

Rhizon sampling of porewaters near the sediment-water interface of aquatic systems

Jens Seeberg-Elverfeldt^{*1,2}, Michael Schlüter¹, Tomas Feseker¹, and Martin Kölling^{2,3}

¹Foundation Alfred-Wegener-Institute for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany

²DFG Research Center Ocean Margins, University of Bremen, P.O. Box 330440, 28334 Bremen, Germany

³Department of Geosciences, University of Bremen, P.O. Box 330440, 28334 Bremen, Germany

Abstract

Rhizon samplers were originally designed as micro-tensiometers for soil science to sample seepage water in the unsaturated zone. This study shows applications of Rhizons for porewater sampling from sediments in aquatic systems and presents a newly developed Rhizon in situ sampler (RISS). With the inexpensive Rhizon sampling technique, porewater profiles can be sampled with minimum disturbance of both the sediment structure and possible flow fields. Field experiments, tracer studies, and numerical modeling were combined to assess the suitability of Rhizons for porewater sampling. It is shown that the low effort and simple application makes Rhizons a powerful tool for porewater sampling and an alternative to classical methods. Our investigations show that Rhizons are well suited for sampling porewater on board a ship, in a laboratory, and also for in situ sampling. The results revealed that horizontally aligned Rhizons can sample porewater with a vertical resolution of 1 cm. Combined with an in situ benthic chamber system, the RISS allows studies of benthic fluxes and porewater profiles at the same location on the seafloor with negligible effect on the incubated sediment water interface. Results derived by porewater sampling of sediment cores from the Southern Ocean (Atlantic sector) and by in situ sampling of tidal flat sediments of the Wadden Sea (Sahlenburg/Cuxhaven, Germany) are presented.

The number of porewater studies to investigate the chemical composition of interstitial fluids and biogeochemical processes in marine and limnic sediments has increased considerably during the last several years. Objectives of these studies were investigations of particulate organic carbon degradation, biogenic silica dissolution, methane formation, and fluxes of nutrients and other dissolved components through the sediment-water inter-

face (SWI). Such data are essential for modeling porewater composition, which allows quantification of biological transport processes, kinetic rates for microbial degradation of particulate organic carbon, and dissolution rates of biogenic silica (Boudreau and Ruddick 1991; Jahnke and Jahnke 2000; Soetaert et al. 1998; Wang and Van Cappellen 1996).

Several techniques exist to sample porewater in aquatic systems. Common ex situ porewater extraction methods are squeezing sliced sediment by pressure (Emerson et al. 1980), flushing the porewater out by a gas stream (Reeburgh 1967), or separating fluids from particles by centrifugation. An ex situ and in situ used sampling method is the so-called whole core squeezing, where the porewater is expelled through sampling ports by compression of an intact sediment core in its liner (Jahnke 1988; Sayles and Dickinson 1991).

Porewater samples obtained by ex situ methods can be affected during coring and core retrieval from the seafloor by a number of factors (de Lange et al. 1992). This includes release of nutrients by cell lysis due to decompression, change of temperature, oxygen contamination during porewater extraction, or degassing of methane from gassy sediments. Furthermore, sediment compaction during coring might bias the depth profiles.

*E-mail: jseeberg@awi-bremerhaven.de; phone: +49-471-4831-1518; fax: +49-471-4831-1425

Acknowledgments

We are indebted to O. Sachs, L. Baumann, and M. Gensheimer for sampling and analyzing porewater during RV *Polarstern* cruise ANT-XXI. Thanks to Michiel Rutgers van der Loeff for critical comments. This manuscript greatly benefited from Gerald Roy Dickens and an anonymous reviewer. We greatly appreciate the technical support in the field and laboratory of U. Knauthe, S. Kurtz, L. and W. Baumann, and several other colleagues of the Alfred-Wegener-Institute. We also acknowledge the generous grant of permission by Nationalparkverwaltung Niedersächsisches Wattenmeer for conducting research on the tidal flat near Cuxhaven/Germany. This work was supported by the Deutsche Forschungsgemeinschaft as part of the DFG-Research Centre "Ocean Margins" at the University of Bremen (Germany, No. RCOM 0314) and the Helmholtz Association of National Research Centers as part of the virtual Institute Marine Technologies (MarTech) (No. awi-n15281).

To minimize sampling artifacts, in situ methods were developed. In addition to the above-mentioned whole core squeezing method, dialysis, like the so-called peeper technique (Hesslein 1976), and suction methods (Bertolin et al. 1995; Rutgers van der Loeff 1980a; Sayles et al. 1976; Watson and Frickers 1990) are applied for in situ sampling. Sampling with a dialysis technique allows a good depth resolution but requires deployment in the range of several hours to days.

Suction samplers basically consist of a vertically aligned array of sampling ports along a tube, which are covered by nylon gauze. The tube is pushed into the sediment and samples are obtained at the extraction points by weak negative pressure (Bertolin et al. 1995; Rutgers van der Loeff 1980a, 1980b).

Sediment coring and the following extraction of porewater as well as some in situ techniques are of limited use for studies on seasonal variations of porewater composition. This applies especially to studies in regions characterized by high spatial variability, due to patchy deposition of organic matter, occurrence of bacterial mats, seasonal variation in bottom water composition, or changing water level along intertidal flats. Such study areas require good reproducibility for positioning the sampling device during the entire course of study to avoid misinterpretation caused by spatial heterogeneity. Therefore, seasonal studies would benefit from sampling devices that can be in place for longer periods without major disturbance of the benthic environment and without requirement of long equilibration times, which might limit interpretation of temporal variability.

Considering studies on fluxes of dissolved components through SWI, benthic chambers are very suitable to assess biological mediate transport and to complement porewater investigations. Several benthic chamber systems were developed for in situ flux measurements (e.g., Berelson and Hammond 1986; Devol 1987; Hall et al. 1979; Jahnke and Christiansen 1989; Smith et al. 1979; Tengberg et al. 2003; Tengberg et al. 1995). Some of them allow the retrieval of the incubated sediment for ex situ studies and porewater extraction or, like the ROLAP²D (Sayles and Dickinson 1991), have equipment for in situ whole core squeezing to obtain porewater samples. From all the above-mentioned methods, only the suction samplers can be used to extract porewater several times at the same place, which is required for studies of seasonal variation, for example in coastal regions characterized by small- to medium-scale variability.

To circumvent some of the artifacts associated with ex situ porewater extraction, a sampling system based on Rhizons was developed during this study. Rhizon soil moisture samplers (Rhizon SMS) are usually used in soil and agriculture sciences. They offer the opportunity to sample fluids from unsaturated soils by a nondestructive technique (Meijboom and van Noordwijk 1991). To the best of our knowledge, there are only a few publications about sampling porewater from saturated soil or sediment with Rhizons: Alberto et al. (2000) used them for determination of dissolved methane in rice fields and Song et al. (2003) investigated ammonium fluxes in a laboratory microcosm.

This study presents the use of Rhizon SMS for sampling pore-

water from aquatic sediments. We introduce the Rhizon sampler, describe the collection procedure for porewater with Rhizons in general and how to sample porewater from sediment cores and present a newly developed Rhizon In Situ Sampler (RISS), which can be easily combined with benthic chamber systems.

Materials and procedures

Rhizon sampler—The key parts of our sampling method are Rhizons (Fig. 1A), distributed by Rhizosphere Research Products (NL-6706 Wageningen) or by Eijkelpark (NL-6987 Giesbeek). They are made of a hydrophilic porous polymer tube, with a typical pore diameter of 0.1 μm , extended with a polyvinyl chloride tube. The outer diameter of a Rhizon is 2.4 mm, and the filter section has a length of 5 or 10 cm. To support the polymer, a wire is fixed to one end of the porous polymer. The wire is made of either stainless steel, carbon fiber, or nylon, the latter in case porewater is used for metal measurements. The fluid sampled from the sediment flows into the tiny space between the porous tube and the supporting wire.

A Rhizon has several advantages compared with other sampling devices: low mechanical disturbance of the sediment due to small diameter (2.4 mm), low dead volume (0.5 mL including standard tubing), minimized sorption processes on the inert polymer, no aging during long-term deployments. The pore size (mean 0.1 μm , max. 0.2 μm) ensures the extraction of microbial- and colloidal-free, ready-to-analyze solution (Knight et al. 1998). Rhizons are several times usable, after ensuring they are intact. They can be rinsed with acid, base, and/or water.

Porewater collection—In this study, we used spring-loaded syringes, vacuum tubes, or peristaltic pumps to extract porewater from sediments through Rhizons (Fig. 1). Especially the application of an in situ peristaltic pump allows very careful extraction of porewater and ensures a well-defined drainage area around the Rhizon.

From sediments, typically 2 mL of porewater was sampled, which is sufficient for analysis of major components, such as chloride; nutrients, such as silicic acid and nitrate; and (via Head Space Technique) methane. For this purpose, standard techniques based on photometric methods, inductively coupled plasma optical emission spectroscopy (ICP-OES), and gas chromatography were applied. In this study, chloride concentrations were analyzed by Mohr-Knudsen titration, and silicic acid was determined photometrically (Grasshoff et al. 1983). The tracer sodium fluorescein (NaF), widely applied in hydrological studies to derive groundwater flow rates and patterns, was measured with a Perkin-Elmer LS-5B Luminescence Spectrometer (Excitation: 478 nm/Emission: 513 nm).

In soil, the following parameters measured from Rhizon sampled soil moisture obtain good results: pH, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe, Mn, Al, Cl^- , NO_3^- , SO_4^{2-} (Spangenberg et al. 1997), Cd, Cu, Ni, Zn (Knight et al. 1998), CH_4 (Alberto et al. 2000), and NH_4^+ (Song et al. 2003). In case of dissolved organic carbon, large complexes, or colloids, filtering effects can occur because of the small pore size (0.1 μm) (Spangenberg et al. 1997).

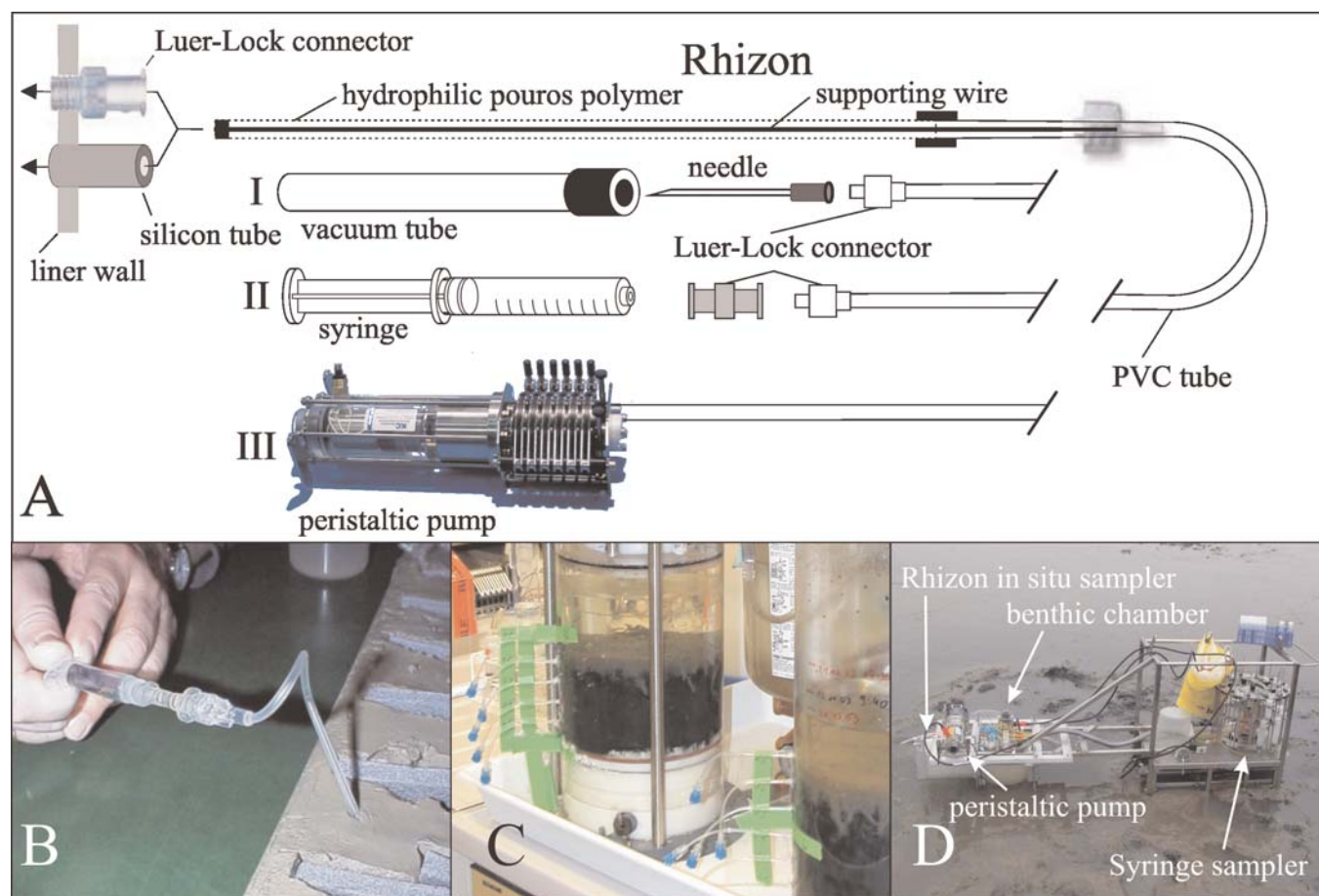


Fig. 1. (A) Schematic diagram of a Rhizon (length 5 and 10 cm, respectively, outer diameter 2.5 mm, dead volume 0.5 mL, pore size 0.1 μm) and the devices used for porewater extraction (vacuum tubes, syringes, and peristaltic pumps, I-III). Modes of application are (B) sampling of porewater with a Rhizon and a syringe from an open sediment core, (C) insertion of Rhizons through predrilled holes in a liner used for sediment sampling or for microcosm experiments, and (D) combined flux and porewater studies using a benthic chamber and an array of Rhizons inserted into the sediment. Typically, 2 mL porewater was sampled from sediments.

Sampling sediment cores—Porewater can be obtained from sediment cores by inserting the Rhizon directly into the sediment, in a gravity core that is cut into two halves or by drilling holes into the liner (Fig. 1B, C). The latter was used for porewater sampling from cores retrieved by a Multicorer (MUC) system. The acrylic liners (inner diameter 10 cm) of the MUC were prepared by drilling holes (diameter of 5.5 mm) into the wall of the liner at the sampling depths. A thread was cut into the predrilled holes, which were tightly sealed by tape or a slug prior to deployment. After retrieval of the sediment cores, the tape/slug was removed and the Rhizons were inserted horizontally into the sediment. In most cases, the Rhizon can be inserted into the sediment directly. For rather consolidated sediments, sands, or sediments with large components (e.g., stones or shells), it might be necessary to generate a small channel with a rod before inserting the Rhizon. To seal the hole-Rhizon connection, tapped-through holes equipped with female Luer-Lock connectors (1/4-inch-28

UNF outer thread) were applied. After inserting the Rhizon into the sediment, the Rhizon can be sealed by screwing together the two slightly modified Luer-Lock connectors.

Rhizon in situ sampler (RISS)—Our pre-investigations (see below) revealed that the filter section of the Rhizon should not be less than 3 cm in muddy sediments. Inserting Rhizons vertically into the sediment results in a rather coarse sample resolution. Therefore, the Rhizon are inserted horizontally into the sediment, allowing porewater retrieval along the entire length of the filter section. An array of horizontally orientated Rhizons vertically aligned by a distance of 1 cm provides a good vertical resolution of porewater profiles (Fig. 2).

The disturbance caused by inserting a sampling device should be minimized. So the basic idea of the Rhizon in situ porewater sampler is to bring Rhizons into the sediment depth where porewater samples should be obtained and then

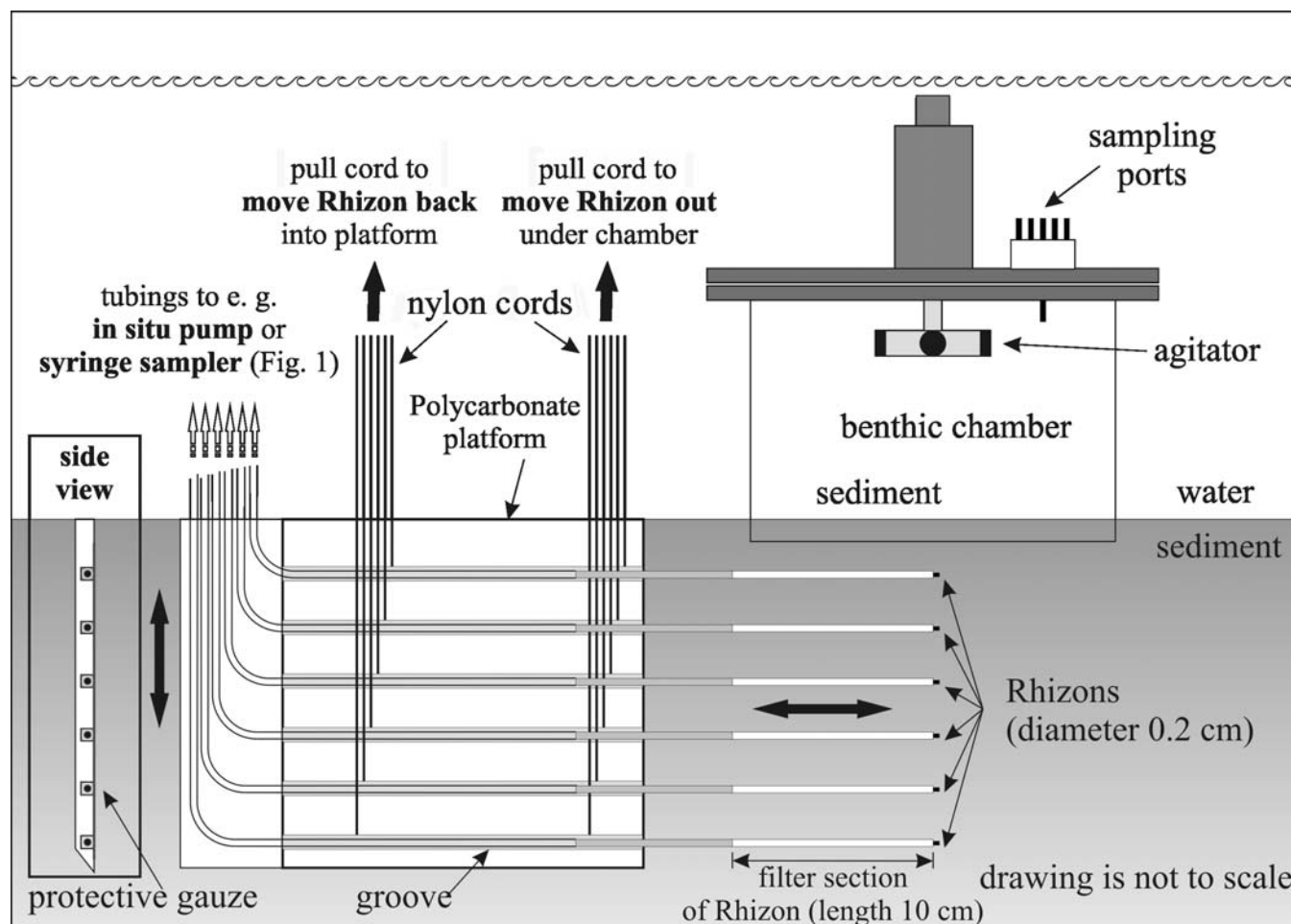


Fig. 2. Schematic diagram of a RISS combined with a benthic flux chamber. The platform made of poly carbonate (thickness 0.6 cm) can be pushed into the sediment with minimum disturbance, and the Rhizons are then moved horizontally into the sediment as well as back into the protective grooves by nylon cords. Porewater profiles can be determined underneath the benthic chamber, with negligible effect for the benthic flux measurement.

move the Rhizons sideways into the sediment. For this purpose, we built the RISS (Fig. 2), which consists of a platform made of poly carbonate (0.6 cm thickness). With a distance of 1 cm, several horizontally aligned grooves were mill-cut into the poly carbonate platform. Within the groove, the Rhizon is protected during insertion of the platform into the sediment. With two nylon cords, the Rhizon can be moved out of the groove as well as back into it and is guided to the sampling location. This ensures that the filter section of the Rhizon is several centimeters away from the platform, which can be pushed gently into the sediment. The Rhizons are connected to a sampling device (e.g., syringe sampler or peristaltic pump) by tubes.

The in situ sampler can also be combined with a benthic chamber to sample porewater during flux measurements directly underneath the incubated sediment (Fig. 2). The combination of the RISS with a benthic chamber system per-

mits simultaneous measurement of the in situ flux and determination of a porewater profile at the same location.

Assessment

Laboratory pre-investigations—To assess the vertical resolution, porewater profiles can be investigated by Rhizons, and to estimate the minimal length of the filter section suitable to extract porewater from sandy and fine-grained muddy sediments, laboratory experiments were carried out. For this purpose, a part of the filter section was covered by an impermeable tube. The Rhizon was carefully moved by a micromanipulator vertically from the top into fine-grained sediment. Using an active filter section of 1 cm length, pump rates of less than 0.1 mL min^{-1} were required to retrieve porewater. At pump rates above 0.1 mL min^{-1} , fine-grained sediments were clotted around the Rhizon. This causes self sealing and cessation of porewater extraction. Clogging runs the risk of sampled fluids that bypass the filter sec-

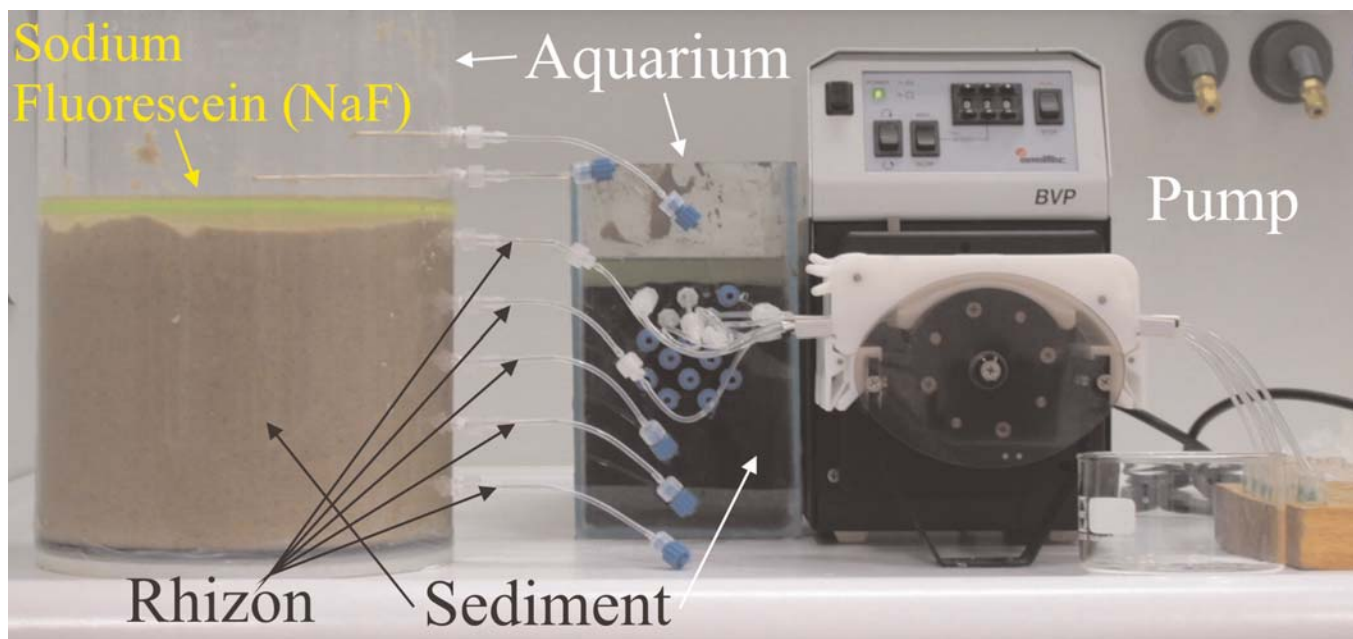


Fig. 3. Laboratory setup for sodium fluorescein (NaF) tracer tests. NaF was added to the water overlying the sediment directly before the peristaltic pump starts to sample from the Rhizons. The retrieved fluids were separated into fractions of 1 mL.

tion and enter the system at, for example, tube connectors in the water column. Furthermore, rather long sampling durations would be required owing to low pump rates.

To avoid long sampling periods without a loss of vertical resolution of porewater profiles, Rhizons (with a filter section of 5 cm or 10 cm length, respectively) were implemented horizontally in the sediment through predrilled holes of the liner used for sediment coring. Due to the increased length of the filter section, porewater extraction without cessation due to clogging was possible up to pump rates of 0.33 mL min^{-1} .

Tracer experiments—Tracer experiments were conducted to assess the interference between adjacent, horizontally aligned Rhizons. This provides information about the vertical resolution of porewater profiles, which can be sampled by Rhizons. These experiments were conducted in the laboratory and in the field. Sediments were sampled with an acrylic liner and Rhizons were installed horizontally. The NaF tracer was carefully added to the overlying water. Immediately afterward, porewater was extracted from all Rhizons inserted into the sediment by the different channels of a peristaltic pump (Fig. 3). A pump rate of 0.33 and 0.15 mL min^{-1} , respectively, was applied, and the retrieved fluids were separated into fractions of 1 mL.

The NaF concentration as function of the volume of extracted porewater for four experimental setups is shown in Fig. 4. Two experiments were conducted with sand (mean grain size: 0.33 mm): one where the Rhizon was located at 1.5 cm below SWI and the other where the Rhizons were located at 0.5 and 3.5 cm below SWI. For field experiments on a tidal flat near Sahlenburg-Cuxhaven/Germany, the RISS, an in situ peri-

staltic pump, and a benthic chamber were used (Fig. 1D, 2). The sampling positions of the Rhizons were in 0.5, 1.5, and 3.5 cm below SWI. From the same tidal flat, a sediment core was taken with an acrylic glass tube (diameter 10 cm) for a laboratory experiment. In the laboratory, porewater was sampled

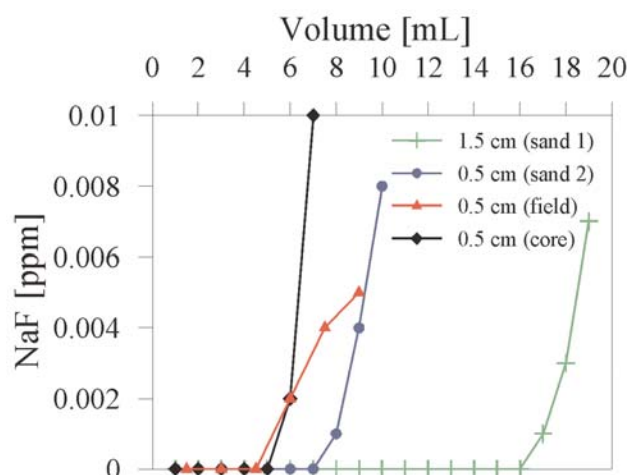


Fig. 4. The concentration of NaF as function of the extracted volume of porewater through Rhizons for 4 tracer experiments. Experiment “sand 1”: Rhizon inserted into fine-grained sand 1.5 cm below SWI. Depth of Rhizons in experiment “sand 2”: Rhizons 0.5 and 2.5 cm. The experiment “field” was conducted near Cuxhaven/Germany on a tidal flat with the RISS and a benthic chamber, Rhizon depths: 0.5, 1.5, and 3.5 cm. The experiment “core”: Rhizons were inserted 0.5, 2.5, and 4.5 cm below SWI into a multicorer tube with sediment taken from the same tidal flat above.

Table 1. Calculated radii of an influenced cylindrical area around a Rhizon (length 10 cm) for different sample volumes (Q) and porosities

| Q (mL) | Porosity | r (cm) |
|--------|------------|--------------|
| 10 | 0.5 to 0.9 | 0.80 to 0.59 |
| 8 | 0.5 to 0.9 | 0.71 to 0.53 |
| 6 | 0.5 to 0.9 | 0.62 to 0.46 |
| 4 | 0.5 to 0.9 | 0.50 to 0.38 |
| 2 | 0.5 to 0.9 | 0.36 to 0.27 |

with Rhizons from 0.5, 2.5, and 4.5 cm depth. The sediments for the field and multicorer laboratory experiment were muddy fine sand (mean grain size: 0.11 mm).

Considering a Rhizon located at 0.5 cm below the sandy SWI, NaF was detected after pumping 7 mL porewater (Fig. 4). More than 14 mL porewater was extracted from the sandy sediment before NaF was detected in fluids pumped from 1.5 cm below SWI (Fig. 4). In muddy sediments, more than 4.5 mL in the field and more than 5 mL from the MUC tube were sampled before detection of NaF in the porewater. The concentration of NaF in the porewater from all other Rhizons in the four experiments was always zero over the entire course of each experiment.

The concentrations of the 2 to 3 samples that were gathered after the first detection of NaF are three orders of magnitude lower than in the water overlying the sediment. This indicates that the percentage of erratic porewater in these 2 to 3 samples is maximum 1% to 5 %. These results show that with a vertical spacing of 1 cm between two Rhizons or a radius of 0.5 cm around a Rhizon up to 7 mL can be sampled. Based on these results, we decided for a vertical resolution of 1 cm and a volume of 2 to 3 mL, which are pumped with 0.33 mL min⁻¹ by a peristaltic pump.

Catchment area calculation—In contrast to suction samplers where porewater is retrieved from an extraction point, the drainage area of a Rhizon is distributed evenly along the entire filter section. The minimum vertical resolution by which porewater profiles can be obtained by Rhizons is equivalent to the drainage area around the filter section. A first estimate of the area of influence is given by calculating the radius of a cylinder, which represents the sediment volume from which the porewater is extracted. The radius of this influenced cylindrical volume around a Rhizon is calculated by

$$r = \sqrt{\frac{V_{\text{sample}}}{\phi \cdot \pi \cdot l}} \quad (1)$$

where V_{sample} is the volume of the sampled porewater in mL, ϕ is the porosity of the surrounding sediment, and l is the length of the filter section in cm, in this case 10 cm. Calculating r for different sample volumes (2-10 mL) and porosities (0.5-0.9), the values range between 0.8 and 0.36 cm (Table 1). The estimated radii (Table 1) are in agreement with the tracer experiments (Fig. 3), where the breakthrough of the tracer was observed for porewater volumes of more than 4 mL extracted from sandy and fine-grained sediments.

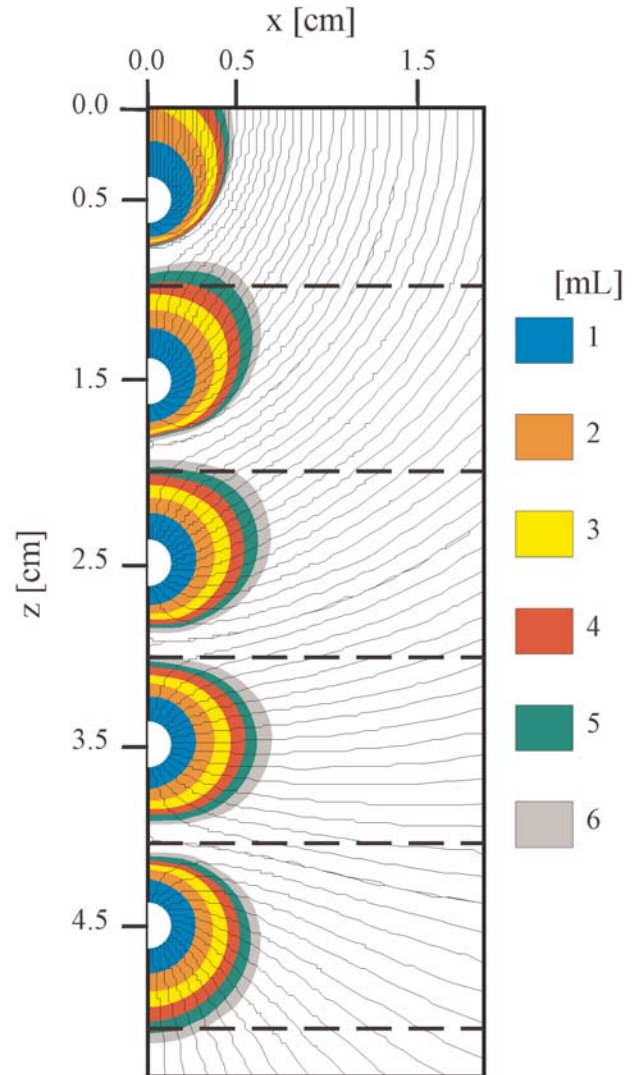


Fig. 5. Results of numerical modeling, applying MATLAB/FEMLAB software package, of the flow field and the catchment areas around Rhizons assuming Darcy flow. The entire model domain of 50 cm in width and 20 cm in depth is considered by a finite element mesh. A porosity of 0.6 and a hydraulic conductivity of 1e-3 m s⁻¹, representative for unconsolidated sand is applied. The Rhizons with a filter section of 10 cm length are located at 0.5, 1.5, 2.5, 3.5, and 4.5 cm depth at the left symmetry plane of the model. The catchment areas representative of fluid volumes of 1 to 6 mL are indicated by the color code. Even for this case of low porosity, a porewater volume of at least 2 mL can be extracted without bias between adjacent sediment layers (indicated by dashed lines) to obtain porewater profiles with 1 cm vertical resolution.

Numerical modeling—Interference of adjacent Rhizons during porewater sampling by the RISS (Fig. 2) was modeled numerically. Applying the Darcy flow, the two-dimensional flow field was computed by application of the MATLAB/FEMLAB software package. In the model, a set of five vertically aligned Rhizons is placed at the left boundary (the symmetry plane) of the model domain (Fig. 5). The entire width of the

Table 2. List of chosen sampling locations for our assessment

| Station | Date | Latitude | Longitude | Depth, m | Gear |
|------------|-----------------|-------------|------------|-----------|------|
| PS65/594-3 | 30 March 2004 | 42° 59.91'S | 4° 59.06'E | 4908.5 | MUC |
| PS65/600-2 | 3 April 2004 | 50° 00.20'S | 2° 19.63'E | 3564.4 | MUC |
| PS65/701-2 | 27 April 2004 | 59° 59.27'S | 3° 32.96'E | 5341 | MUC |
| Cuxhaven | 29 October 2004 | 53° 51.26'N | 8° 35.23'E | 0 to 1.5* | RISS |

*Field study in Wadden Sea

model domain is 50 cm and a depth of 20 cm is considered. The Rhizons are 2.5 mm in diameter and 10 cm long. The uppermost Rhizon is located 0.5 cm below the sediment surface, and the distance between two adjacent Rhizons is 1 cm. A constant hydraulic head of 1 m at the upper boundary ($z = 0$ m) represents the bottom water. Since the relative pressure and flow between the upper boundary and the Rhizons is considered, changing the hydraulic head does not affect the computed flow field. Porewater is extracted at a constant pumping rate of 2.5×10^{-3} mL s^{-1} for each Rhizon. Dividing this pumping rate by the intake area of the Rhizons yields a normal flux of approximately 3.18 mL $m^{-2} s^{-1}$ at the boundaries representing the Rhizons.

In Fig. 5, the result for homogenous sediment with porosity of 0.6 is shown. The hydraulic conductivity is set to 1×10^{-3} m s^{-1} , representative for unconsolidated sand and assumed to be isotropic. Numerical experiments showed that a near steady-state pressure distribution is reached in less than 1 min after the porewater extraction starts. Therefore, the steady-state solution is used to delineate the catchment area for fluids around the filter section of each Rhizon. The retrieved fluids are representative for a sediment layer of 1 cm thickness (indicated by dashed lines in Fig. 5), if the catchment area is restricted to this layer.

The simulation results for sampling times corresponding to a fluid extraction of 1 through 6 mL, applying a flow rate of 2.5×10^{-3} mL s^{-1} , are shown in Fig. 5. For the given hydraulic properties of the sediment, samples of up to a volume of 2 mL clearly represent sediment layers of 1 cm thickness. After approximately 20 min, which corresponds to a sample volume of 3 mL, the first bottom water has reached the uppermost Rhizon, while the samples obtained from the Rhizons below are still unbiased. For a Rhizon located in 1.5 cm depth, the 4 mL sample consists of a mix of porewater from the uppermost and the second layer.

The chosen set of hydraulic parameters, e.g., porosity and hydraulic conductivity, is considered as a conservative estimate. In the field, the porosity of marine sediments often exceeds 0.6 and the hydraulic conductivity in the horizontal direction is usually greater than in the vertical direction. Considering Rhizons aligned with a vertical spacing of 1 cm, this would even reduce the catchment area required to extract a porewater volume of 2 mL.

Our calculations did not take into account the total loss of volume during sampling. This is true for all applications but is

obvious for multicorer sampling, where the sediment is confined within a liner. For example, if samples of 6 mL at 15 Rhizons from a core (diameter: 10 cm, area: 78.5 cm²) will be taken, the volume of the core will decrease by 90 cm³. For a core that can compact, the surface will drop by 1.15 cm, and for a core that cannot compact, the bottom water flows into the upper 1.15 cm of the sediment (assuming a porosity of 0.5). A clear error is implicit in these applications, which can be minimized by keeping the volume of each sample as low as possible and by optimizing the number of Rhizons required.

Considering the tracer experiment (Fig. 4), the numerical modeling (Fig. 5) and minimizing the totally extracted volume, we applied a vertical distance of 1 cm between adjacent Rhizons and a porewater extraction of 2 mL from each Rhizon. This seems to be suitable for sampling porewater profiles of most sediments. With advanced analytical techniques (e.g., ICP-OES, inductively coupled plasma mass spectrometry [ICP-MS], flow through sensors, and auto analyzer) a porewater volume of 2 mL is sufficient for studies on nutrient cycling, mobilization of manganese, or CH₄ distribution in gassy sediments.

Porewater sampling from cores—During cruise ANT-XXI of the RV *Polarstern* to the Atlantic sector of the Southern Ocean, surface sediments were retrieved with an MUC equipped with 12 acrylic liner tubes (10 cm diameter). Porewater sampling was carried out on the MUC cores in the laboratory onboard ship. Immediately after retrieval of the MUC, the cores were transferred to and processed in the cooling lab (4°C) of the ship. At three different sites (Table 2), porewater was sampled in two different ways. At least one sediment core was segmented into slices that were squeezed to obtain porewater with a low pressure Teflon squeezer using 0.2 μ m membrane filters (Schlüter 1990). In addition, porewater was sampled from at least one parallel core using Rhizons. For this purpose, holes predrilled into the liner in a distance of 2 cm over the whole core length, were sealed with tape prior to core sampling. In the cool lab, female Luer-Lock connectors with threads (Fig. 1A) were screwed in the predrilled holes. The Rhizons were pushed through them and sealed tightly by a male Luer-Lock connector. Then porewater samples were taken with syringes. For the cores sampled with Rhizons, the overlying water was still present in the MUC tube during extraction. The comparison of porewater profiles obtained by low pressure squeezing and Rhizons are shown in Fig. 6.

The depth profiles of dissolved silica concentrations show an asymptotic decrease with depth for every core (Fig. 6). At

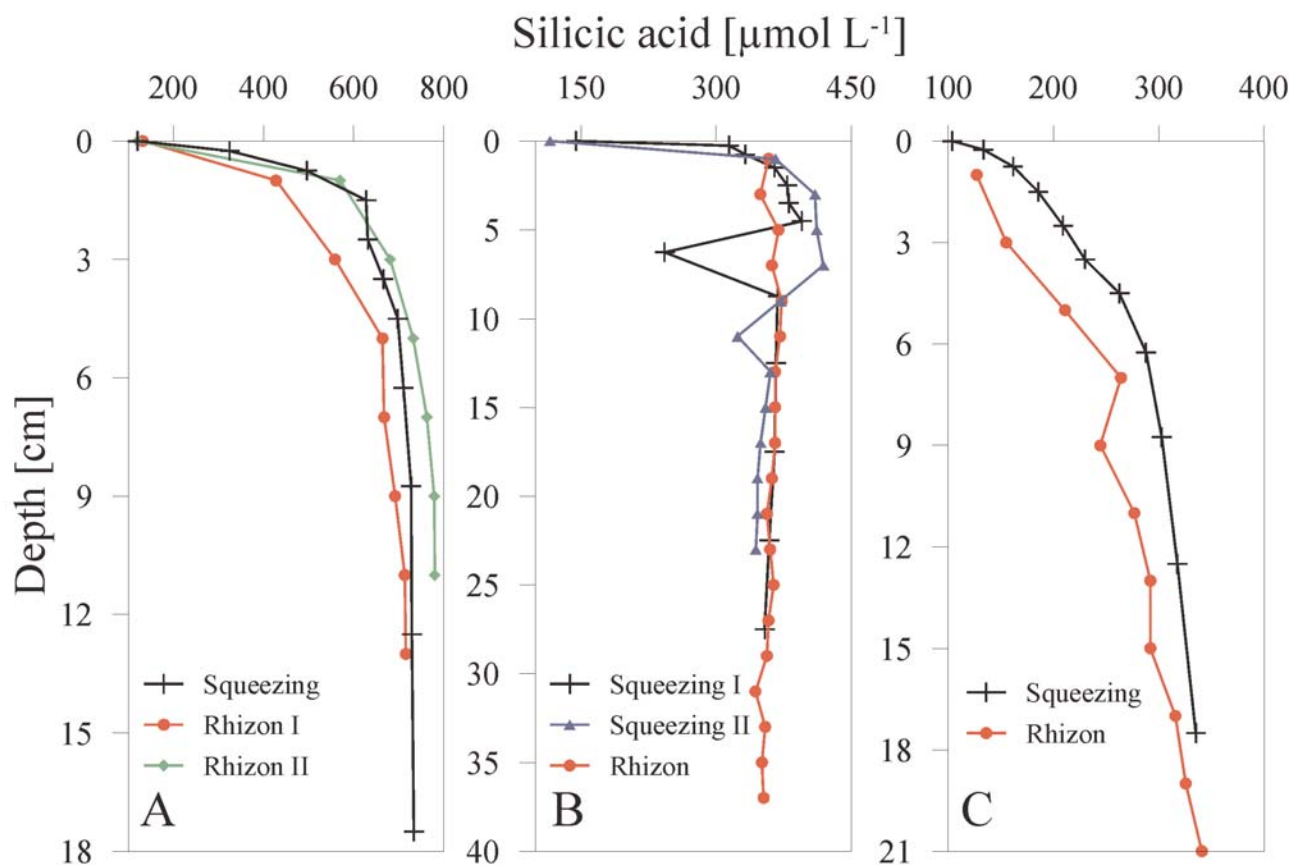


Fig. 6. Silicic acid profiles from three stations in the Atlantic sector of the Southern Ocean: (A) PS65/600-2, (B) PS65/701-2, and (C) PS65/594-3. At each site, at least two cores from the Multicorer system were processed either by low pressure squeezing or with Rhizons for porewater sampling.

site PS65/600-2, two cores of the MUC were sampled with Rhizons (Fig. 6A), where the results obtained by Rhizons correspond closely with those from the squeezed core. The data obtained by the two different sampling methods at site PS65/701-2 (Fig. 6B) correlates well; especially in the lower part they are almost identical. Only in the upper centimeters, a few data points mismatch. For station PS65/594-3 (Fig. 6C), one MUC core was sampled by squeezing, whereas another core was used for Rhizon sampling. The silicic acid concentrations in the core sampled with Rhizons are lower than from the core used for porewater squeezing. This might be caused by high bioturbation observed at this site or high spatial variations between the 12 cores retrieved by one MUC deployment. It should be mentioned that slight deviations in porewater composition derived from different cores of a Multicorer system were observed before (e.g., Ragueneau et al. 2001).

In situ chamber and porewater sampling—Combining in situ chamber incubation and porewater sampling, a RISS with a benthic chamber (Fig. 2) was deployed in muddy sediments at the station Cuxhaven in the Wadden Sea (coastal area of the North Sea; Table 2). The study area is influenced by groundwater discharge (Schlüter et al. in prep. unref.). During low

tide, the chamber and the in situ sampler (Fig. 2) were installed in the sediment for almost 4 h. The RISS was connected to an in situ peristaltic pump for sampling from the Rhizons, and a multiple syringe water sampler was connected to the benthic chamber (Fig. 1D). In the beginning and in the end of the chamber deployment, porewater samples (2 to 3 mL) were obtained from six depths (4, 5, 7, 9, 12, and 15 cm beneath SWI) applying a pump rate of 0.33 mL min⁻¹. The results of the chamber incubation showed that silicic acid and chloride behaved oppositely (Fig. 7A). Silicic acid rose by about 20 μmol L⁻¹ in the chamber, whereas at the same time, the chloride concentration declined by about 20 mmol L⁻¹. It seems that chloride and silicic acid correlate and the transport of freshwater in this region also transport high amounts of silicic acid to the surface water. This is supported by the porewater profiles underneath the chamber. The silicic acid profiles show an asymptotic increase with depth. Transport of freshwater to the SWI is indicated by chloride profiles. Both profiles of silicic acid and chloride show hardly any difference between the two sampling times (Fig. 7B), which confirms that no channeling of bottom water to the upper Rhizons occurs during porewater sampling. We considered this as a

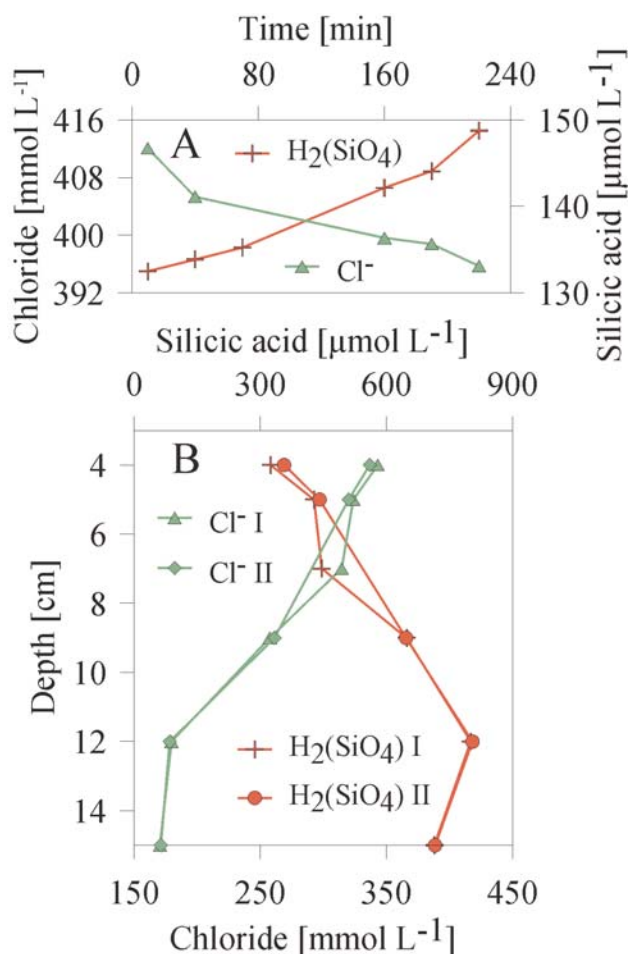


Fig. 7. (A) Change of chloride and silicic acid over time in a benthic chamber deployment on a tidal flat near Sahlenburg/Cuxhaven Germany. (B) Two silica and two chloride profiles taken with a Rhizon in situ sampler beneath the benthic chamber at the (I) beginning of chamber deployment and (II) end of chamber deployment.

first example for the suitability of simultaneous chamber and porewater sampling, which allows improved calculation of transport and reaction processes.

Discussion

In this study, we showed applications of Rhizons to sample porewater from sediments. The comparison of the composition of porewater, obtained from sediment cores by different techniques, suggests the suitability of Rhizons. This is supported by tracer experiments and numerical modeling.

Rhizons are well suited to sample porewater from cores, especially if the core material is limited and has to be shared by a scientific party. For most applications, a glove box for sampling under inert gas is not required since the core liner does not have to be opened and contact with ambient oxygen can be avoided. Thus eliminating not only the need for

glove box sampling, but also the need for cumbersome pressure filtration. The method is very rapid and the technical and labor effort is low.

The results from the RISS indicate that it is a very useful tool to sample porewater with minimum disturbance, and it is even possible to apply a RISS underneath devices used for investigating SWI (e.g., benthic chamber). Due to the horizontal distance of the filter section to the platform used to place the Rhizon in the sediment, this technique is less prone to artifacts such as channeling of bottom water along sediment corers or suction samplers. This allows long-term deployment and repetitive sampling of porewater at one site. For example, a RISS sampler was built, which can be buried in the sediment of tidal flats. The advantage of burying the sampler is that tidal currents cannot cause scour around the sampler as often happens with other samplers used so far for long-term in situ studies (Montgomery et al. 1979; Rutgers van der Loeff 1980a). So the sampler causes no local depression where organic matter can accumulate and influence the diagenetic processes heavily, which really allows the study of in situ changes of porewater constituents.

Porewater sampling in highly bioturbated sediments by horizontally aligned Rhizons might show high variability. In such settings, the sampler may not resolve gradients caused by burrows or burrowing activity and water from penetrated burrows might be withdrawn preferentially.

Rhizons provide an easy and inexpensive way to sample pore fluids from aquatic sediments, ex situ as well in situ. Only for in situ sampling in deeper water, the deployment of the Rhizons is more complex because a diver, a Lander system, or an underwater vehicle (e.g., remotely operated vehicle [ROV]) is needed.

During laboratory studies by microcosms, for example, it is often not suitable to take sediment samples during the course of the experiment. Often taps are used for sampling during a column experiment where only a local sample near the wall is obtained and not an average over a whole cross-section of a horizon or at least a certain part of it. This disadvantage can be covered by application of Rhizons.

Compared to sampling techniques like whole core squeezing (Jahnke 1988; Sayles and Dickinson 1991), the depth resolution that can be achieved by Rhizons is limited to 1 cm.

This present limitation of sampling by Rhizons has to be considered with the restriction caused by technically advanced procedures or caused by long equilibrate times.

The RISS might improve other methods when combined with benthic chamber measurements or in combination with microprofilers. The latter allows studies of the chemical composition of pore fluids with a vertical resolution of 0.025 cm within the upper few centimeters of sediments.

Comments and recommendations

Further fields of application might be achieved by combination of in situ porewater sampling with in situ measurements of, e.g., pH, O₂, and conductivity by flow through

sensors and microsensors. The advantage to retrieving pore-water fluids without contact to air might support studies on trace gases such as ^{222}Rn for studies of bioirrigation or fluid flow. Samples with high dissolved gas content (methane) can be easily pumped into gastight bags, so no out-gassing can occur during transport on-board ship. Rhizons can also be used to inject substances into the sediment. This can be used, e.g., for tracer injection under benthic chambers.

References

- Alberto, M. C. R., J. R. M. Arah, H. U. Neue, R. Wassmann, R. S. Lantin, J. B. Aduna, and K. F. Bronson. 2000. A sampling technique for the determination of dissolved methane in soil solution. *Chemosphere* 2(1):57-63.
- Berelson, W. M., and D. E. Hammond. 1986. The calibration of a new free-vehicle benthic flux chamber for use in the deep sea. *Deep-Sea Res.* 33(10):1439-1454.
- Bertolin, A., D. Rudello, and P. Ugo. 1995. A new device for in-situ pore-water sampling. *Mar. Chem.* 49(2-3):233-239.
- Boudreau, B. P., and B. R. Ruddick. 1991. On a reactive continuum representation of organic matter diagenesis. *Am. J. Sci.* 291:507-538.
- de Lange, G. J., R. E. Cranston, D. H. Hydes, and D. Boust. 1992. Extraction of pore water from marine sediments: A review of possible artifacts with pertinent examples from the North Atlantic. *Mar. Geol.* 109(1-2):53-76.
- Devol, A. H. 1987. Verification of flux measurements made with *in situ* benthic chambers. *Deep-Sea Res.* 34(5-6):1007-1026.
- Emerson, S., R. Jahnke, M. Bender, P. Froelich, G. Klinkhammer, C. Bowser, and G. Setlock. 1980. Early diagenesis in sediments from the eastern equatorial Pacific, I. Pore water nutrient and carbonate results. *Earth Planet. Sci. Lett.* 49(1):57-80.
- Grasshoff, K., M. Erhardt, and K. Kremling. 1983. *Methods of seawater analysis*, 2nd ed. Verlag Chemie.
- Hall, C. A. S., N. Tempel, and B. J. Peterson. 1979. A benthic chamber for intensely metabolic lotic systems. *Estuaries* 2(3):178-183.
- Hesslein, R. H. 1976. An in situ sampler for close interval pore water studies. *Limnol. Oceanogr.* 21(6):912-914.
- Jahnke, R. A. 1988. A simple, reliable, and inexpensive pore-water sampler. *Limnol. Oceanogr.* 33(3):483-487.
- and M. B. Christiansen. 1989. A free-vehicle benthic chamber instrument for sea floor studies. *Deep-Sea Res.* 36(4):625-637.
- and D. B. Jahnke. 2000. Rates of C, N, P and Si recycling and denitrification at the US Mid-Atlantic continental slope depocenter. *Deep-Sea Res. I* 47(8):1405-1428.
- Knight, B. P., A. M. Chaudri, S. P. McGrath, and K. E. Giller. 1998. Determination of chemical availability of cadmium and zinc in soils using inert soil moisture samplers. *Environ. Pollut.* 99(3):293-298.
- Meijboom, F., and M. van Noordwijk. 1991. Rhizon soil solution samplers as artificial roots, p. 793-795. *In* L. Kutschera, E. Huebl, E. Lichtenegger, H. Persson, and M. Sobotnik [eds.], *Root ecology and its practical application 3*. ISRR Symposium. Verein für Wurzelforschung, A-9020 Klagenfurt Austria.
- Montgomery, J. R., C. F. Zimmermann, and M. T. Price. 1979. The collection, analysis and variation of nutrients in estuarine pore water. *Estuar. Coast. Mar. Sci.* 9:203-214.
- Ragueneau, O., and others. 2001. The benthic silica cycle in the Northeast Atlantic: annual mass balance, seasonality, and importance of non-steady-state processes for the early diagenesis of biogenic opal in deep-sea sediments. *Prog. Oceanogr.* 50(1-4):171-200.
- Reeburgh, W. S. 1967. An improved interstitial water sampler. *Limnol. Oceanogr.* 12:163-165.
- Rutgers van der Loeff, M. M. 1980a. Nutrients in the interstitial waters of the southern bight of the North Sea. *Neth. J. Sea Res.* 14(2):144-171.
- . 1980b. Time variation in interstitial nutrient concentrations at an exposed subtidal station in the Dutch Wadden Sea. *Neth. J. Sea Res.* 14(2):123-143.
- Sayles, F. L., and W. H. Dickinson. 1991. The ROLAP²D lander: a benthic lander for the study of exchange across the sediment-water interface. *Deep-Sea Res.* 38(5):505-529.
- , P. C. Mangelsdorf, Jr., T. R. S. Wilson, and D. N. Hume. 1976. A sampler for the in situ collection of marine sedimentary pore waters. *Deep-Sea Res.* 23:259-264.
- Schlüter, M. 1990. Zur Frühdiagenese von organischem Kohlenstoff und Opal in Sedimenten des südlichen und östlichen Weddelmeeres. *Berichte zur Polarforschung* 73:1-156.
- Smith, J., K. L., G. A. White, and M. B. Laver. 1979. Oxygen uptake and nutrient exchange of sediments measured in situ using a free vehicle grab respirometer. *Deep-Sea Res.* 26(3):337-346.
- Soetaert, K., P. M. J. Herman, J. J. Middelburg, and C. Heip. 1998. Assessing organic matter mineralization, degradability and mixing rate in an ocean margin sediment (North-east Atlantic) by diagenetic modeling. *J. Mar. Res.* 56:519-534.
- Song, J., Y. M. Luo, Q. G. Zhao, and P. Christie. 2003. Novel use of soil moisture samplers for studies on anaerobic ammonium fluxes across lake sediment-water interfaces. *Chemosphere* 50(6):711-715.
- Spangenberg, A., G. Cecchini, and N. Lamersdorf. 1997. Analysing the performance of a micro soil solution sampling device in a laboratory examination and a field experiment. *Plant Soil* 196(1):59-70.
- Tengberg, A., E. Almroth, and P. Hall. 2003. Resuspension and its effects on organic carbon recycling and nutrient exchange in coastal sediments: in situ measurements using new experimental technology. *J. Exp. Mar. Biol. Ecol.* 285-286:119-142.
- and others. 1995. Benthic chamber and profiling landers in oceanography—A review of design, technical solutions and functioning. *Prog. Oceanogr.* 35(3):253-294.

Wang, Y., and P. Van Cappellen. 1996. A multicomponent reactive transport model of early diagenesis: Application to redox cycling in coastal marine sediments. *Geochim. Cosmochim. Acta* 60(16):2993-3014.

Watson, P. G., and T. E. Frickers. 1990. A multilevel, in situ

pore-water sampler for use in intertidal sediments and laboratory microcosms. *Limnol. Oceanogr.* 35(6):1381-1389.

Submitted 16 November 2004

Revised 13 June 2005

Accepted 12 July 2005