

sity of Michigan, Physics Instrument Shop, by P. Racicot. Exact specifications are available from us on request. This work is supported through Argonne National Laboratory subcontract 31-109-38-2468 and E.P.A. grant R-803086.

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Chemical water sampling in lakes and sediments with dialysis bags¹

Abstract—An inexpensive interstitial water sampler using dialysis bags for the in situ separation of water from particulate matter in lake waters and sediments is described, and an example of dissolved silica is given.

Natural waters frequently change in chemical composition during the period of time between sampling and analysis, through biological action or re-equilibra-

tion between water and suspended sediment. Techniques of sample preservation can usually solve problems arising from biological action, but occasionally the process of preserving a sample leads to other complications. For example, refrigeration or the addition of acid will inhibit biological action, but will also affect water and suspended sediment equilibria (Siever and Woodford 1973). Thus the in situ separation of dissolved from particulate

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constituents is sometimes desirable. The methods most commonly used to overcome these problems are various filtration and centrifugation techniques. For some applications, however, these methods are awkward or expensive.

Sampling of interstitial waters, in sediments results in similar problems. Methods currently in use fall into two categories: coring-squeezing and in situ. The problems associated with coring-squeezing techniques are primarily due to changes in temperature and pressure in the sediment before the pore waters are extracted (Fanning and Pilson 1971). In situ techniques of equilibration with water enclosed in Tygon tubing (Rudd and Hamilton 1975) or in situ filtration by vacuum (Sayles et al. 1973; Barnes 1973) resolve these problems somewhat but such construction is beyond the means of many limnologists.

Dialysis bags, for some applications, can serve as a simpler and cheaper alternative to these methods. They also filter very fine particles (such as colloids and smaller bacteria) which often pass through conventional filters. The technique essentially consists of placing a dialysis bag filled with particle-free distilled water in the location to be sampled and leaving it there long enough for equilibration between the water in the bag and the ambient water. The dialysis bag is then retrieved, cut open, and the water poured into a sample bottle (if the sample is left in the dialysis bag, water will evaporate, concentrating the sample).

For water samples, both field and laboratory measurements have shown that equilibration takes place in 7–8 h at 25°C. Although this work has been all performed with waters of a salinity equal to 500–1,000 mg liter⁻¹, the variation of equilibration time with salinity should be nil for most limnological systems. This is easily seen by reference to the general solution to Fick's second law of diffusion, given by Crank (1956) as

$$C = (C_0/2)\text{erfc}[x/2(Dt)^{1/2}]$$

where C is the concentration at a point x ,

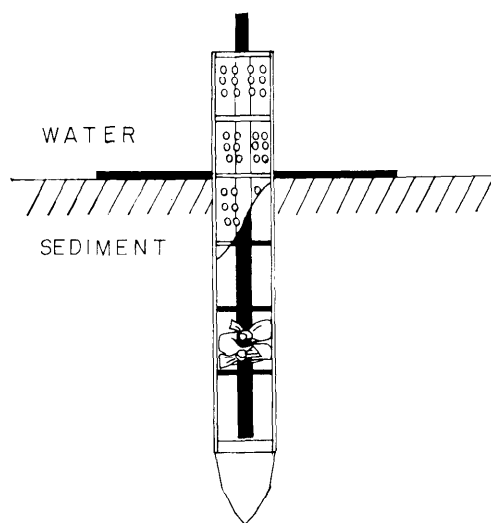


Fig. 1. Schematized interstitial water sampler with one dialysis bag in place.

C_0 is its original concentration, erfc is the error function complement, and D is the diffusion coefficient. The change in the ratio $C : C_0$ from 0 to 1 as equilibration takes place, then, is a function only of the diffusion coefficient at a given time and point. The equilibration time will change, however, as a function of the temperature and type of ion, because of the effects of these variables on D . Computer modeling of this equation yields a roughly linear, inverse correlation of equilibration time with D . Thus, if equilibration times in the Na-Ca-Mg-HCO₃-Cl-SO₄ waters used in this study are of the order of 7–8 h at 25°C, equilibration times should be roughly doubled in waters of 5°–10°C due to halving of the diffusion coefficients (Li and Gregory 1974). The equilibration time for chloride should be about half that for sulfate in water, since D for chloride is twice that for sulfate. In areas with inquisitive fish, enclosure of the bag in a protective shell such as a perforated plastic bottle is necessary to prevent the fish from pecking the bag open.

For sampling of interstitial waters, I have found a device such as that schematized in Fig. 1 to work satisfactorily. This

consists of a perforated Lucite tube, fitted with a removable cone, and separated into chambers by rubber washers fitted over an inserted Lucite rod. The washers are separated at the desired intervals (as might be determined after examination of a core of the sediment) by spacers of Lucite tubing which just fit over the inner rod. One dialysis bag per chamber is wrapped around the inner rod, which is then inserted into the perforated tube. The device is then plunged into the sediment. One or two chambers are left exposed above the sediment to sample the overlying waters. A rubber apron fitted around the outer tube and placed at the sediment-water interface prevents seepage of the overlying waters down the outside of the sampler. The device is very inexpensive, requires only a few hours to build, and weighs <0.5 kg.

Equilibration times for this sampler will vary much more than those for dialysis bags in the water column. This is because diffusivities in sediments are subject to the variables of porosity, tortuosity, and ion exchange reactions (Berner 1971; Manheim 1970) in addition to those of ion type and temperature. I have found times of 100 h in unconsolidated clay and silt sediments to be sufficient for equilibration in the 20° – 25° C range and have tested this in the laboratory by immersing the sediment sampler in artificial sediments of about 50 : 50 sediment : water ratios. After the dialysis bags are removed, the water is analyzed for conductivity. The interstitial waters of the sediments are then extracted with a stainless steel filter press through a $0.4\text{-}\mu$ Nucleopore filter under 2 atm of compressed air. Conductivities for the waters extracted both ways agree generally to within 1%. Although the variation of equilibration time discussed above should result in much shorter sampling times with clay-free sediments (because of the inhibiting effect of clays on cation diffusivities) and longer sampling times for sediments at lower temperatures, I have not determined these variances. Because of the many different variables at work, the investigator should

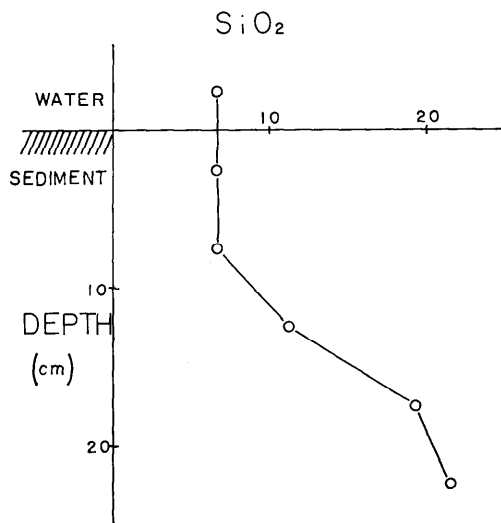


Fig. 2. Variation of dissolved silica (in mg liter⁻¹) in water column and interstitial waters of sediments.

determine the relevant parameters for his own needs and experiment accordingly before field sampling.

Figure 2 shows a sample interstitial water profile for dissolved silica taken with this instrument. The sediment is actually a buried desert sand recently transgressed by rising water level in an artificial reservoir (Lake Powell, Utah). The increase in silica with depth probably reflects evaporative concentration in the sand before actual submergence. A sample of the water above the sediment taken by hand gave a value identical to that obtained by the dialysis bag which was exposed to the same water (6.6 mg liter⁻¹).

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An in situ sampler for close interval pore water studies¹

Abstract—A sampler for defining compositional changes over distances on the order of 1 cm in aqueous systems operates by equilibration of water contained by a dialysis membrane with the surrounding water. Depth profiles of methane and phosphate in Hudson Estuary sediments are presented as examples.

Small-scale structure of dissolved species in natural aquatic systems has become of increasing interest. Much of the difficulty in studying this small-scale structure is the inability to precisely sample at small intervals (<10 cm) without disturbing the structure to be measured. The sampler described here was designed for measuring concentrations of dissolved components of sediment interstitial waters, but can be used equally well for sampling in the overlying water.

I credit J. Rudd for seeding this idea in my mind; R. Lupton, T. Protus, and B. Deck gave technical and analytical assistance. M. Zickl typed the manuscript and P. Catanzaro drafted the figures. W. S. Broecker criticized the manuscript.

The principle of operation of the sampler is the equilibration of a contained quantity of water with the surrounding water through a dialysis membrane. The contained water is then removed from the

system and container for analysis. The use of dialysis or other membrane as the separating material allows the sampler to discriminate against various large size molecules depending on the membrane chosen and eliminates the need for filtering the sample as particulate matter is totally excluded. As the contained water is equilibrated in situ the amount of the species of interest in the compartment will not be altered by processes such as precipitation on exposure to air (e.g. iron, manganese, phosphate, etc.). One may have to rinse the compartments in such a way as to remove these altered forms quantitatively.

The sampler is made of clear acrylic plastic (Plexiglas, Lucite, etc.), with nylon machine screws to avoid any problems associated with metals. For the version shown in Fig. 1 two 8- × 60-cm sheets of acrylic, one 1/8 inch (0.3 cm) and one 1/2 inch (1.3 cm) thick were used. The pieces were held together and the compartments simultaneously machined through the thinner piece and into the thicker piece on an overhead mill. The compartments were cut 1 cm on center. Holes for the screws were drilled and threaded to accept nylon machine screws.

The sampler was prepared for use by filling the compartments with distilled water and carefully laying a piece of dialysis membrane over the full compartments

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