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Notes and Discussions

A Comparison of Ceramic and Teflon *in situ* Samplers for Nutrient Pore Water Determinations^a

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A laboratory comparison study of porous Teflon® and porous ceramic samplers which can be used to collect sediment pore water was performed for varying concentrations of NH₄, PO₄, NO₃, NO₂ and Si. Significant differences were evident between nutrient concentrations before and after being filtered through ceramic samplers. Mean per cent recoveries were 11% ± 0.9 for NH₄, 43% ± 1.1 for PO₄, 96% ± 0.1 for NO₃, 85% ± 0.0 for NO₂, and 111% ± 0.2 for Si (standard deviations for *N* = 5). Per cent recoveries using the Teflon® sampler were from 98–106% for all nutrients tested. The Teflon samplers can be placed in shallow estuarine sediments and samples collected over a 14-day period without disturbing the sediment or clogging the sampler.

Introduction

One of the important needs in sampling sediment pore water is a device which can be used at a specific site, to take multiple samples over time and be able to sample at discrete depths.

Cores have been used to obtain sediment samples and the water collected for chemical analysis by squeezing. Several problems arise using this method. Mangelsdorf & Wilson (1969) and Fanning & Pilson (1971) have found that the warming of seawater-clay suspensions significantly alters the chemical composition of the interstitial waters. The collection of a core disturbs the sediment and only one sample can be taken from a specific spot. Squeezers are characteristically messy and the quantity of pore water collected is minimal.

Dialysis type samplers have also been used to sample sediment pore waters (Mayer, 1976). Drawbacks to this type of sampling procedure are biodegradation of the tubing, the problems encountered using various molecular weight dialysis tubing and the inability of the sampler to take more than one sample.

Porous ceramic cups have been used in many studies to obtain water samples from soil for nutrient determinations (Devitt *et al.*, 1976, Mansell *et al.*, 1975). In our preliminary attempts to adapt porous ceramic samplers to measure *in situ* nutrient exchange in estuarine sediments, we recorded poor and erratic recovery of soluble nutrients passing through the sampler.

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These observations led us to experiment with porous Teflon® (TFE). Per cent recovery studies were performed on both porous ceramic (Soilmoisture Equipment Corp, Santa Barbara, Calif.) and the TFE samplers.

The purpose of this paper is to describe the results of this comparison study and to describe the advantages of the TFE sampler for use in sampling marine and fresh water sediment pore waters.

Materials and methods

The TFE was purchased in rod form (Fluorocarbon, Anaheim, Calif.) and machined into cups (length, 80 mm; diameter 51 mm o.d., 32 mm i.d.; tops indented 13 mm × 3 mm from outer edge). These cups were then cemented to 30 cm lengths of 3.5 cm o.d. PVC pipe.

To obtain a sample in the field, a porous cup attached to a length of PVC pipe is inserted in the sediment or soil at the desired depth. The sample is allowed to equilibrate for 48 h. A vacuum is then placed on the sampler through the vacuum/purge line and both lines clamped off (Figure 1). The pore water surrounding the cup is then allowed to infiltrate for a predetermined time. After releasing the clamp on the vacuum-purge line, a sample is drawn through the sample line. This process halts the further inflow of pore water and reduces the vacuum required to remove the sample.

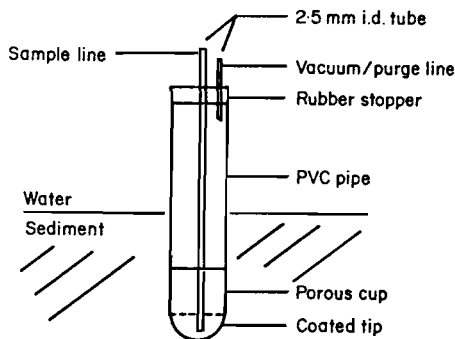


Figure 1. Sample collection using porous samplers.

Treatment of the ceramic cups prior to field use is important in reducing sources of contamination (Grover & Lamborn, 1970; Wolff, 1967; Wood, 1973). In this study, both types of samplers were cleaned by pumping 200 ml of 1 N-HCl through the cups and pipe, followed by numerous deionized water rinses. Seven liters of known concentrations of ammonia (11.4 $\mu\text{g-at. l}^{-1}$) nitrate, (2.6 $\mu\text{g-at. l}^{-1}$), nitrite (0.33 $\mu\text{g-at. l}^{-1}$), ortho-phosphate (3.6 $\mu\text{g-at. l}^{-1}$), and silicate (27.0 $\mu\text{g-at. l}^{-1}$) were placed in each of two acid washed polyethylene containers containing three ceramic and three TFE samplers, respectively. These solutions were continually stirred with a magnetic stirrer. Five replicates were taken from each container before and after the samplers were inserted. To each ceramic sampler a vacuum of 50 cm Hg for 10 min was applied and the collected sample discarded. This procedure was followed for each TFE sampler using 20 cm Hg for 5 min. All samplers were evacuated a second time; 50 cm Hg for 20 min for ceramic samplers and 20 cm Hg for 5 min for TFE samplers. Five replicates of the collected water were analysed. Differences in vacuums used were required to equalize the low porosity of the ceramic with the high porosity of the TFE. This procedure was repeated using lower concentrations of each

nutrient (ammonia—5.5 $\mu\text{g-at. l}^{-1}$, nitrate—1.7 $\mu\text{g-at. l}^{-1}$ ortho-phosphate—1.5 $\mu\text{g-at. l}^{-1}$, and silicate—17.1 $\mu\text{g-at. l}^{-1}$).

A separate study was conducted to determine the effect of vacuum on nutrients in water. A standard solution containing known concentrations of nitrate, ammonia, ortho-phosphate, and silicate was placed under a vacuum of 50 cm Hg for 10 min. The solution was stirred to maximize air-water contact and to insure adequate mixing. Five replicate samples were run before and after vacuum. Results indicate no significant difference between nutrient concentrations before and after vacuum.

All nutrient determinations were analysed on a Technicon AutoAnalyzer II[®] using modified Technicon[®] procedures (Zimmermann *et al.*, 1977).

An experiment was also performed to establish the particle size distribution of the liquid being filtered by the TFE sampler. Prior to analysis, a slurry of artificial seawater and silty sand was prepared. The sampler was placed in this slurry and allowed to equilibrate for 1 h. A vacuum of 25 cm Hg was applied to the sampler and the filtrate withdrawn after each of five 20-min intervals. The first, third and fifth filtrate samples were analysed for particle size distribution using a Coulter Counter TA II[®] (Coulter Electronics, Sarasota, Fla.)

Results

The nutrient experiments showed that significant differences occur between the standards and filtrates of the porous ceramic samplers. Per cent recoveries using the ceramic cups ranged from 11% for ammonia to 111% for silicate. The TFE samplers consistently recovered 98–106% of the standards for all nutrients (Table 1).

TABLE 1. Mean nutrient values of standards ($N = 10$) and filtrate ($N = 15$) from samples in $\mu\text{g-at. l}^{-1}$ calculated to 95% confidence interval

	Teflon			Ceramic		
	Standard \bar{x}	Sampler \bar{x}	Mean % recovery	Standard \bar{x}	Sampler \bar{x}	Mean % recovery
Ammonia	11.42 \pm 0.10	11.6 \pm 0.40	102	11.38 \pm 0.06	1.26 \pm 0.52	11.1
	5.46 \pm 0.07	5.67 \pm 0.17	104	5.73 \pm 0.06	1.60 \pm 0.67	27.9
Phosphate	3.58 \pm 0.08	3.80 \pm 0.12	106	3.58 \pm 0.07	1.53 \pm 0.60	42.7
	1.45 \pm 0.11	1.48 \pm 0.02	102	1.52 \pm 0.15	1.21 \pm 0.28	79.6
Nitrite	0.33 \pm 0.01	0.33 \pm 0.01	100	0.34 \pm 0.00	0.29 \pm 0.01	85.3
Nitrate	2.62 \pm 0.02	2.64 \pm 0.02	101	2.59 \pm 0.05	2.50 \pm 0.04	96.5
Silica	1.70 \pm 0.12	1.71 \pm 0.03	101	1.89 \pm 0.04	1.78 \pm 0.03	94.2
	27.04 \pm 0.08	26.72 \pm 0.03	99	26.93 \pm 0.06	29.87 \pm 0.11	110.9
	17.06 \pm 0.07	16.77 \pm 0.03	98	17.24 \pm 0.17	17.91 \pm 0.01	103.9

The most significant changes occurred in the ammonia and phosphate analyses. Figures 2 and 3 indicate the variability of results using ceramic samplers and the stability of the same analyses using TFE samplers. These results are in agreement with Hansen & Harris (1975), who found substantial variability of nitrate and phosphate concentrations using porous ceramic cups.

Particle size analysis of the TFE samplers indicated that the majority of particles passing through the sampler were 2 μm or less and that the percentage of the particles less than or equal to 2 μm increased over time (Table 2). The mean pore size of the porous ceramic cups is 2.9 μm (Soilmoisture Equipment Corp., 1974).

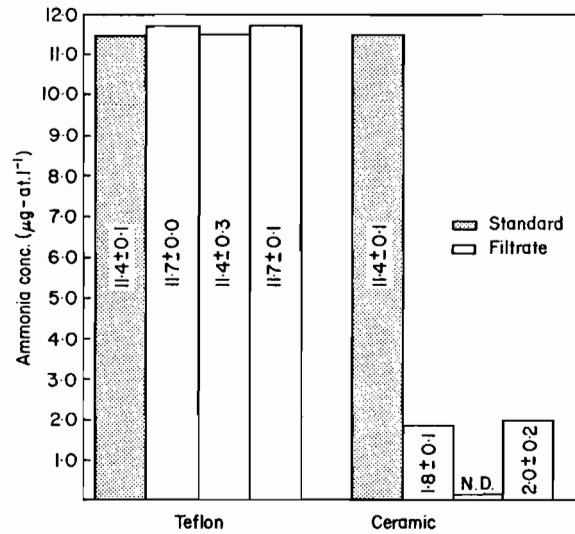


Figure 2. Comparison of ammonia concentrations for Teflon® and ceramic standards and filtrates (95% confidence limits for $N = 5$ replicates/sampler; $N = 10$ replicates/standard).

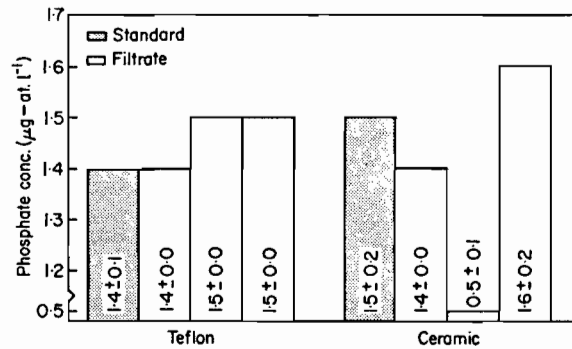


Figure 3. Comparison of ortho-phosphate concentrations for Teflon® and ceramic standards and filtrates (95% confidence limits for $N = 5$ replicates/sampler; $N = 10$ replicates/standard).

TABLE 2. Per cent particle size distribution of TFE filtrate over time

Size in µm	$t = 0+20$ min	$t = 0+60$ min	$t = 0+100$ min
< 5	4.1	2.5	1.7
< 4	13.9	12.3	12.2
< 3	12.9	14.8	16.0
< 2	48.0	59.8	64.5
Total < 5	78.9	89.4	94.4

Discussion

Creaser (1971), performing interstitial salinity determinations using an allundum cup, indicated that these could be used for nutrient studies with minor modifications. A drawback to this method is the need for frequent cleaning of the cup to prevent clogging, causing

removal of the sampler from the sediment after collection. The porous TFE sampler has many advantages in measuring nutrient concentrations of pore water. It can be placed in the sediment for long periods of time without clogging. Studies to date indicate that 125 ml of pore water can be collected once per day (25 cm Hg for 20 min) over a 14-day period without clogging the sampler or diminishing the sample volume. The sampler can be precisely located at a desired depth, then left in place without disturbing the sediment when sampling. The TFE is inert and, as this study indicates, does not alter nutrient concentrations. With minor modifications, the sampler can be used to analyse salinity, chlorinity and trace metals as well as nutrients in pore waters and would be especially valuable when frequent sampling at the same depth and location may be necessary over an extended period of time (i.e., diurnal or tidal studies).

These teflon devices are presently being used in a study of nutrient exchange in seagrass beds. A method is being developed whereby the anaerobic properties of pore water are being maintained from collection to final analysis.

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