BERNER, R. A. 1971. Principles of chemical sedimentology. McGraw-Hill.

CRANK, J. 1956. The mathematics of diffusion. Oxford.

FANNING, K. A., AND M. E. Q. PILSON. 1971. Interstitial silica and pH in marine sediments: Some effects of sampling procedures. Science 173: 1228–1231.

LI, Y., AND S. GREGORY. 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmochim. Acta 38: 703–714.

MANHEIM, F. T. 1970. The diffusion of ions in unconsolidated sediments. Earth Planet. Sci. Lett. 9: 307–309.

RUDD, J. W., AND R. HAMILTON. 1975. Two samplers for monitoring dissolved gases in lake water and sediments. Limnol. Oceanogr. 20: 902–906.

SAYLES, F. L., T. R. WILSON, D. N. HUME, AND P. C. MANGELSDORF. 1973. In situ sampler for marine sedimentary pore waters: Evidence for potassium depletion and calcium enrichment. Science 181: 154–156.

SIEVER, R., AND N. WOODFORD. 1973. Sorption of silica by clay minerals. Geochim. Cosmochim. Acta 37: 1851–1880.

An in situ sampler for close interval pore water studies[1]

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 ⅛ inch (0.3 cm) and one ½ 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

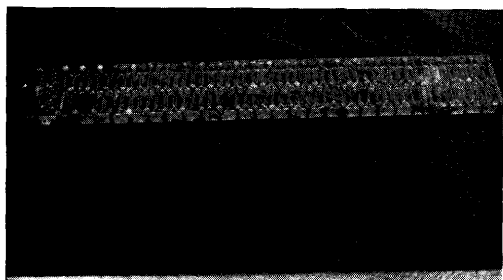Fig. 1. The sampler.

Fig. 2. Equilibration with chloride in well mixed water.

so as to exclude any air bubbles (easily done with the help of a squeeze bottle). The thinner acrylic sheet was then laid over the membrane, holes were poked to accommodate the screws, and the sheet was screwed down tight. The whole sampler was then placed in a closed bath of degassed distilled water and allowed to lose most of its dissolved gases by equilibration.

The sampler was inserted in the sediment and allowed to equilibrate with the interstitial water (~1 week). Upon removal, the compartments were sampled by tilting the sampler slightly from horizontal, piercing the upper end of the membrane covering each compartment, and withdrawing from the lower end by syringe. The samples were then injected into helium-filled serum bottles for gas analysis and later transferred and diluted for other analyses. The sample size is 4 ml. Unfortunately, suitable apparatus was not available for comparison with the usual method of coring and squeezing.

As mentioned above, the sampler was allowed to equilibrate for 1 week in the sediment. As can be seen from Fig. 2 this is much longer than necessary in water, but in sediments the interstitial water directly adjacent to the membrane becomes depleted of dissolved constituents by flux into the compartment and additional time must be allowed for this zone to be replenished by flux from the surrounding interstitial water. A very small amount of sediment is, of course, "subducted" with the emplacement of the sampler. This should be a problem only if there is a large gradient
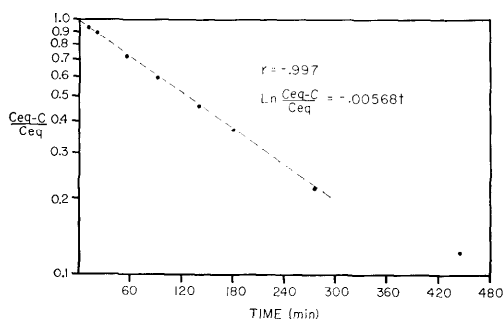
in exchangeable species or degradable material. With gases, a correction must be made for loss to air during the draining procedure. This is easily measurable and an example for methane is shown in Fig. 3. Characteristic equilibration and loss times of various species should, for any one sampler configuration, be dependent on the limiting diffusion rate, whether that be in the compartment, membrane, or in the sediments. In the type of equations that describe diffusive problems as presented by the sampler, the diffusion coefficient and time appear as a product (Dt). The same nearness to equilibrium will be achieved at a time inversely proportional to the diffusion coefficient of interest relative to the time for some known species. Diffusion coefficients do vary with molecular size,
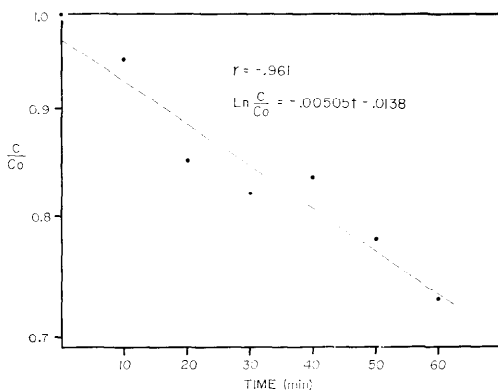

Fig. 3. Loss of methane in air vs. time after removal.
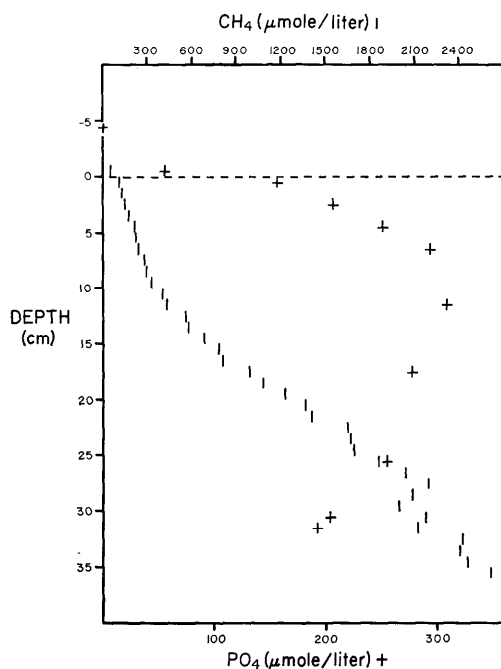
CH₄ (μmole/liter) ı

Fig. 4. Methane and phosphate distribution with depth in Hudson River sediments.

temperature, salinity, and, of course, with porosity and tortuosity in the sediments. Discussions of these problems are available in the literature. If a substance were rapidly freed from the sediments (to solution in pore water), the depletion mentioned above would be small and equilibrium more rapid. The diffusion approach should give an upper limit in equilibration time. Before any measurements are made using this sampler both equilibration and loss characteristics should be determined in the laboratory for the species of interest.

An example of the kind of measurements that can be made with the sampler is shown in Fig. 4 for shallow water ($\simeq 1$ m) Hudson River sediments of silty clay about 15 km upstream from New York City. Methane was measured by equilibrating a known sample volume (4 cc) with a known gas volume (19 cc) and injecting an aliquot of the gas into a gas chromatograph (Rudd et al. 1974). Phosphate was measured as soluble reactive phosphorus (Murphy and Riley 1962). Phosphate was not measured on all compartments to save samples for other measurements.

The sampler can be modified depending on the system to be studied. D. Schindler (personal communication) has used small vials covered with membrane filter material at various fixed intervals in sampling chemical gradients in lakes. Modifications for use of the sampler in deep water (not accessible by diving) and filling the compartments with other than distilled water are under consideration.

Raymond H. Hesslein

Lamont-Doherty Geological Observatory
  of Columbia University,
Palisades, New York   10964

References

MURPHY, J., AND J. P. RILEY.   1962.   A modified single solution method for the determination of phosphate in natural waters.   Anal. Chim. Acta **27**: 31–36.

RUDD, J. W., R. D. HAMILTON, AND N. E. CAMPBELL.   1974.   Measurement of microbial oxidation of methane in lake water.   Limnol. Oceanogr. **19**: 519–524.