A Close-Interval Sampler for Collection of Sediment Pore Waters for Nutrient Analyses[1]

ABSTRACT: An *in situ* sediment pore water sampler is described. It can simultaneously and continuously sample at four discrete 1 cm levels at one location without disturbing the sediment or the sample. The sampler can maintain an anaerobic environment, and can be used over extended periods of time. Laboratory tests indicate 98 to 100 percent recoveries for ammonium, silicate, reactive phosphate, nitrate and nitrite. Vertical profiles for ammonium, reactive phosphate and silicate are shown from field studies.

A knowledge of the properties of the sediment-water interface and, in particular, the upper few centimeters of sediment are critical to the understanding and description of both the kinetics and mass transfer of chemical species in estuarine systems. The boundary conditions at this interface are often poorly known or undefined due to the difficulty of sample collection using classical methods, such as the gravity or piston corer, which disturb the sediment water interface (Vanderborght, et al. 1977; McRoy, et al. 1972). In particular, the determination of nutrients for this area is especially difficult, due to the problems of degassing (Rudd and Hamilton 1975), air contamination, and temperature changes (Fanning and Pilson 1971; Bischoff, et al. 1970). A second problem associated with the classical methods of gravity or piston cores is their limited scope. One core represents one finite set of data, as it is impossible to sample the exact location a second time. Most of these problems have been overcome by an *in situ* sampling device (Montgomery, et al. 1979) which both maintains the anaerobic state of the sample and can be sampled over extended periods of time in the same location. This method has two disadvantages, it requires one sampler for each depth and because of the non-homogeneity of the sediment, produces large variances.

This paper describes a single, *in situ* sampler which simultaneously samples four 1 cm sampling surfaces at 2 cm intervals. This sampler requires minimal sample manipulation, minimizes sediment disturbance, maintains an anaerobic sample environment, and can be used over extended periods of time to sample at one location.

The close interval sampler was designed to locate 4 each, 1 cm porous Teflon® filter rings at levels 1 cm apart on a cylinder 4.5 cm in diameter. The chamber behind each filter ring is discrete, and the filtrate withdrawn from each of the four chambers is independent of the other three.

The sampler is composed of a tube with a nose cone which facilitates insertion into the sediment. The tube is separated into a layered filter section, a tubular extension to facilitate handling, and a top section which provides the necessary connections to the internal sample chambers. Except for the porous Teflon® filter rings, clear acrylic plastic (Plexiglas) was used exclusively for the construction (Fig. 1).

The filter section is made from three identical separator pieces (middle separator) plus two more (top and bottom separator) which are modified to connect the nose cone at one end and the extension section at the other. Four sample tubes run the entire length of the sampler. Each separator piece is drilled through for all four tubes. A ridge near the edge of the separator pieces holds the Teflon® filter ring in place and forms a chamber in the center. The ridge is drilled through to provide passage for the filtrate from the filter ring into the chamber. Although all four sample tubes go through each chamber, only one tube is open at each level. All joints are sealed at each level, making a particular tube part of only one chamber; all chambers are equal volume, and the bottom of all four chambers is the joint between the filter section and the nose cone.

The extension section is simply the extended sample tubes surrounded by a protective 4.5 cm diameter tube. The length of the extension is not critical.

The top piece is made from solid Plexiglas, drilled for the four sample tubes. The location of each sample tube is enlarged into a chamber by drilling a larger hole part way through the Plexiglas. A cover plate containing eight polyethylene tubing connectors (Technicon 116-0003-01, Type A) is sealed in place over the chambers. Each of the tubing connectors (inner) is in line with the larger sample tubes and is made contiguous with the bottom of the sample tubes by the use of a smaller plastic tube (Acidflex, Technicon AutoAnalyzer 1.59 mm I.D.). The other connectors (outer) are also connected in turn to each of the four larger sample tubes and are used to apply vacuum or purge gas for each discrete level. The sample and vacuum/purge connectors on the cover plate are joined to plastic tubing (Acidflex, Technicon, Inc. 1.59 mm I.D.). The tubing for the sample compartments are connected to a Technicon pump. The pump (Technicon, Inc., Proportioning pump) was modified for field use with a 12V DC motor and an in-line speed reducer (Dayton models M2M272 and 27821, respectively).

Prior to all experiments, the sampler was cleaned by flushing one liter of 6 N HCl through each level, followed by numerous deionized water rinses. All sample cups and sample containers were pre-washed with acid and rinsed with deionized water.

Laboratory tests were conducted to determine possible nutrient sorption or contamination by the sampler. Both spiked and unspiked deionized water were sampled and compared with concentrations in the sample reservoirs. The spiked sample contained known concentrations of ammonium, nitrogen, dissolved reactive phosphorous, soluble reactive silicon, nitrate and nitrite nitrogen (5.8, 1.6, 5.0, 2.0, and 0.3 μM, respectively). All nutrient analyses were performed in triplicate on a Technicon AutoAnalyzer II® using modified Technicon procedures (Zimmermann, et al. 1977). The precision for NH_4^+ was 0.2 to 6.6% relative standard deviation (RSD) at 25 to 125 μM, 1.0 to 5.4% RSD for

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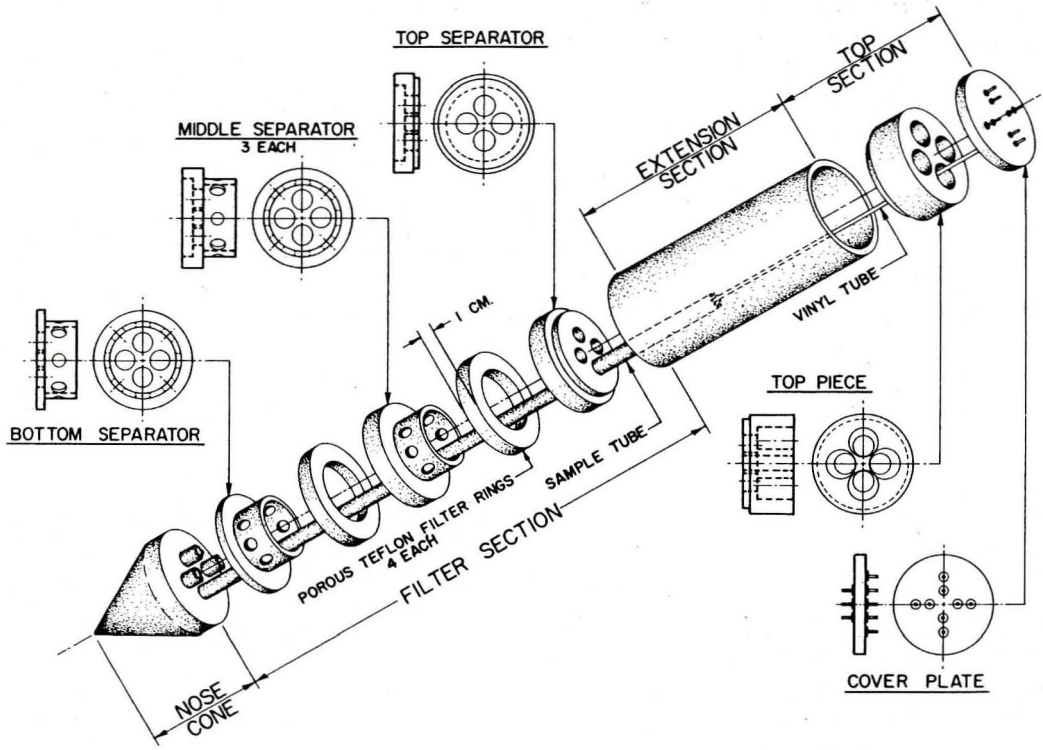

Fig. 1. Exploded view of the close interval, pore water sampler. For simplification, only two Teflon® filter rings are shown.

DRP at 10–20 μM and 0.4 to 2.6% RSD for silicate at 300-450 μM.

Field testing of the sampler was carried out in the Indian River, near Fort Pierce, Florida (Latitude 27°32′, Longitude 80°21′). This field test was conducted to sample the upper 8 cm of sediment although the sampler could have been placed at any depth by increasing the length of the extension section and internal sample tubes (Fig. 1). We were primarily interested in the upper 10 cm of sediment because previous data (Montgomery, et al. 1979) had shown a sharp increase in nutrient concentrations between 2 cm and 10 cm with subsequent decrease to relatively constant level at 30 cm. This gradient could not be resolved using the larger *in situ* sampler with the 2 cm porous Teflon rings. The close interval sampler was placed in the sediment of a mixed *Halodule wrightii* (Ascherson), *Syringodium filiforme* (Kützing) bed, with the sampling surfaces located at 2, 4, 6 and 8 cm beneath the sediment-water interface. The sampler was purged with Freon gas, the sample and purge lines sealed and the sampler was equilibrated for 72 h.

To initiate sampling the sampler and purge lines were opened and Freon gas was used to purge the sampler. Any sample which had collected over the 72 h equilibration period was discarded. Purging with Freon was contained for 1 min after all sample was expelled. The purge lines were sealed and the excurrent end of the sample tubes were connected in series with a Gelman in-line filter holder with 25 μm dia., 0.4 μm pore size filters and then force fitted to a #21 gauge needle. The sample lines were inserted through the septum of a prepurged 50 ml glass vial. A second needle was used to vent each sample vial. Sampling commenced with activation of the pump. The sampling rate was 4 ml min^{-1}. At the conclusion of sampling the needles were withdrawn and the septum vial was stored in the dark on ice for later analysis.

Three sets of samples were taken during 30 min, with each collection period averaging 10 min. Samples were also collected at the surface and at 10 cm using the larger *in situ* sampler as a further check on the close interval sampler.

All nutrient concentrations were determined within a few hours of collection. The anaerobic condition of the samples was maintained throughout the analyses utilizing the method described by Montgomery, et al. (1979). Oxidation/reduction potential (Eh) was measured using a double junction electrode (Orion model 96-78) coupled with a Corning pH/mV meter (model 110).

Results of the laboratory experiments indicated no nutrient contamination of unspiked deionized water. Percent recoveries for the spiked series ranged from 98 to 100 percent for all five nutrients at all four sample levels.

During the field experiment, maximum concentrations of ammonium (NH_4^+), reactive phosphate (PO_4) and silicate (SiO_3) occurred at 8 cm for all three sample periods (Fig. 2). This depth was also the most reduced, as shown by the Eh value (−344 mV). Nitrate values were maximum at 2 cm (2.08 μg-at l^{-1} to μM) but were

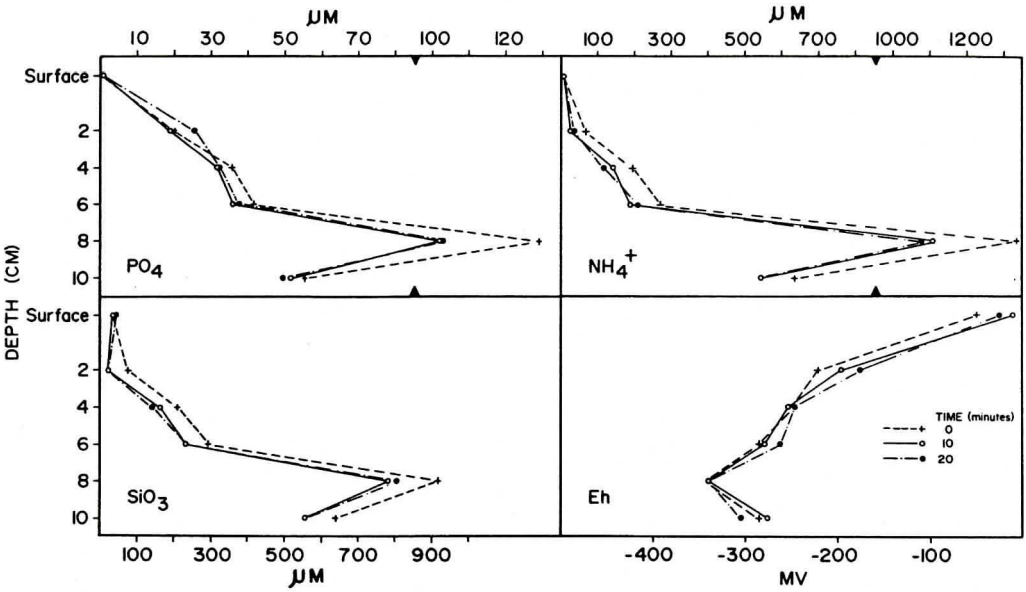

Fig. 2. Nutrient profiles from sediment pore waters of a mixed *Halodule wrightii, Syringodium filiforme* grassbed. Ammonium (NH_4^+), reactive phosphate (PO_4) and reactive silicate (SiO_3) values shown are for three consecutive sample periods (0, 10, 20 minutes). The nutrient concentrations are μM. The Eh is millivolts.

below our detection limit (0.2 μg-at l^{-1} to μM) for other depths, as were all nitrite values (0.04 μg-at l^{-1} to μM).

There was no significant difference (Student's t statistic, $P \leq 0.05$) between the second and third sample periods, at all depths for ammonium, reactive phosphate and silicate. However, while overall profiles remained the same, the first sample period was significantly higher for these three nutrients for most depths.

Significant differences between the initial sample and subsequent samples was probably due to a "carry over" from the high nutrient concentrations of the sample remaining in the sampler from the 72 hr equilibration period. It is not due to drawdown from other levels because drawdown is primarily a function of flow rate and sediment permeability. Our flow rate (0.067 ml sec^{-1}) with a sediment permeability (K) of 0.052 cm sec^{-1} (Montgomery, unpublished data) would only cause a drawdown of 0.04 cm at the maximum. Previous studies using radioactive ^{14}C as bicarbonate have shown no drawdown at the low flow rates we are using (Montgomery, et al. 1979). Laboratory tests in aquaria containing anaerobic sediment, show no significant oxygen contamination using the present technique as compared to sampling Eh *in situ* (Student's t test $P < 0.05$). We suggest that the first sample withdrawn be discarded and successive samples be used for quantitative analysis.

In both field and laboratory studies where multiple water samples need to be collected from one site this *in situ* sampler has great potential. There is no need to withdraw sediment cores to squeeze and therefore kinetic studies of the nutrients in pore waters can more easily be determined. Potential applications include analysis of pore waters for trace metals, dissolved organic carbon, sulfides, sulfates, salinity, Eh, dissolved oxygen and pH.

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