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The Collection, Analysis and Variation of Nutrients in Estuarine Pore Water

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A series of field experiments were performed using *in situ* porous Teflon® samplers to determine the nutrient concentrations of anoxic pore waters in estuarine sediments. A method is described where pore water may be collected, stored and analyzed in an inert atmosphere. Multiple samples may be collected over long time periods without disturbing the sediment. High variability of nutrient levels within a one meter square plot of a subtidal mud flat were detected. The variation of ammonium (NH_4^+), reactive phosphate (RP) and silicate (SiO_3) in pore water were 34·3, 30·7 and 40% respectively, for four samplers placed at the same depth in this one meter square area, while sampler variability under laboratory conditions was 5·0, 7·0 and 0·3% for these nutrients respectively.

Introduction

The determination of nutrients in pore waters from marine sediments is difficult because certain chemical and physical interactions affect the concentration and 'state' of the chemical to be measured. For example, temperature (Fanning & Pilson, 1971; Bischoff *et al.*, 1970), oxygen (Emerson, 1976; Bray *et al.*, 1973), and carbon dioxide (Emerson, 1976) affect the concentration of nutrients in sediment pore waters collected using sediment squeezers. Temperature affects changes in ion exchange selectivity. Oxygen and carbon dioxide cause precipitation or co-precipitation by ferric hydroxides and calcium carbonate, respectively. Bray *et al.* (1973), suggested that these problems may be overcome by performing all sampling and analytical determinations in an inert atmosphere so that any possible oxygen contamination is avoided. An *in situ* sampling device where pore water could be collected in an inert atmosphere would greatly diminish the effects of temperature and gas exchange on nutrient pore water concentrations.

The purposes of this paper were to determine the precision of the *in situ* samplers for the collection of nutrients, the horizontal and vertical variations of nutrients in a 1 m^2 area in a seagrass bed and to determine whether the apparatus sampled from a predetermined sampling depth.

The procedures and samplers utilized in these experiments have several advantages over other methods. Multiple pore water samples can be collected from precise locations and depths in sediments while maintaining their anaerobic properties with minimal manipulation

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of the sample or perturbation of the substrate. The samplers are particularly useful in diurnal studies or longer time series investigations where multiple samples and replicates are required.

Materials and methods

Sampler description

The Teflon® (TFE) sampler consists of a machined porous TFE cup 5·0 cm long and 4·8 cm in diameter. The upper 1·5 cm is threaded and indented 0·7 cm from the cup. The cup is attached to a threaded length of PVC pipe and Silastic® (Dow-Corning) used as a sealant between the threads to insure an airtight seal. This allowed the PVC pipe to lie flush against the porous TFE. A 2 cm section of TFE was utilized to obtain a sample. The bottom 1·5 cm of the cup was also indented 0·7 cm, and a plastic PVC well head attached (Figure 1). This well head protects the Teflon and allows the samplers to be directly inserted into the sediment. Prior to field use, the samplers were cleaned by flushing with 1 l of 6 N-HCl followed by 6 l of deionized water. All sample containers and sample cups were washed with acid and rinsed with deionized water. Sample containers were flushed with Freon gas prior to sample collection. Laboratory studies (Zimmermann *et al.*, 1978) have shown 98–100% recovery for known concentrations of nutrients passing through the sampler. More than 65% of the particles passing through the TFE cup are 2 μm or less with the remaining particles being 5 μm or less.

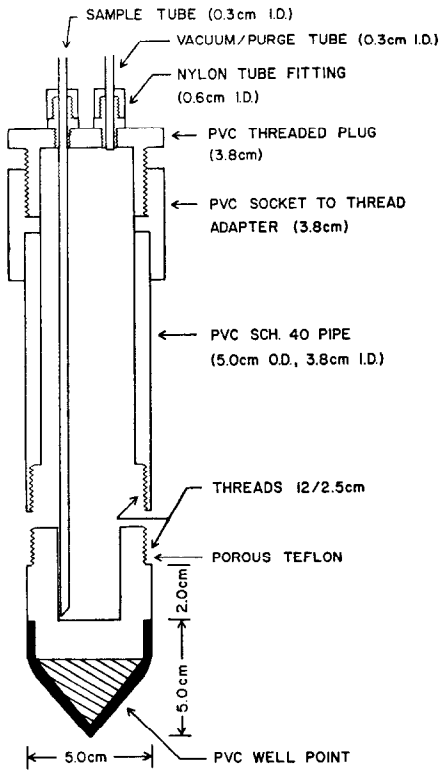

Figure 1. Schematic diagram of porous Teflon® sampler. Sample tip is shown separated from PVC pipe for clarity and length of PVC pipe is variable.

Study area and collection procedure

The study site was a subtidal mud flat located in the Indian River estuary on the east coast of Florida (Latitude: 27°32′, Longitude: 80°21′). All experiments were performed in this flat, in water approximately 0·5 m deep where the mean tidal range is 0·15 m. The sediment was composed of muddy sand (Thompson & Wolcott, 1976).

The samplers were inserted to various depths in the sediment and allowed to equilibrate for one week to eliminate any possible oxygen contamination from the overlying water (Hesslein, 1976). To establish sampler depth, PVC collars were attached to the PVC pipe at the desired depth, measured from the base of the sampler. The desired sampling depth was reached when the collar contacted the sediment surface.

The samplers were initially purged with Freon to remove accumulated seawater and provide an inert atmosphere. To collect pore water samples the sample line was sealed, a vacuum of 50 cm Hg was applied to the gas/purge line of the sampler for 15 min. A portable Freon gas bottle was then connected to the vacuum/purge line of the sampler. A portable hand-held vacuum pump was joined to another line on the septum vial. To retrieve a sample the Freon gas valve was opened and sufficient gas dispensed to provide an inert atmosphere in the sampler. The sample was then withdrawn from the sampler into a previously purged 50 ml septum vial by applying 35 cm Hg vacuum to the septum vial. Gas flow is critical during this part of the procedure. Too much pressure will force the sampler out of the sediment and/or push the sample back through the sampler into the sediment. With this procedure, several samples may be collected from the same site and depth during a specific time period without disturbing the sediment.

Laboratory procedures

Laboratory procedures included preparing dilutions and sample trays in an argon purged glove box. All dilutions were prepared using argon purged artificial seawater. Freon and argon gas were used in the field and laboratory respectively to provide an anaerobic atmosphere. In a separate field experiment, no significant differences were found in the concentration of nutrient samples collected with Freon or argon gas. Freon gas was used in the field because the gas container was portable. Ammonium (NH_4^+), nitrite (NO_2), nitrate and nitrite (NO_3+NO_2), reactive phosphate (RP) and silicate (SiO_3) were determined a few hours after collection using modified Technicon procedures (Zimmermann *et al.*, 1977). A minimum of three replicates were analyzed for each sample. To maintain anaerobic conditions throughout analysis, a Plexiglas® box was constructed to cover the Technicon® automatic sampler. Air and diluent tubing for the Technicon AutoAnalyzer® were routed through this box to maintain an inert atmosphere throughout analysis. Oxygen was maintained at less than one percent in both the glove box and the Technicon® automatic sampler and was monitored using a Beckman Oxygen Analyzer, Model D2.

The Eh of each sample was measured in the laboratory under an inert atmosphere with an Orion combination redox specific ion electrode and a Corning digital 110 expanded scale pH meter. Readings were made within 2 h of collection, and indicated stable conditions after approximately 1 min equilibration.

Laboratory and field experiments

A series of laboratory and field experiments were performed to determine, (1) if a lateral flow of water was collected from the sampler or if migration of water occurred either from above or below this depth, (2) sampler precision in the field, (3) horizontal variations of

nutrient concentrations within a defined area and depth in the pore waters of a subtidal mud flat, and (4) variability of nutrients in sediment pore water at various depths at both seagrass and non-seagrass sites.

Experiment 1—sampler resolution

Experiments were performed using radioactive carbon, to determine whether the *in situ* apparatus sampled within a discrete 5 cm area or from above or below this area. Marine sediment was collected and stored in a plastic bucket. The sediment was frozen to limit biological activity and thawed 36 h before use. The diffusion constant for radioactive carbon was determined, using the method of Duursma & Bosch (1970), to be less than $0{\cdot}8 \times 10^{-5}$ cm^2 s^{-1} under our experimental conditions.

A sampler was placed to a depth of 10 cm in the sediment. A boundary layer of Whatman no. 4 filter paper was placed over the sediment surface. Radioactive carbon 'spiked' seawater ($3{\cdot}982$ μCi ml^{-1}) was added to a depth of 2 cm over the sediment. Six pore water and surface water samples were collected at 10, 20, 30, 40, 50, 60 and 90 min after addition of the ^{14}C 'spiked' water.

A second test involved placing a $2{\cdot}5$ cm radioactive 'spiked' sediment slurry in the bottom of a plastic bucket. The slurry was covered by a filter paper boundary. The boundary paper was covered by 1 cm of unspiked sediment slurry. The sampler was placed at this depth and an additional 15 cm layer of unspiked sediment added around the sampler. Sample collection times of pore water and overlying water after the addition of spiked slurry were 10, 20, 30, 40, 50, 60, 90 and 120 min.

The samples were prepared for scintillation analysis using 1 ml of sample in 14 ml of PCS® 'cocktail' (Amersham Searle). All samples were counted for 10 min on a Searle Mark III liquid scintillation counter.

Experiment 2—sampler precision

This second experiment was designed to determine sampler precision and to detect any significant changes in nutrient concentrations when multiple samples were collected at one depth from one sampler over a short time period. One TFE sampler was placed at a depth of 20 cm in the experimental mudflat. Eight samples were collected at approximate 10-min intervals using a vacuum of 50 cm Hg. Sample volume ranged from approximately 50–75 ml. Collection, storage, and analysis of these samples were performed in an inert atmosphere.

Experiment 3—horizontal variations

This experiment was initiated to determine horizontal variations in the nutrient concentrations of pore water. The precision for all samplers was determined under laboratory conditions for ammonia, silicate and reactive phosphate prior to the field experiment. Before placing the samplers in the field the samplers were thoroughly cleaned, placed in deionized water and a sample withdrawn. This sample was analyzed for nutrients and if detected the samplers were recleaned. The mean coefficient of variation in the laboratory for the four samplers used in this experiment was $5{\cdot}0$, $7{\cdot}0$ and $0{\cdot}3\%$ for ammonium, reactive phosphate and silicate respectively. Four samplers were equally spaced 20 cm below the surface of the sediment in a 1 m square area. Nutrient samples from each sampler were collected using a vacuum of 50 cm Hg for 10 min. Two separate sets of samples were collected from each sampler within a 90 min period.

Experiment 4—vertical variations

A fourth experiment was performed to study the variability of nutrients in sediment pore water at various depths beneath a seagrass bed and a non-seagrass area. Eight samplers were placed in the sediment of a *Halodule* sp. grass bed, two at each of 10, 20, 30 and 40 cm depths. The samplers were placed at 1 m intervals in a double diamond pattern with the two center samplers 0·5 m apart. The samplers were situated in a $1{\cdot}5 \times 3{\cdot}0$ m area. Care was taken not to place two samplers next to each other at the same depth. The non-seagrass area was sampled in replicate at 11, 20 and 40 cm. This site was within 70 m of the seagrass site.

Surface water and sediment pore water, from 2 cm, were also analyzed for nutrient concentrations for both sites. Two centimeter pore water samples were collected using a modified syringe assembly (Johnson, 1967).

Ammonium, reactive phosphate, silicate, and Eh were measured from these samplers on three separate occasions; 30 January, 27 February and 17 April 1978, sampling periods 1, 2 and 3 respectively for the seagrass area and on April 1977 for the non-seagrass site.

Estimation of flux

Flux was estimated using the diffusion constants from Manheim (1976) corrected for temperature (Duursma & Bosch, 1970) as well as porosity and tortuosity (Manheim, 1970; Tzur, 1971) and the following equation:

$$F = D_0 \frac{\Delta c}{\Delta x} t$$

where F is the flux in $\mu g\ cm^{-2}\ year^{-1}$, D_0 is the diffusion constant in $cm^2\ s^{-1}$, Δc is the amount in $\mu g\ cm^{-3}$ by which the concentration of the ion in the pore water at a particular level differs from that in the immediately overlying seawater, Δx is the distance (cm) which the ion has to migrate from that level to the sediment surface and t the number of seconds in a year ($3{\cdot}15 \times 10^7$). The flux was measured from 10 cm depth for all ions and at 20 cm for sample two for reactive phosphate.

Results

Experiment 1—sampler resolution

The results of this radioactive ^{14}C experiment, whose purpose was to determine whether the *in situ* sampler collected pore water at the desired depth or whether the sample was withdrawn from a higher or lower depth, show that the sampler collected pore water only from its preset depth. The samples yielded a mean radioactive count of $47{\cdot}4 \pm 58$ disintegrations per minute (d.p.m.) versus a mean radioactive ^{14}C level of 65×10^3 d.p.m. in the slurries 5 cm above and 1 cm below the sampler, indicating no transport of radioactive carbon.

The hydrological characteristics of the *in situ* sampler simulate those of a partially penetrating well. Hydrology theory (Todd, 1958) states that for this type of well the crucial factors affecting water level 'drawdown' are flow rate and permeability. Assuming a low permeability of 1 with a flow rate of $0{\cdot}2\ cm^3\ s^{-1}$ the maximum intrusion of pore water, from other depths, would be 0·3% of the total sample volume. The crucial factor in determining 'drawdown' from above or below the sample site is flow rate and not total sample volume.

Experiment 2—sampler precision

When samples collected from one depth and one sampler over an 80 min time period were examined, no significant difference in Eh, silicate, ammonium or reactive phosphate was noted. The results are shown in Table 1.

TABLE 1. Multiple samples from one sampler at 20 cm depth over an 80 min time period. Mean values in μg-at. l^{-1} for nutrients and MV for Eh

Time (min)	Eh	SiO_3	NH_4^+	RP
0	+32	204·7	107·1	9·43
+10	−115	196·7	101·4	10·21
+20	−160	189·2	102·4	10·70
+30	−235	—	97·2	10·50
+40	−220	190·4	92·3	8·27
+50	−232	191·7	95·3	8·47
+60	−206	192·9	109·0	10·07
+70	−225	193·3	97·4	8·22

The coefficients of variation among the replicates were 3, 6 and 13% for silicate, ammonium and reactive phosphate, respectively.

Eh was slightly positive for the first sample probably due to oxygen contamination but then became negative for the remaining seven samples.

Experiment 3—horizontal variations

Horizontal variations in nutrient concentrations observed for four samplers placed at the same depth in a 1 m^2 area, during the two time periods tested, showed coefficients of variation (CV) for SiO_3 of 40%, NH_4^+, 34%; and RP, 30·7% (Table 2). The mean CV between replicates of the same sample set were 1%, 2·8% and 3·4% respectively. This indicates a relatively low variation due to our analytical techniques and that the variability between sample location is real.

In this experiment, samplers 11 and 12 were placed beside each other at a 1 m interval while samplers 9 and 10 were placed in a like manner 1 m closer to shore. When samplers 9 and 10 are compared to samplers 11 and 12 the results indicate that relatively low coefficients of variation exist within the two sets of samplers but that the variation between both sets of samplers is high (Table 3). The high CV for RP between samplers 9 and 10 may be due to oxygen contamination of sampler 9 at the first time period. Corresponding nitrate values were higher also. Eh values also confirm the presence of two distinct populations. No significant differences occurred for RP and NH_4^+ between samplers 11 and 12 or for NH_4^+ and SiO_3 for samplers 9 and 10. All other combinations of samplers and nutrients indicated significant differences (paired t statistic, $P<0{\cdot}05$).

Experiment 4—vertical variation

The maximum concentrations of ammonium, reactive phosphate and silicate occur at the 8–10 cm depth in the seagrass as do the highest negative Eh values (Table 4). Nitrate values were highest at 2 cm (3·27 μg-at. l^{-1}) and less than 0·1 μg-at. l^{-1} throughout the other depths.

It is also interesting to note the horizontal variations, at the seagrass site, between replicates in this experiment. The highest CV for silicate was found between the 18–20 cm samplers (16·1%); for ammonium, the 8–10 cm samplers (24·4%); and for reactive phosphate all 4 depths had a CV of approximately 30%.

The change with depth in the pore water concentrations of ammonium, silicate, reactive phosphate and Eh over the three sample periods is shown in Figure 2.

The results for the non-seagrass area are shown in Table 5. The maximum concentration for the nutrients studied are at 40 cm, but the concentration gradient is greatest from the surface to 10 cm after which the values appear to level off.

TABLE 2. Mean ($\bar{x}$), standard deviation and coefficient of variation (CV) for samplers 9–12 at 20 cm depth. Two sample series taken at 45-min intervals. Nutrient concentrations in μg-at. l^{-1}, Eh values in M.V.

Series	Eh		SiO_3			NH_4^+			RP		
Sample number	1	2	1	2	CV	1	2	CV	1	2	CV
9	−140	−59	163·5±0	102·2±0	25%	83·4±0·4	42·5⊥1·2	36%	7·69±0·09	9·43±0·63	12%
10	−45	−70	138·3±0·5	107·7±0·6	14%	66·2±0·7	70·4±5·4	6%	19·23±0·13	12·84±0·31	22%
11	−188	−183	266·4±1·5	254·2±0	3%	111·7±2·8	127·9±0	6%	10·40±0·50	9·60±0·89	8%
12	−243	−224	228·3±2·1	212·4±0·3	4%	105·6±3·6	127·7±1·9	11%	10·45±0·16	10·08±0·06	2%
%CV			27·0	41·0		20·7	44·8		38·0	15·0	
%CV overall			40·0			34·3			30·7		

TABLE 3. Mean ($\bar{x}$), standard deviation (S.D.) and coefficient of variation (CV) for pairs of samplers. Nutrient concentrations in μg-at. l^{-1}

		SiO_3			NH_4^+			RP		
Series	Samplers	$\bar{x}$	S.D.	CV	$\bar{x}$	S.D.	CV	$\bar{x}$	S.D.	CV
1	9 and 10	150·9	13·79	9%	74·8	9·45	12·6%	13·46	6·32	47%
	11 and 12	247·4	20·93	8%	108·7	4·37	4·0%	10·43	0·33	3·2%
2	9 and 10	104·9	3·05	3%	56·5	15·7	27·8%	11·13	1·91	17·2%
	11 and 12	233·3	22·91	10%	127·8	1·21	0·95%	9·79	0·68	6·9%
Mean values of nutrients over 2 sampling periods	9 and 10	127·9	25·82	20%	65·62	15·6	23·8%	12·30	4·6	37·4%
	11 and 12	240·3	22·18	9%	118·2	10·4	8·8%	10·14	0·59	5·8%

TABLE 4. Depth profile of nutrients (μg-at. l^{-1}) and Eh (M.V.) in the pore waters of a *Halodule* sp. grass bed. Mean ($\bar{x}$), standard deviation (S.D.) and coefficient of variation (CV) given. 1 and 2 represent duplicate samplers

Depth	Eh		SiO_3		NH_4^+		NO_3+NO_2		RP	
	1	2	1	2	1	2	1	2	1	2
Surface	+232		15·5		0·4		0·27		0·99	
2 cm	−38		128·1		25·5		3·27		11·45	
8–10 cm	−208	−263	200·3	178·4	72·2	113·6	*	*	9·82	17·76
$\bar{x}$			189·4		92·9				13·79	
S.D.			11·9		22·7				4·35	
CV (%)			6·0		24·4				31·50	
18–20 cm	−146	−147	141·9	105·4	55·7	48·0	*	*	6·42	4·48
$\bar{x}$			123·6		51·9				5·64	
S.D.			19·9		4·3				1·59	
CV (%)			16·1		8·2				28·20	
38–40 cm	−33	−155	125·0	119·2	44·5	37·7	*	*	3·51	5·18
$\bar{x}$			122·1		41·1				4·35	
S.D.			3·24		3·9				1·09	
CV (%)			2·6		9·5				25·10	
38–40 cm	−157	−102	102·3	98·8	44·3	36·7	0·11	0·18	3·42	2·32
$\bar{x}$			100·6		40·5				2·87	
S.D.			5·2		4·1				0·95	
CV (%)			5·2		10·2				33·10	

* Undetectable, MDC less than 0·2 μg-at. l^{-1}.

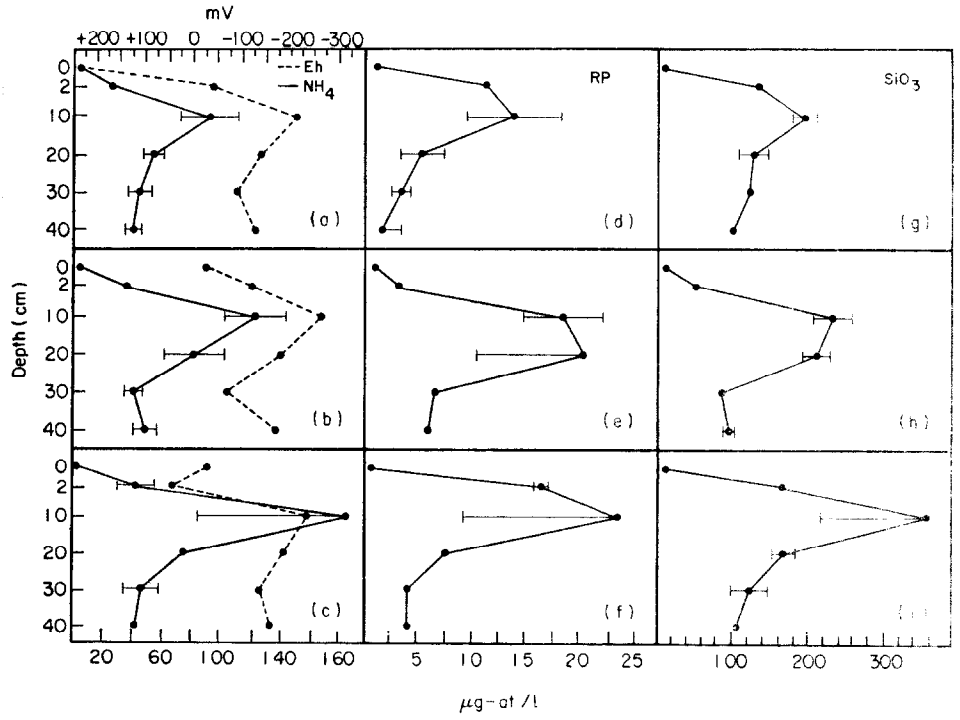

Figure 2(a)–(i). Nutrient and Eh depth profiles for three sampling periods; 30 January 1978, 27 February 1978 and 17 April 1978 in the sediment of a *Halodule* sp. grassbed. Values shown are means of two samplers at the same depth ± one standard deviation.

Flux estimations

The data used to calculate flux, for the seagrass data, F, and the values for F are shown in Table 6.

TABLE 5. Depth profile for ammonium, reactive phosphate and silicate in sediment pore water underlying a non-seagrass area (April, 1977). Values are in μg-at. l^{-1}

Depth	NH_4^+	SiO_3	RP
Surface	7·40	20·0	1·03
S.D.	4·40	2·40	0·220
5 cm	62·0	61·7	1·15
S.D.	2·90	1·40	0·180
10 cm	59·9	109·0	3·42
S.D.	5·70	10·6	2·04
20 cm	111·6	178·0	7·63
S.D.	14·4	78·9	3·89
40 cm	149·0	307·0	9·67
S.D.	48·6	61·9	0·780

TABLE 6. Flux estimations (F) in μg cm^{-2} $year^{-1}$, for ammonium (NH_4^+), reactive phosphate (RP), and silicate (SiO_3) for three sampling periods 30 Jan. 78 (1), 27 Feb. 78 (2), and 17 Apr. 78 (3). Flux calculations were computed using $F = D_0(\Delta c/\Delta x)/t$ where t was $3{\cdot}15 \times 10^7$ s $year^{-1}$, Delta C (Δc) was measured at 10 cm except as noted. Where Δc is the amount (g cm^{-3}) by which the concentration of the ion in the pore water at a particular level differs from that in the immediately overlying seawater. Delta x (Δx) is the distance (cm) which the ion has to migrate from that level to the sediment surface. Temperature in °C, of sediment at 10 cm except as noted. D_0 values corrected for temperature (2·5% increase per °C) and porosity/tortuosity of sediment assuming 50% porosity (Manheim, 1970)

Nutrient	Sample	$\Delta c/\Delta x$ (μg cm^{-1})	D_0 (cm^2 s^{-1}[a])	F (μg cm^{-2} $year^{-1}$)	T (°C)
NH_4^+	1	$1{\cdot}3 \times 10^2$	$2{\cdot}8 \times 10^{-6}$	$1{\cdot}1 \times 10^4$	[c]9·0
	2	$1{\cdot}7 \times 10^2$		$1{\cdot}5 \times 10^4$	16·7
	3	$2{\cdot}5 \times 10^2$		$2{\cdot}2 \times 10^4$	24·2
RP	1	$4{\cdot}1 \times 10^1$	$1{\cdot}2 \times 10^{-6}$	$1{\cdot}5 \times 10^3$	9·0
	2	[b]$3{\cdot}1 \times 10^1$		$1{\cdot}2 \times 10^3$	16·7
	3	$7{\cdot}4 \times 10^1$		$2{\cdot}8 \times 10^3$	24·2
SiO_3	1	$4{\cdot}9 \times 10^2$	$1{\cdot}4 \times 10^{-6}$	$2{\cdot}2 \times 10^4$	9·0
	2	$6{\cdot}2 \times 10^2$		$2{\cdot}7 \times 10^4$	16·7
	3	$9{\cdot}8 \times 10^3$		$4{\cdot}3 \times 10^5$	24·2

[a] Manheim, 1976. Corrected for temperature effect (2·5% increase in D_0 per °C) and porosity/tortuosity effect (Manheim, 1970; Tzur, 1971) assuming a porosity of 50%.

[b] Delta C (Δc) measured at 20 cm depth.

[c] Temperature of surface water, temperature data for 10 cm depth in sediment not available.

Discussion

When the precision of the *in situ* samplers is examined, the total variation can be partitioned into four major sources: the variability due to the analytical technique; the variation due to the samplers; the variation due to sampling in the field; and variance due to spatial heterogeneity. The total precision of the samplers in the field, at one depth (Exp. 2), including variance due to the sampler plus analysis error but excluding variance due to spatial heterogeneity was, 3% (SiO_3), 6% (NH_4^+), and 13% (RP). The mean analytical precision for the

three nutrient determinations was 0·85%. When the precision of the samplers and analytical technique is subtracted from the total variation, the results show that the field variation of the samplers is much greater than the variation found in the laboratory. This increased variation can be attributed to the increased difficulty of sampling in the field and within sampler variation. The precision of the *in situ* samplers and the samplers' vertical resolution were far exceeded by the variability of the pore water nutrient concentrations within a 1 m^2 area. These variations ranged from 40% for SiO_3 to 30·7% for RP.

Matisoff *et al.* (1975) in their work on interstitial waters of Chesapeake Bay indicated spatial variations of 10%, 15% and 16% for silicate, ammonium and dissolved reactive phosphate, respectively, for five cores taken at approximately 100 foot intervals in a '*T*' pattern.

The results shown in our research demonstrate the spatial heterogeneity of nutrient concentrations of interstitial water. More than one sampler per depth is necessary for accuracy in flux determinations. This is in agreement with the conclusions of Ristvet *et al.* (1973).

Our pore water concentration profiles of NH_4^+ and RP in *Halodule* sp. grass beds do not agree with those of Patriquin (1972) obtained in the pore waters of sediments underlying *Thalassia testudinum*. The best explanation for our disagreement with Patriquin's results was the difference between sample collection techniques. Our analyses and sampling were all performed under an inert atmosphere. As a result, the average value of NH_4^+ at 2·0 cm was thirteen times the value found by Patriquin. Multiplying Patriquin's value for the total NH_4-N reservoir of 340 mg m^{-3} by thirteen yields a 62 to 212 day supply of nitrogen for *Thalassia testudinum* leaf growth rather than the 5 to 15 day supply he postulated.

In our vertical profiles of ammonium, reactive phosphate, and silicate the concentration increased to a maximum at 10 cm and then decreased. This type of profile was also found by McRoy *et al.* (1972) beneath *Zostera* beds. This profile is apparently maintained by the seagrass system as the profile is different in an area devoid of seagrass.

Matisoff *et al.* (1975), Vanderborght & Billen (1975), Nriagu (1978) and Martens *et al.* (1978) found similar maximum concentrations of ammonia, phosphate and silicate in the interstitial waters of other non-seagrass areas. The nitrate profile determined in this research is also in agreement with other investigators as shown by the results of Vanderborght & Billen (1975) who found maximum concentrations of nitrate at approximately 2 cm with undetectable concentrations at 10 cm. Bender *et al.* (1977) found maximum concentrations of nitrate at 5 cm with undetectable concentrations of 40 cm. Grundmanis & Murray (1977) indicated intermediary nitrate maxima at 20–30 cm which they believed due to burrowing organisms. It is interesting to note that the Eh values obtained by them never approached reducing conditions.

The possibility then arises that the chemical character of the organic matter and biological activity of the seagrass, or burrowing organisms, on the organic matter are responsible for the particular ammonium profiles. The decrease of phosphate and silicate below 10 cm is probably due to authigenic mineral formation (Troup, 1974) and to silica diagenesis (Berner, 1971). At this time we have no evidence to support either of these two reactions but they are reasonable hypotheses.

Most of the work using stoichiometric reactions to describe the decomposition of organic matter and the regeneration of nutrients specifically excludes the biogenic zone (Martens *et al.*, 1978; Berner, 1971) because mixing occurs by bioturbation and other physical processes rather than molecular diffusion. Preliminary data in our laboratory indicate depth profiles similar to the nutrients for sulfide and dissolved organic carbon. We are initiating

analysis for sulfate and plan to intensify our sampling intervals at both seagrass and non-seagrass sites in an attempt to determine whether the biological activity of the seagrasses is responsible for the peculiar nutrient depth profiles. Our initial estimates of flux indicate a phosphate flux ranging from 1·2 to $2{\cdot}8 \times 10^3$ μg cm^{-2} $year^{-1}$. When this estimated flux value is compared to 62·4 mg m^{-2} day^{-1} ($2{\cdot}3 \times 10^3$ μg cm^{-2} $year^{-1}$) (McRoy *et al.*, 1972), we find that the values are similar.

The transport of nutrients, phosphorous in this case, need not entirely depend on the active transport by the seagrasses as our flux estimates show. Further confirmation of these conclusions are also shown by McRoy & Barsdate (1970) where 50% (87% for the 'dark' experiment) of radioactive ^{32}P tracer remained in the water and 33% (8% in the 'dark' experiment) was transported through the eelgrass plants to the upper water within 24 h.

Although an active transport of phosphate by eelgrass plants was shown by McRoy, the total system transport of nutrients may equal or exceed that of transport by seagrasses alone.

Byrnes *et al.* (1972) indicated, in lakes, that the flux of NH_4^+-N will proceed from interstitial waters to lake water with the 0·4 cm sediment layer providing the immediate source of nitrogen. Sediment from 5 to 16 cm provides a long-term source of NH_4^+-N. Vanderborght & Billen (1975), quoting unpublished data from Wollast, state that diffusion, aided by turbulence and bioturbation, can increase flux rates by a factor of one hundred.

From work done by investigators cited in the Introduction, the need for inert conditions while collecting, storing and analyzing anoxic pore water samples cannot be over-emphasized. The TFE sampler and procedure described here meets this important requirement. This system is presently being used to measure trace metals, pH, salinity, organic carbon as well as nutrients and Eh in an intensive sampling program of the sediments of seagrass beds.

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