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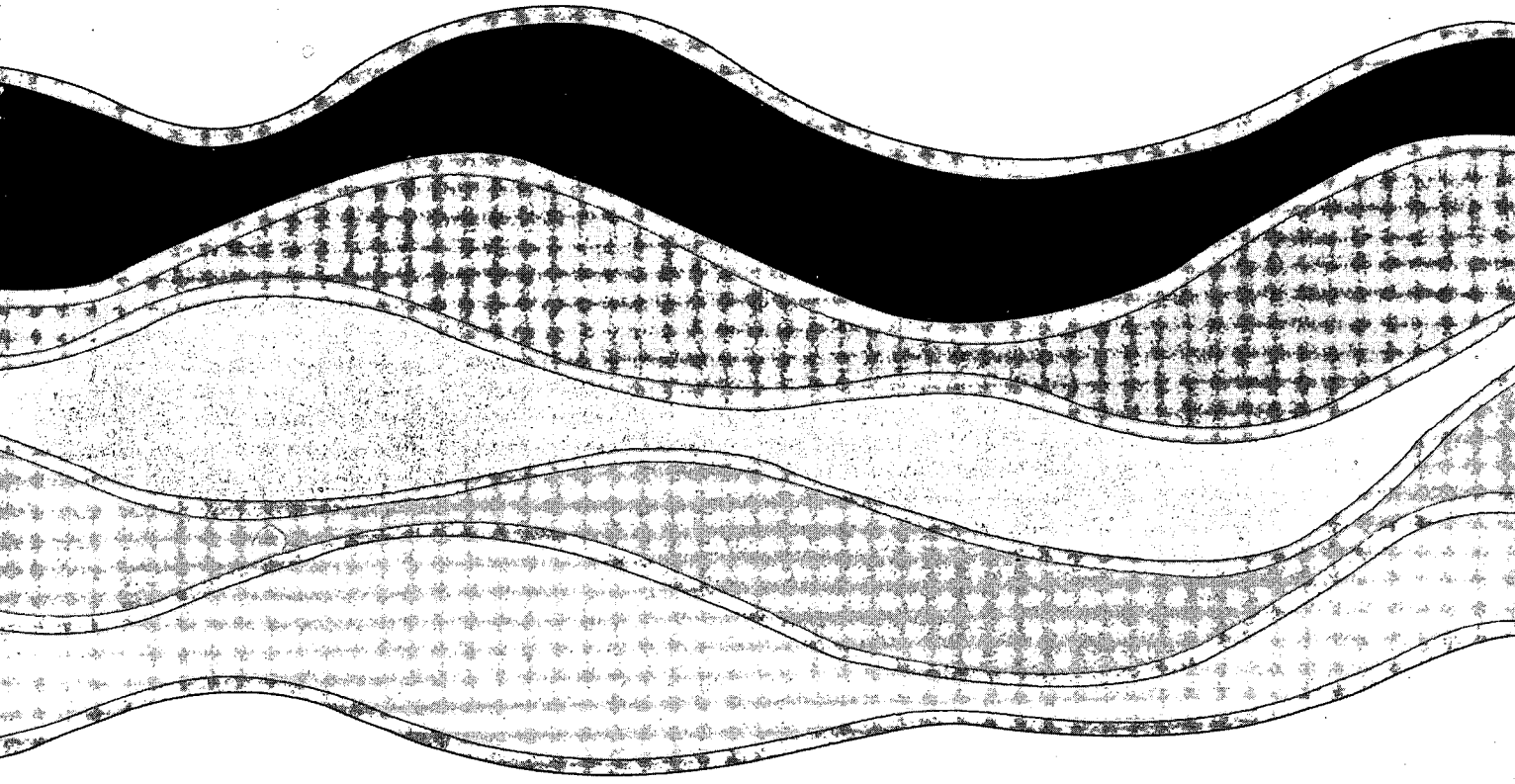

"PESPER METHODOLOGY"
A DETAILED PROCEDURE FROM FIELD EXPERIENCE

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NWRI Contribution N° 93-33

"Peeper Methodology "

- A Detailed Procedure from Field Experience -

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MANAGEMENT PERSPECTIVE

Sampling of sediment pore water has become a very instrumental tool in the studies of transport and accumulation of contaminants. The techniques involving sediment manipulation outside the benthic environment (such as centrifugation and squeezing) are subjected to significantly concentration changes due mainly to temperature-, oxidation- and pressure-related changes during recovery. The sampler developed by Hesslein in 1976 to collect pore water *in situ*, based in diffusion-controlled transport, minimizes all these sampling artifacts. The principle of operation of this sampler (called "*peeper*") is the equilibration of a quantity of water with the surrounding water through a dialysis membrane.

Data obtained by sampling sediment pore water can provide valuable information on the chemical changes occurring in the sediment profile, and on the transport and fluxes of contaminants into the sediment/water interface and overlying water. It is recognized that this information has an enormous application fundamentally for the study of sediments from mine or industrial waste deposits. However, the technique involved in the collection of sediment pore water using *peepers* is complex and susceptible to contamination. The present report summarizes all the different steps involved in the *peeper* methodology, from the cleaning and assembly of the peeper to retrieval and preservation of the samples. In the past year there have been many requests from outside agencies to provide NWRI scientists for pore water measurements and advice. The main objective of this report is to

fill the gap in the literature providing a simple and complete "manual of instructions" in the use of the *peepers* which could be widely used by many outside agencies which are now initiating their field research in sediment pore water. The information presented in this review is based on field experience from the authors and other scientists from NWRI who have previously worked with *peepers*.

ABSTRACT

Sediments are one of the main repositories of contaminants in the environment. After the sediment is deposited, changes in the redox conditions can alter the availability and mobility of the contaminants. Sediment pore water, referred also as interstitial water, is the linking agent between the bottom sediments and the overlying water. The technique involved in the collection of sediment pore water plays a crucial role in studies of pore water quality. The *in situ* pore water sampler ("*peeper*") developed by Hesslein (1976), and its modifications have been used in many sediment pore water investigations. However, the "*peeper*" technique is complex and susceptible to contamination. This report provides a simple and complete "manual of instructions" in the use of the *peepers*, such as cleaning, assembly, retrieval, and preservation.

1. INTRODUCTION

Sediment pore water, referred also as interstitial water, is defined as the water filling the space between sediment particles and not held by surface forces, such as adsorption and capillarity, to sediment particles. The water content in typical sediments ranges from about 30% for sand and mixtures of silt and sand, to up to 99% in fine-grained surface sediments containing large amounts of organic matter. Sediment pore water is a linking agent between the bottom sediments and the overlying water. Negligible changes in sediment composition often cause noticeable variations in the quality of sediment pore water. Increasing number of studies of concentrations of contaminants in sediment pore water in marine and lacustrine environments reflects the significance of this compartment. The sediment pore water chemistry can explain many diagenetic processes. However, the technique involved in the collection of sediment pore water play a crucial role in investigating of pore water quality. Pore water sampling can provide valuable information on chemical changes occurring in the sediment profile, on the equilibrium reactions between the sediment's solid phase and water, and on the transport and fluxes of contaminants into the sediment/water interface and overlying water.

With the exception of the sediment/water interface, sediments are generally anoxic, and become rapidly oxidized upon exposure to air. The oxidation of the sediments induce immediate changes of the redox-sensitive chemical species of different elements in the pore water usually followed by their precipitation. For example, Krom and Berner (1980), found that the adsorption of phosphate by anoxic marine sediment is greatly increased when the system is aerobic, probably due to the adsorption of phosphate on iron oxyhydroxides. Therefore, the speed of the sampling procedure and the maintenance of an oxygen-free atmosphere are critical factors in sediment pore water sampling.

Up to 1970 pore water was extracted from recovered sediments through various techniques, such as centrifugation, pressure filtration, gas displacement (as well as other methods involving sediment manipulation outside of the benthic environment). However, several authors showed significant concentration changes due mainly to temperature- and pressure-related changes during recovery. The major problem during sediment pore water sampling and handling has been shown to be the potential for oxidation. Since then many methods have been developed to collect pore water *in situ* to minimize sampling artifacts. Samplers based in diffusion-controlled transport were first developed by Mayer (1976) and Hesslein (1976). The principle of operation of these samplers is the equilibration of a contained quantity of water with the surrounding water through a dialysis membrane.

2. THE SAMPLER - "*PEEPER*"

The in situ pore water sampler developed by Hesslein (1976), and its modifications have been used in many sediment pore water investigations. The sampler (called a "*peeper*" by Hesslein, or dialyser) is based on the principle that, given enough time, a contained quantity of water in the sampler will diffuse and equilibrate through a dialysis membrane, or other materials, with the surrounding water and its dissolved solutes. The in situ sampler can either be removed by divers or the pore water can be collected through attached tubing while the *peeper* remains in the sediments. The use of dialysis or other membranes as the separating material allows for discrimination against various size molecules, depending on the chosen membrane, and eliminate filtering of the sample since particulate matter is totally excluded (Hesslein, 1976).

Minor modifications of the sampling device and the membrane used have occurred since Hesslein introduced it, but the principle of the in situ pore water sample has remained the same. A modified version of Hesslein's sampler is shown in Figure 1. Generally, samplers of this type are made of clear acrylic plastic (Plexiglass, Lucite, etc.). Two sheets of acrylic (one 0.3 cm thick cover and other 1.3 cm thick body for the original sampler developed by Hesslein (1976) are held together by a series of nylon or stainless steel screws. Elongated sampling compartments are

machined, usually 1 cm apart, through the 0.3 cm cover and into the acrylic body.

Many scientists have changed the design of the sampler to better achieve the objectives of their studies. For example, greater compartments when larger sample volumes where needed, or *peepers* with thinner walls to facilitate the penetration in very compact sediments. The use of dialyses or other membranes as the separating material allows for the discrimination of various size molecules, depending on the chosen membrane, and eliminates filtering of the sample. Simon et *al.* (1985) made some modifications to the sampler design by Hesslein. They used two 3 mm thick cover sheets and 0.2 μm polycarbonate membranes mounted in the sampler with the shine side out to provide less surface area for attachment of microorganisms. Because of microbial attack, cellulose-based dialyses membranes have proven to be less resistant, therefore should not be used. For an extensive review of applications of membranes of different pore sizes in sediment pore water sampling refer to Adams (1991). A nonporous 75 μm (3 mL Teflon) membrane would allow for diffusion of gases but not ionic chemical species into the sampling compartments of the in situ equilibrator, Adams (1991).

3. PROCEDURE FOR THE PREPARATION OF *PEEPERS*

3.1 Cleaning and Storage Before Assembly

The risks of contamination are considerable when sampling sediment pore water, due to considerably lower concentrations of elements than those in the sediments. Therefore, special attention has to be paid to avoid contamination when sampling and cleaning all sampling equipment and containers for collection of the pore water samples. To avoid cross-contamination, the cleaning of the apparatus and the *peepers* become a critical stage. For cleaning, deoxygenation and storage of *peepers*, complete the following steps:

i) A large pre-cleaned polyethylene tank with lid is filled with doubly distilled water (DDW).

ii) *Peepers* which have been acid-soaked in another tank with 1M HNO_3 for 2 weeks (4 weeks for new *peepers*) are transferred to the polyethylene tray. After the acid-soaking period the *peepers* are rinsed first with tap water followed by doubly distilled water(two rinses), and then placed in the tank mentioned in 3.1.i.

iii) Attach a rubber tubing with an adapted end to a N_2-cylinder, to release small bubbles. Place tubing end in one of the corners, at the bottom of the DDW tank, using a **slow** bubbling rate.

iv) To conserve N_2 consumption, tape an airtight clean plastic cover over the tank, and place the lid over it.

v) After 1-2 days of N_2 bubbling, purge once or twice daily with N_2, through a small hcle which is covered with masking tape after each purge.

vi) Refill with N_2 gas and place polyethylene lid back on plastic-covered tank. The gas above the DDW should be almost pure N_2 by this time, and thus, the DDW should be totally deoxygenated.

3.2 *Peeper* Assembly

For a efficient *peeper* assembly two people are needed, one at each side of the table. A heavy duty polyethylene tray (55 x 80 x 14 cm) should be used to facilitate procedure for *peeper* assembly. Have clean acid-soaked utensils ready for use: a new plastic-bristled brush, an artist's brush, a glass rod and a plastic bar.

i) Place 10 to 15 cm of N_2-purged DDW in the tray.
ii) Take one *peeper* from the storage tank and submerge it in the tray. Use the clean bristled brush to sweep away all air bubbles from the bottom of the tray. Then use the small artist's brush to remove all air bubbles from *peeper* cells (a slow tedious step). ***IT CANNOT BE OVERSTRESSED THAT THE REMOVAL OF ALL AIR BUBBLES IS IMPORTANT BOTH EXPERIMENTALLY AND PROCEDURALLY.*** (It is very time-consuming to loose screws to release 1 or 2 bubbles).

Have *peeper* cover plate, screws and a screwdriver (preferably a battery operated) ready. Put the cover plate against the other side of the tray next to the *peeper*, with the glass rod and the plastic bar on top of the cover plate (easily accessible).

iii) Cut length of dialysis paper (membrane) about 3 cm longer than required, using a ruler and a 45° pull after using a small starter rip to neatly tear paper (instead of tearing, a sharp blade or scissors can be used).

iv) Submerge the paper in the tray and do not allow any part of it to surface above DDW. Pull paper gently between the glass rod and the plastic bar by placing glass rod on paper above the bar, as shown (Figure 2). The glass rod and plastic bar are used in conjunction to gently scrape in visible bubbles from the surfaces of the submerged dialysis paper. After this step, the dialysis paper should be kept under water at all times until assembly.

Adjust finger pressure by gently squeezing the paper between the bar and the glass rod. Once the submerged paper is bubble-free, slip a cover plate over the paper and gently slide a bubble-free *peeper* under the paper and cover plate.

v) Line them (cover, paper and *peeper*) up neatly and place all centre screws, end screws, and about every 4th side screw in place. Tighten these screws only with the pressure one can exert by using

the thumb and forefinger on the screwdriver handle (see note below). Be careful not to slip the screwdriver off the screw and puncture the cell membrane.

vi) Flip the *peeper* over and inspect for air bubbles. If an air bubble is present, flip the *peeper* back over and "burp" it by undoing the nearest screw on the side and gently prying the *peeper* and cover plate up in the vicinity of the bubble. Tap lightly and tilt the end or side of the *peeper*, where the bubble is, upward to allow the air to escape. Once all the bubbles are removed, put in all screws, making the *peeper* airtight.

NOTE: If using metal screws, don't overtighten them or you will ruin the plastic threads. If using metal-insert-in-plastic-thread screws, don't overtighten or the metal insert will break free from the plastic part of the screw; if this happens, carve a slot into the plastic portion of the screw head and screw it out slightly off centre.

vii) Remove the assembled *peeper* from the tray and place in deoxygenated DDW in a portable polyethylene tank (bubbling chamber), previously filled with deoxygenated water. One chamber may hold 2 to 4 *peepers*, depending on the size of *peepers*. Assembled peepers are transported to the field sealed in the bubbling chambers with deoxygenated DDW.

3.3 List of Equipment for Assembly

- Approximated volumes of double distilled water (DDW)
  20 L for each papering trayload
  25 L for each transportation tank
  20 L for each Gerry Can (polyethylene) (to take into the field)

- Heavy duty polyethylene tray 55 x 80 x 14 cm
- N_2 gas cylinder and regulators
- Rubber tubing with adapted end for releasing small bubbles
- clean polyethylene containers (washing tank and water storing)
- rubber tubing for releasing bubbles
- bubbling chamber
- deoxygenated water
- screws for *peepers* (#6-32 x 1/2" stainless steel screws)
- *peepers*
- cleaning utensils brushes, glass rod and plastic bar
- dialysis membrane
- screwdriver (recommended battery operated screwdriver)

4. DEPLOYMENT OF *PEEPERS*

At the sampling site, the *peepers* are inserted perpendicularly to the sediments surface in flat areas. In areas with prevalent currents, the sampler is oriented with the narrow side parallel to the direction of the waves and tide (if known) and manually pressed into the sediments. This orientation minimizes tilting and possible the dislocation of the *peeper* during the equilibration period. An apparatus called '*peeper* placer" can also be used if SCUBA diver support is not feasible or in deep areas (>25m). *Peepers* are attached by a rope to an anchor, and allowed to equilibrate with the sediment interstitial water. Reported pore water equilibration times varied from six to thirty days (Bolliger *et al.*, 1992; Carignan *et al.*, 1985; Simon *et al.*, 1985). The most important factors affecting the equilibration time are the diffusion coefficient of the substance of interest, its degree of adsorption to the solid phase, the temperature, and the porosity of the sediments (Carignan, 1984). For most recent sediments, 20 days for cold (4°-6°C) and 15 days for warm (20°-25°C) sediments, appear to be safe equilibration periods for major ions and nutrients (Carignan, 1984).

5. *PEEPER* RETRIEVAL

As mentioned before equilibration times of 6 to 30 days were found adequate for most sediments. Shortly before *peepers* are going to be retrieved, pre-treat all the sample containers (plus a few spare ones) with the appropriate type and quantity of preservative based on the analysis to be performed. For nonvolatile species, pore water samples will be collected in pre-acidified (HNO_3) vials to a final pH of 2.5-3.5, stored at 4°C, and analyzed within two weeks. The pretreatment requirements for the different analysis of pore waters are shown in Table 4.4. All acidified containers are placed in trays for easy manipulation on the boat. These trays should provide enough space between sample containers, for easy uncapping and capping, and clearly show the sample number. Before retrieval of the *peeper*, two boxes should be arranged, one with the new syringes with the attached hypodermic needle, and a second box for the disposal of the used syringes. It is recommended to use one syringe for each cell.

It is recommended that sampling be completed within five minutes from the time the *peeper* is withdrawn from the sediments. More delayed sampling increases the risk of oxidation of the sample during the sampling procedure, which could significantly change the concentrations of dissolved elements, such as reactive phosphorus and iron. It is therefore essential that, following its removal from anoxic sediments, the air-exposed *peeper* be handle efficiently

and quickly. The *peepers* are removed from the sediment by he diver or pulled with a rope from the boat. Once at the surface, the *peeper* is momentarily agitated in the water to remove any visible sediment particles adhering to the membrane surface. The compartments are sampled by tilting (20°) the *peeper* from horizontal to facilitate drainage of the cells. The pore water contained in each cell is withdrawn from the lower end by syringe. Special care is taken to avoid drawing any air into the syringe, especially for samples to be used for gas analysis. Ideally three or four persons will assist in sampling the *peeper*. Two persons using the syringes to empty the *peeper* cells, beginning in the middle and working in opposite directions. On the opposite site of the *peeper* one or two persons emptying the syringes in the appropriate numbered and pretreated sample containers. For each *peeper* retrieved, the visual sediment water interface observed by the diver; the position of the oxic-anoxic interface as indicated by the ferric oxyhydroxide staining on the *peeper* membrane; and the exposure time since *peeper* removal from sediment until last cell is emptied; have to be recorded.

5.1 Preparation in Laboratory

i) Prepare enough sample tubes to collect all samples, and if necessary to hold diluted samples. For most analyses, a 5 or 10 cc polypropylene tube is appropriate. For trace metal analysis, polypropylene tubes and caps are acid-leached in 1 N HCl for about 1 day, then rinsed with DDW, dried and capped (Nriagu *et al.*,

1993). This type of sample tubes are not for the storage of CH_4/DIC samples (see section 5.1.iii). Keep caps on (to keep tubes sterile) and label all tubes using waterproof ink. Label a second set of tubes for dilutions, if necessary, and set aside.

ii) Have solutions ready for the use as sample preservatives (or anti-oxidants). Shortly before samples are to be collected, pre-treat all sample tubes (plus a few spare tubes) with the appropriate type and quantity of preservative based on the analysis, to be performed.

iii) Place acidified tubes in trays for transport to the boat. One arrangement that will serve well as a sample tube tray is a box of scintillations vials, numbered around the necks of the vials, with one sample tube being placed in each vial. The box should be partitioned internally to hold vials securely in place. Another option for a sample tube tray is to use sheets of sturdy styrofoam in which rows of holes are bored (use a cork borer of appropriate dimensions to hold sample tubes snugly). The later trap is recommended since the tubes will be held snugly, and will not fall out in case the tray is tilted or dropped.

iv) Prepare new syringes by attaching the appropriate size of hypodermic needle and arranging syringes in a box to facilitate easy and safe handling, i.e. no needles pointing up. Have enough syringes for emptying each *peeper*: allow one syringe for each

peeper cell. In the deep section of the peeper, less active chemically (shown by a constant concentration), the study leader may determine that some syringe can be used to empty several *peeper* cells. Each *peeper* has about 60 cells (some 54, some 70). For most sampling, a 5 cc syringe fitted with an 18G1 1/2 needle is appropriate. However, for CH_4/DIC sampling, a 3 cc syringe fitted with a 21G1 needle is used to prevent making too large a hole in the rubber septum of the Vacutainers.

5.2 Retrieval Procedures and Sample Recovery in the Field

Peepers are to be retrieved from the anoxic sediment and their contents quickly removed and preserved. There is threat of oxidation of the sample during this sampling procedure, which could give rise to erroneous results for certain chemicals species (specially Fe). It is therefore essential that, following *peeper* removal from the anoxic sediments, the air-exposed *peeper* be handled efficiently and quickly, emptying and preserving pore water samples before oxidation-precipitation reactions can occur.

i) *Peepers* are retrieved from the sediment by a SCUBA diver, who either transports the *peeper* by hand or clips a rope to the *peeper* so that it can be hauled quickly to the surface by a person in the boat. Through a 25 m water column, the diver requires about 1-2 min to reach the surface, while pulling from the boat takes approximately 30 seconds.

ii) While the *peeper* is being retrieved, the sample tubes are set out on the board (sample tube board) and the caps are removed, placing them in a clean container handy for recapping.

iii) When the *peeper* arrives at the surface, momentarily swish (agitate) it in the lake water to remove any visible sediment particles adhering to the membrane surface. The *peeper* is leaned lengthwise on the *peeper* board, titling it back about 20 to 30° angle to facilitate drainage of the cells.

iv) Have 3-4 persons assist in sampling the *peeper*: using syringes, 2 persons empty the *peeper* cells beginning in the middle of the *peeper* and working toward the ends, and 1 or 2 persons (preferably 2) emptying the syringes into the appropriately numbered, pretreated sample tubes. Each *peeper* cell is numbered. It takes about 2 minutes to empty 60 m cells, giving a total exposure time of about 4 minutes from the time the *peeper* is withdrawn from the sediment until the last cell is sampled.

The persons emptying the *peeper* sit opposite the persons injecting the sample into the sample tubes, and hand the full syringe across and call out the cell number. Capping the tube as each sample is injected will help prevent errors, i.e. mixing two samples in one tube. The study leader will determine if syringes are either discarded in a box after each use, or passed back for re-use.

v) Empty *peeper* cells by puncturing the very bottom of the cell membrane (dialysis paper) with the hypodermic syringe, the needle angled downwards, and quickly withdraw the sample from the cell. For all samples, but especially for samples for gas analysis such as CH_4, special care is taken to avoid drawing any air into the syringe.

vi) Quickly inject the pore water into the pre-treated sample tube, but not so forcefully as to splash the sample back out of the tube. The acid will readily mix. Cap the tube. When a *peeper* has been completely emptied, the tray of sample tubes is placed in the cooler and next tray is prepared, i.e. uncapped, and ready to receive samples.

vii) To measure pH, insert the thin pH probe directly through the cell membrane into the *peeper* cell, or use Carignan's (1984) method.

viii) For each *peeper* retrieved, record the following information:
a) When visibility permits divers should record the number of cells located above the sediment water interface to estimate sediment disturbances of *peeper* movement during the exposure period.
b) position of the oxic-anoxic interface as indicated by ferric oxyhydroxide staining on the *peeper* casing and membrane; and
c) approximate draining time for *peeper*, i.e. time from removal from sediments until last cell is emptied.

ix) When sampling a double *peeper*, the second side to be emptied should be quickly and closely covered with Saranwrap or other suitable material to reduce evaporation or air contamination from the exposed membrane surface while the first side is being emptied. Note that a double set of sample tubes must be ready and uncapped when a double *peeper* is being sampled, taking care to avoid contamination of the open tubes.

5.3 Sample Storage and Dilution

Nutrients should be preferably stored at 4°C and analyzed as soon as possible. Most pore water samples will require dilution prior to nutrient analysis, as concentrations of nutrients are usually enhanced by factor of 10 to 100 in the pore waters. Samples from above the sediment-water interface require less dilution than samples from below the interface. Carefully performed dilutions using an automatic diluter should be easily reproducible.

Properly preserved samples for trace metals, CH_4,DIC and $RSiO_2$ analysis are apparently stable for several weeks to several months. Table 1 summarizes the conditions for storage and preservation for the analysis of different elements.

5.4. List of Equipment

The following chemicals and equipment are used in preparation for and during *peeper* retrieval. Some items are specifically for certain analyses.

- Solutions:

Ultrex concentrated hydrochloric and nitric acids

Saturated $HgCl_2$ (dissolve $HgCl_2$ in H_2O; allow to set for 2 hrs. and shake; if crystals are visible then solution is saturated)

7% H_2SO_4 (dilute 10 ml of 30% P-free H_2SO_4 with 50 ml of P-free DDW)

1N HCl (use it as an acid bath for polypropylene sample tubes)

- Pipettes (10 μL Eppendorf & tips)
- Syringes & Needles:

5 cc Becton-Dickinson syringe fitted with Yale 18G1 1/2 needle

3 cc Becton-Dickinson **PLASTIPAK** syringe fitted with 21G1 needle

(10 cc syringe fitted with 21G1 needle can also be used)

50 μL Hamilton syringe (as chromatographic) (for injecting preservative into Vacutainers)

- sample tubes 5 or 10 cc polypropylene, translucent with caps
- small Vacutainers (approx. 5 cc volume)
- P-free double distilled water
- diluter Brinkman Diluette model
- *peeper* Board (to support *peeper* during emptying)
- sample Tube Board (to support trays of sample tubes)
- test tube racks (to hold sample tubes)

- numbered racks or boxes of scintillation vials (to serve as sample tube trays during sampling in the boat)
- saranwarp or Parafilm
- tuck tape
- pen (waterproof ink)
- cooler
- boxes for syringe disposal
- field notebook

6. CONCLUSIONS

1. Syringes and Needles

- 5 cc syringes are preferable to 10 cc syringes as they are easier to manipulate.
- 3 cc syringes are easy to manipulate and ideal for small volumes where a safeguard is needed to prevent completely emptying the *peeper* cell and thereby introducing air into the sample.
- 18G needles are preferable to 21G needles as they create less back-pressure and withdraw the sample faster.
- 1 or 1/2 inch needle length are unnecessary and the hypodermic tips are dangerous; a shorter or blunter tip would be safer to handle and equally functional.

A hypodermic tip **is** necessary to inject samples to be stored in Vacutainers.

2. Sampling Time

Sampling time has two components, retrieval time and time to empty the *peeper*. Retrieval time can be kept under 30 seconds by hauling the *peeper* to the water surface on a rope. Emptying time is about 2-3 minutes for 60 cells with 4 persons assisting. To reduce sampling time, an apparatus might be devised which would manipulate many syringes at once, thus emptying many *peeper* cells simultaneously. A possible disadvantage of such an apparatus might be a loss of maneuverability and the increased possibility of air being drawn into the syringe.

3. Working Space in Boat

It is essential that adequate bench surface exists in the boat for supporting *peeper* and tray sample tubes during sampling. Work space can be increased by using portable boards, such as the *peeper* board and the sample tube board which can be clamped to the boat bench, thus stabilizing and effectively extending the working space.

4. Sample Tube Trays

This tray should have ample space for the sample tubes to facilitate speedy uncapping and capping, and should not obscure the sample tube numbers. If test tube racks are used, allow for double spacing of tubes. A box of scintillation vials can also be used as a sample tube tray (as described in Section 4.2). The use of trays that can be stacked and easily transported in the boat is recommended, particularly when collecting large numbers of samples.

5. Double *Peepers*

The disadvantage of double *peeper* is that the total draining time is about doubled. If one side is completely emptied before the second side is started (rather than emptying opposite cells simultaneously), it is recommended that the second side be covered with Saranwrap or Parafilm to reduce evaporation or oxygen contamination through the membrane. If oxygenation is a problem for sample analysis, then use of a N_2-filled bag or some other measure such to cover the second side of the *peeper*. Another disadvantage is the number of samples to be handled at once, which is awkward in the limited working space of a small boat. Therefore the use of a single *peeper* is recommended.

6. Collecting Large Numbers of *Peepers*

Since each *peeper* generates about 50-60 samples, all sample tubes must be clearly labelled with waterproof ink to facilitate quick identification. Use of sample tub trays which stack securely and which show sample tube numbers is recommended. Waterproof the bottom of trays or pack in plastic, as the bottom of the boat may become quite wet.

During sampling, allow time between retrieval of consecutive *peepers* to remove caps ahead of time and covering uncapped tubes with a sheet of Saranwrap or other clean material to prevent contamination of open tubes. Have sample tube trays in order, and have enough trays so no tubes have to be transferred between trays and racks in the boat.

7. Efficiency

Organization of the work surface in the boat facilitates an efficient sampling process. For example, have ready a box for holding clean caps for sample tubes, a box for syringe disposal, and have all necessary items within arm's reach.

Have four persons assisting with sampling one *peeper* for optimal efficiency. Verbally cross-check the cell number being sampled to avoid any mix-ups of samples. Have a few spare parts (i.e. caps, pre-acidified tubes, etc.) along.

Each sampling event is constrained by working space available in the boat being used and other considerations; organize the work space accordingly.

We emphasize that due to its complexity, sediment pore water sampling is not suitable in any monitoring program, and should only be carried out by personnel with experience in sediment pore water sampling. Typical sediment pore water profiles obtained with peeper sampler are shown in Figure 3.

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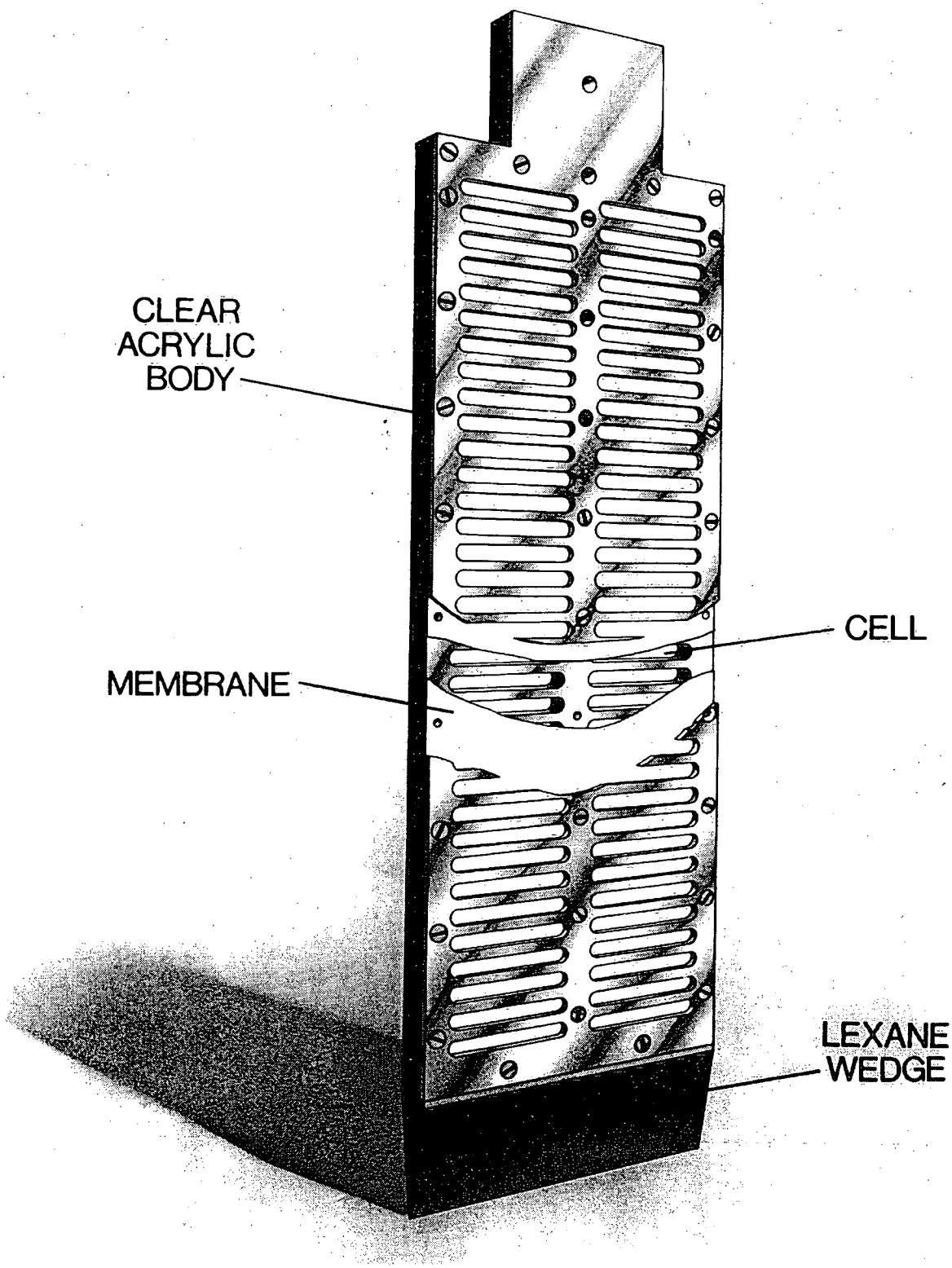
Table 1. Preservation requirements for the analysis of different elements in sediment pore water samples (volumes of preservatives are based in 5 ml samples)

Element	*pH of treated sample*	*Preservative*	*Sample containers (5 or 10 ml)*	*Time for analysis*
trace metals	2.5-3.5	10 μl of concentrated HNO_3 and stored at 4°C	polyethylene (high or low density), or Teflon	within 14 days
Nutrients	2.5-3.5	10 μl of 7% H_2SO_4	polypropylene	ASAP
DIC and CH_4 (a)		0.05 ml of saturated $HgCl_2$	glass tubes (Vacutainers)	within 3 days
$RSiO_2$	1.5-2.5	10 μl of concentrated HCl	polypropylene	within 14 days
Gases		equilibration to atmospheric pressure with N_2	glass tubes (Vacutainers)	within 3 days

(a) - use the 50 μL Hamilton syringe to inject $HgCl_2$ into Vacutainers

DIC = dissolved inorganic carbon

Figure 1.


PORE - WATER SAMPLER
CLEAR ACRYLIC BODY
CELL
MEMBRANE
LEXANE WEDGE

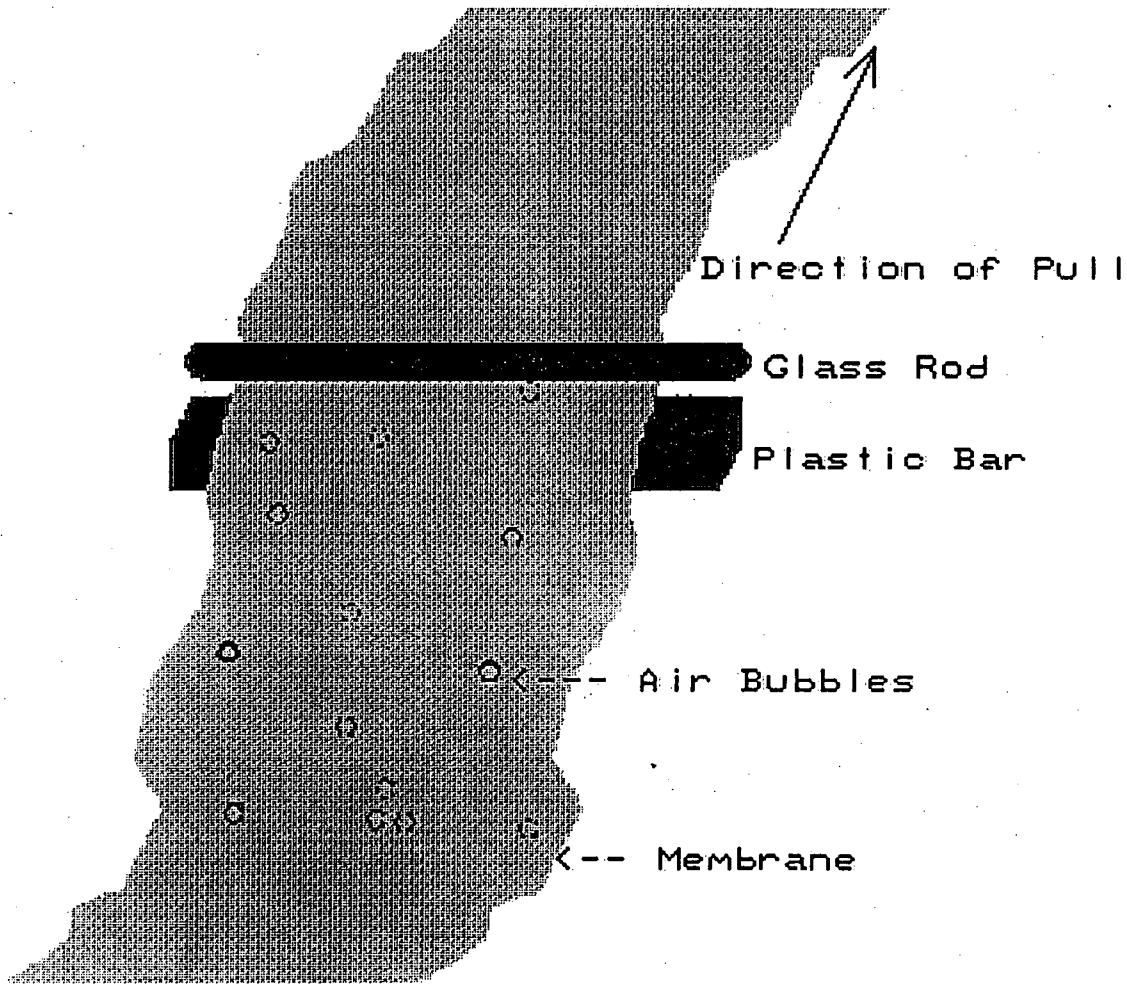
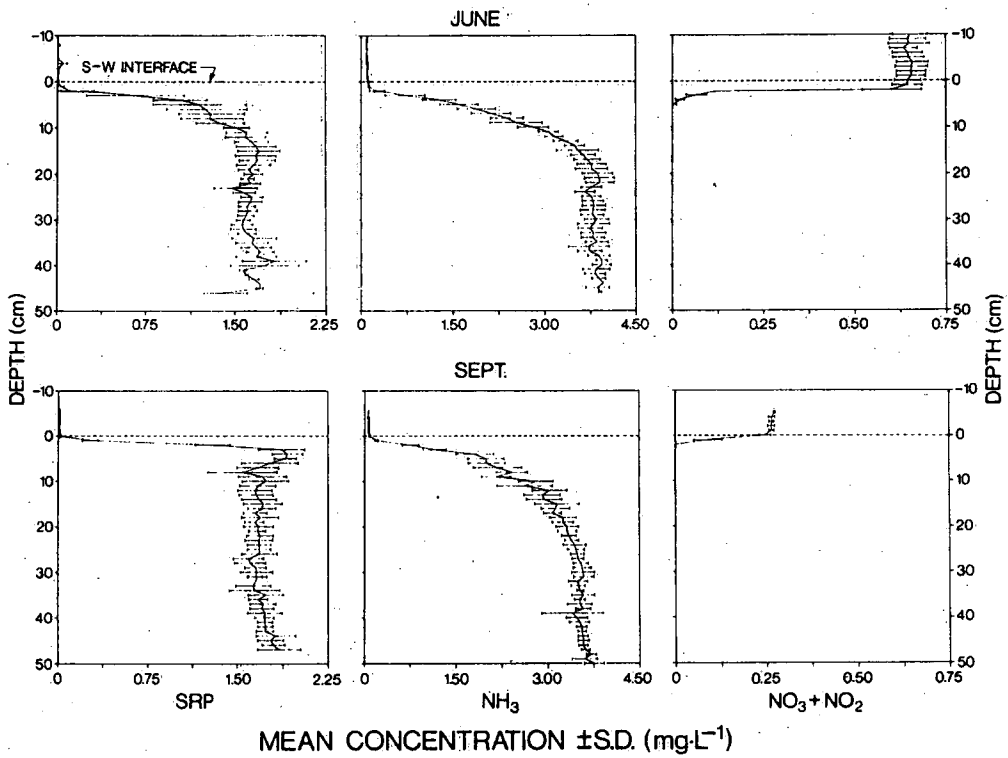
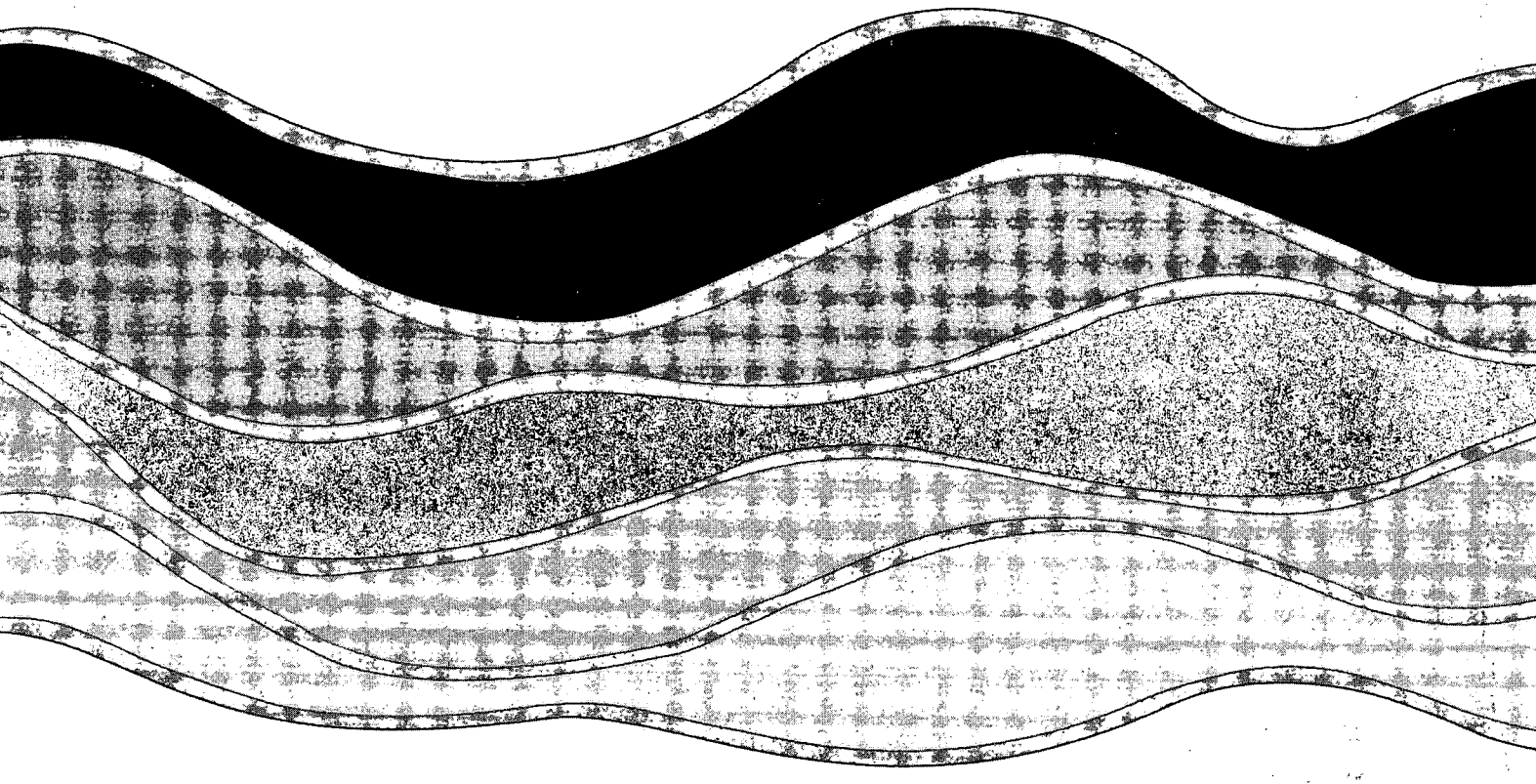


Figure 2. Schematic Diagram for Air Bubbles Removal

Figure 3. Examples of sediment porewater profiles obtained with *peepers*





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