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Ion chromatography of organic-rich natural waters from peatlands

II. Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}

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ABSTRACT

Organic-rich natural waters from peat bogs in continental (Switzerland) and maritime (Shetland Islands, Scotland) environments were analysed for Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} using ion chromatography. These cations were determined simultaneously in surface and pore water samples from the continental bogs using a 250-μl injection loop in an isocratic separation. Using this loop, detection limits of the order of 1 ng/g were achieved. An organics-removal cartridge (Dionex OnGuard P) was used to remove humic materials. Analyses of deionized water filtered through these cartridges showed acceptably low blank values (*e.g.*, *ca.* 5 ng/g) and appeared to have no significant effect on the measured cation concentrations. For the maritime bog waters, the low concentrations of NH_4^+ (*ca.* 1 μg/g) compared with Na^+ (*ca.* 100 μg/g) required improved peak separation. This was accomplished by using a gradient separation beginning with 40 m*M* HCl–1 m*M* D,L-2,3-diaminopropionic acid monochloride (DAP) and switching to 40 m*M* HCl–12 m*M* DAP after 2 min. Using a 25-μl injection loop, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} were determined simultaneously in less than 25 min. In this instance, even with $Na^+/NH_4^+ > 100$, there was no interference from Na^+ in the determination of NH_4^+ (baseline separated).

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]. As a result, Ca concentrations are relatively low, typically of the order of 1 mg/l or less, and sodium is the dominant cation. In "minerotrophic" (groundwater-fed) peatlands such as fens and swamps, Ca concentrations are much higher and Ca is the dominant cation [2]. By measuring the concentration of Ca in peatland surface waters, ombrotrophic bogs may be distinguished from minerotrophic fens and swamps. Thus, the concentration of Ca has become one of the most important criteria for describing the trophic status of peatlands.

Unfortunately, the utility of Ca measurements has given rise to extensive interest in this element at the expense of other major metallic cations. For example, very little is known about the geochemistry of K and Mg in peatland ecosystems. Analyses for each of the major cationic species are necessary in order to calculate the electrical charge balance of the waters; the total cationic charge is needed to calculate the total inorganic anionic and organic anionic charges. Because peatlands are anaerobic below the water table, ammonium may also be a quantitatively important cation. In addition, the determination of ammonium may be helpful for describing the oxidation–reduction status of the peatland system [1].

Today, Na, K, Mg, and Ca are usually determined using either atomic absorption spectrometry

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(AAS) to measure the metal concentrations one at a time, or inductively coupled plasma spectrometry (ICP) to measure the metals simultaneously. Ammonium is typically determined using ion-selective electrode potentiometry, which measures the concentration of free ammonium [3]. One of the principle advantages of ion chromatography (IC) is the possibility of determining each of these cationic species simultaneously, in a relatively short time, with minimum sample preparation [4,5]. The use of IC has already been applied to measurements of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} in dilute natural waters such as rainwater [6].

The results presented here show that IC is a convenient method for the determination of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} in organic-rich peatland waters. Even in bog waters in maritime areas with more than 100 ppm of sodium, NH_4^+ can be clearly separated from Na^+, allowing all five cations to be determined in less than 25 min. To illustrate the applicability and reproducibility of the methods, examples of the abundance and distribution of these cations in representative 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. Fleck o' da Lochs is on the Island of Foula, approximately 50 km west of the main island ("The Mainland") of Shetland in Scotland.

Sampling of waters and sample preparation

The sampling and sample handling procedures have been described elsewhere [7].

Ion chromatography

The theoretical basis for the determination of cations using IC has been described in detailed in several recent books [4,5]. All cation determination were performed using a Dionex 4500i IC system with Dionex columns, conductivity detector and computer interface. The entire system was operated using the Dionex AutoIons program (version 3.2). The cations were separated on a CS10 separation column after a CG10 guard column and the background conductivity of the eluent was suppressed using a CMMSII membrane suppressor. The suppressor was continually regenerated using 100 m*M* tetramethylammonium hydroxide (Fluka, Buchs, Switzerland).

The eluent and all standard solutions were prepared using 18-MΩ deionized water. Merck 1000 mg/l cation stock standard solutions were used to prepare all of the cation working standard solutions. All working standard solutions were prepared in clean polypropylene bottles and stored in a refrigerator. Fresh standard solutions were prepared prior to each set of pore water analyses.

Isocratic separation of cations in continental waters. The eluent was 40 m*M* HCl–12 m*M* D,L-2,3-diaminopropionic acid monochloride (DAP) (Fluka), which allows the separation and determination of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. 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 cation standards (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) using linear regression. The linearity of the calibration graph for each of the cations over this concentration range was excellent ($r^2 = 0.999$ or better).

Gradient separation of cations in maritime waters. This was accomplished using a gradient beginning with 40 m*M* HCl–1 m*M* DAP (E_1) and switching to 40 m*M* HCl–12 m*M* DAP (E_2) as follows: 0.0–2.0 min, E_1; 2.0–4.0 min, switching to E_2; 4.0–15.0 min, E_2; 15.0–17.0 min, switching to E_1; 17.0–25.0 min, E_1. The last step (17–25 min) is simply a rinse following the elution of Ca^{2+}. This step was necessary to ensure reproducible separation of the monovalent cations in the following sample. Although 5 m*M* HCl–4 m*M* DAP can also be used as E_1, the difference in background conductivities (E_1 *versus* E_2) was much greater.

Using a 25-μl injection loop, the instrument was calibrated with the following standards: 10, 20, 50, 100 μg/g (ppm) Na^+; 1, 5, 10, 20 μg/g Mg^{2+}; 0.1, 0.5, 2.0, 10.0 μg/g NH_4^+, K^+ and Ca^{2+}. Again, linear regression was used to calculate the calibration graphs and the fit was excellent ($r^2 = 0.999$ or better).

RESULTS

Continental bog waters

Typical chromatograms of standards and samples. A typical chromatogram of a 500 ng/g cation standard is shown in Fig. 1a. The first peak is Na^+, followed by NH_4^+, K^+, Mg^{2+} and Ca^{2+}. A representative chromatogram of a subsurface bog pore water sample is shown in Fig. 1b. Note that NH_4^+ is by far the dominant cation in the bog pore water.

Effect of organics-removal filter. A 1000 ng/g cation working 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 cation concentrations in the cation standard which has been passed through a rinsed OnGuard-P cartridge are not significantly different from those in the corresponding standard which has not been so filtered. Hence the use of the organics-removal cartridge has no significant effect on the measured cation concentrations.

Analyses of blanks. The deionized water was analysed after calibrating the instrument with 1, 2, 5 and 10 ng/g standards. In the deionized water only Mg^{2+} (<1 ng/g) and Ca^{2+} (<2 ng/g) peaks are visible. Five deionized water samples filtered through a rinsed OnGuard-P organics-removal cartridge yielded concentrations of Na^+ 5.3 ± 0.6, NH_4^+ 5.9 ± 0.5, Mg^{2+} 2.5 ± 1.0 and Ca^{2+} 3.5 ± 1.3 ng/g. These concentrations are well below the lowest concentrations measured in the bog waters and represent acceptable blank values.

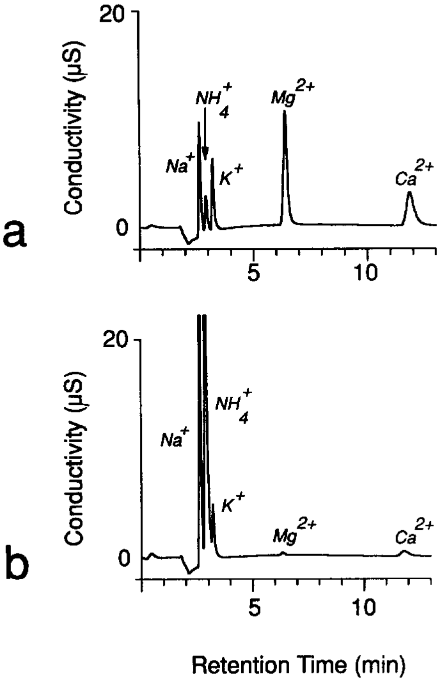

Fig. 1. Chromatograms of (a) a 500 ng/g cation standard using a 250-μl injection and (b) a pore water sample (90–93 cm) from Etang de la Gruyère.

TABLE I

EFFECT OF ONGUARD P PRE-TREATMENT CARTRIDGE ON MEASURED CATION CONCENTRATIONS

A 1000 ng/g working standard was analysed in triplicate with and without an OnGuard P cartridge.

Cation	Concentration (ng/g)	
	No filter	OnGuard P
Na^+	999 ± 12	1028 ± 47
NH_4^+	947 ± 35	992 ± 7
K^+	1009 ± 9	1010 ± 14
Mg^{2+}	1000 ± 9	1003 ± 5
Ca^{2+}	991 ± 12	1013 ± 8

Sensitivity and limits of detection. Under ideal operating conditions and using the 250-μl injection loop, the limit of detection of each of the cations is *ca.* 1 ng/g. Hence, the limits of determination are *ca.* 2 ng/g. One example of the sensitivity of the method is the measurement of each of the cations in dilute natural waters such as rainwater (Fig. 2). However,

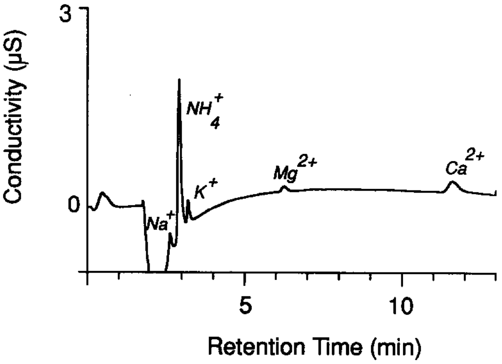

Fig. 2. Chromatogram of rainwater collected in Berne on 31.10.91. The average measured concentrations ± one standard deviation of the water analysed in triplicate are Na^+ 7 ± 1, NH_4^+ 265 ± 3, K^+ 24 ± 1, Mg^{2+} 5 ± 1 and Ca^{2+} 25 ± 0 ng/g.

the concentrations of inorganic cationic species in peatland waters are generally much higher than the limits of detection. Hence, the sensitivity of the method is certainly adequate for measurements of cations in bog waters.

Variability of analytical procedure. An estimate of the variability of the analytical procedure was made by analysing a blind working standard (500 ng/g) in triplicate after every tenth injection. These results were pooled to calculate the mean ± one standard deviation for fifteen analyses of the 500 ng/g working standard: Na^+, 511 ± 19; NH_4^+, 518 ± 37; K^+, 489 ± 21; Mg^{2+}, 508 ± 12; Ca^{2+}, 496 ± 7 ng/g.

Precision of pore water analyses. The precision of the pore water analyses is most clearly illustrated by examining the reproducibility of duplicate analyses of the dominant cations in the pore waters (Fig. 3). The average standard deviations of the 35 duplicate pairs were estimated according to ASTM Designation D 4210 [3] and are Na^+ 17.3, NH_4^+ 71.1, K^+ 9.5, Mg^{2+} 4.3 and Ca^{2+} 8.8 ng/g.

Maritime bog waters

Typical chromatograms of standards and samples. A sample of bog surface water from an Irish bog analysed using the isocratic separation of cations is shown in Fig. 4a. In this instance, the NH_4^+ peak (*ca.* 5 μg/g) is masked by that of Na^+ (*ca.* 27 μg/g). At higher Na^+/NH_4^+ ratios the separation becomes increasingly poor.

Examples of chromatograms obtained using the gradient method are shown in Fig. 4b and c. A chromatogram of a standard containing 100 μg/g of Na^+ and 10 μg/g of NH_4^+ shows that the two peaks are clearly separated (Fig. 4b). In this instance, with $Na^+/NH_4^+ > 10$, there is no interference of Na^+ (3.1 min) in the determination of NH_4^+ (3.9 min). Even when $Na^+/NH_4^+ > 100$, these two peaks are

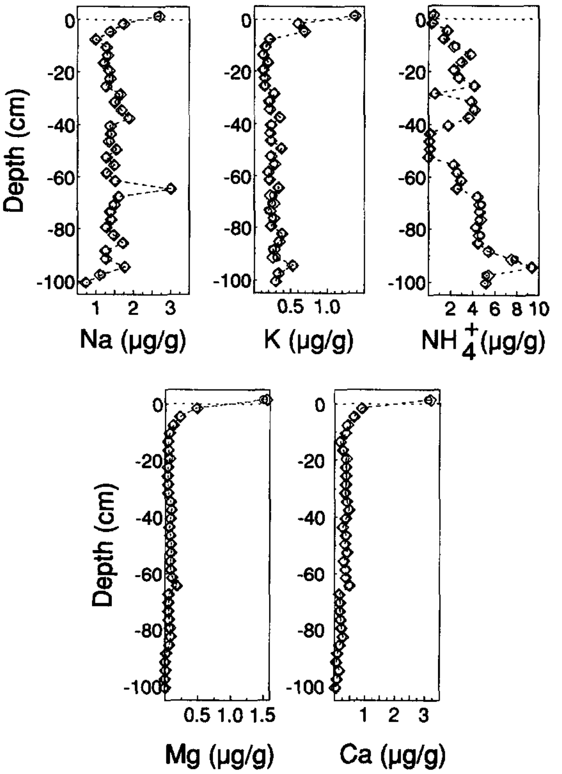

Fig. 3. Cations in pore waters at Etang de la Gruyère. The circles and diamonds represent two separate sets of analyses (duplicates).

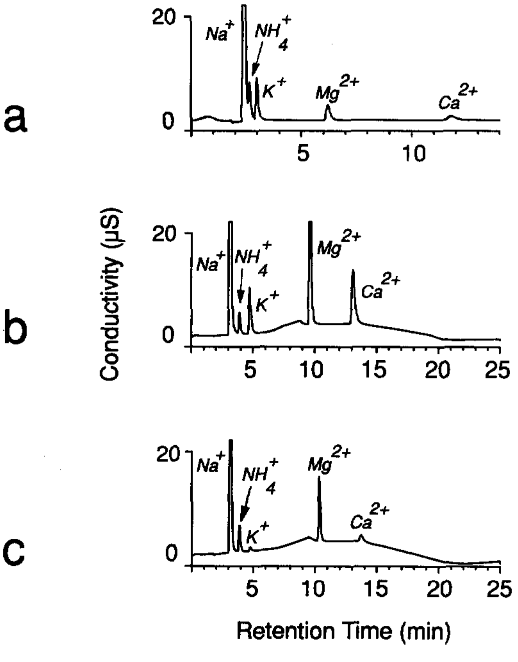

Fig. 4. (a) Isocratic separation of cations in surface water from an Irish bog. Note that NH_4^+ (*ca.* 5 μg/g) is masked by Na^+ (*ca.* 27 μg/g). With increasing Na^+/NH_4^+ ratio the separation becomes increasingly poor. (b) Gradient separation of cations in a standard containing: 100 μg/g of Na^+, 10 μg/g each of NH_4^+, K^+ and Ca^{2+} and 20 μg/g of Mg^{2+}. (c) Gradient separation of cations in pore water (63–66 cm) from Lochs o' da Fleck. Note that NH_4^+ is clearly separated from Na^+.

still baseline separated. A pore water sample from Lochs o' da Fleck is shown in Fig. 4c. The sample contains 53.4 μg/g of Na^+ and 11.3 μg/g of NH_4^+, but the two peaks are clearly separated.

The isocratic and gradient methods for cation separations were compared by analysing a sample of water from Tourbière des Veaux using both methods. The results of the analyses are not significantly different (Table II). The main advantage of the isocratic method is the shorter time required for analysis (15 min *versus* 25 min for the gradient method). The isocratic method provides adequate separation of sodium and ammonium when the Na^+ to NH_4^+ ratio is relatively low (continental bog waters). The main advantage of the gradient method is the improved separation of Na^+ and NH_4^+ in waters with a high Na^+ to NH_4^+ ratio (maritime bog waters).

Variability of analytical procedure. After every tenth injection a blind standard containing 50 μg/g of Na^+, 10 μg/g of Mg^{2+} and 2 μg/g each of NH_4^+, K^+ and Ca^{2+} was analysed in triplicate. These results were pooled to calculate the mean ± one standard deviation for twelve analyses of the working standard: Na^+, 55.2 ± 4.3; NH_4^+, 2.1 ± 0.1; K^+, 2.2 ± 0.1; Mg^{2+}, 10.6 ± 0.5; Ca^{2+}, 2.3 ± 0.3 μg/g.

Precision of the water analyses. Again, the precision is best illustrated by comparing duplicate sets of analyses of the dominant cations in a maritime bog (Fig. 5). The average standard deviations of the 27 duplicate pairs estimated according to ASTM Designation D 4210 [3] are Na^+ 1.8, NH_4^+ 0.2, K^+ 0.1, Mg^{2+} 0.2 and Ca^{2+} 0.2 μg/g.

TABLE II

COMPARISON OF ISOCRATIC AND GRADIENT METHODS OF CATION DETERMINATION

A sample of surface water from Tourbière des Veaux was analysed six times using each method.

Cation	Concentration (ng/g)	
	Isocratic separation	Gradient separation
Na^+	505 ± 1	485 ± 22
NH_4^+	1605 ± 30	1507 ± 50
K^+	1126 ± 47	1191 ± 44
Mg^{2+}	173 ± 7	171 ± 6
Ca^{2+}	763 ± 12	723 ± 26

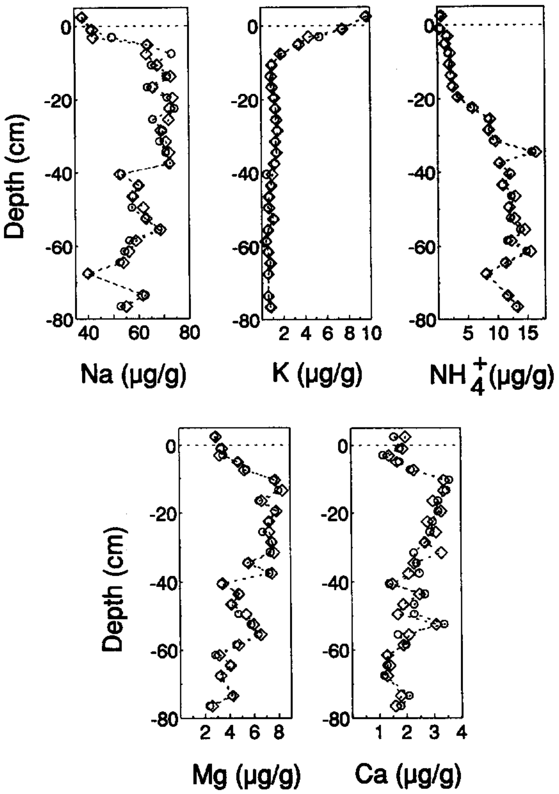

Fig 5. Cations in pore waters at Lochs o' da Fleck. The circles and diamonds represent two separate sets of analyses (duplicates).

Comparison of the determination of Na, K, Mg and Ca by IC versus ICP

Na, K, Mg and Ca were determined by both IC and ICP methods in one complete set of pore waters from Etang de la Gruyère. The relationship between the two sets of values is illustrated in Fig. 6. The results obtained by ICP are 20–40% higher than the corresponding data obtained using the IC. The concentrations of dissolved organic carbon (DOC) in the pore water samples were also measured and found to vary from 50 to 120 mg/l. The ratios of measured metal concentrations (ICP/IC), however, are independent of DOC concentration. The ratios of measured metal concentrations (ICP/IC) were also compared with the pH values of the pore waters, which range from 3.8 to 4.2. The measured differences between the ICP and the methods IC are also independent of the pH values of the

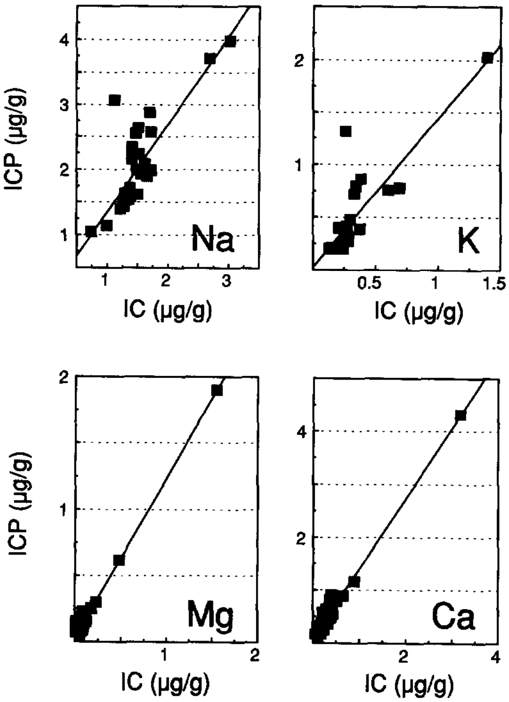

Fig. 6. Comparison of measured metal concentrations using ICP *versus* IC. The data represent a complete set of pore waters (32 samples) from Etang de la Gruyère in which the metal cations were measured by both methods. The detection limits using ICP are Na 30, K 200, Mg 40 and Ca 10 ng/g. The linear regression equations are as follows: Na, ICP = 1.35 IC − 0.07 (r^2 = 0.664); K, ICP = 1.42 IC + 0.02 (r^2 = 0.708); Mg, ICP = 1.21 IC + 0.03 (r^2 = 0.986); Ca, ICP = 1.33 IC + 0.08 (r^2 = 0.975). All of the correlation coefficients are significant at the 0.01 level of probability.

solutions analysed. Additional studies are needed to explain the differences in measured metal concentrations between the two methods.

CONCLUSIONS

The dominant cations in peatland waters (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) can be measured simultaneously in less than 15 min and with adequate sensitivity and precision using IC. The principle advantage of IC over AAS and ICP is the measurement of NH_4^+, in addition to the metallic cations. This may be especially valuable with pore waters from continental bogs because NH_4^+ may be the dominant cation. An organics-removal cartridge is used with each injection, but this has no significant effect on the measured cation concentrations.

In waters from continental bogs with relatively low Na^+ to NH_4^+ ratios, the isocratic method allows adequate separation of these two cations. In waters from maritime bogs with large Na^+ to NH_4^+ ratios, a gradient method must be used to separate these two peaks clearly.

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