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Ion chromatography of organic-rich natural waters from peatlands

III. Improvements for measuring anions and cations

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Abstract

Organic-rich, anaerobic pore waters from peatlands have been sampled using peepers which filter the waters in situ. Pore waters collected using these devices are neither oxidized nor degassed. Anions (F^- , acetate, formate, Cl^- , HCO_3^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and $S_2O_3^{2-}$) and cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) were analyzed using ion chromatography (IC). With a Na borate gradient increasing from 4.9 to 24.5 mM, F^- , acetate, formate, Cl^- , HCO_3^- , NO_3^- , PO_4^{3-} and SO_4^{2-} can be quantified in one run (12 min). The high concentrations of dissolved CO_2 in the pore waters are manifested as a broad HCO_3^- peak in the chromatograms. This allows HCO_3^- to be quantified (with a linear calibration curve from 40 to 800 $\mu g/g$), but interferes with the Br^- and NO_2^- peaks. Measurement of these two species requires sample degassing to remove dissolved CO_2 . While $S_2O_3^{2-}$ can also be determined using a modified borate gradient (7 to 35 mM), its concentration in the pore water samples is below the detection limit of approximately 30 ng/g. In an earlier report, IC measurements of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} in peat bog pore waters were found to yield significantly lower concentrations compared to inductively coupled plasma analyses of the same samples. Here, 20 mM methanesulfonic acid was used to acidify the pore waters to pH 2 prior to injection. Following this sample pretreatment, the measured concentrations of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} obtained by IC were significantly higher than in the unacidified samples and were in good agreement with the concentrations determined independently using inductively coupled plasma mass spectrometry.

1. Introduction

Ion chromatography (IC) has been used to measure both anions (Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} and oxalate) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) in organic-rich natural waters from peatlands [1,2]. The pore waters in these previous studies had been

squeezed from peat cores and vacuum-filtered through a 0.2- μm membrane filter. As a result, the samples were both degassed and partly oxidized. Unfortunately, HCO_3^- is completely removed from the pore waters when they are degassed, and the concentrations of other important ionic species (NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , NH_4^+) may be greatly increased or decreased because of oxidation. Therefore, in these vacuum-filtered water samples, reliable measure-

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ments could be obtained only for Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} .

In the present study, IC methods are applied to peat bog pore waters sampled with peepers. Peepers are in situ diffusion-equilibrium pore water samplers and provide pore water samples which are neither oxidized nor degassed. The species determined, typical concentration ranges of these ions in bog pore waters and retention times are given in Table 1. Because the peeper samples are not degassed, they may contain high concentrations of dissolved carbon dioxide. Using a borate eluent, however, HCO_3^- can be quantified in these samples in addition to Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-} . The borate eluent may be modified so that $\text{S}_2\text{O}_3^{2-}$ also elutes.

In the previous study [2], IC measurements of Na^+ , K^+ , Mg^{2+} and Ca^{2+} in peat bog pore waters were found to yield significantly lower concentrations compared to inductively coupled plasma (ICP) analyses of the same samples. In

the present investigation this discrepancy was resolved by acidifying the pore waters to pH 2 prior to injection.

2. Experimental

2.1. Location of sites

The pore waters studied were collected from two continental bogs in the Franches-Montagne region of the Jura Mountains, Switzerland. One of the bogs, Tourbière de Genevez (TGe), consists of 1.5 m of peat, while at the other site, Etang de la Gruyère (EGr), peat accumulation is more than 6 m. More detailed descriptions of the sites are given elsewhere [3].

2.2. Sampling of peat pore waters

The pore waters analyzed in this study were obtained using peepers [4]. Peepers were originally designed for studying pore waters in lake or sea sediments [5]. They consist of a single Plexiglas housing made up of individual 30-ml chambers that are filled with deionized, deaerated water and covered with a 0.2- μm membrane filter. The chambers are inserted into the bog at different depths and are allowed to equilibrate with the pore waters for about five weeks. To prevent oxidation during sample collection and handling, the peepers are pulled directly from the bog into N_2 -filled glove bags. Individual chambers are then sampled through the glove bag using syringes. The samples are brought to the laboratory in the closed syringes, which are kept in a cold-storage bag, and then analyzed immediately. Because a 0.2- μm filter is built into the sampler, there is no need to vacuum-filter the pore waters prior to analysis and therefore there is no degassing.

2.3. Ion chromatography

The IC system used was a Dionex 4500i equipped with Dionex AG4A SC/AS4A-SC (anions) and CG12/CS12 (cations) analytical columns. Suppressed conductivity detection was

Table 1
Typical range of solute concentrations found in organic-rich peat bog pore waters sampled with peepers

Species	Concentration range ($\mu\text{g/g}$)	Retention time (min)
Fluoride	<0.03	2.1
Acetate	<0.02–2 (17)	2.3
Formate	<0.02	2.8
Chloride	0.3–2	4.2
Nitrite	<0.02	5.1
Bicarbonate	100–350 (700)	5.5
Bromide	<0.02	6.7
Nitrate	<0.02	7.3
Phosphate	<0.02–1 (2)	9.5
Sulfate	<0.01–0.3	11
Thiosulfate	<0.05	40
Sodium	0.25–1.1	4.1
Potassium	0.02–0.8 (4)	6.2
Magnesium	0.03–0.3 (2.5)	7.6
Calcium	0.1–4 (35)	9.6

The pH range is typically 4–5, while DOC concentrations range from 30 to 80 mg/l. The exceptional values given in parentheses are mainly found in deeper peat layers where groundwater can infiltrate. Retention times refer to the elution conditions given in the text. Note that thiosulfate was determined with the special gradient described in the text.

accomplished by using ASRS-I and CSRS-I suppressors, respectively. Injection volume was 100 μl .

Anions were analyzed using a gradient method with a sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) eluent (flow-rate: 2 ml/min). With this method the column was equilibrated with the weaker eluent (4.9 mM sodium borate) for 5 min prior to injection; 0.5 min after injection the strength of the eluent was increased linearly to reach 24.5 mM sodium borate 7 min after injection. This eluent concentration was held to the end of analysis at 12 min.

The CS 12 column was eluted with 20 mM methanesulfonic acid (MSA) at a flow-rate of 1 ml/min. Eluents were degassed and pressurized with N_2 gas.

Carbonate standards were made by dissolving sodium bicarbonate in degassed, deionized water in a closed, completely filled bottle. Preparation of all other standards, resulting calibration curves and limits of detection, as well as the use of OnGuard-P cartridges were described previously [1,2].

Typical retention times for the ions are given in Table 1. The retention times of all peaks decreased continually in the course of a day, probably because the columns became progressively contaminated by humic acids which are abundant in the organic-rich samples. However, the columns were readily reconditioned by rinsing with 0.1 M NaOH for 30–60 min at the end of each day.

3. Results

3.1. Chloride, nitrate, phosphate and sulfate

A typical anion chromatogram of a pore water sample (collected with peepers) obtained with the above borate gradient is shown in Fig. 1. The peaks attributed to Cl^- , PO_4^{3-} and SO_4^{2-} are well separated and the concentrations of these species (cf. Table 1) are readily quantified. A nitrate peak would also be separated from the other peaks, but nitrate concentrations were below the

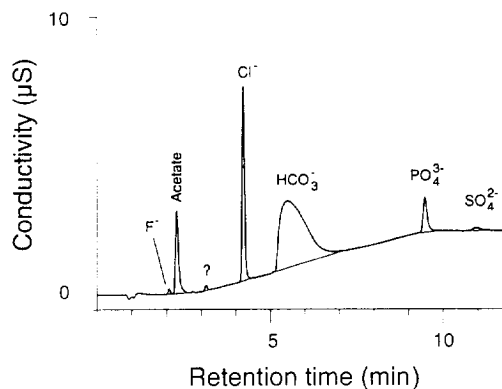


Fig. 1. Chromatogram of fresh pore water from a peat bog collected with a peeper. Gradient: 4.9 to 24.5 mM Na borate. The solute concentrations are: < 25 ng/g fluoride, 1.6 $\mu\text{g/g}$ acetate, 1.15 $\mu\text{g/g}$ chloride, 227 $\mu\text{g/g}$ bicarbonate, 1.31 $\mu\text{g/g}$ phosphate, < 25 ng/g sulfate. The peak labeled “?” is possibly due to acrylate.

detection limit in most peeper samples (cf. Table 1).

The samples obtained using peepers showed PO_4^{3-} concentrations up to five times higher and SO_4^{2-} concentrations up to ten times lower than pore water samples squeezed from peat cores which were taken from the same bogs [1]. The lower PO_4^{3-} concentrations in the squeezed pore waters were probably the indirect result of sample oxidation; PO_4^{3-} was precipitated together with Fe^{3+} resulting from the oxidation of Fe^{2+} [6]. The higher SO_4^{2-} concentrations in the squeezed pore waters were probably also created during sample oxidation. Because only very low concentrations of inorganic reduced sulfur species have been measured in the pore waters from the peeper samples [7] the higher concentrations of SO_4^{2-} in the squeezed samples must have been due to the oxidation of organic sulfur compounds.

3.2. Bicarbonate

The large amount of dissolved CO_2 results in the broad bicarbonate peak seen in Fig. 1. Although the shape of the peak is not ideal, the calibration curve for bicarbonate was linear in

the range 40–800 $\mu\text{g/g}$ bicarbonate. The equation of a typical calibration curve (obtained from standards at 50, 100, 200, 400 and 800 $\mu\text{g/g}$ bicarbonate) is

$$\text{concentration} = -13.1 + 1.98 \cdot \text{area} \quad (r^2 = 0.9999)$$

where area is the peak area ($\mu\text{S s}$) and concentration is the bicarbonate concentration in $\mu\text{g/g}$. The ability of the method to measure simultaneously high bicarbonate concentrations and low concentrations of other anions meets ideally with the composition of peatland pore waters (see Table 1). Due to the irregular peak shape the method is not suitable for measuring bicarbonate concentrations below approximately 10 $\mu\text{g/g}$. Note that during IC analysis all of the dissolved CO_2 species ($\text{CO}_2 + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$) are converted to HCO_3^- . The measured HCO_3^- concentration, therefore, corresponds to the concentration of total dissolved CO_2 , $[\text{CO}_2]_{\text{T}}$, in the waters.

3.3. Organic anions and fluoride

Acetate and formate were found in the pore water samples. These peaks were identified by standard addition of acetate or formate to the samples (retention times are given in Table 1). Acetate may occasionally occur in high concentrations (up to 17 $\mu\text{g/g}$). High acetate concentrations are also sometimes observed in lake sediments [8]. The possible co-elution of other organic acids with formate and fluoride cannot be excluded. For formate and fluoride, therefore, only maximum concentrations can be given. Another organic anion spiked to samples was acrylate. The acrylate peak was separated from acetate and formate and only low concentrations of acrylate were found in the samples (Fig. 1). Acrylate was presumably leached from the sampling device, which consists of acrylic glass (Plexiglas).

3.4. Thiosulfate

Various inorganic sulfur species can be measured using IC (e.g. Ref. [9]). In an effort to

measure thiosulfate, the borate gradient method was modified as follows: 7 mM Na borate for 10 min, increasing to 35 mM Na borate from 10 to 40 min and maintaining at 35 mM for 5 min. Thiosulfate eluted after 40 min with a detection limit of about 30 ng/g $\text{S}_2\text{O}_3^{2-}$. However, no thiosulfate peaks were recorded in the peat bog pore water samples.

3.5. Nitrite and bromide

At high HCO_3^- concentrations it is impossible to measure low concentrations of NO_2^- and Br^- because both peaks are overlapped by the huge HCO_3^- peak. However, nitrite and bromide can be measured using the isocratic method described previously [1]. Unfortunately, in CO_2 -charged waters analyzed isocratically, the broad HCO_3^- peak overlaps the Cl^- and the NO_2^- peak. Accurate measurement of Cl^- , NO_2^- and Br^- in these samples requires degassing prior to injection.

3.6. Measurements of Na, K, Mg, and Ca by IC versus ICP mass spectrometry (MS)

As noted previously [2] concentrations of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} in organic-rich pore waters measured by ICP were found to be 20–40% higher than those measured by IC. One possible explanation for these differences is that the OnGuard-P cartridges used to remove dissolved humic materials had also retained the fraction of these cations that were bound to the humic acids. To dissociate the metal–organic complexes the pore water samples studied here were acidified to approximately pH 2 with MSA. MSA was added to give a final concentration of 20 mM in the samples, the same concentration of MSA as in the eluent. Sodium, K, Mg and Ca were determined in a set of 21 pore water samples using both IC and ICP-MS methods. Good agreement was found between the two methods, with the regression curves having slopes close to 1 and high coefficients of correlation (Fig. 2). When the results shown in Fig. 2 are compared with those shown in Fig. 6 of Ref. [2], it is clear that organic-rich waters must be acidified before

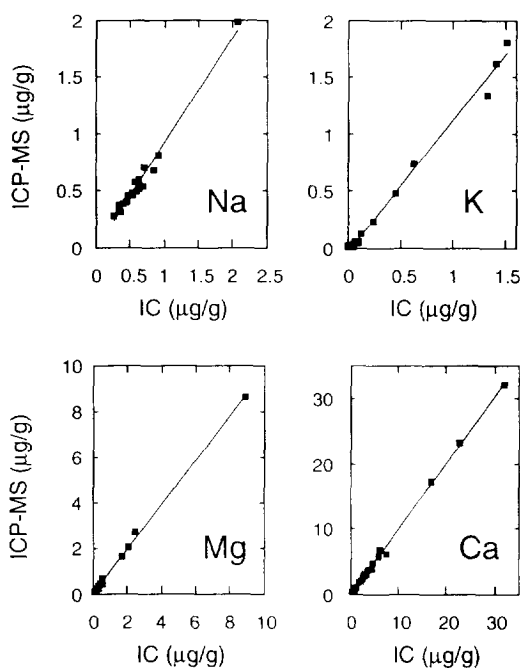


Fig. 2. Comparison of measured metal concentrations using ICP-MS versus IC. A set of 21 samples from the bogs at EGr and TGe was analyzed using both methods. The linear regression equations are as follows: Na, ICP-MS = 0.93 IC - 0.01 ($r^2 = 0.979$); K, ICP-MS = 1.14 IC - 0.02 ($r^2 = 0.993$); Mg, ICP-MS = 0.97 IC - 0.03 ($r^2 = 0.998$); Ca, ICP-MS = 1.01 IC - 0.07 ($r^2 = 0.998$).

analyzing cations by IC. Moreover, because humic substances are less soluble at low pH values, sample acidification should improve the efficiency of the organics-removal cartridges, thereby extending the life of the analytical columns.

4. Summary and conclusions

IC was used to analyze anions and cations in pore waters obtained using in situ diffusion-equilibrium samplers (peepers). These results were compared with those of an earlier IC study in which the pore waters were obtained from the same bogs by squeezing peat samples and vacuum-filtering the expressed solutions. Individual water samples were removed from the peeper chambers by syringe in a N_2 -filled glove bag in the field. The samples were injected into the ion

chromatograph using the same syringe, and this procedure guarantees minimal sample degassing and oxidation.

The isocratic separation of anions described previously [1] is inappropriate for these samples, because a broad HCO_3^- 'peak' interferes with the determination of Cl^- and NO_2^- . For quantitative measurement of anions with the isocratic method, the samples must be degassed prior to injection.

Alternatively, the borate gradient method described here allows the samples to be injected without degassing and allows the quantitative determination of HCO_3^- , in addition to F^- , acetate, formate, Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-} in a single run (12 min). Because HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and PO_4^{3-} are by far the dominant inorganic anions in peat bog pore waters collected in situ, this new method is ideally suited for the analysis of inorganic anions in these samples.

A second gradient method extends the analytical capability to include $S_2O_3^{2-}$, but this species was not detected in the pore waters.

To measure Na^+ , K^+ , Mg^{2+} and Ca^{2+} in organic-rich waters by IC, the samples must first be acidified to pH 2. This was accomplished by adding sufficient 20 mM MSA to each sample. Following this pretreatment, the measured cation concentrations were significantly higher than in the unacidified samples and were in good agreement with the concentrations determined independently using ICP-MS. Acidification of the samples appeared to liberate the organically bound fraction of each of these cations, an essential step in analyzing these waters by IC.

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