

A high-resolution pore water sampler for sandy sediments

Abstract—In this paper, we present a new technique for collecting pore-water samples in coarse- to fine-grained sandy sediments. We have used the technique both for in situ sampling and for pore-water extraction from sediment cores brought back to the laboratory, in both cases with a depth resolution as fine as 1 cm. The key device is a long, thin (~2 mm) stainless steel tube with a specially designed tip that functions as a filter. Pore-water samples are collected by inserting the tube into the sediment at the desired depth and applying a light suction from a syringe connected to the tube. The sample is injected immediately into a vial through a syringe filter and stored for later analysis. The technique has some clear advantages over other methods that are used commonly in sandy sediments. In comparison with lysimeters or sippers, it gives pore-water samples with a much higher depth resolution, which often is needed to accurately estimate fluxes across the sediment-water interface or transformation rates of solutes within the sediments. In comparison with dialysis cells or peepers, the new technique gives measurements that truly represent the time of collection. This can be crucial when non-steady-state systems are studied. Furthermore, disturbance of the sediment is minimal because of the small dimension of the tube. This is especially important in vegetated sediments, in which the deployment of larger conventional samplers is likely to cause significant disturbance. Finally, sample extraction is

less laborious than other techniques, requiring only one site visit and typically <1 min of sampling time per sample. In laboratory tests using a dye tracer, we showed that pore water was drawn evenly toward the tube tip from all directions in the surrounding sediment. On the basis of these results, we provide guidelines for choosing the appropriate sampling depth intervals as a function of the sample size. Data from representative pore-water profiles are presented for PO_4^{3-} from vegetated coarse-grained carbonate sediments in the Bahamas and NH_4^+ from fine-grained unvegetated sands in a temperate coastal lagoon in Virginia.

Concentration profiles of pore water in sediments are used extensively in studies of biogeochemical processes. Vertical gradients of pore-water solutes have been used to calculate fluxes across the sediment-water interface (Glud et al. 1995; Charpy-Roubaud et al. 1996; Urban et al. 1997). Furthermore, estimates of carbon, nitrogen, and phosphorus transformations within the sediments, such as mineralization, denitrification, and benthic photosynthesis, can be obtained from the profile curvature (Revsbech et al. 1981; Dalsgaard and Revsbech 1992; Berg et al. 1998; McGlathery et al. pers. comm.). Microelectrodes (Revsbech et al. 1980) provide an

excellent tool to measure profiles on a submillimeter scale in the upper few centimeters of sediments. Pore-water profiles on a macroscale (cm) that extend deeper into sediments can be determined by a variety of techniques for pore-water extraction based on (1) suction sampling, (2) diffusion equilibration, and (3) sectioning of whole sediment cores, followed by squeezing or centrifuging.

Sandy sediments present a special challenge for obtaining such pore-water profiles. The most commonly used technique in these sediments is suction sampling with sippers (lysimeters) (Montgomery et al. 1979; Short et al. 1985; Fourqurean et al. 1992). These typically consist of a PVC pipe (outside diameter [OD] 2–5 cm) fitted with a porous (Teflon or polyethylene) collar or cap at the base which is placed at the sampling depth in the sediment. Sippers, one for each sampling depth, are usually deployed with a depth resolution of 5–10 cm, and then allowed to equilibrate for 1 d to 1 week, to avoid disturbance effects before samples (10–50 ml) are collected by vacuum. Since many pore-water constituents change significantly within the top 5 or 10 cm of the sediment, this coarse depth resolution becomes a serious limitation. Given the dimension of the sipper and the typical sample size, it is not possible to refine the depth resolution markedly. An improved depth resolution has been achieved in a more specialized suction sampler, the drive-point sampler, that was developed recently for pore-water extractions in the hyporheic zones of sand-bottom streams (Duff et al. 1998). This sampler relies on an array of six 0.32-cm stainless steel tubes, located at 2.5-cm depth intervals; pore water is extracted through 0.8-cm-long slots in the tubes by continuous suction delivered by a peristaltic pump.

In comparison with suction samplers, peepers (dialysis cells) (Hesslein 1976; Emerson et al. 1984; Brandl and Hanselmann 1991; Urban et al. 1997) and the gel sampler (Krom et al. 1994; Mortimer et al. 1999) both rely on diffusion equilibration to extract sediment pore water and can give a significantly higher depth resolution of a few mm (gel sampler) to 1 cm (peeper). The peeper (typically 30–60 cm long with a cross section of 8×2 cm) consists of an array of cells filled with deionized water or filtered seawater and covered by a dialysis or similar membrane. The water in each cell equilibrates with the surrounding pore water when embedded in the sediment for a period of 1 week to 1 month. The gel sampler ($50 \times 4 \times 0.7$ cm) relies on diffusion of solutes into a thin layer of polyacrylamide gel over a period of hours to 1 d, after which the gel is sectioned into slices and allowed to back-equilibrate in distilled-deionized water. Both devices give samples that reflect average concentrations over the time the sampler has equilibrated in the sediment. Given the time requirement for this equilibration, it can be difficult or impossible in dynamic systems to relate pore-water concentrations to water-column measurements at specific points in time or to capture dynamic events (e.g., diurnal cycles) influencing pore-water constituents. The high permeability of sandy sediments also represents a potential problem with peeper measurements, as emphasized in a recent study by Grigg et al. (1999). They showed that density differences between the pore water and the cell fluid in peepers can induce a convective motion in the sediment that may give misrepresentative sample concentrations. This phenom-

enon is obviously most pronounced in sandy sediments and must also be of concern for the gel sampler, although that device was not included in their study.

Sectioning of whole sediment cores and pore-water extraction by centrifugation or squeezing (Reeburgh 1967; Emerson 1976; Thamdrup et al. 1994) is a widely used technique in muddy sediments, giving a depth resolution as fine as a few mm (Rysgaard et al. 1998). It is, however, difficult or impossible to use in coarser-grained sandy sediments, because the pore water drains off almost instantly when the sediment cores are sectioned. Another potential problem for all sediment types is that sediment squeezing and centrifugation can result in artificially high concentrations of both organic and inorganic nutrients because of bacterial cell or plant root damage (Howes et al. 1985; Henrichs and Farrington 1987).

In this note, we present a new technique for collecting pore-water samples in coarse- to fine-grained sandy sediments. In previous studies, we have used sippers extensively for pore-water extractions from both vegetated and unvegetated carbonate sediments (McGlathery et al. 1992, pers. comm; Jensen et al. 1998). Part of our motivation for developing this new technique was the need to obtain pore-water samples at a much finer depth resolution, to accurately estimate fluxes across the sediment-water interface and transformation rates of solutes within the sediments. It also was important to minimize the disturbance associated with larger conventional samplers, especially since some of our work involves vegetated sediments. Finally, since we wanted to capture possible diurnal variations of pore-water concentrations in these sediments, we needed a technique that would give measurements that would be representative of a specific point in time. The key device in our technique is a long, thin stainless steel tube (referred to below as the probe) with a specially designed tip that functions as a filter.

The probe and accessory devices—The probe itself is constructed from a 45-cm-long stainless steel tube (OD 2.4 mm, inside diameter [ID] 1.8 mm). One end of the tube is closed by silver soldering and is rounded at the tip (Fig. 1). Four holes (diameter [D] 0.38 mm) are drilled perpendicular to the tube 2 mm above the rounded tip. The probe can be manufactured easily in a metal workshop with use of standard tools and machinery. A small piece of Tygon tubing (~1 cm long) is mounted on the probe and used for depth adjustments (Fig. 1). This piece of tubing fits the probe tightly but can be moved easily with a firm push. When we initially developed the technique, we worked with more sophisticated designs for depth adjustments. However, after several tests, including in situ and laboratory measurements, we found that this simple solution works well and also provides for faster adjustments. A longer piece of Tygon tubing (ID ~1.8 mm) is connected to the open end of the probe and serves, in addition to the probe volume, as a reservoir for the sample. The length of the tube is adjusted so that the volume of the probe and tube is ~5% larger than the desired sample size. Since our sample size in most situations varies from 1.5–3.0 ml, we have used tube lengths ranging from 20–80 cm. The probe and tube lengths both can be adjusted to accommodate larger sample sizes or deeper sediment pro-

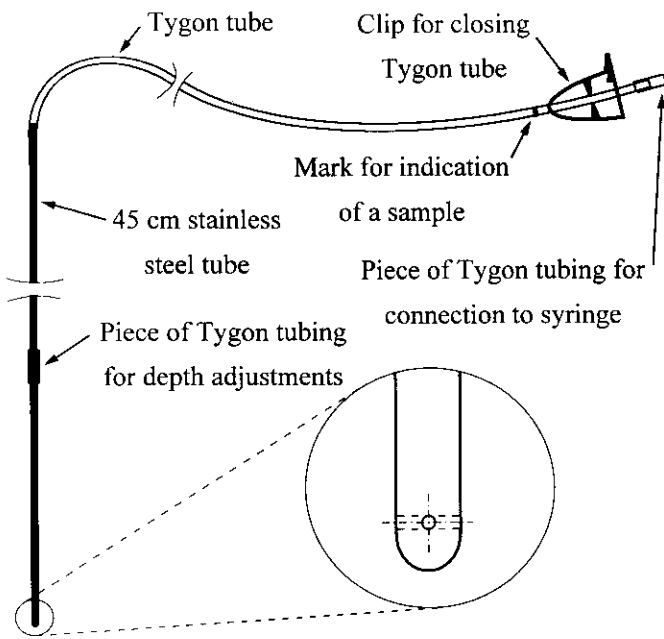


Fig. 1. Pore-water sampler.

files. A plastic clip is attached to the long Tygon tube (Fig. 1), and, when in a closed position, it prevents any spill of sampled pore water when the probe is retrieved. A piece of Tygon tubing (~2 cm long) that fits the long tube tightly serves as a connection to a syringe. Finally, a mark on the long tube is used as an indicator as to when a full sample is collected.

As a guide for the probe when it is inserted into the sediment, and also to ensure precise depth adjustments during in situ sampling, we use a device made of an acrylic plate

(2.5 × 17 × 22 cm) that is elevated from the sediment surface by four stainless steel "legs" attached to the corners of the plate (Fig. 2a). Each leg has the shape of a disk (D 5.0 cm, 2.0 cm high) with a spike (5.0 cm long, D 1.0 cm at the base) in the center of one of the plane disk surfaces. The legs are attached to the plate with countersunk nylon screws (D 8 mm). Six holes (D 2.41 mm) are distributed evenly on a circle (D 4.7 cm) centered in the middle of the acrylic plate. During the sampling process, these holes serve as a guide for the probe, and the upper surface of the plate is used as a fixed level for depth adjustments.

When the probe is used for pore-water sampling in sediment cores brought back to the laboratory, we use a similar device (Fig. 2b), which consists of two acrylic disks connected by a 6.5-cm-long cylindrical (D 2.5 cm) acrylic rod. The device is designed to be used with sediment cores collected in acrylic tubes (ID 8.2 cm) in which the sediment-water interface is located at least 8 cm below the top of the tube. The upper disk (2.5 cm thick) has an indentation 1.9 cm from the surface that functions as a lid that clips onto the top of the acrylic tube. The top part of the disk has the same diameter as the tube (OD 8.8 cm), and the lower part, as well as the lower disk (0.6 cm thick), has a diameter of 8.19 cm, to give a precise but not tight fit into the tube. Each of the disks has six holes (D 2.41 mm) evenly distributed on a circle (D 4.7 cm) centered in the middle of the disk. In addition, the lower disk has six larger holes (D 1.2 cm), which allow the water to flow unhindered into the space between the two disks when the device is immersed into the water above the sediment core. These six holes are also evenly distributed on a centered circle (D 6.2 cm). The two disks are attached to the rod by countersunk nylon screws (D 8 mm) and are positioned such that the six 2.41-mm holes in each disk are in line. During the sampling process, when the device is mounted on top of the acrylic tube, the six

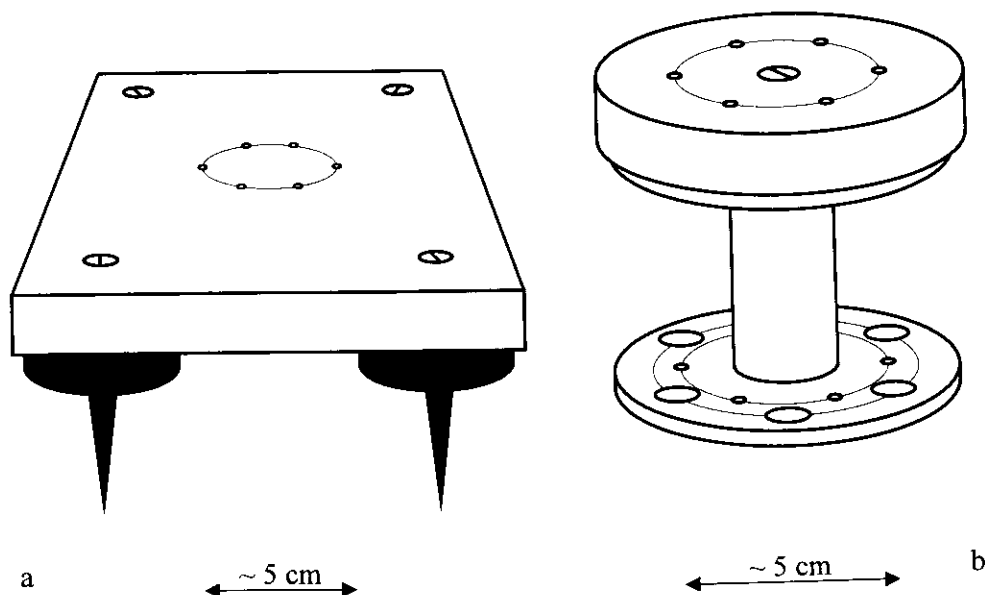


Fig. 2. Accessory devices (a) for in situ sampling and (b) for sampling in sediment cores. The array of holes in both devices serves as a guide for the probe when inserted in the sediment.

holes in each of the two disks serve as a guide for the probe, and the upper surface of the device is used as a level for depth adjustments.

Protocol for in situ sampling—Before a sampling series is started, the guiding plate (Fig. 2a) is placed on top of the sediment, and the spikes are carefully pressed down into the sediment until the bottom of the stainless steel disks is even with the sediment surface. At the beginning of a sampling sequence, the piece of Tygon tubing on the probe (Fig. 1) used for depth adjustments is positioned such that the sampling holes in the probe will be at the correct depth when the probe is inserted into the guiding plate. The probe and the long attached Tygon tube are filled with air or an inert gas (i.e., N₂ or argon). A syringe, also filled with air or inert gas, is connected to the other end of the tube, and the clip is in the open position, so that there is free passage from the syringe to the tip of the probe. The inert gas is used if the pore-water sample is to be analyzed for any solute that might react with O₂. As the sampling device is brought down to the sediment surface, the probe partially fills with water when the air or gas volume in the probe, tube, and syringe is compressed because of an increasing hydrostatic pressure. This water volume is expelled by pushing the syringe piston to the bottom position. The probe is now inserted into the sediment through one of the guiding holes in the plate until the lower edge of the piece of tubing for depth adjustments is level with the upper surface of the plate. By pulling back the syringe piston in a slow steady movement, pore water is drawn into the probe and then into the attached Tygon tube. It is easy to see the front of a sample through the clear tube as it fills, and when the front reaches the indication mark on the tube (Fig. 1), the clip is immediately closed and the probe retrieved carefully from the sediment. Usually the first part of a sample (<1 cm in the tube) contains a cloud of small particles that has passed through the sampling holes in the probe, and the rest of the sample consists of clear pore water. We have experienced that a sampling rate of 0.02–0.1 ml s⁻¹ (see discussion below) generally will produce samples containing few particles that can be removed easily by filtering. Above the water, the sample is drawn into the syringe and the sample is immediately filtered through a syringe filter (e.g., a Gelman Supor 0.45 μm) directly into a vacutainer. Depending on the depth resolution used and also on the sample size (see discussion below), the next sample is collected through the neighboring guiding hole in the plate. In this way, the same guiding hole is only used once for every sixth sample collected, which effectively minimizes interference between the samples. This interference is discussed in detail below.

As the probe is inserted into the sediment, the air or gas volume in the probe and tube compresses further because of an increase in hydrostatic pressure, and a small amount of pore water enters the probe. This amount of pore water can be estimated from Boyle-Mariotte's law, which states that $V_{sd}p_{ss} = V_{sd}p_{sd}$ where V is the air or gas volume in the probe and tube, p is the pressure acting on this volume, and the indices "ss" and "sd" refer to the sediment surface and the sampling depth, respectively. When the unit atmosphere is used for p , the two pressures can be expressed as $p_{ss} = 1 +$

$0.1H$ and $p_{sd} = 1 + 0.1H + 0.1h$, where H is the water depth and h is the sampling depth below the sediment surface, both in units of meters. Insertion of these expressions into Boyle-Mariotte's law gives the result that the relative compression of the air or gas volume in the probe and tube is $V_{sd}/V_{ss} = (1 + 0.1H)/(1 + 0.1H + 0.1h)$. Clearly, this compression is most pronounced in shallow waters (small values of H). In the worst-case scenario ($H = 0$), and if the probe is inserted to a depth of, for example, 0.4 m below the sediment surface, the relative compression equals 0.96. This means that 4% of the probe and tube volume gradually fills with pore water as the probe tip is moved from the sediment surface to the sampling depth. Although 4% of a sample volume is a relatively small fraction, the artifact can be significantly larger in terms of solute concentrations in cases in which the pore water above the actual sampling depth contains higher concentration levels. This artifact can be avoided by expelling the first part of a collected sample before the remaining part is drawn into the syringe.

When sampling at a water depth at which diving is needed, we use more than one sampling device (probe, tube, and syringe), and the preparation of each device (height adjustment, filling the probe, tube, and syringe with air or inert gas) is done ahead of time. This makes it possible to collect all samples in one dive. The samples are left in the probes and attached Tygon tubes until all samples are collected, and then they are brought back on the surface, where they are filtered as described above.

Protocol for sampling in cores—The procedure for sampling in sediment cores is almost identical to the one for in situ measurements. After the guide (Fig. 2b) is carefully immersed into the acrylic tube containing the sediment core, the previously described sampling protocol is followed. Only one probe is used, and each sample is filtered immediately after collection. Since a sediment core only contains a finite amount of pore water, there is a constraint on how much pore water can be collected. This affects the size of each sample in combination with the depth resolution that can be used. This is discussed in detail below.

Tracer tests—When we developed the technique initially, we were concerned that an artifact could arise if the pore water did not move evenly toward the sampling holes from all directions. Since there is more resistance to water movement in the sediment than in the water column, such an unevenly distributed flow pattern would be expected to be most pronounced when sampling near the sediment-water interface. Proportionally more pore water could be sampled from the sediment above the holes in the probe. To investigate the flow pattern during sampling, we performed a series of tracer tests in the laboratory.

The dye tracer Rhodamine WT was added to the water column in two fine-grained, sandy, and undisturbed sediment cores that were collected in a shallow coastal lagoon on the eastern shore of Virginia at the Virginia Coast Reserve Long Term Ecological Research Site (VCR LTER). Immediately after the tracer was added, six samples were collected at a sampling rate of ~0.02 ml s⁻¹ in each core, 1 cm below the sediment-water interface. Different sample sizes were used

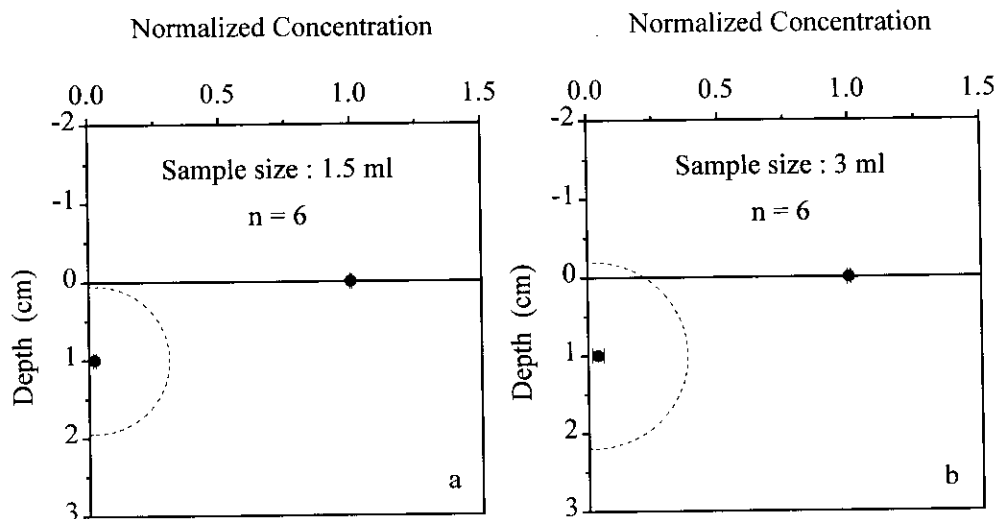


Fig. 3. Normalized concentrations from tracer tests where samples of (a) 1.5 ml and (b) 3 ml were collected 1 cm below the sediment surface (error bars represent SEs). The dashed lines represent the spherical volumes of pore water collected under the assumption that the pore water moved evenly toward the sampling holes in the probe from all directions.

for the two cores: 1.5 and 3.0 ml. Additional samples were collected in the overlying water column. The Rhodamine WT concentration in standard samples ($n = 4$) containing 100%, 25%, 5%, 2.5%, 1.25%, and 0% of the expected concentration in the water column were measured on a spectrophotometer and used to produce a standard curve ($R^2 = 0.9998$). The means of the measured pore-water concentrations, normalized to the respective water column concentrations, are shown in Fig. 3. For both sample sizes, the mean concentrations were small, 0.022 ± 0.005 for the 1.5-ml samples and 0.039 ± 0.021 for the 3.0-ml samples (error estimates represent standard errors).

In order to estimate the spatial extent of a sample collected, the porosity was determined at 0–1 and 1–2 cm depth intervals as weight loss after drying (60°C) in three additional cores. Since there was no variation between the porosities for the two depth intervals, the mean porosity was calculated as 0.427 ± 0.007 (vol/vol; error estimates represent standard errors; $n = 6$). Under the assumption that the pore water moved from all directions toward the sampling holes in an evenly distributed flow pattern, the sample would be collected from within a sphere centered at the sampling holes. A good approximation for the volume of this sphere that also takes into account the volume of the probe itself is $V_{\text{sample}} = \varphi(4/3)\pi r^3 - \varphi(1/4)\pi D^2 r$, where r is the radius of the sphere, D is the diameter of the probe, and φ is the porosity. Knowing the two sample sizes (1.5 and 3.0 ml), the radii of the two spheres are calculated to be 0.95 and 1.19 cm. These radii are indicated on Fig. 3, and their extent suggests that no Rhodamine WT should be expected in the 1.5-ml samples, whereas a small amount should be found in the 3.0-ml samples. A simple estimate for the 3.0-ml samples based on the volume fractions of the sphere above and below the sediment surface gives a normalized mixing concentration of ~ 0.04 . These results, in conjunction with the actual measured concentrations of 0.022 ± 0.005 and 0.039 ± 0.021 in the two cores, show that an evenly distributed flow

pattern was present in the sediment during sampling. In other words, the samples collected give a true representation of pore water at the depths of the sampling holes. It should be noted that we have obtained similar results in tracer tests performed in cores with more coarse tropical sands from Bermuda.

When sampling near the sediment-water interface (~ 1 –5 cm), we consider it essential to use relatively slow sampling rates (~ 0.02 ml s^{-1}) to maintain an evenly distributed flow pattern, whereas faster rates can be used deeper in the sediment (up to ~ 0.1 ml s^{-1}).

Sample sizes and depth intervals—The pore-water movements in the sediment that inevitably are induced during sampling put some limitations on the combinations of sample sizes and depth resolutions that can be used. We have estimated how much the pore water moves at different distances from the sampling holes in the probe depending on the volume sampled. We use these estimates as guidelines for choosing appropriate sample sizes and depth intervals.

The pore-water movement (Δr) is defined as the distance that an infinitely small volume of water located at a given distance (r) from the sampling holes moves when a sample is collected. Under the assumption that the pore water moves evenly toward the sampling holes from all directions, a volume of pore-water equivalent to the sample volume is contained in a spherical shell with the thickness Δr , which can be approximated as $V_{\text{sample}} = \varphi(4/3)\pi r^3 - \varphi(4/3)\pi(r - \Delta r)^3$. For a porosity of 0.5 and for sample sizes of 1.5, 3, and 4.5 ml, Δr is shown as a function of r in Fig. 4. The horizontal distance between two neighboring guiding holes in the accessory devices (Fig. 2) is 2.4 cm, and if we use a depth interval of 1 cm, the distance between two sampling points is 2.6 cm. If, for example, 1.5 ml is collected, Fig. 4 shows that at a distance of 2.6 cm from the sampling holes, the pore water moves < 0.04 cm, indicating that there is insignificant interference between the samples collected.

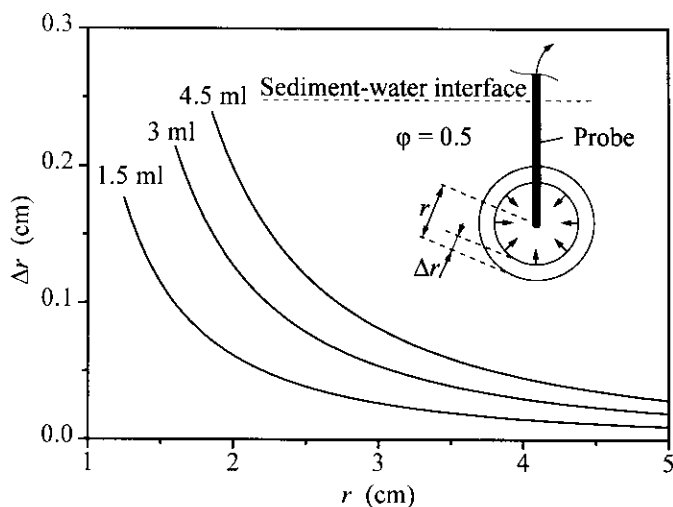


Fig. 4. Pore-water movement (Δr) at different sample sizes as a function of the distance (r) from the sampling holes in the probe. The Δr values are calculated with the assumption that the pore water moves evenly toward the sampling holes from all directions.

In order to keep the movement of the pore water at a minimum during a sampling series, we generally chose our sample sizes to be as small as possible (1.5–3 ml). This is especially important when sampling in a sediment core, since a secondary vertical pore-water movement, in addition to the movement toward the sampling holes, is induced because of the limited volume of water in the sediment core. Since the core has a fixed bottom, this movement is directed downward and it occurs almost exclusively above the actual sampling depth in sediment layers from which samples already have been collected. The vertical movement is relatively small for the sample sizes we normally use and will not lead to any serious artifacts. If, for example, 1.5-ml samples are collected in a sediment with a porosity of 0.5, this movement is <0.06 cm per sample (sediment core diameter 8.2 cm).

In situ sampling—As an example of an application of our technique where larger sampling devices are difficult to deploy without significant disturbance to the sediment, we present some *in situ* measurements from a dense seagrass bed in coarse-grained tropical carbonate sediments in the Bahamas. Triplicate samples of 3 ml were collected at 3-cm depth intervals in the top 39 cm of the sediment, following the sampling protocol described above. The filtered samples (Gelman Supor 0.45- μm syringe filters) were frozen for later analysis of PO_4^{3-} after reaction with molybdate-antimony (Stainton et al. 1974) on a Perstorp Flowsolution III autoanalyzer. The mean concentration profile (Fig. 5; error estimates represent standard errors) clearly shows a subsurface concentration maximum and then a decrease with depth. The same general pattern also has been found in other studies of tropical vegetated sediments on a coarser depth scale (McGlathery et al. 1992, pers. comm.; Erfteimeijer and Middelburg 1993; Jensen et al. 1998). The shape of the profile is the net result of sources of PO_4^{3-} (mainly decomposition of organic matter and sediment dissolution), sinks of PO_4^{3-}

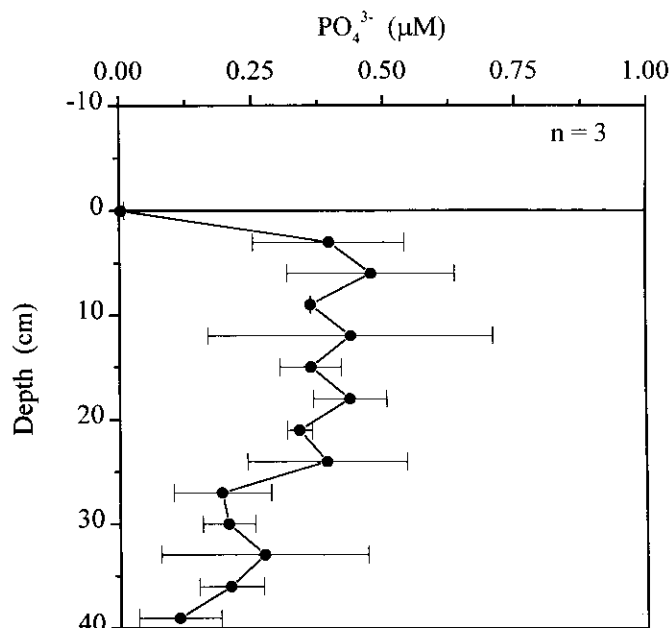


Fig. 5. Pore-water profile (*in situ* extractions) in a dense and heavily rooted seagrass bed in a tropical coarse-grained sandy sediment. The large error bars (standard errors) reflect a highly heterogeneous sediment with microenvironments of high release or uptake of PO_4^{3-} .

(primarily uptake by seagrasses and sediment immobilization), and a loss of PO_4^{3-} (presumably dominated by molecular diffusion) to the water column and, to some extent, to the sediment below our measurements. Under the assumption that the profile represents a steady-state situation, the sources of PO_4^{3-} are larger than the sinks in the upper part of the sediment, causing the build-up of PO_4^{3-} . Deeper in the sediment the sinks of PO_4^{3-} are larger than the sources, causing the concentration to decrease with depth. The relatively large error bars reflect a highly heterogeneous sediment with microenvironments of high release or uptake of PO_4^{3-} . The diffusive flux out of the sediment (calculated as $-\phi D_s dC/dx$, where D_s is the sediment diffusivity and dC/dx the concentration gradient approximated from the two upper measurements) yields $0.3 \mu\text{mol m}^{-2} \text{d}^{-1}$ (ϕ estimated as 0.7 and D_s as $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). On the basis of the steep gradient at the sediment-water interface (Fig. 5), it is obvious that a markedly smaller flux would be calculated if the profile was determined with a coarser depth resolution. Likewise, we cannot rule out that a resolution finer than the 3 cm we used would give a larger flux. This suggests that a depth resolution of 1 cm, for example, should be used for such pore-water extractions, at least in the upper part of the sediment.

Laboratory sampling—Three sediment cores were collected in a fine-grained, sandy and unvegetated sediment in a shallow lagoon at the VCR-LTER site on the eastern shore of Virginia. The cores were immediately brought back to the laboratory, where the pore-water sampling was done according to the protocol described above. In each core, one 1.5-

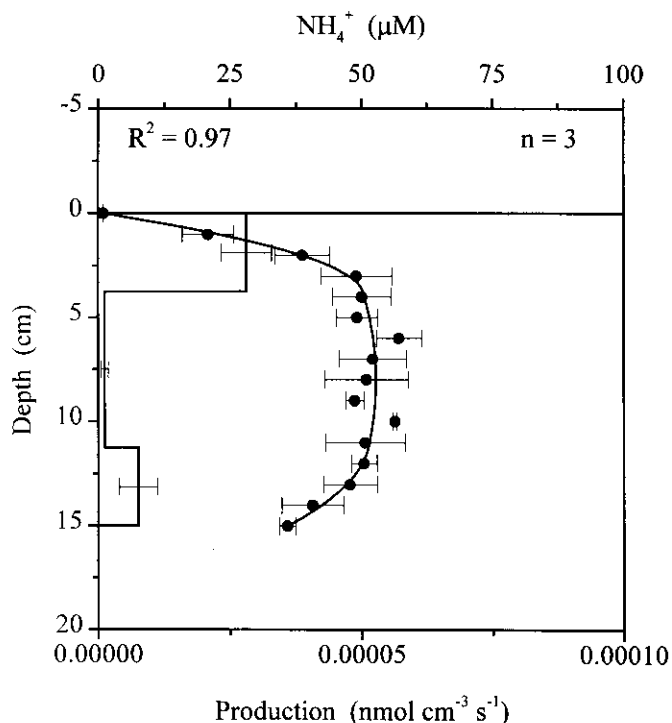


Fig. 6. Pore-water profile (laboratory extractions) in fine-grained sandy sediment cores. The small error bars (SEs) indicate a relatively homogeneous sediment. The curved line is a fit to the NH_4^+ concentrations. The fit was used to estimate the shown net production profile. Error bars are standard errors.

ml sample was collected at 1-cm depth intervals in the top 15 cm of the sediment. The filtered samples (Gelman Supor 0.45- μm syringe filters) were frozen for later analysis of NH_4^+ by use of the indophenol blue method modified from Strickland and Parsons (1972). The smoothness and the relatively small error bars on the mean concentration profile (Fig. 6; error estimates represent standard errors) indicates a relative homogeneous sediment. The NH_4^+ profile was interpreted with use of the procedure of Berg et al. (1998), which calculates net rates of production (or consumption) on the basis of least-squared fitting of a concentration profile and F statistics to select the appropriate fit. The procedure assumes steady-state conditions and neglects pore-water convection but can include the transport mechanisms of vertical molecular diffusion, bioturbation (i.e., the diffusion-like transport caused by random movements of fauna), and irrigation (i.e., the pumping activity of tube-dwelling animals). Since the purpose of this interpretation was to get a first-order estimate of the NH_4^+ production and its depth distribution, we only included molecular diffusion in our interpretation (ϕ estimated as 0.4 and D_s as $10^{-5} \text{ cm}^2 \text{ s}^{-1}$). This resulted in a fit to the NH_4^+ profile with an R^2 value of 0.97 and three distinctive zones of different net production rates (Fig. 6). The error bars for these rates (standard errors) were calculated from additional interpretations of the three individual NH_4^+ profiles. The highest production rate was found near the top of the sediment surface, as anticipated. The near-zero production rate further down in the sediment and,

in particular, the peak at the bottom of the profile, are more difficult to explain. Since the production of NH_4^+ in the sediment results primarily from decomposing organic matter, we would expect a steady decrease in NH_4^+ production with depth (Berner 1980; Boudreau 1997). The effects of irrigation could have formed the NH_4^+ profile we measured, but no tube-dwelling animals were seen in the sediment cores when they were inspected after the pore-water samples were collected. We believe that the most plausible explanation for the shape of the NH_4^+ profile is that it does not represent a steady-state situation. The fact that the profile was measured ~ 3 weeks after a large storm supports this explanation. In shallow waters, and especially in sandy sediments, wave action can induce a significant mixing of pore water in the upper sediment layers (Rutgers van der Loeff 1981), and it is also likely that some fraction of the sediment was resuspended during the storm. The combined effect of these two transport phenomena could lower the pore-water concentration of NH_4^+ through some depth in the sediment, perhaps even at a level similar to the water-column concentration. We believe that the profile as we measured it represents a dynamic situation in which NH_4^+ was building up in the sediment after such a major disturbance. Since our technique gives measurements at specific points in time, we would have been able to test this idea by following the development of the NH_4^+ profile over the weeks following our measurements.

We have tested and used the probe successfully in different sediments varying from coarse-grained tropical carbonate sediments to fine-grained sandy sediments. These applications include vegetated and unvegetated sediments. We consider the probe to be a valuable replacement for sippers, which we have used in the past. By using a significantly smaller sampling device and collecting a smaller sample volume, we can obtain pore-water profiles with a much finer depth resolution and minimal disturbance of the sediment.

Although the probe was specifically developed to be used in sandy sediments, we have also recently used it in a tropical carbonate mud. However, it is not possible to draw any general conclusions on the functionality of the probe in muddy sediments on the basis of this one successful application. It is possible that clogging of the sampling holes can become a serious problem in some muddy sediments. We do believe, however, that this problem can be solved by decreasing the diameter of the sampling holes significantly, to 0.2 mm or perhaps even to 0.1 mm. In this case, the number of holes should also be increased to eight or even more. With this altered design of the probe tip, a new series of tests must be done, including tracer test to determine appropriate sampling rates, to examine the functionality of the probe in muddy sediments.

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