsequent slices (in increments of 3 cm) represent peat samples varying in degree of decomposition. Each slice was placed in a plastic bag and the bag was squeezed by hand to express the pore water. The volume of pore water obtained in this way ranges from 0 to more than 100 ml, depending on the degree of decomposition of the peat.

Pore water filtration

Prior to ion chromatographic analyses, all water samples were filtered to exclude all material larger than 0.2 μm. Filtering raw peat pore waters directly through a 0.2-μm filter without pre-filtering may be extremely slow (up to 2 h for a 50-ml sample, depending on the degree of decomposition of the peats) and require several filters. To speed up this process and to minimize the number of filters required, the pore waters were first centrifuged at 5000 *g* in clean polyethylene centrifuge tubes. This procedure approximately halves the time required for filtration. The centrifuged samples were then filtered under vacuum using the sequence of nominal pore sizes 3.0, 0.8 and 0.2 μm.

All peatland water samples were injected through an organics-removal cartridge (Dionex OnGuard-P) prior to injection. This cartridge consists of polyvinylpyrrolidone and its sole purpose was to remove humic materials which otherwise would progressively damage the separation column. One cartridge was used per sample. Each cartridge was first rinsed with 4 ml of deionized water and 2 ml of sample.

Sample preservation

The measured concentrations of chloride, bromide, phosphate and sulphate are not directly affected by sample oxidation. In order to maintain the integrity of nitrite and oxalate, which are both sensitive to oxidation, however, the peat core would have had to be collected and subsampled under an inert atmosphere such as nitrogen and the pore waters expressed and filtered under nitrogen. These capabilities were not available at the time of sample collection and preparation. Thus, by the time the samples had been filtered there may have been considerable oxidation of nitrite and oxalate. The measured concentrations of nitrite, nitrate and oxalate are not presented because they may not necessarily reflect their concentrations in the pore waters at the time of sample collection. Although the analytical method described here is suitable for the quantitative measurement of these species, improvements are required in sample collection, preparation and preservation against oxidation.

Ion chromatography

The theoretical basis for the quantitative measurement of anions using ion chromatography has been described in detail [6,7]. All anion analyses were performed using a Dionex 4500i ion chromatographic system with Dionex columns, conductivity detector and computer interface. The entire system was operated using the Dionex AutoIons program (version 3.2). The anions were separated on an AS4A separation column after an AG4A guard column and the background conductivity of the eluent was suppressed using an AMMSII membrane suppressor. The suppressor was continuously regenerated using an anion membrane suppressor regenerant cartridge and 50 m*M* H_2SO_4.

The eluent used was 1.8 m*M* Na_2CO_3–1.7 m*M* $NaHCO_3$, which allows the separation and determination of Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-} and oxalate. Analytical-reagent grade Na_2CO_3 and $NaHCO_3$ (Merck) were used to prepare the eluent. All standards were prepared using 18 MΩ deionized water. Merck 1000 mg/l anion standards were used for all of the anion standards except oxalate, which was prepared from oxalic acid dihydrate (Merck). All standards were prepared in clean polypropylene bottles and stored in a refrigerator. Fresh standards were prepared prior to each set of pore water analyses.

For continental bog waters, a 250-μl injection loop was employed and the instrument was calibrated with 20, 50, 250 and 1000 ng/g (ppb) mixed anion standards (Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-} and oxalate). The linearity of the standards over this concentration range was excellent (r^2 = 0.999 or better for each species).

For maritime bog waters with Cl^- concentrations up to 100 μg/g (ppm), two separate runs were required. In each instance an OnGuard P cartridge was used to remove humic materials. For Cl^-, Br^- and SO_4^{2-}, a 10-μl injection loop was used and the instrument was calibrated with 10, 50 and 100 μg/g Cl^-, 2, 10 and 50 μg/g SO_4^{2-} and 0.1, 0.5 and 2.5 μg/g Br^-. These standards also contained 0.1, 0.5 and 2.5 μg/g NO_3^- and HPO_4^{2-} because the pore waters closest to the surface (the plant rooting zone) contain elevated concentrations of these species. Thus, in near-surface pore waters all of the anions of interest can be determined in a single run. For NO_2^-, NO_3^-, HPO_4^{2-} and oxalate in deeper pore waters, a 250-μl injection loop was used and the instrument was calibrated with 10, 20, 50, 250 and 1000 ng/g standards. In this instance, a chloride-removal cartridge (Dionex OnGuard AG) was used to remove Cl^-. Again, the linearity of the standards was excellent in each instance (r^2 = 0.999 or better).

RESULTS

Continental bog waters

Typical chromatograms of standards and samples. A typical chromatogram of a 100 ng/g anion standard is shown in Fig. 1a. The first peak is F^-, followed by Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-} and oxalate.

A typical chromatogram for a peatland water sample is shown in Fig. 1b. Note that there are more peaks (and therefore more anions) in this chromatogram compared with the standard. These additional peaks are probably due to organic anions and were consistently seen in most of the chromatograms of bog water samples. In general they are clearly separated from the inorganic anions of interest and do not interfere with their measurement. However, the peak at 1.2 min which appears to be F^- (Fig. 1b) is actually F^- plus some organic anions (probably formate plus acetate, propionate, butyrate and lactate, but possibly also some others) which co-elute using the carbonate–hydrogenbicarbonate eluent.

The chemical complexity of these waters can be illustrated using a weaker (borate) eluent. For example, using a gradient elution ranging from 7 to 21 m*M* $Na_2B_4O_7$, as many as 30 anionic species were found in a chromatogram of bog water (Fig. 2).

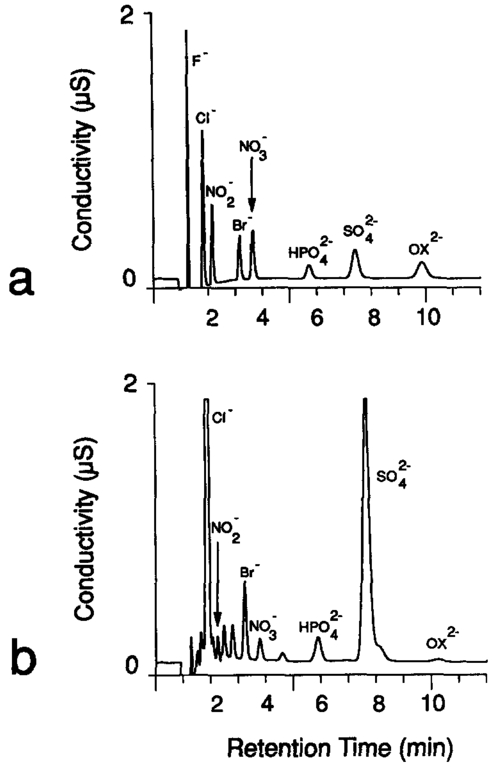

Fig. 1. (a) Chromatogram of a 100 ng/g anion standard using a 250 μl injection loop. (b) Chromatogram of a pore water sample squeezed from peat 6–9 cm below the bog surface of La Tourbière des Veaux. Concentrations (ng/g) were as follows: Cl⁻, 1413 ± 37; NO$_2^-$, not determined; Br⁻, 220 ± 15; NO$_3^-$, 83 ± 1; HPO$_4^{2-}$, 198 ± 2; SO$_4^{2-}$, 824 ± 20; oxalate, not determined. The peaks before chloride include fluoride plus some organic anions. No attempt was made to determine fluoride. The other unknown peaks (between NO$_2^-$ and Br⁻, between NO$_3^-$ and HPO$_4^{2-}$ and the shoulder on SO$_4^{2-}$) are probably organic anions.

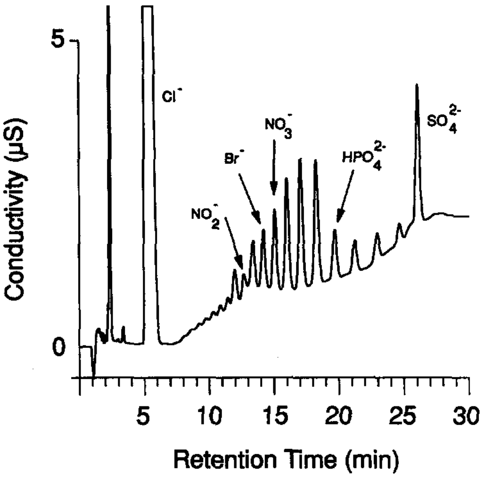

Fig. 2. Chromatogram of bog water using a borate gradient. The two eluents consisted of deionized water (E_1) and 70 m*M* $Na_2B_4O_7 \cdot 10\,H_2O$ (E_2). The gradient was performed as follows: 90% E_1 from 0.0 to 10.0 min; decreased to 80% E_1 from 10.0 to 20.0 min; decreased to 70% E_1 from 20.0 to 25.0 min; held at 70% E_1 from 25.0 to 30.0 min; increased to 90% E_1 from 30.0 to 35.0 min. The chromatogram shown corresponds to a pore water (36–39 cm) from La Tourbière des Veaux. In addition to the species identified in the figure, formate and glycolate were found. The other peaks have not yet been identified.

Approximately ten peaks are seen before Cl⁻ elutes and another 20 peaks before SO$_4^{2-}$. Except for the inorganic anions plus glycolate and formate, most of these peaks have not yet been identified.

Changing retention times. During the analyses of peatland waters the retention times of the anions typically decreased slightly with time, compared with those of the standard. This may be due to the presence of dissolved organic material in the peatland water samples adsorbing on the resin of the separation column and slightly changing its anion retention properties. In order to confirm the retention times of the anions, a blind standard was injected in triplicate after every tenth sample injection.

Effect of organics removal cartridge. A 1000 ng/g anion standard was analysed in triplicate before and after filtration through an OnGuard-P humics-removal cartridge and the results are given in Table I. The anion concentrations in the anion standard that had been passed through a rinsed OnGuard-P cartridge were not significantly different from the concentrations in the corresponding standard that had not been filtered through an OnGuard-P cartridge. Hence the OnGuard-P cartridge does not appear to contribute any significant error to the analyses of anions in peatland waters.

Analyses of blanks. The deionized water used in the laboratory was analysed after calibrating the instrument with 1, 2, 5 and 10 ng/g standards. In the deionized water only chloride (*ca.* 3 ng/g) and nitrate (*ca.* 1 ng/g) were measurable. The concentrations of anions in a sample of this water filtered through a rinsed OnGuard-P organics-removal cartridge were not significantly different from those in

TABLE 1

EFFECT OF ONGUARD P PRETREATMENT CARTRIDGE ON MEASURED ANION CONCENTRATIONS

Anion	Concentration (ng/g)[a]	
	No filter	OnGuard P
Cl^-	1024 ± 14	1025 ± 19
NO_2^-	1005 ± 19	991 ± 10
Br^-	948 ± 19	935 ± 22
NO_3^-	992 ± 9	981 ± 36
HPO_4^{2-}	985 ± 2	982 ± 4
SO_4^{2-}	992 ± 2	993 ± 4
Ox^{2-}	987 ± 1	986 ± 7

[a] Mean ± S.D. ($n = 3$).

the unfiltered deionized water. Hence the organics-removal filters used did not contribute significantly to the measured anion concentrations.

Sensitivity and limits of detection. Using the 250-μl injection loop, the anions Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-} can be measured down to *ca.* 1–2 ng/g and HPO_4^{2-} and oxalate down to 5 ng/g. Hence the limits of detection were *ca.* 5 ng/g for the first group of anions and 10 ng/g for phosphate and oxalate. Using this injection volume, each of these anions is easily quantified even in dilute natural waters such as rain water (Fig. 3). Because the concentrations of inorganic anionic species in peatland waters generally are significantly higher than the limits of detection, the sensitivity of the method is not expected to restrict its application. In some deep pore water samples, concentrations of phosphate as low as 10 ng/g were observed. However, a larger injection loop (500 μl or more) may be used in such instances to improve the detection limit for this species further.

Analytical procedure variability. An estimate of the analytical procedure variability was made by analysing a blind working standard (250 ng/g) in triplicate after every tenth injection. These results were pooled to calculate the mean ± one standard deviation for nine analyses: Cl^-, 245 ± 10; Br^-, 281 ± 10; NO_3^-, 249 ± 29; HPO_4^{2-}, 255 ± 8; SO_4^{2-}, 274 ± 11 ng/g.

Precision of pore water analyses. The reproducibility of the analyses is best illustrated by comparing the results of the duplicate pore water analyses.

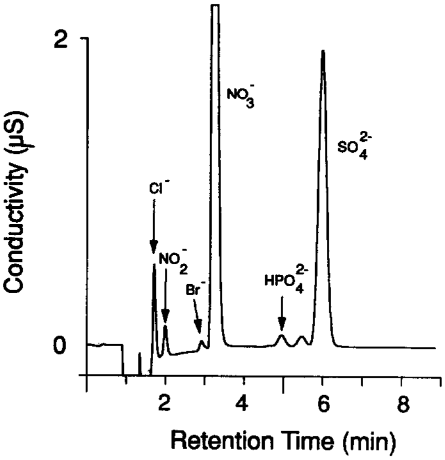

Fig. 3. Chromatogram of rain water collected in Berne on 31.10.91. Concentrations (ng/g) are as follows Cl^-, 17; NO_2^-, 51; Br^-, 5, NO_3^-, 1329; HPO_4^{2-}, 50; and SO_4^{2-}, 519. Cl^-, NO_2^-, Br^- and HPO_4^{2-} were determined using a single-point calibration against a 20 ng/g standard. NO_3^- and SO_4^{2-} were calculated using a three-point linear calibration (50, 250 and 1000 ng/g standards).

The vertical distribution of the four major anions in the pore waters at Etang de la Gruyère are shown in Fig. 4. The average standard deviations of the 35 duplicate pairs were estimated according to ASTM Designation D 4210 [4] and are Cl^-, 40; Br^-, 39; HPO_4^{2-}, 26 and SO_4^{2-}, 13 ng/g.

The reproducibility was generally good except for Br^- at depths between 20 and 30 cm and HPO_4^{2-} in the deeper layers (Fig. 4). The relatively large variation in Br^- in some of the samples may be due to the combined effect of changing retention times and relatively abundant (organic?) anions in the pore waters causing incorrect peak identification. In pore waters expressed from strongly decomposed peats, the position of the Br^- peak should be confirmed regularly with spiked samples. The relatively large variation in HPO_4^{2-} may be due to the instability of phosphate in Fe-rich anoxic water samples exposed to the air [9]. Subsequent studies of these pore waters maintained in an anoxic condition have yielded significantly higher concentrations of HPO_4^{2-} [10].

Maritime bog waters

Effect of chloride-removal filter. A typical chromatogram for a 250-μl injection without a chloride removal cartridge is shown in Fig. 5a. A chromato-

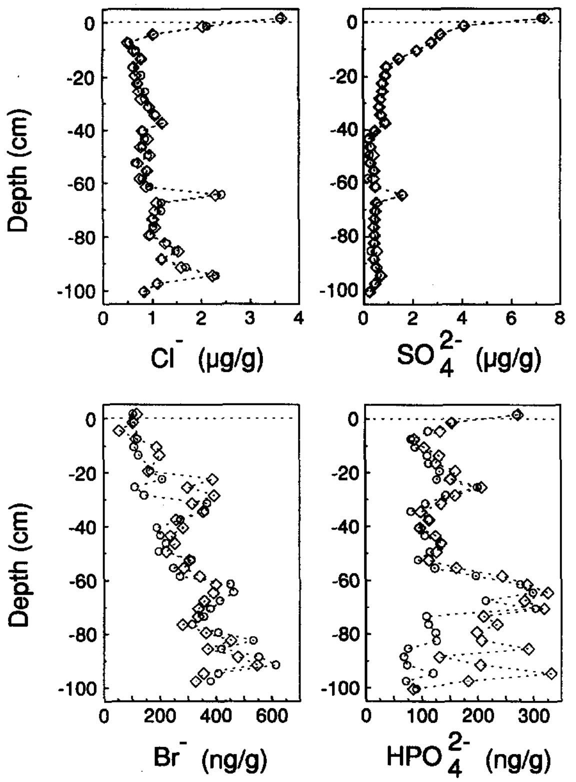

Fig. 4. Major anions (Cl^-, SO_4^{2-}, Br^-, HPO_4^{2-}) in pore waters at Etang de la Gruyère. The circles and squares represent two separate sets of analyses (duplicates). The poor reproducibility for Br^- at a depth of 30 cm may be due to interfering unknown (organic) anions. The poor reproducibility for HPO_4^{2-} from 70 to 100 cm may be due to the oxidation of Fe^{2+} during sample handling (see text).

gram of a sample that had been passed through a chloride-removal cartridge prior to injection is shown in Fig. 5b. To evaluate the effect of the cartridge on the measurement of low concentrations of phosphate, a blind standard containing 20 ng/g of phosphate was analysed seven times with and without a cartridge. The measured phosphate concentrations were 22.9 ± 1.6 and 20.8 ± 2.2 ng/g, respectively. Therefore, although this cartridge successfully removes most of the chloride, it has no significant effect on the measurement of phosphate at the concentrations present in the bog pore waters.

A representative chromatogram for a 10-µl injection of a maritime bog water is shown in Fig. 6a.

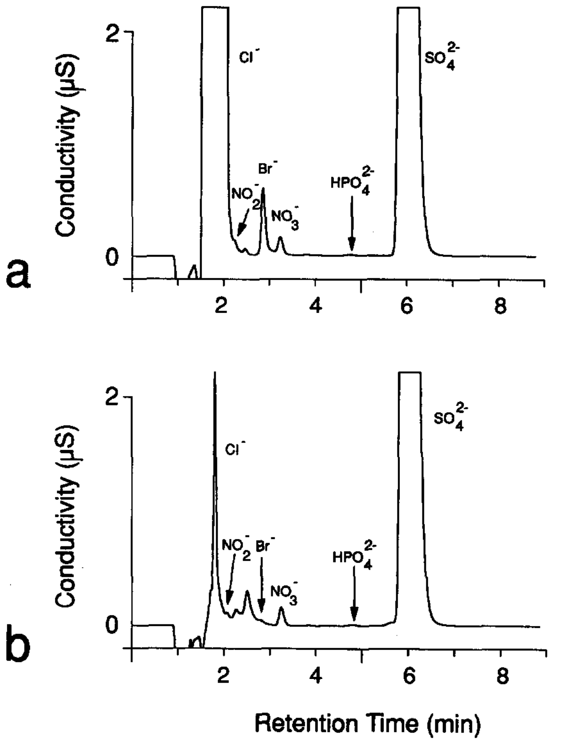

Fig. 5. Effect of chloride-removal cartridge (Dionex OnGuard AG) on maritime bog waters (250-µl injection). (a) No cartridge. Concentrations were *ca.* 95 µg/g Cl^-, 24 ng/g NO_3^-, 16 ng/g HPO_4^{2-} and 16 µg/g SO_4^{2-}. (b) Same sample as in (a), but filtered through an OnGuard AG cartridge. Measured concentrations of nitrate, phosphate and sulphate were not significantly different.

In the near-surface samples, nitrate and phosphate may be measured, in addition to Cl^-, Br^- and SO_4^{2-}. A chromatogram for a 250-µl injection of a maritime bog water filtered through an OnGuard AG chloride-removal cartridge is shown in Fig. 6b. Both nitrate and phosphate were conveniently measured with this method at concentrations down to 10 ng/g.

Analytical procedure variability. After every tenth injection a blind standard containing 50 µg/g Cl^-, 10 µg/g SO_4^{2-} and 250 ng/g Br^- was analysed in triplicate. These results were pooled to calculate the mean ± one standard deviation for the six analyses: Cl^-, 50.6 ± 1.6 µg/g; SO_4^{2-}, 9.6 ± 0.0 µg/g; and Br^-, 270 ± 17 ng/g.

Precision of the pore water analyses. The reproducibility of the methods is best assessed from duplicate analyses of the four major anions in the pore

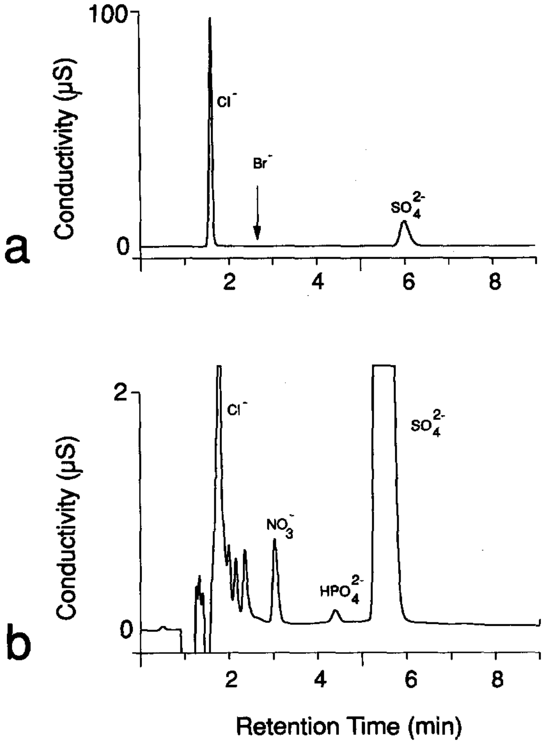

Fig. 6. Chromatograms of surface water from a Lochs o' da Fleck. (a) 10-µl injection for Cl^-, Br^- and SO_4^{2-}. In subsurface samples (plant rooting zone), nitrate and phosphate concentrations are significantly higher than deeper in the profile and can be measured in the same run. (b) 250-µl injection through an On-Guard AG chloride-removal cartridge for the determination of nitrate and phosphate.

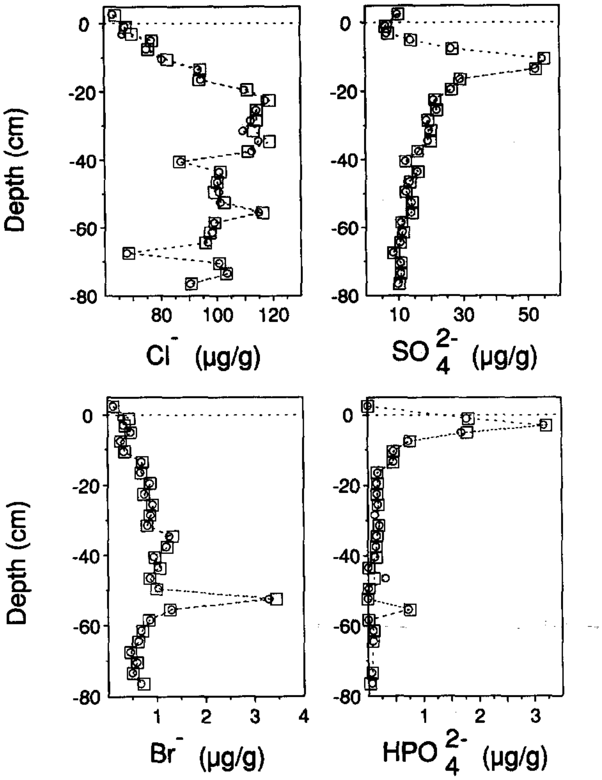

Fig. 7. Major anions (Cl^-, SO_4^{2-}, Br^-, HPO_4^{2-}) in pore waters at Lochs o' da Fleck. The circles and squares represent two separate sets of analyses (duplicates).

waters at the Lochs o' da Fleck (Fig. 7). The average standard deviations of the 27 duplicate pairs estimated according to the ASTM Designation D 4210 [4] are as follows: Cl^-, 0.7 µg/g; SO_4^{2-}, 0.1 µg/g; Br^-, 15 ng/g; and HPO_4^{2-}, 11 ng/g.

The precision of Br^- in these samples was much better than in the continental bog waters because the Br^- concentrations were significantly higher (owing to sea spray).

CONCLUSION

The dominant inorganic anions in peatland waters (Cl^-, Br^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}) plus nitrite and oxalate may be measured rapidly (in less than 10 min) and with adequate sensitivity and precision using ion chromatography. An organics-removal cartridge was used to filter the water prior to injection, but appeared to have no significant effect on the measured anion concentrations. In addition, for nitrate and phosphate determination in chloride-rich bog waters from marine sites, a chloride-removal cartridge was used prior to injection. However, this cartridge has no significant effect on measured phosphate concentrations down to 20 ng/g.

A large number of unknown anionic species in the bog waters eluted when a weak (borate) gradient was used. These are probably organic anions. The size of these peaks compared with those for the inorganic anions suggests that they also may be important constituents of the waters. Further studies are in progress to identify them.

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