High-resolution pore-water sampling with a gel sampler

Abstract—Sediment pore-water profiles were sampled at high resolution (millimeter scale) with a polyacrylamide gel probe. This simple procedure involves inserting a 1-mm-thick gel held in a plastic probe into sediment. The gel reaches diffusive equilibrium in <1–2 h. For anions, the gel was sectioned, back-equilibrated into distilled-deionized water, and anions determined by high-performance liquid chromatography. Laboratory trials showed recovery of 104±4% Cl, 102±2% NO_3, 101±1% SO_4, and 102±2% NH_4. For Fe and Mn, the gel was fixed in 0.01 M NaOH for ~3 h, subsectioned, extracted with 1 M HNO_3, and analyzed by atomic absorption spectrometry. Field trials were undertaken in Esthwaite Water, a seasonally anoxic lake in the English Lake District. Gel probe data compared well with conventional pore-water extractions.

The chemistry of interstitial waters, both freshwater and marine, has been used to study biogeochemical processes in Recent sediments (e.g. Santschi et al. 1990), and gradients at the sediment–water interface have been used to calculate the fluxes of geochemically important solutes into or out of the sediment (e.g. Kelly et al. 1987; Kuivila et al. 1989). Pore waters have been sampled by a variety of techniques, including centrifugation (Hamilton-Taylor and Morris 1985), in situ sampling (Kuivila et al. 1989), and peepers (Hesslein 1976). These conventional methods have a common limitation in that sampling at a resolution of finer than several millimeters to centimeters is problematic because of construction and practical handling difficulties. In order to study biogeochemical processes in organic-rich sediments or fluxes through the benthic boundary, it is desirable to sample at higher resolutions.

Over the past decade, oxygen microelectrodes have been used to resolve concentration

gradients in the benthic boundary on a scale of ~25 μm (Revsbech et al. 1980). This improvement has enabled major advances to be made in understanding the principal processes that control the flux of dissolved oxygen to and through the benthic boundary layer (Hall et al. 1989; Gundersen and Jørgensen 1990; Rasmussen and Jørgensen 1992). There are, however, only a limited number of biogeochemically important ions that have been measured with microelectrodes. Dialysis cells (peepers), in which a membrane separates distilled water from the sediment, have been shown to provide good estimates of pore-water concentrations (Hesslein 1976). After the cells have been immersed in the sediment for several days to a week, diffusive equilibrium is established, and the enclosed solution assumes the same composition as the pore waters.

The gel sampler relies on a similar equilibration principle, but rather than confining the solution to compartments, it uses a thin film of polyacrylamide gel. The thin film is convenient to prepare, stable, easy and clean to use, and requires a relatively short time for solution equilibration. Fick's law indicates that for a typical dialysis cell (1 cm deep), complete equilibration is established in ~3 d, for a diffusivity of 10^{-5} cm^2 s^{-1}. By contrast, a 1-mm-thick gel with the same diffusion coefficient will be completely equilibrated in only 42 min.

Reeburgh and Erickson (1982) developed a thin-film polyacrylamide gel sampler impregnated with lead acetate to detect dissolved sulfide in marine sediments. Although they noted that equilibrated gel segments could be removed and either solubilized or extracted, they did not go on to produce such a system. Davison et al. (1991, 1994) developed a pore-water sampler that used a thin (~1 mm) polyacrylamide gel for sampling pore waters from lake sediments. After equilibration with pore water, the gel was treated with sodium hydroxide to immobilize the iron and manganese and subsequently analyzed by proton induced X-ray emission (PIXE) or acid extraction followed by atomic absorption spectrometry
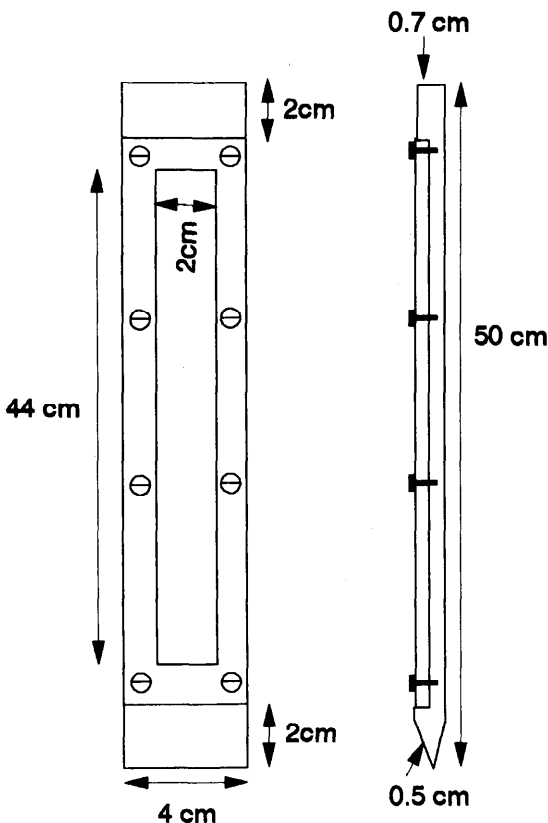
Fig. 1. Diagram and dimensions of the sediment sampling probe. The materials are Perspex with nylon screws.

(AAS). We have adapted and developed the gel sampler to allow it to be used to sample pore waters for the geochemically important ions, chloride, nitrate, sulfate, and ammonia-N, as well as for iron and manganese by AAS. Although the developmental work has been carried out in freshwater sediments, the sampling procedure should also be applicable to marine systems. Here, we describe the gel sampling method in detail, as well as laboratory experiments carried out to confirm its viability. We show a set of representative results of pore waters sampled by this technique from Esthwaite Water, a small productive lake in NW England.

The gel polymer is 15% acrylamide and 0.3% crosslinker (AcrylAide). The major components are mixed and diluted with distilled-deionized water (DDW) or Milli-Q water to the required concentration. The polymerization process is initiated with ammonium per-oxodisulfate (60 μl of 10% wt/vol for 20 ml of solution) and catalyzed by TEMED (20 μl for 20 ml of solution). The initiator and then the catalyst are added, and the solution is again mixed. All reagents are analytical grade.

Gel casting between glass plates produces the required sheets. Plastic spacers are placed between the glass to seal a cavity and set the gel thickness. The casting assembly is then clamped in position. The glass plates and spacers are acid washed and rinsed in DDW, then air-dried before use. The casting assembly is warmed in an oven at 30–40°C before it is filled. The casts are filled with the gel solution while carefully avoiding trapping air bubbles. The filled mold is then returned to the oven for 15–20 min until polymerization is complete. When set, the gels are ~85% water by mass. Once removed from the mold, the gel is placed in an excess of DDW for 24 h to fully hydrate before mounting in the probe. This procedure brings the water content up to 96% by mass and causes a considerable increase in volume. The thickness of the gel is ~0.5–1 mm after hydration.

The probes designed to carry the gel are made of Perspex; they are 50 cm long and 4 cm wide, with a sharpened end for insertion. A 4-cm-wide plate 1 mm thick and with a 2-cm-wide window running the length of the probe is screwed in place to secure the gel (Fig. 1). The gel sheet is laid on the acid-washed probe and covered with a 0.45-μm cellulose-acetate filter membrane. The top plate with the window is then laid on top. The gel and membrane are punctured to allow passage to the screws. When assembled, the anion probes are stored in canisters of DDW and bubbled with nitrogen for 12–24 h before use. The Fe/Mn probes are placed in Milli-Q water and bubbled with nitrogen for 2–3 d before use.

The sampling and handling procedures for anion probes and for Fe/Mn probes were somewhat different. The anion probes were inserted into sediment and left to equilibrate for 6–7 h. Once a probe was withdrawn from the sediment, it was washed briefly with a few milliliters of DDW to remove any adhering sediment. The central exposed section of the probe was cut out and removed. The covering membrane was discarded, and the resulting 2-cm-wide strip of gel was quickly and carefully sectioned into 1-cm-long pieces. These were sec-

tioned further into 1–2-mm strips (or to the required resolution) on a dry and clean cutting board and placed into preweighed 1.5-ml microcentrifuge tubes for weighing. Gel mass was ascertained by difference. The precise depth of the sample in the sediment was calculated by dividing the total mass of the 1-cm section by the masses of the individual subsections. The sectioning of the gel was done as quickly as possible (generally within 10–15 min) to minimize errors due to lateral diffusion within the gel. At 10 min, the mean diffusive path can be expected to be ~1 mm. The gel sections were transferred to the laboratory and stored in a refrigerator at 4°C until analysis.

Analysis was conducted as soon as possible after sample collection (generally within a few days). We added 100 μl of DDW to the gel and centrifuged the solution at 13,000 rpm for 5 min (lower speeds would probably be acceptable) to ensure that all the added liquid was in contact with the gel. The gel was allowed to back-equilibrate with the solution for ~1 h, after which the liquid was drawn off with a microsyringe and injected into a Dionex 4500i anion chromatography module (HPLC). The HPLC was fitted with a 20-μl sample loop which allowed ~3× sample loop volume to flush through before sample analysis. The leachate was eluted with a CO_3^{2-}/HCO_3^- -eluant over a 12-min period. The initial anion concentration within the gel (and so in the sediment pore water) was calculated assuming complete equilibration between the measured mass of gel (of known water content) and the added DDW. In a subsequent set of experiments, ammonium was determined in the gel. In these experiments, dipotassium peroxodisulfate (240 μl of 0.11 M for 20 ml of solution) was used as the initiator. A similar procedure was followed for sample handling as for the major anions. The concentration of ammonia-N in the leachate was determined by flow injection analysis (Hall and Aller 1992).

The Fe/Mn probe was allowed to equilibrate for 24 h, then removed from the core and immediately immersed in a sodium hydroxide solution (0.01 M) for ~3 h to oxidize and hydrolyze Fe and Mn, fixing them as insoluble and immobile forms (Davison et al. 1994). The gel sample was cut into 1.25-mm slices. Each slice was equilibrated in 500 μl of HNO_3 (1 M) for ~6 h and then analyzed by Zeeman
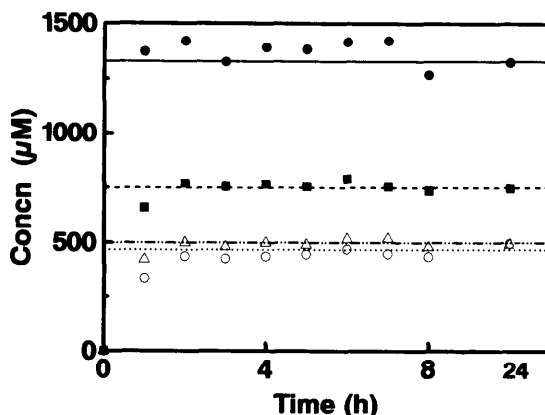

Fig. 2. The concentration of anions in the gel after immersion in standard solutions for up to 24 h. Back-equilibration time for this experiment was 2–3 h. The horizontal lines represent the original concentrations of anions in the standard solutions. Concentrations: chloride—●; nitrate—■; sulfate—△; phosphate—○.

graphite furnace AAS after further dilution. The relative standard deviation of the analysis is < ±3%.

To verify complete equilibration of the gel with the sample, we placed a series of identical gel probes in beakers containing a mixed standard solution (47.5 ppm) of chloride, sulfate, nitrate, and phosphate. After a series of time intervals from 1 to 24 h, the gel was removed, sampled, and analyzed as described above. The back-equilibration time for these experiments was 2–3 h. The gel was found to be fully equilibrated with the surrounding water within 1–2 h (Fig. 2) and gave no further change in concentration over the remaining 22 h of the experiment. The measured recovery of chloride (2→24 h) was 104±4%, nitrate (102±2%), and sulfate (101±1%). The recovery of phosphate, while showing a similar profile to the other anions, reached a value of only 89±3%. Further tests are planned to determine the reason for this somewhat lower recovery. The measured recovery of ammonia-N in a similar experiment was 102±2%.

Once the gel had been sampled into 1–2-mm-wide slices, it was necessary to determine the time needed for the gel to back-equilibrate with added distilled water. To determine the time needed for this back-equilibration, we equilibrated samples of gel with standard solutions for 6–7 h, removed the samples and cut them into 1.5-mm slices. The gel slices
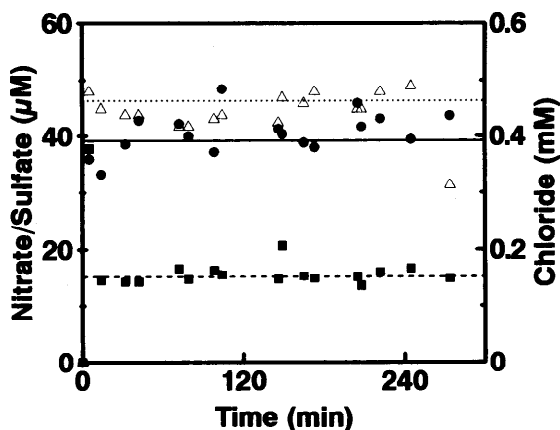
Fig. 3. The concentration of anions recovered from the gel samples after they had been cut into thin (1–2 mm) strips (~30 μl) and back-equilibrated by being placed in 100 μl of DDW vs. time. Equilibration time in the standard solution was 6–7 h. Zero time represents the time at which DDW was added to the sample. Horizontal lines represent the original concentrations of anions in the standard solutions. Concentrations: chloride—●; nitrate—■; sulfate—△.

were stored in microcentrifuge tubes for 1 d in the dark at 4°C. We added 100 μl of distilled water to each gel, and centrifuged the sample for 5 min to ensure complete solution coverage of the gel. The distilled water was sampled and analyzed with the HPLC after differing time intervals as described above. Back-equilibration was so rapid that, with the handling procedure used, all samples showed similar (~100%) recovery from 10–20 min (from the first addition of DDW) to 270 min (Fig. 3). A routine of 60-min back-equilibration proved convenient for practical purposes.

We conducted a set of sample preservation experiments with known concentrations of chloride, sulfate, and nitrate in distilled and eutrophic tank water. Gels were placed in these waters for 2 h to reach equilibrium. The gels were then cut into subsamples. One set of duplicate gels was analyzed within 1 h ($t = 0$). The remaining samples were analyzed after 1–7 d. There was no significant change in anion concentration after up to 7 d storage, both in a refrigerator (4°C) or on the bench, although the degree of scatter of the data was smaller for the samples stored in the refrigerator. Initial tests for ammonia-N suggested that under these storage conditions, samples cannot be stored for more than 24 h before a significant change in concentration is observed. Further tests will determine the reasons for this and develop suitable storage conditions for ammonia-N.

Jenkin cores (Mortimer 1971) of the sediment–water interface were taken from the deepest part of Esthwaite Water, a productive lake in the English Lake District. The cores were taken on 20 May and 8 July 1993. Samples of filtered overlying water were taken with a peristaltic pump system fitted with a sensor to sample close to the sediment–water interface (i.e. within 5–10 cm). The cores were transported to a boathouse where gels were inserted within 1 h of collection. The cores
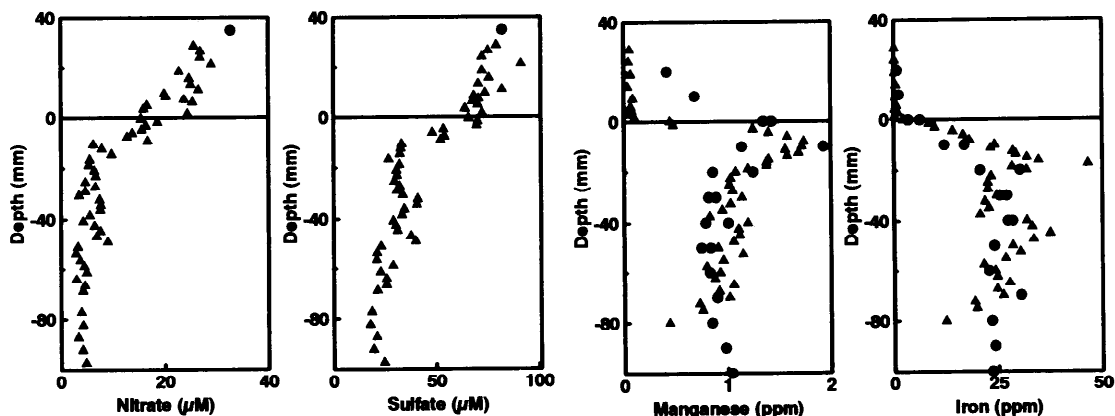

Fig. 4. Concentration of nitrate, sulfate, manganese, and iron in the pore waters of sediment sampled by high-resolution gel sampler from Esthwaite Water, 20 May 1993. Samples from the gel—▲; samples from the overlying water sampled by water-column interface sampler or from pore waters sampled by syringe—●.
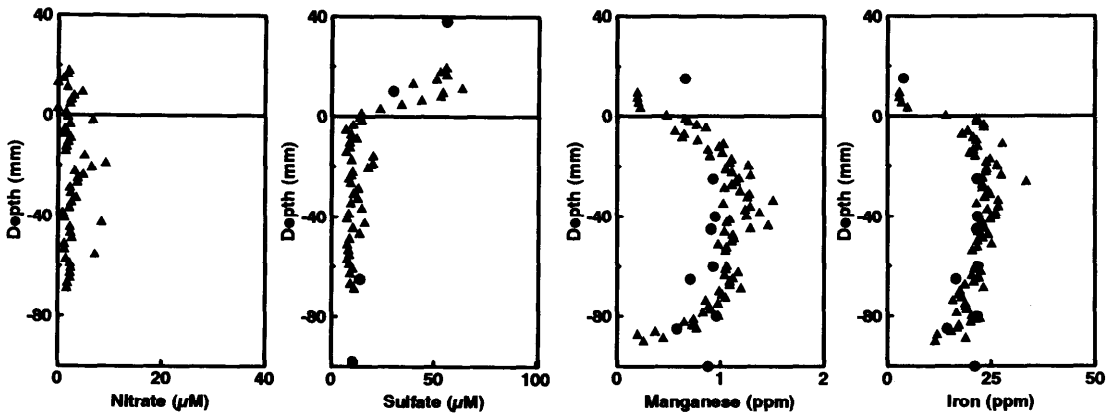
Fig. 5. As Fig. 4, but for 8 July 1993.

were left to incubate in the dark for 6 h. During the July sampling, pore waters were also extracted by syringe from a duplicate core (Davison et al. 1982). These pore-water samples were passed through 0.45-μm filters and stored at 4°C until they were analyzed (within 2 d) by the same HPLC system used for the gel extractions. Total precision (1 s), determined by analyzing 5 replicate samples of anion gel taken from the water column several centimeters above the benthic boundary, was 0.357±0.009 mM for chloride, 0.283±0.061 μM for nitrate, and 28.8±1.1 μM for sulfate.

The high recoveries obtained in the laboratory experiments were confirmed by field studies. Gel samples of the overlying water reached or asymptotically approached the value measured on filtered water samples taken close to the sediment–water interface (Figs. 4, 5). The results for interstitial water iron, manganese, and sulfate obtained by the gel sampler were similar to those measured by conventional (syringe) sampling (Figs. 4, 5). Unfortunately, because the pore-water samples were also being used for trace metal determinations, the filter holders had been pretreated with nitric acid; thus, the nitrate values, although determined, were contaminated.

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Aquatic fulvic acids in algal-rich antarctic ponds

Abstract—We isolated fulvic acids from two antarctic coastal ponds by means of preparative scale column chromatography with XAD-8 resin. Both ponds are on Ross Island. Pony Lake at Cape Royds has abundant phytoplankton populations, and Feather Pond at Cape Bird has a luxuriant benthic algal mat. Neither site has higher plants in the watershed. The dissolved organic carbon (DOC) concentration in Pony Lake was very high, but the percentage of DOC accounted for by fulvic acid was low, as has been observed for other lakes with algal-derived DOC sources. Fulvic acid from Pony Lake was more enriched in nitrogen than fulvic acid from Feather Pond, with a C:N atomic ratio of 13 in Pony Lake and a C:N ratio of 24 in Feather Pond. The [^{13}C]NMR spectra for the coastal pond samples showed that the content of sp^2-hybridized carbon atoms (aromatic or olefinic) was only 16.5% of the total spectral area for Pony Lake and only 20.1% for Feather Pond.

Aquatic fulvic acids are a class of biomolecules present in some concentration in all natural waters. From a chemical perspective, aquatic fulvic acids are defined as a heterogeneous mixture of moderate-molecular-weight (400–2,000 Da) yellow organic acids (Aiken et al. 1985). They are complex substances that

can be operationally defined (Aiken et al. 1985). Further, fulvic acids function as part of the detrital organic material in aquatic ecosystems. These detrital organic compounds are not readily degraded and have the potential to alter the aquatic environment in several ways, including absorption of light, behavior as weak acids (contributing to pH buffering), complexation of required or toxic trace chemical species, and sorption on mineral and oxide surfaces (conveying an overall negative charge to surfaces). The isolation procedure used in this study—preparative scale column chromatography with XAD-8 resin (Thurman and Malcolm 1981)—produces a fulvic acid sample that is operationally defined relative to a set of chemical properties, or a set of ecological functions, or both.

In temperate lakes and streams, aquatic fulvic acids are derived from soils and plants of the surrounding watershed and from algae and bacteria in the water or sediments. The chemical properties of the fulvic acid pool within a lake or stream are influenced by these differing sources. Although much has been learned about the chemical characteristics of terrestrially derived fulvic acids (Aiken et al. 1985), knowledge of algal-derived fulvic acids remains limited. In previous studies, we examined fulvic acids from two permanently ice-covered lakes in the McMurdo Dry Valleys of Antarctica (McKnight et al. 1991, 1993; Aiken et al. 1991). The desert areas surrounding the dry valley lakes have no higher plants, and degradation of algal material in the lake sediments is the main source of dissolved organic carbon (DOC). The distinguishing characteristics of