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# Sediment porewater extraction and analysis combining filter tube samplers and capillary electrophoresis

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Careful extraction and analysis of porewater from sediment cores are critical for the investigation of small-scale biogeochemical processes. Firstly, small sample volumes and high spatial resolution are required. Secondly, several chemical species in the anaerobic porewater are sensitive to oxidation when brought in contact with ambient air. Here we present the combination of a special sampling technique and an analytical method for the porewater extraction of a varved sediment core from Lake Baldegg in central Switzerland, using MicroRhizon samplers and a portable capillary electrophoresis (CE) instrument. MicroRhizon filter tubes of 1 mm diameter and 20 mm length are suitable for fast retrieval of particle-free porewater samples directly from the sediment core. Since the time-span between sampling and analysis is less than 20 seconds, oxygen-sensitive $Fe(II)$ can be analyzed in one go together with $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$, and $Mn(II)$ without splitting, acidification or dilution of the sample. The major inorganic cations and anions of the sediment porewater can be determined in less than 15 minutes. Detection limits are in the sub-micromolar concentration range. The capillary electrophoresis instrument used in this study requires sample volumes of only 20 μL. These remarkable small sample volumes allow the minimization of disturbance of the sediment cores and a high spatial resolution of the sediment profile, even in sediments with low water content. The equipment is inexpensive, easy to handle, fully portable and therefore suitable for environmental on-site applications.

### Environmental impact

Early diagenetic processes in lake sediments can be traced and quantified from porewater concentration gradients. Exemplified for the sediments of Lake Baldegg (Switzerland), a eutrophic lake whose sediment oxygen consumption rate remained unchanged despite significantly decreased phosphate concentrations, we demonstrate the advantages of a new combination of porewater extraction and subsequent analysis of inorganic cations and anions. Remarkably small sample volumes are collected with minimal disturbance of the sediment and immediately analyzed without any pretreatments steps. The procedure allows high sample throughput and spatial resolution with a short time-span between sampling and analysis allowing the determination of oxygen-sensitive $Fe(II)$ together with the major inorganic ions.

## 1 Introduction

The extraction and analysis of porewater from sediments are some of the most important techniques for the investigation of small scale biogeochemical processes and cycles, *e.g.* for the estimation of fluxes from and to the sediment–water interface, quantification of burial and mineralization rates of organic matter and production rates of climate affecting methane, or for

quality assessments to estimate chemical contamination and toxicity.[1,2] Because of the high sensitivity of porewaters to changes in pressure, temperature, and redox potential, suitable extraction techniques are essential. They should be easy to use, avoid contamination risks, and provide sufficient vertical resolution as well as a good porewater yield at high throughput. Artefacts such as sorption/desorption processes or cell lysis should be avoided. For remote areas it is important to have lightweight and simple equipment. In general, on-site methods are to be preferred because the long transport of the sediments can cause temperature changes, outgassing due to decompression, mixing, diffusion, and redox changes at the sediment–water interface.

Since the 1960s porewater extraction techniques have been improved with regard to simplicity, rapidity, spatial resolution, and integrity of the sediments. The most widely used methods are, because of easy handling and inexpensiveness, *ex situ*

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techniques including squeezing and centrifugation[3] of the sediment. The squeezing methods are classified into core section squeezers[4–6] and whole core squeezers.[7,8]

Centrifugation is widely used but requires subsequent filtration to remove remaining suspended particles.[1] Moreover, it is difficult to avoid contact with ambient air. To minimize sampling artefacts such as chemical alterations of the porewater induced by oxygen, temperature changes and decompression,[1] *in situ* sampling techniques, like diffusion plates ("peepers") were introduced by Hesslein[9] and refined for the two-dimensional mapping of sediment sections by Lewandowski *et al.*[10] Peepers rely on the passive diffusion of dissolved compounds from the porewater across a filter membrane into compartments filled with distilled water.[11] For the improvement of equilibration time, a gel sampler[12] was developed, which reduced the required exposition time from days to hours. Profiling the sediment–water interface with ion-selective electrodes allowed the measurement of porewater concentration gradients with a spatial resolution of around 25 µm, but were only available for the detection of particular ions in the top few centimeters.[13–15]

Many of these limitations (artefacts with *ex situ* methods on the one hand and difficult handling with *in situ* methods on the other hand) can be overcome by using MicroRhizons (Rhizosphere Research Products, Wageningen), for porewater extraction. The MicroRhizons consist of a microporous polymer tube of 0.15 µm pore size[16] and a PEEK tubing, which can be connected to a syringe. A vacuum can be applied by a peristaltic pump or a syringe. Only a few authors[2,17,18] used this technology, which was originally designed for soil science to collect seepage water, despite the fact that this material is chemically inert and without ion exchange properties, permeable only for liquids, durable, fast, easy to use, inexpensive and reusable after rinsing.[19–21] Seeberg-Elverfeldt *et al.*[2] showed with tracer experiments and numerical modeling that approximately 2 mL sample volumes can be extracted attaining a resolution of ~1 cm even with low sediment porosities. Short-term processes can be investigated because of the fast and easy sampling procedure. The contamination with oxygen is minimal and anaerobic sampling does not require the installation of a glove box.[17] Despite the many advantages of the method, however, sample handling and analysis remain a challenge due to the small volume, the need for splitting and preservation, and the risk of contamination.[14,22] Field-portable instrumentation can overcome these problems by the immediate analysis of the extracted sample.[23–25] Therefore, a combination of MicroRhizons and a portable capillary electrophoresis (CE) instrument is ideal. Only a few microliters of sample volumes are needed and the analysis can be carried out on-site.

Kubáň *et al.*[26] developed and optimized a portable capillary electrophoresis instrument with capacitively coupled contactless conductivity detection (C[4]D)[27] for the sensitive field measurements of ionic compounds in environmental samples. Inorganic ions could be determined with detection limits in the range of ~0.2 to 1 µM. CE can be implemented in lightweight portable equipment as only a separation capillary, a high voltage power supply, and small volumes of buffer solutions are needed. The very small and contact free detector system requires a data acquisition system connected to a laptop computer for immediate data storage and processing.[28] Only tiny water volumes (<20 µL) are required for analysis. The CE instrument with C[4]D has been successfully tested in several environmental applications, *e.g.* the determination of major inorganic cations and anions in natural waters.[26,28,29]

Here we present an application for porewater sampling and analysis combining MicroRhizon samplers and a portable CE instrument. The facility combines the advantages of fast sampling with minimal bias and high spatial resolution and coincidentally the analysis of extremely small volumes and portability. The design and performance of the method is presented and exemplified with sediment cores from a eutrophic lake in Switzerland where porewater concentration measurements were compared with simultaneous analysis by ion chromatography (IC).

## 2 Experimental

### 2.1 Sampling site and sediment coring

Sediment cores were sampled from the deepest location (66 m) of Lake Baldegg, a eutrophic lake in central Switzerland of 5.2 km² surface area which has been artificially aerated since 1982 (geographic position: Lat 47°11.907′, Lng 8°15.590′).[30] The sediments of Lake Baldegg are varved as a consequence of anaerobic deep water since 1885[31] caused by the discharge of nutrients from household sewage, and intensified agriculture. Cores for the measurements of anions and cations were collected in April and June 2012, respectively, using a Uwitec gravity corer (www.uwitec.at). The tube of 65 cm diameter and 60 cm length was made of PVC and holes of 0.1 cm diameter were drilled staggered with a vertical resolution of 0.5 cm. The holes were sealed with a tape before coring. For the retrieval of porewater the tapes covering the sampling holes were cut open with a paper knife. A MicroRhizon sampler (Rhizosphere Research Products, Wageningen, Netherlands) of 2 cm length and 1 mm diameter connected to a 1 mL syringe was inserted horizontally and 10 to 50 µL of porewater were drawn out gently. The MicroRhizon sampler consists of a hydrophilic membrane (composed of a blend of polyvinylpyrrolidine and polyethersulfone) of 0.15–0.20 µm pore size. Sampling of one location takes less than 30 seconds. For the present experiments relatively large porewater volumes of 50 to 100 µL were collected until a 5.5 cm depth to allow verification of the CE data by IC measurements. Otherwise, the retrieval of 10 µL was sufficient for determinations with CE. The extracted porewater samples were transferred to 1 mL PE centrifugation tubes and immediately injected into the capillary for the CE measurement. Blanks (Nanopure water collected with MicroRhizon samplers) and certified multielement ion chromatography standard solutions (Fluka, Buchs, Switzerland) were intermittently measured to ensure a high data quality. All samples were stored at 5 °C in the dark for subsequent analysis with IC.

### 2.2 Apparatus and procedures

The determination of cations and anions was carried out using a portable capillary electrophoresis (CE) instrument with

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capacitively coupled contactless conductivity detection ($C^4D$). The instrument was a modification of the model developed by Kubáň et al.[26] A sketch is given in Fig. 1. It consists of a box with dimensions of $310 \times 220 \times 260$ mm made of Perspex plates, which can be opened at the front. The left side contains the sample and the vial holder, and the right side, separated by a Perspex plate, a vial holder and the detector holder. The high voltage supply from Spellman High Voltage Electronics Corporation, New York, was attached to the back, and the purpose-made electronic controller was fixed at the left side of the box.

A TraceDec® $C^4D$ detector (Innovative Sensor Technologies GmbH, Strasshof, Austria) was used and the signal was recorded with the Tracemon software application. The peaks were analyzed using the Chart Software (version 5.2) from eDAQ, Australia. A fused silica capillary (50 μm i.d., 360 μm o.d., 55 cm length) (BGB Analytik AG, Böckten, Switzerland) was used for the separation. The capillary was preconditioned with 1 M NaOH for 5 minutes, rinsed with Nanopure water for 5 minutes and 1 M HCl for 5 minutes, rinsed with Nanopure water for 5 minutes, and finally equilibrated with the electrolyte solution for at least 30 minutes. A voltage of 15 kV was applied to the buffer vials at both ends of the capillary. The polarity of the applied separation voltage could be set by a switch, depending on whether anions or cations were recorded. The sample was injected hydrodynamically by elevating the capillary end immersed in the sample vial. Best results were obtained for an injection time of 20 seconds at 15 cm height for anions and 8 cm for cations. The detector settings were as follows. Frequency: $2\times$ high, voltage level: 0 dB, gain: 200%, offset: 185. The electrolyte solution for both, the separation of cations as well as anions, consisted of 11 mmol $L^{-1}$ L-histidine, 50 mmol $L^{-1}$ acetic acid, 1.5 mmol $L^{-1}$ 18-crown-6 and 0.1 mmol $L^{-1}$ citric acid.[26] All solutions were ultrasonicated for 30 minutes. Chemicals were of p. a. grade (purchased from Sigma-Aldrich, Steinheim, Germany, or from Fluka, Buchs, Switzerland) and only used with Nanopure water purified on a Purelab Ultra (ElGA LabWater, UK). The stock solutions of cations were prepared immediately before use from the corresponding chloride salts, except of the ferrous iron stock solution, which

**Table 1** Concentrations of standards (STc) for the calibration of the instrument adapted to the concentration ranges in the sediment porewater of Lake Baldegg

| Ions | Blank, μmol $L^{-1}$ | STc 1, μmol $L^{-1}$ | STc 2, μmol $L^{-1}$ | STc 3, μmol $L^{-1}$ | STc 4, μmol $L^{-1}$ |
|---|---|---|---|---|---|
| $NH_4^+$ | 0 | 70 | 100 | 200 | 500 |
| $K^+$ | 0 | 17.5 | 25 | 50 | 125 |
| $Ca^{2+}$ | 0 | 140 | 200 | 400 | 1000 |
| $Na^+$ | 0 | 70 | 100 | 200 | 500 |
| $Mg^{2+}$ | 0 | 70 | 100 | 200 | 500 |
| $Mn^{2+}$ | 0 | 17.5 | 25 | 50 | 125 |
| $Fe^{2+}$ | 0 | 50 | 150 | 300 | 600 |
| $Cl^-$ | 0 | 25 | 50 | 100 | — |
| $NO_3^-$ | 0 | 25 | 50 | 100 | — |
| $SO_4^{2-}$ | 0 | 25 | 50 | 100 | — |
| DIP | 0 | 25 | 50 | 100 | — |

was prepared from its sulfate salt. The stock solutions of anions were prepared from the corresponding sodium or potassium salts. The multi-ion standard solutions for the calibration were freshly prepared from these stock solutions. Cation standard solutions were prepared in $10^{-4}$ M HCl (suprapure). The concentration range of the standards was adjusted to the range expected for the sediment porewater samples (Table 1).

Samples, extracted from 0 until 5.5 cm core depth, were additionally measured by IC (Metrohm, Switzerland). $NH_4^+$, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and $Mn^{2+}$ were determined with a Metrosep C4 100/4.0 column (eluent: 1.7 mmol $L^{-1}$ nitric acid, 0.7 mmol $L^{-1}$ dipicolinic acid, flow: 0.9 mL $min^{-1}$). $Cl^-$, $NO_3^-$ and $SO_4^{2-}$ were determined with a Metrosep A Supp 5 column (eluent: 3.2 mmol $L^{-1}$ $Na_2CO_3$, 1.0 mmol $L^{-1}$ $NaHCO_3$, flow: 0.7 mL $min^{-1}$). The concentrations of dissolved inorganic phosphorus (DIP) and $Fe^{2+}$ ions were not determined with IC, because acidification would be necessary to avoid oxidation and precipitation. The sample volume obtained by the MicroRhizons was too small for an accurate dilution with acid.

## 3 Results and discussion

### 3.1 Performance and validation of CE measurements

The analysis of the entire core was accomplished within less than five hours after coring. Electropherograms from the analysis of sediment porewater concentrations of cations and anions are shown in Fig. 2. All peaks could be fully resolved in undiluted samples. The amount injected was optimized in order to allow this resolution while still providing the required sensitivity. For the cations, a high sensitivity was required to allow the determination of $K^+$, which was present at a low concentration, but at the same time a signal overlap with $Ca^{2+}$, the ion with the highest concentration, had to be avoided. Results were at an optimum for an injection time of 20 seconds at 8 cm height for cations and at 15 cm height for anions (hydrodynamic injection by syphoning). Inorganic cations of the sediment porewater, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$ including Mn(II) and Fe(II), could be analyzed in less than six minutes. Anions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$, DIP) were analyzed in less than ten minutes ($Cl^-$, $NO_3^-$, $SO_4^{2-}$ in less than five minutes).
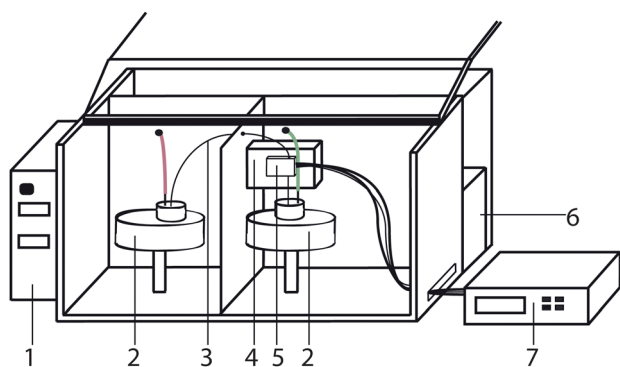


**Fig. 1** Sketch of the portable capillary electrophoresis instrument with a $C^4D$ detector. (1) Electronic control box, (2) buffer vial holder, (3) capillary, (4) detector cell holder, (5) detector cell, (6) Spellman High Voltage power supply, and (7) detector.
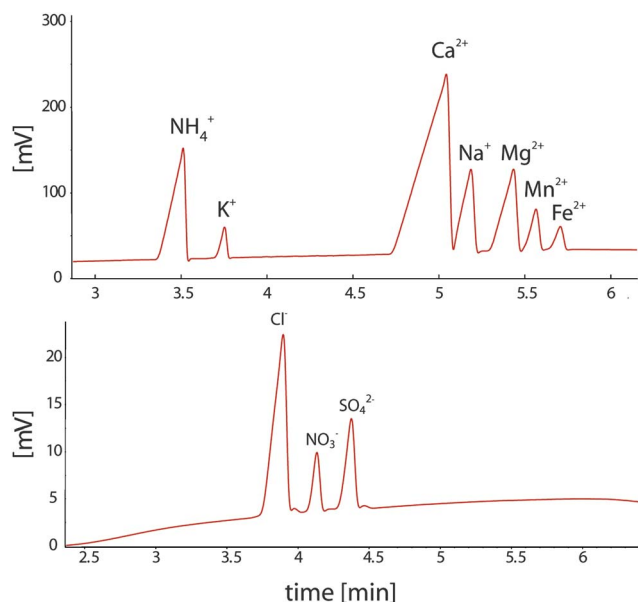
**Fig. 2** Determination of cations (sample from a 15 cm sediment depth) and anions (sample at the sediment–water interface) from the Lake Baldegg sediment porewater. The concentrations were 700 μmol L$^{-1}$ NH$_4^+$, 100 μmol L$^{-1}$ K$^+$, 1500 μmol L$^{-1}$ Ca$^{2+}$, 500 μmol L$^{-1}$ Na$^+$, 320 μmol L$^{-1}$ Mg$^{2+}$, 120 μmol L$^{-1}$ Mn$^{2+}$, and 70 μmol L$^{-1}$ Fe$^{2+}$ for the cations and 610 μmol L$^{-1}$ Cl$^-$, 120 μmol L$^{-1}$ NO$_3^-$, and 120 μmol L$^{-1}$ SO$_4^{2-}$ for the anions.

Lines of best fit and coefficient values were determined based on four to five-point calibrations in the expected concentration range (Table 2). All calibration functions were very reproducible over time, and intercepts were close to zero. Slopes of five calibration functions recorded on different days in September 2012 varied only by 6%, even without thermostating of the detector cell. The limits of detection (LOD) are in the sub-micromolar range and were determined corresponding to a three times signal to noise ratio ($3 \times S/N$).

The CE instrumentation has a number of advantages such as the possibility to detect a large set of cations and anions within

**Table 2** Analytical parameters for the determination of inorganic ions. The relative standard deviation (RSD) was calculated from peak areas of standard solutions used for the calibration of the porewater samples (Table 1). Each standard solution was measured three times. The correlation coefficients, $r^2$, were obtained for the corresponding calibration curves. The limits of detection (LOD) were defined as three-fold of the signal/noise ratio ($3 \times S/N$)

| Ion | RSD (%), peak area | $r^2$, peak area | LOD, μmol L$^{-1}$ |
|---|---|---|---|
| NH$_4^+$ | 2.43 | 0.998 | 0.46 |
| K$^+$ | 2.20 | 0.997 | 0.76 |
| Ca$^{2+}$ | 1.32 | 0.994 | 0.47 |
| Na$^+$ | 3.25 | 0.997 | 0.79 |
| Mg$^{2+}$ | 2.72 | 0.998 | 0.53 |
| Mn$^{2+}$ | 3.22 | 0.996 | 0.82 |
| Fe$^{2+}$ | 2.47 | 0.998 | 1.55 |
| Cl$^-$ | 4.79 | 0.982 | 0.98 |
| NO$_3^-$ | 3.23 | 0.997 | 0.29 |
| SO$_4^{2-}$ | 1.37 | 0.999 | 0.28 |
| DIP | 7.80 | 0.988 | 0.83 |

minutes, requiring negligible sample volumes. The determinations are highly reproducible with low detection limits, and the equipment is inexpensive and lightweight. These characteristics and the portability of the measuring device are important, *e.g.* in the analysis of sediment porewaters requiring fast sampling of only small volumes and the sensitive measurement of as many compounds as possible avoiding dilution and preservation of samples. A representative application to freshwater sediment porewater analysis in combination with a fast and easy sampling principle is presented in the following section.

### 3.2 Lake sediment porewater sampling and analysis applying MicroRhizons and CE

Fig. 3 depicts porewater concentrations of cations and anions from sediment cores of Lake Baldegg sampled with Micro-Rhizon tubes (red lines). Measurements of the same samples by IC as an established routine method are shown in blue. Values agree very well, and the average deviation of all values is 6% (IC value = 100%). The IC samples had to be diluted 2–8-fold to obtain the volume required for the injection by the autosampler (100 μL for cations and 800 μL for anions), while CE measurements were done with undiluted porewater and immediately after sampling. Dilution of small volumes introduces an additional error and bears the risk of contamination. Moreover, it is increasingly difficult to retrieve the relatively large volumes of porewater required by IC with increasing sediment depth as the water content decreases with depth from close to 100% at the surface to 80% at 5 cm and 70% at 15 cm. Collection of larger volumes required extended sampling time and thus increased the risk of Fe(II) oxidation and loss of vertical resolution. In our experiments, it was not feasible to collect enough porewater for IC analyses below a 5.5 cm core depth. In addition, the detection limits of IC for Fe(II) and DIP were insufficient, and analysis with other methods could not be accomplished due to the small sample volume.

Subsurface peaks of NH$_4^+$, Mn(II) and Fe(II) in the top sediment layer originate from the most recent settling of a spring algae bloom. The high amount of organic matter was subject to immediate mineralization consuming easily available electron acceptors such as oxygen O$_2$, NO$_3^-$ and SO$_4^{2-}$ and subsequently even Mn(IV)- and Fe(III)-oxy-hydroxides releasing NH$_4^+$, Mn(II) and Fe(II).

The simultaneous fluctuations of the profiles (Fig. 3) may be caused by the laminated structure of the sediment. The varves consist of alternating layers of biogenically precipitated calcite of 1–2 mm magnitude deposited after the first algae bloom in spring, and black layers of organic rich material of similar thickness deposited during summer and autumn. The average sedimentation rate of Lake Baldegg is 3.4 mm *per annum*.[31] The diameter of the MicroRhizon sampler tube is only 1 mm and thus in the same range as the sediment laminae. Incidental insertion of the sampler in a calcite-rich sediment layer may thus result in slightly different concentrations of porewater constituents than in an organic rich layer.

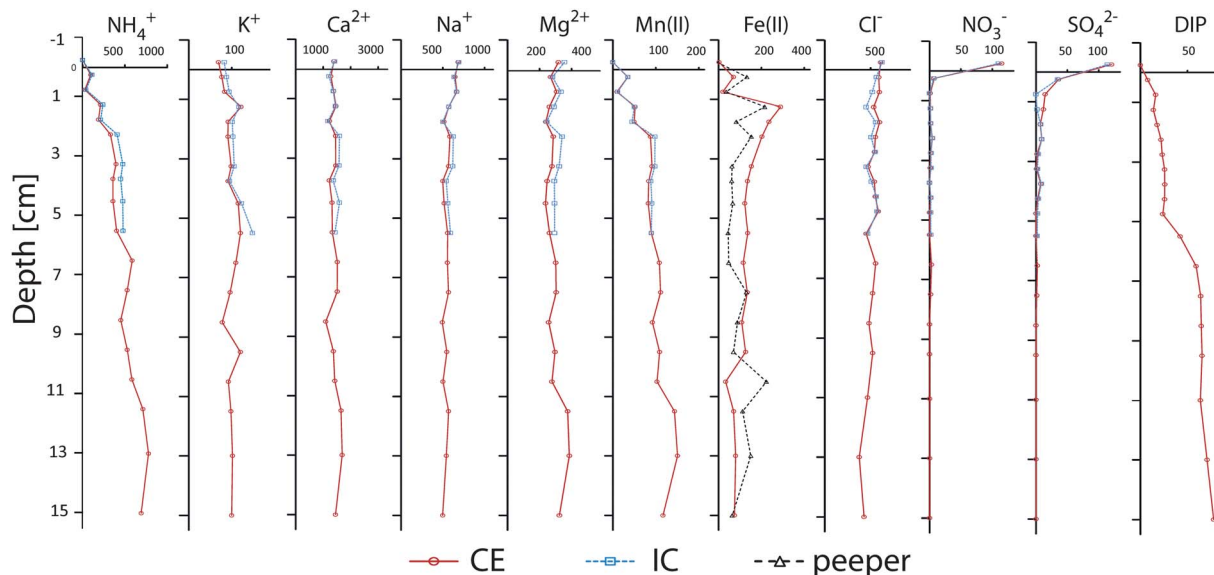While the sampling and analysis of Mn(II) is usually straightforward, the collection of Fe(II) from porewater is

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**Fig. 3** Porewater concentration (μmol L$^{-1}$) profiles from sediment cores of Lake Baldegg collected in April (cations) and June (anions) 2012. Blue dots are IC measurements of the same samples (sufficient volume was available until 5.5 cm) and archived Fe$^{2+}$ samples were collected directly from the bottom of the lake with a "peeper" and measured with AAS (dashed line; B. Wehrli, unpublished results).

difficult due to its immediate abiotic oxidation when in contact with O$_2$. Its sensitivity towards O$_2$ usually requires handling of sediment cores in a N$_2$ atmosphere and therefore in glove boxes. Porewater collection by diffusion plates (peepers) is subject to unknown bias due to the contact of the facility with oxic water during retrieval.[32] Here, the porewater collection with Micro-Rhizon samplers from closed sediment cores reduces the contamination with O$_2$ to a minimum, and injection into the CE capillary is accomplished in less than 20 seconds allowing analysis of Fe(II) within the set of cations (Fig. 2) without sample splitting, acidification or dilution. Data obtained in previous studies[17] showed no significant difference between sampling in a glove box and sampling in ambient air with the MicroRhizons.

Fig. 4 shows a simple kinetic experiment to investigate the potential loss of Fe(II) in the vial after sampling. Three porewater samples were injected and measured at different time intervals after retrieval from the sediment core. The first injection was made immediately after sampling (<20 seconds). Three to four further measurements of the same samples, stored in the vials without shaking, were carried out at even time intervals to estimate the oxidation rate. In spite of the oxidation of Fe(II) being a second order process (depending on the concentration of the Fe$^{2+}$ species and O$_2$ (ref. 33)) we observed an initial linear decrease of Fe(II) concentrations (Fig. 4), originating from the diffusion of O$_2$ from the atmosphere to the sample solution.

The entire Fe(II) content was found to be oxidized after less than 30 minutes. Linear extrapolation of the initial consumption rate to time zero shows that the loss of Fe(II) in the time between sampling and measurement (20 seconds) is negligible and within the range of the standard deviation of ~5%. These results demonstrate that our method is fast enough to analyze Fe(II) with a minimum error. It emphasizes the high practical value of the proposed method for fast, simple and inexpensive porewater analysis with a minimum bias.

## 4   Conclusion

The new method, consisting of a combination of MicroRhizons for sampling and a portable capillary electrophoresis instrument for analysis, was successfully applied in the investigation of sediment porewaters of Lake Baldegg. We achieved a full separation of the major inorganic anions and cations, inclusive of manganese(II) and ferrous iron, in less than 15 minutes. MicroRhizon tubes allowed safe handling and sampling of sediment cores in high spatial resolution with minimal disturbance of the sediment structure and zero-oxygen conditions
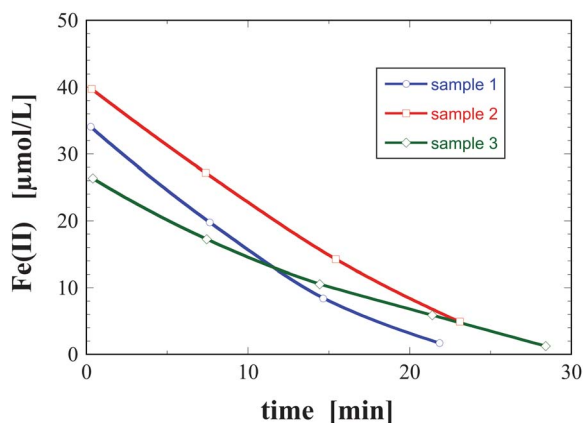


**Fig. 4** Kinetic experiment depicting the loss of Fe(II) with time between sampling and injection of the sediment porewater into the capillary (buffer pH 4.1). The initial oxidation of Fe(II) follows a zero-order kinetic.

during sampling without laborious precautions. Due to the fact that porewater from sediment cores can be analyzed accurately without sample splitting, acidification or dilution, the presented method probably is the most rapid technique for sediment porewater analysis without losing accuracy. The accuracy was verified by analyses using ion chromatography. The light-weight and low-cost CE analyzer runs on mains power as well as battery power and is thus well suited for environmental on-site measurements.

Sediment porewater concentration gradients allow the estimation of fluxes of oxidizing agents involved in the mineralization of organic matter in the sediment ($NO_3^-$, $SO_4^{2-}$, Mn(II) and Fe(II)), and released nutrients ($NH_4^+$, DIP). The possibility of accomplishing fast and unsophisticated sediment porewater sampling and reliable measurements of these ions is essential for the monitoring of seasonal variations and for extended investigations of the mineralization of organic matter at different depths of lakes, from littoral to profundal zones,[34] and to complement monitoring of the water column. To date, only a few of such measurements have been carried out due to the great effort that porewater sampling and measurements require. The combination of the methods presented here will significantly facilitate such projects in the future.

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## References

1 S. E. Bufflap and H. E. Allen, *Water Res.*, 1995, **29**, 165–177.

2 J. Seeberg-Elverfeldt, M. Schlüter, T. Feseker and M. Kölling, *Limnol. Oceanogr.: Methods*, 2005, **3**, 361–371.

3 S. Emerson, V. Grundmanis and D. Graham, *Earth Planet. Sci. Lett.*, 1980, **43**, 57–80.

4 N. J. Lusczynski, *Filter-press method for extracting water samples for chloride analysis*, United States Geological Survey, 1961, vol. 1544-A, http://pubs.usgs.gov/wsp/1613f/report.pdf.

5 B. J. Presley, R. R. Brooks and I. R. Kaplan, *J. Mar. Res.*, 1967, **25**, 355–357.

6 W. S. Reeburgh, *Limnol. Oceanogr.*, 1967, **12**, 163–165.

7 M. Bender, W. Martin, J. Hess, F. Sayles, L. Ball and C. Lambert, *Limnol. Oceanogr.*, 1987, **32**(6), 1214–1225.

8 R. A. Jahnke, *Limnol. Oceanogr.*, 1988, **33**(3), 483–487.

9 R. H. Hesslein, *Limnol. Oceanogr.*, 1976, **21**(6), 912–914.

10 J. Lewandowski, K. Rüter and M. Hupfer, *Environ. Sci. Technol.*, 2002, **36**(9), 2039–2047.

11 H. Brandl and K. W. Hanselmann, *Aquat. Sci.*, 1991, **53/1**, 1015–1621.

12 M. Krom, P. Davison, H. Zhang and W. Davison, *Limnol. Oceanogr.*, 1994, **39**(8), 1967–1972.

13 N. P. Revsbech and B. B. Jørgensen, *Adv. Microb. Ecol.*, 1986, **9**, 293–352.

14 D. De Beer and J.-P. R. Sweerts, *Anal. Chim. Acta*, 1988, **219**, 351–356.

15 B. Müller, M. Märki, C. Dinkel, R. Stierli, and B. Wehrli, in *Environmental Electrochemistry: Analyses of Trace Element Biogeochemistry*, ed. M. Taillefert and T. F. Rozan, American Chemical Society Symposium Series 811, Washington DC, 2002, pp. 126–143.

16 J. Seeberg-Elverfeldt, M. Schlüter, M. Kölling and T. Feseker, Rhizon – an excellent pore water sampler for low maintenance collection and filtration of small volume samples, in EGU General Assembly, 25–29 Apr., Vienna, Austria, 2005.

17 L. Shotbolt, *J. Paleolimnol.*, 2010, **44**(2), 695–700.

18 J. Song, Y. Luo, Q. Zhao and P. Christie, *Chemosphere*, 2003, **50**, 711–715.

19 B. P. Knight, A. M. Chaudri, S. P. McGrath and K. E. Giller, *Environ. Pollut.*, 1998, **99**(3), 293–298.

20 A. Spangenberg, G. Cecchini and N. Lamersdorf, *Plant Soil*, 1997, **196**(1), 59–70.

21 T. Tiensing, S. Preston, N. Strachan and G. I. Paton, *J. Environ. Monit.*, 2001, **3**, 91–96.

22 J. Parr, M. Bollinger, O. Callaway, and K. Carlberg, in *Principles of Environmental Sampling*, The American Chemical Society, 2nd edn, 1996.

23 Y. Xu, W. Wang and S. F. Y. Li, *Electrophoresis*, 2007, **28**, 1530–1539.

24 J. P. Hutchinson, C. Johns, M. C. Breadmore, E. F. Hilder, R. M. Guijt, C. Lennard, G. Dicinoski and P. R. Haddad, *Electrophoresis*, 2008, **29**, 4593–4602.

25 M. Ryvolová, J. Preisler, D. Brabazon and M. Macka, *Anal. Chem.*, 2010, **29**, 339–353.

26 P. Kubáň, H. T. A. Nguyen, M. Macka, P. R. Haddad and P. C. Hauser, *Electroanalysis*, 2007, **19**(19–20), 2059–2065.

27 P. Kubáň and P. C. Hauser, *Electrophoresis*, 2009, **30**, 176–188.

28 T. Mai, S. Schmid, B. Müller and P. Hauser, *Anal. Chim. Acta*, 2010, **665**, 1–6.

29 P. Kubáň, M. Reinhardt, B. Müller and P. C. Hauser, *J. Environ. Monit.*, 2004, **6**, 169–174.

30 B. Wehrli, A. Lotter, T. Schaller and M. Sturm, *Aquat. Sci.*, 1997, **59**(4), 285–294.

31 A. Lotter, M. Sturm, J. Teranes and B. Wehrli, *Aquat. Sci.*, 1997, **59**(4), 304–325.

32 N. R. Urban, C. Dinkel and B. Wehrli, *Aquat. Sci.*, 1997, **59**, 1–25.

33 W. Stumm and J. Morgan, *Aquatic Chemistry*, John Wiley and Sons, New York, 1996.

34 B. Müller, L. Bryant, A. Matzinger and A. Wüest, *Environ. Sci. Technol.*, 2012, **46**, 9964–9971.

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