

In situ pore water sampling in deep intertidal flat sediments

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Abstract

In this study, we present a multilevel in situ pore water sampler that allows pore water sampling down to 5 m sediment depth. The sampler forms a crucial tool to study biogeochemical processes on different time scales in advective pore water systems. After insertion into the sediment, the sampler stays on site, allowing repetitive sampling at identical locations and depth intervals. The sampler has been successfully tested for 1 year in sandy sediments in the backbarrier tidal flats of Spiekeroog Island at the German North Sea coast. Depth profiles of redox-sensitive elements show a high depth resolution and are not affected by oxidation artifacts during extraction. Seasonal variations because of advection and changing microbial activity are apparent for some element species even at sediment depths of 5 m.

Introduction

Pore water studies are essential to understand early diagenetic exchange processes between the sediment and water column in aquatic ecosystems. In permeable systems such as tidal flats or salt-marshes, they are crucial for a better understanding of biogeochemical cycles and fluid flow. Chemical transformations in pore waters, often mediated by microbial activity and redox conditions, regulate exchange processes between the solid and dissolved phase within the sediment. For example, particulate Mn(IV) is transformed into dissolved Mn(II) under anaerobic conditions (e.g., Sundby and Silverberg 1981; Burdige 1993; Thamdrup et al. 1994), whereas dissolved Mo(VI) in sulfide-containing solutions is converted to a series of Mo(VI) thioanions ($\text{MoO}_x\text{S}_{4-x}^{2-}$, $x = 0-3$) (Erickson and Helz 2000; Vorlicek et al. 2004). In solutions containing both sulfide and S(0)-donors (i.e., polysulfides), Mo is transformed into Mo(IV) or Mo(V)₂ polysulfide/sulfide anions,

which are easily scavenged by Fe compounds and organic matter (e.g., Helz et al. 1996; Erickson and Helz 2000; Zheng et al. 2000; Vorlicek et al. 2004).

Numerous techniques have been developed to sample sediment pore water. These can be divided into ex situ and in situ methods. Ex situ methods, which are widely used at present, comprise squeezing or centrifugation of slices of sediment cores. During squeezing, pressure applied to the core forces pore water through a sampling port. In core section squeezers, sediment samples are compressed to retrieve the pore water (Reeburgh 1967; Sasseville et al. 1974; Robbins and Gustinis 1976). In whole core squeezers, an intact sediment subcore is pressurized and pore water is expelled through a single sampling port at the top or through several sampling ports located at specific depths along the core liner (Bender et al. 1987; Jahnke 1988). For the extraction of pore water from sediments by centrifugation, special centrifuge tubes are used combining the separation of particles from pore water and the filtration of the resulting fluid (Saager et al. 1990).

A number of artifacts are inherent to ex situ methods because the sediment has to be removed from the natural environment for pore water retrieval. Differences in temperature and pressure between the natural environment and the location where the cores are processed potentially affect samples (Bischoff et al. 1970), and oxygen contamination of anaerobic sections can occur even if samples are handled under an inert atmosphere.

In contrast, in situ methods such as dialysis, rhizon extraction, or suction filtration have less potential for artifacts. In

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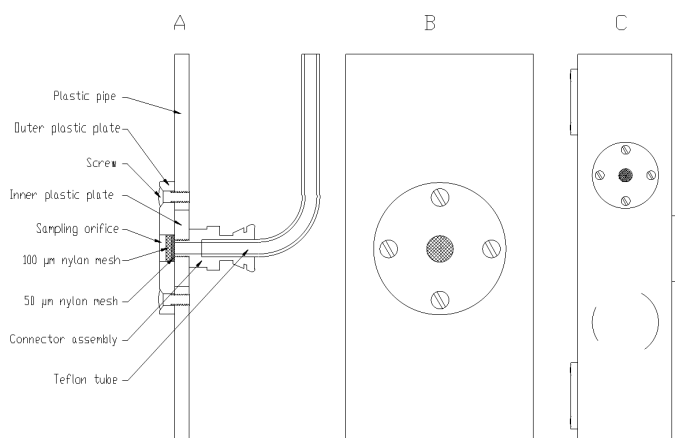


Fig. 1. In situ pore water sampler. (A) Vertical cross section of a single sampling port. (B) Close-up of one sampling port from the outside. (C) Part of the sampler showing 5 sampling ports with a distance of 5 cm between adjacent ports and a rotation angle of 90 degrees around the sampler pipe.

dialysis samplers, a volume of originally deionized water is allowed to equilibrate with sediment pore water (Hesslein 1976). Dialysis sampling permits a high spatial and temporal resolution. For example, osmosamplers were developed to autonomously collect continuous water samples in remote locations for up to several years (Jannasch et al. 2004). Recently, Seeberg-Elverfeldt et al. (2005) developed a rhizon system consisting of a hydrophilic porous polymer tube that is inserted horizontally into the sediment. Pore water flows from the sediment into the space between this porous tube and a central supporting wire, from where it can be sampled via an elastic tube.

Suction filtration forms a third in situ method employed for the extraction of pore water. Several apparatus have been developed, with the simplest a single-level sampler consisting of a modified glass pipette (Makemson 1972). Howes et al. (1985), Berg and McGlathery (2001), and Nayar et al. (2006) developed modified, more robust versions of single-level samplers. Multi-level suction filtration samplers were proposed by Sayles et al. (1973), Montgomery et al. (1981), Watson and Frickers (1990), Hursthouse et al. (1993), and Bertolin et al. (1995). In general, the latter suction samplers consist of a tube equipped with sampling ports at different depths. They are installed in the sediment, mostly by manually driving them into the sediment, and pore water is obtained by the use of suction. For the extraction of pore water, Charette and Allen (2006) presented the application of a suction filtration system that was originally designed for soil gas sampling by AMS (AMS Gas Vapor Probe System, USA). This system can be used to sample multiple depths down to 10 m and is recovered after sampling.

The AMS sampling system represents the only in situ method described in the open literature that allows sampling of pore water in sediment depths exceeding 1 m. Most in situ samplers were constructed for the extraction of pore water

from the upper decimeters of the sediment at high spatial resolution. Furthermore, most sampling devices were not designed for long-term pore water sampling at one location or, in case of osmosamplers, long-term sampling would only be possible at a few distinct depth intervals. To investigate processes occurring in advective deep pore water systems at depths down to 5 m throughout the year, we constructed a new suction sampler. In this article, we describe the new in situ, multilevel pore water sampler, which is used for sampling pore waters in porous tidal flat sediments at different time scales. We show the construction of the sampler, its insertion into the sediment, and the sampling procedure and present examples of pore water profiles obtained.

Material and procedures

In situ pore water sampler—Sampler construction. A scheme of the new in situ pore water sampler designed for retrieval of pore water from depths down to 5 m is shown in Fig. 1. Each sampler is composed of a polyethylene (PE) pipe with an outer diameter of 64 mm. Holes were drilled into the sampler walls, allowing the insertion of a connector assembly into the pipe which connects the sampling port to Teflon tubes with an inner diameter of 4 mm located inside the plastic pipe. The connector is screwed into disc-shaped PE plates, outer diameter 26 mm, which are glued to the outer sampler wall. The sampling ports are covered by 2 plies of nylon gauze, 100 and 50 µm pore size, which serve as prefilters. The gauzes are attached to the pipe by a second disc-shaped PE plate with an outer diameter of 45 mm and a central opening of 9 mm. These plates are fixed to the pipe by stainless steel screws or, in our latest design, nylon screws. But according to our own experience stainless steel screws had no contamination effect on trace metal analysis. The plates around the sampling ports were installed to prevent vertical flow along the sampler walls while extracting pore water from the sediment. The distribution of the sampling orifices forms a spiral along the pipe to minimize the effect of local sampling on adjacent ports via lateral and vertical flow. The Teflon tubes inside the sampler pipe link the sampling orifice to sampling devices at the sediment surface. At the top, the sampler is sealed with a removable cap to prevent seawater from entering the Teflon tubes.

Because of the limited space available within the plastic pipe for Teflon tubes, each in situ pore water sampling system consists of two samplers. The short sampler (1 m length) has 11 sampling ports at 0.05, 0.07, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.50, 0.75, and 1.0 m sediment depth. The long sampler (5 m length) has 10 sampling ports located at 1.0, 1.25, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 m sediment depth.

Insertion of the samplers. For the insertion of the pore water sampler into the sediment, an aluminum tube with an inner diameter of 76 mm was driven into the sediment by a vibro corer to a depth equivalent to the length of the sampler. The sediment inside the aluminum tube was removed by a sediment corer, and the pore water sampler was inserted into

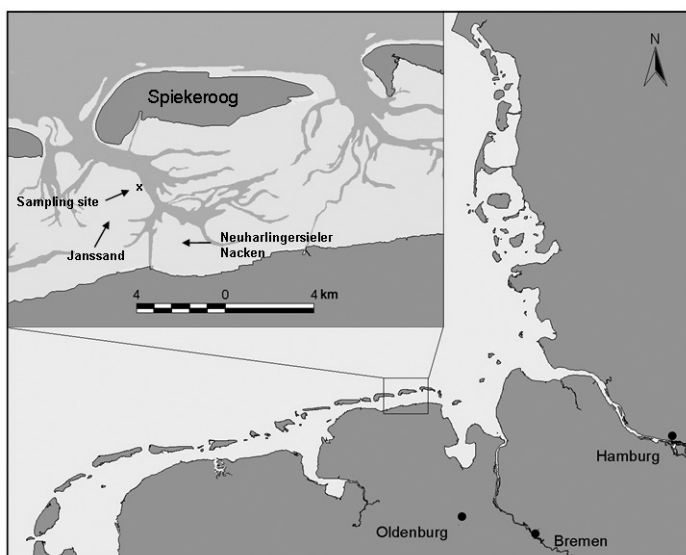


Fig. 2. Sampling area located in the tidal backbarrier area of the Island of Spiekeroog, one of the barrier islands of the NW German Wadden Sea. The cross marks the sampling location (Janssand: 53°44.183'N, 007°41.904'E).

the empty aluminum tube. Then the aluminum tube was drawn out of the sediment by a tripod while the pore water sampler remained in the sediment. To ensure that the sampler stayed positioned and was not slacked by tidal currents, the inside of the sampler pipe was filled with sand.

Pore water sampling. In sandy water-saturated sediments, the pore water sampler enables the extraction of pore fluids via 50-mL PE-syringes. The vacuum generated by a syringe is sufficient to retrieve pore water even from depths of 5 m. However, a transportable vacuum pump (VK2, UMS GmbH, München, Germany) was used where pore water was extracted from sediments with higher contents of clay and silt and from less water-saturated sediments in salt-marshes. The maximum negative pressure applied to the sampling system by the vacuum pump was 700 hPa. Depending on the sampling depth and the diameter of the Teflon tubes used, different volumes of pore water were discarded before taking the sample for analyses. For depths of up to 1 m, at least 20 mL pore water was discarded, increasing to at least 40 mL for depths of up to 3 m and 60 mL for depths exceeding 2 m. The volume necessary to discard resulted from the volume of tubing from the port to the sampling device. The volume of the tubing was 4, 25, and 65 mL for sampling depths of 0.3, 2, and 5 m, respectively. At all sampling ports, pore water samples of 100 mL were extracted for later analysis.

Sampling area—The sampling area is located in the German Wadden Sea, a large tidal flat area located between the Frisian coastline and its barrier islands in Northwest Germany. This study was conducted in the East-Frisian Wadden Sea, which is characterized by mesotidal conditions (tidal range 2–4 m). Pore water samples were taken on a sand flat (Janssand) and

on a mixed flat (Neuharlingersiel Nacken) of the backbarrier area of the Island of Spiekeroog (Fig. 2). The tidal flat is covered by 1–2 m of water during high tide and becomes exposed for approximately 4–6 h during low tide. In the sand flat area, sandy sediments predominate; however, at depths exceeding 3 m the sands are intermingled with silt-clay layers. The sand flat surface is almost horizontal, except for the margin where the sediment surface slopes toward the main tidal creek. At low tide, the distance between the sampling location and the water line is approximately 70 m, and the difference in altitude 1.5 m. As an example, results are presented (see below) from the sampling location on the sand flat which is situated near the main tidal creek (53°44,183'N; 007°41,904'E).

Sample analysis—The samples were analyzed for trace elements (Mn, Mo, U, V), SO_4^{2-} , and dissolved organic carbon (DOC). In this study, some results for selected redox-sensitive species (SO_4^{2-} , Mn, Mo, U, and V) are presented, and refer to the full set of data which will be published elsewhere.

For the analysis of dissolved metals, the samples were filtered through 0.45- μm SFCA (surfactant-free cellulose acetate) syringe filters. Subboiled HNO_3 was added to obtain a concentration of 1% (vol/vol) in all samples. Mn, Mo, U, and V were analyzed by ICP-MS (Thermo Finnigan MAT Element) in 25-fold dilution. The applied analytical procedure is similar to the method published by Rodushkin and Ruth (1997). Precision and accuracy were checked by the reference seawater standard Cass 4 (Seawater reference material for trace metals, National Research Council, Canada). A solution containing Mn was added to the reference standard to control accuracy and precision of the analyses, as Mn concentrations are much higher in the Wadden Sea pore water than in the original reference material. Precision/accuracy were 4.0%/2.2% for Mn, 5.8%/0.8% for Mo, 4.4%/–5.0% for U, and 7.3%/4.4% for V. Samples for sulfate analysis were filtered through 1.2- μm GF/C filters. Sulfate was analyzed by ion chromatography (Dionex DX 300) in a 250-fold dilution, with standard Atlantic seawater (salinity $35.0 \pm 0.2\%$; OSIL, UK) used to control the precision (3.0%) and accuracy (–5.3%) of the measurements. Samples for DOC analysis were filtered through 1.2- μm GF/C filters, and 1 mL HCl (6 M) was added to 40 mL sample. DOC was analyzed by high-temperature catalytic oxidation using a multi N/C 3000 analyzer (Analytik Jena).

Assessment

Comparison of sampling techniques—Before our newly developed samplers were installed, the in situ AMS gas vapor probe kit was used to sample pore water at a nearby location. Because of technical problems, sampling was possible down to only 2 m depth; nevertheless, the general trends with depth obtained for SO_4^{2-} , Mn, Mo, and U were similar to those using the new in situ sampler (Figure 3). Regarding Mo and U, the decrease in concentration shifted slightly toward greater depths when the AMS system was used for sampling. This is probably not due to the different sampling techniques, but to

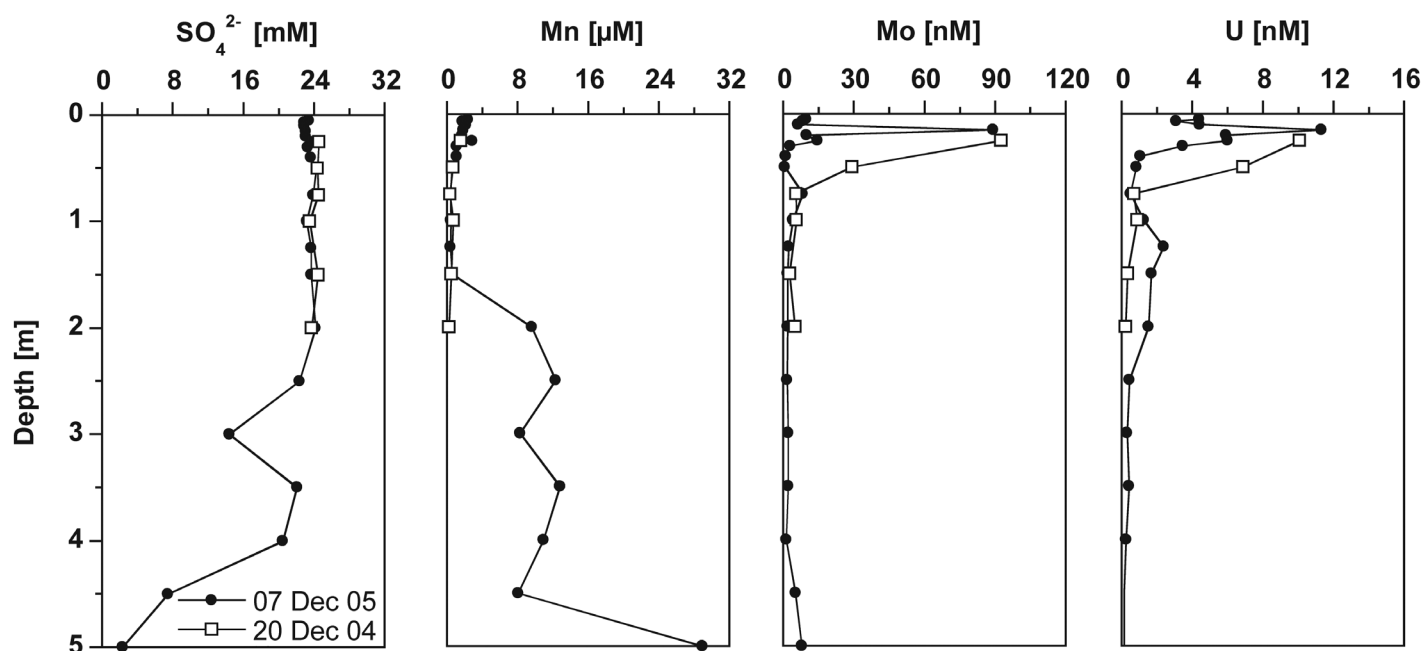


Fig. 3. Comparison of two in situ sampling techniques, our newly developed sampler (filled dots) and the AMS gas vapor probe kit (open squares). Samples taken with the AMS sampler were extracted at a location close to our permanently installed samplers.

the distance between the two sampling locations and the different sampling dates. The results for Mo and U furthermore partly differ in the upper 0.5 m of the sediment, as the resolution with depth is better using our sampling technique. Both sampling techniques seem to be suitable to obtain in situ pore water samples without altering concentrations of redox-sensitive elements by oxidation effects. Preferential flow along the samplers which could falsify the depth profiles would even be more likely to occur using the AMS system, as it has to be redeployed in the sediment for each sampling. However, preferential vertical flow does not seem to occur, as it would have an impact on Mo and U concentrations, which decrease from seawater concentrations in the near-surface layers to much lower concentrations at depths where reducing conditions prevail. Unlike the AMS system, the new sampler stays on site after its insertion into the sediment. This offers the possibility of the sediment/pore water system to equilibrate before conducting repetitive samplings at identical locations. We regard this as an important advantage of the new sampling system.

Oxidation effects during sampling—First samples were taken 2 weeks (April 2005) and 7 weeks (May 2005) after the insertion of the samplers into the sediment. At several sampling depths exceeding 0.5 m, Mo and U concentrations were higher in April than in May (Fig. 4). These changes can be ascribed to oxidation effects still seen in redox-sensitive elements like Mo and U even after 2 weeks of equilibration. The depth profiles obtained from May 2005 onward remained essentially stable at lower concentration levels in depths exceeding 0.5 m, which supports our hypothesis that oxygen introduced into the sediment during the insertion of the sampler caused the

initially high Mo and U concentrations. We therefore regard both elements as sensitive proxies for oxygen contamination. The oxidation effect seemed less pronounced for Mn and V, as the depth profiles of these elements were similar in April and May 2005. V is known to form complexes with DOC (Brumsack and Gieskes 1983, Wehrli and Stumm 1989), which are supposed to be less sensitive to oxidation. Regarding Mn, the reaction with O₂ is slow, resulting in a half-life for Mn(II) disappearance of 340 days at pH ~8 in seawater with Po₂ ~0.21 atm (Morgan 2005). The results from these first sampling sequences suggest the need for a prolonged equilibration time, which was achieved at least 7 weeks after insertion. The accurate equilibration time unfortunately could not be determined, as the oxidation artifacts in April 2005 were not evident before a comparison of data with those obtained during later sampling campaigns.

In November 2004, pore water samples were obtained in situ by using the AMS gas vapor probe kit and ex situ by centrifugation of sediment core material during a sampling carried out on a mixed tidal flat (Neuharlingersielser Nacken). As the sediment core sampling was not performed under N₂ atmosphere, pore water results show the potential oxidation effect on concentrations of redox-sensitive elements. Severe artifacts are seen when comparing the results of the two sampling techniques (Table 1). For example, the sample at 1 m sediment depth showed a Mo concentration of 18 nM using the in situ AMS technique compared with 865 nM in the centrifuged sample. Concentrations of Mo exceeding the seawater level (approximately 105 nM) by more than 8-fold represent oxidation artifacts, as the study site is known to be

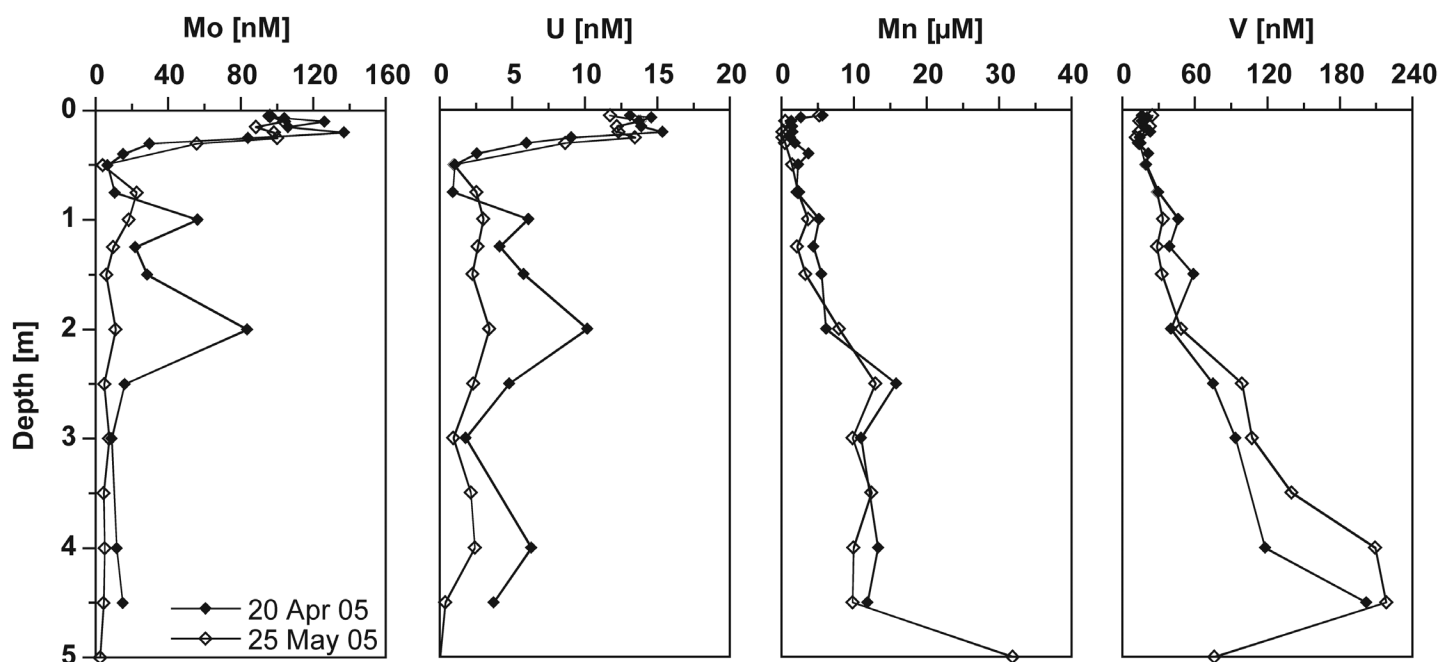


Fig. 4. Pore water depth profiles of Mn, V, Mo, and U. Samples were taken with the in situ sampler in a sandy tidal flat sediment, NW Germany, in April and May 2005. The samples in April were extracted after 2 weeks' equilibration time, whereas the samples in May were taken 7 weeks after the insertion of the samplers into the sediment.

anaerobic below a few centimeters' depth. U concentrations in centrifuged pore waters were also significantly higher than in the in situ samples. An opposing effect was seen for Mn, as the oxidation of Mn during the sampling of the core led to lower concentrations in centrifuged pore water samples than in samples taken in situ.

Sample volume—The sediment volume from which pore water is extracted by the in situ sampler at each sampling port can be calculated via the assumption that this volume is of approximately half-spherical shape around the sampling port. The radius (in cm) of the hemisphere can be described via equation (1)

$$r = \sqrt[3]{\frac{3 \cdot V_{\text{sample}}}{2 \cdot \phi \cdot \pi}} \quad (1)$$

Table 1. Comparison of the in situ AMS sampling technique and the ex situ centrifugation of sediment core slices.

Depth, m	Mn, μM		Mo, nM		U, nM	
	In situ	Ex situ	In situ	Ex situ	In situ	Ex situ
0.5	2.2	2.2	19	331	1.1	16.5
1.0	3.4	1.6	18	866	3.6	40.3
1.8	8.8	0.1	6	528	0.3	38.1

Results of the sediment core sampling show the effect of oxygen on concentrations of redox-sensitive elements. The sediment core was not treated under a nitrogen atmosphere.

where V_{sample} is the volume of pore water sampled (ml), and ϕ is the porosity of the sediment. In this study, about 120 to 160 mL of pore water was extracted at each sampling port, depending on the depth of the sampling port and the volume within the tubing necessary to be discarded. The porosity of sandy sediments in the sampling area is approximately 0.45 (B.W. Flemming, personal communication). Based on these parameters, a radius of 5.0 or 5.5 cm is derived for the resulting hemisphere, extracting 120 or 160 mL pore water, respectively. This radius is larger than the smallest distance between the sampling ports in the uppermost part of the sediment. As the rotation angle from one sampling port to the other is 90 degrees, the distance of adjacent sampling ports is 7.3 or 11.5 cm, for a difference in depth of 5 or 10 cm, respectively. Consequently, for a difference in depth of 5 cm, the hemispheres of adjacent sampling ports may partly overlap, whereas no overlap of the hemisphere will occur for differences in depth >10 cm. The sampled hemispheres therefore may have partly interfered for ports located at <0.3 m depth. To avoid mixing of pore water in the upper sections of the sediment, smaller volumes of pore water should be sampled at these depths. For a difference in depth of 5 cm between adjacent sampling ports, the maximal pore water volume sampled should be 45 mL. Because the volume of the tubing is <10 mL at depths <0.3 m, at least 35 mL of sample can be taken for analysis. The volume of pore water, which can be extracted without any overlap of the hemisphere, increases to 180 mL if the difference in distance of adjacent ports is 10 cm. At greater depths, an overlap of the hemispheres around adjacent sampling ports

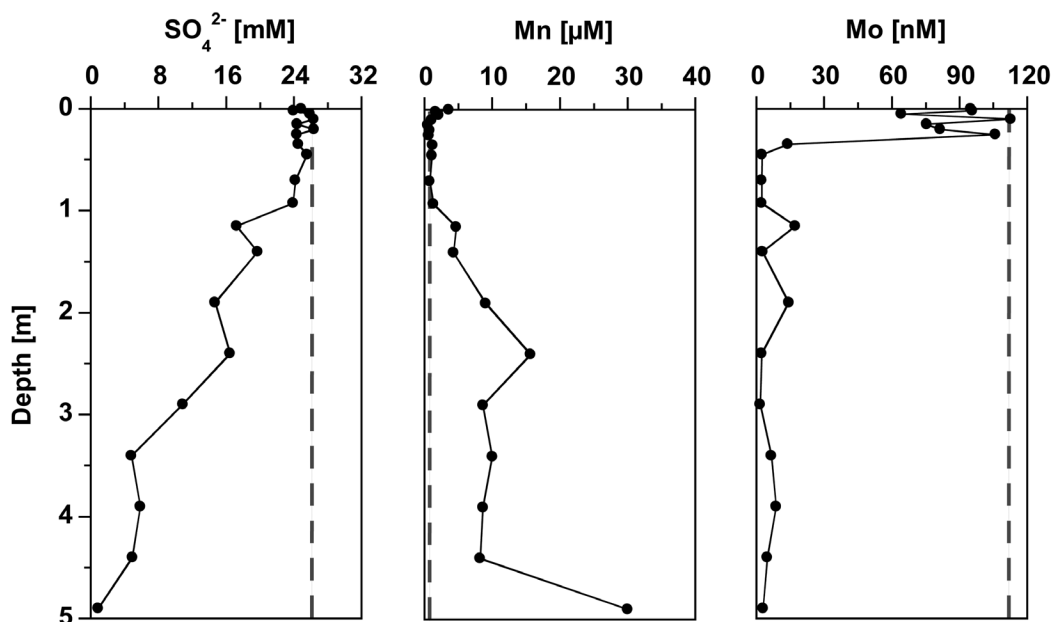


Fig. 5. Pore water depth profiles of SO_4^{2-} , Mn, and Mo. Samples taken with the in situ sampler in a sandy tidal flat sediment, NW Germany, on July 19, 2005. Dashed lines mark concentrations in the open water column of the tidal flat: SO_4^{2-} calculated for 31 psu, Mn from Dellwig et al. (2007), and Mo from O. Dellwig (unpublished data).

can generally be excluded, because the distance between the ports by far exceeds the calculated radius of the hemisphere.

We are assuming that the volume of extracted pore water forms a hemisphere. The extracted volume could also be of ellipsoidal shape, especially at higher flow velocities or during extraction of pore water from sediment layers with changing permeabilities, such as alternating sand/mud layers. If the ellipsoid extends perpendicular to the sampler, then the length and width of the ellipsoid would be even smaller than the radius calculated for a hemisphere. In this case, the overlap of pore water volumes extracted from adjacent sampling ports would be reduced. Nevertheless, the adaptation of the volume sampled to the distance between the sampling ports remains an important aspect. As the main application of our sampling device is the sampling of pore waters from greater depths, a vertical resolution of <5 cm was not considered to be essential. Well-adapted sampling devices do exist for high-resolution applications in surface sediment. A suitable vertical spacing of the sampling ports of 10 cm is recommended if large pore water volumes of ~ 100 mL are required. By reducing the extracted pore water volume to 35 mL, a vertical spacing of 5 cm is possible. Changing the construction of the sampler by mounting the sampling ports at an angle of 120 degrees around the sampler tube would allow interference-free sampling of 110 mL at 5-cm depth intervals. Preferential flow along the sampler seem unlikely to occur, as the concentrations of several redox-sensitive metal species sharply decrease from seawater-like values in the upper part of the sediment to significantly lower concentrations in deeper layers. For example, Mo concentrations close to the seawater level of 105 nM

would have been determined at depths exceeding 0.3 m if seawater percolated along the sampler walls into the sediment.

Pore water profiles—The in situ sampler was successfully used to sample pore waters in tidal flat sediments in the coastal area of NW Germany. Examples shown here represent samples from a sandy tidal flat. They highlight both the importance of obtaining in situ pore water samples of depths exceeding 1 m, as huge changes in element concentrations can be observed below this depth, and the necessity for a high density of sampling ports in the upper 100 cm of the sediment body, as many processes occur especially in this section (Huettel et al. 1998; Huettel and Rusch 2000; Rusch and Huettel 2000).

At the study site, aerobic conditions prevailed only in the upper few cm of the sediment (Billerbeck et al. 2006b). Thus, shortly below the sediment surface, other electron acceptors such as SO_4^{2-} are used for microbial organic matter degradation. Consequently, SO_4^{2-} retained seawater concentrations (26 mM at 31 psu) only in the upper 0.5 m of the profile and decreased below this depth (Fig. 5). Owing to the reducing conditions in the sediment, high concentrations of dissolved Mn(II) are apparent in the pore waters (Fig. 5). Mo concentrations showed only slight deviations from seawater concentration (110 nM) in the upper part of the sediment (Fig. 5). However, concentrations sharply decreased at depths exceeding 0.3 m, suggesting that soluble MoO_4^{2-} was converted into Mo species that were subsequently scavenged by organic matter or Fe compounds (Helz et al. 1996).

Seasonal variation—Depth profiles resulting from repetitive sampling at the same location for different seasons are shown for DOC and SO_4^{2-} (Fig. 6). The depth profile for May 2005

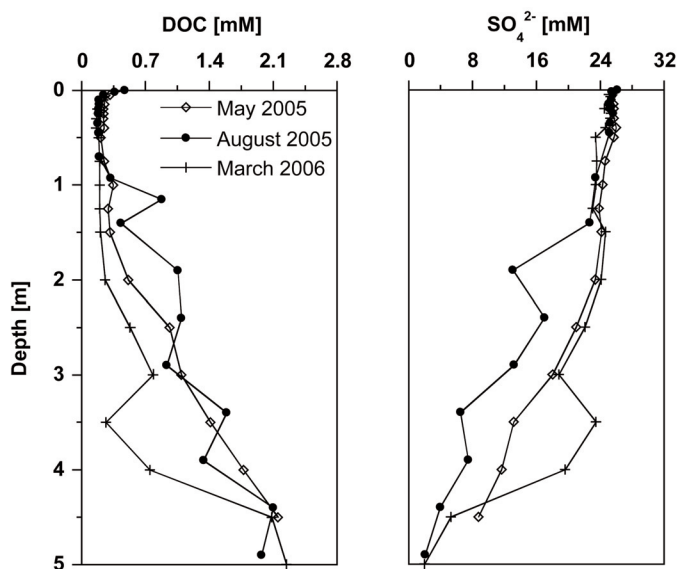


Fig. 6. Seasonal variation of the pore water depth profiles of DOC and SO_4^{2-} . Samples were taken with the in situ sampler in a sandy tidal flat sediment, NW Germany.

represents a characteristic profile for spring and early autumn, whereas the profile for August 2005 is shown as a typical example for the summer months June, July, and August. The depth profile for March 2006 forms a representative profile for samplings from November to April. During the summer months, concentrations of SO_4^{2-} decreased more strongly with depth than during the other seasons, whereas the concentrations of DOC increased in the same time period at depths of about 1 to 3 m. During autumn and winter, the contrary was seen in the deeper part of the sediment, i.e., increased concentrations of SO_4^{2-} and decreased concentrations of DOC. These changes in concentration seem to be caused by advection (Billerbeck et al. 2006a,b; Wilson and Gardener 2006) and by changing microbial activity due to variations in temperature (Vosjan 1974).

Discussion

Bufflap and Allen (1995) discuss possible reasons why pore water sampling methods may alter trace metal concentrations in pore waters. As potential sources of error, they list oxidation of anoxic pore waters and sediments, disturbance of sediment cores leading to disruptions of sediment layers, metal contamination, and temperature artifacts. In this study, pore water samples were extracted in situ and consequently temperature artifacts can be ruled out. With regard to the analysis of trace metals, the sampler was constructed avoiding metal components, and therefore the possibility of metal contamination by components of the sampler is rather unlikely. Oxidation artifacts are the source of error which are most difficult to prevent. However, the installation of the new sampling system definitely prevents any contact of the sample with oxygen.

Another potential source of error is the formation of preferential water paths along the sampler walls, hence smoothing the trends in the depth profiles. The depth profile of Mo with its sharp decrease in concentrations at about 0.3 m depth (Fig. 5), but also strong variations in the concentrations of other elements observed between adjacent sampling ports, suggest that this phenomenon can be neglected. If samples are not filtered immediately after extraction, particles present in the pore water can form another source of error, as trace metals can be adsorbed to or released by such particles. Using the proposed sampler, all samples are prefiltered during extraction. Furthermore, the samples were filtered immediately after extraction via syringe filters. In principle, it would be possible to use 0.45- μm filters at the sampling ports of the sampler to avoid an additional filtration step. However, this bears the risk of clogging sampling ports by particles.

The in situ pore water sampler described in this study offers several new possibilities to gain meaningful insights into the biogeochemical processes occurring in permeable sediments. Compared to in situ samplers currently in use, the new sampler allows the extraction of pore waters from depths of several meters. For the determination of chemical transformation processes occurring in pore waters of intertidal sediments influenced by advection, sampling of pore waters down to depths of at least several meters is essential. Depth profiles of major and trace elements demonstrate that chemical transformations do not occur only at the sediment-water interface or shortly below the sediment surface, but at greater depth as well.

The new sampler is suitable for studies of seasonal pore water composition, as samples can be taken at an identical location for extended periods of time. In permeable sediments influenced by advection, the replacement and re-equilibration of pore water is assumed to occur within some hours, allowing the determination of pore water compositions within tidal cycles. Furthermore, the permanently installed samplers allow to clearly distinguish between temporal variations and spatial heterogeneity. So far, the new samplers have been used for a period of 1 year and are still working properly. Even the necessary equilibration time of several weeks is not considered to be disadvantageous in light of its long life span. All these aspects indicate that the new in situ sampler is a powerful tool to investigate biogeochemical cycles in tidal flat sediments, salt-marsh soils, or other temporarily inundated environments.

Comments and recommendations

The sampler proved to be very suitable to sample pore water in permeable water-saturated sandy sediments. For the extraction of pore water from muddy sediments (mixed flat Neuhaaringersielener Nacken) or partly unsaturated sediments (salt-marsh sediments of Langeoog Island) the sampler is also appropriate; however, the sampling is much more time consuming. A further improvement to adapt the sampler to such environments seems possible, e.g., via the enlargement of the sampling port to facilitate the extraction of pore water by

extending the area through which suction directly acts on the sediment.

Further fields of application are the analysis of CH₄, N₂O, or H₂S contents in the pore water. However, degassing of the sample has to be taken into account once the sample is transferred into sampling containers. In general, pore waters retrieved by this sampler seem to be as suitable for the analysis of dissolved gases as sediment cores where losses of gas are also supposed to occur. For example, a first comparison of CH₄ concentrations determined in samples taken with the in situ sampler and in samples from sediment cores showed similar results.

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