Biogeochemistry 7: 55-75 (1989)

The sedimentary flux of nutrients at a Delaware salt marsh site: A geochemical perspective

JOSEPH R. SCUDLARK & THOMAS M. CHURCH
College of Marine Studies, University of Delaware, Lewes, DE 19958, USA

Key words: salt marsh, nutrients, sediments, diffusion

Abstract. A basic geochemical approach has been used to study the diagenetic cycling and sediment-water exchange rates of essential nutrients at a site in a Delaware salt marsh. The pore water nutrients $Si(OH)_4$, NH_4^+, PO_4^{-3}, and NO_3^- were analyzed and compared seasonally, and potential diffusive fluxes were calculated from the corresponding pore water concentration gradients. Concurrent direct flux measurements were also made using closed chambers deployed on the salt marsh surface under ambient and controlled conditions. The differences in these two approaches allows for estimation of nutrient production and consumption in the root zone and at the salt marsh surface. Silicate and phosphate appear to be primarily geochemically controlled, while the nitrogen species undergo dynamic seasonal redox fluctuations resulting from microbial mediation (e.g., nitrification and denitrification). Specifically:

- silicate behaves rather conservatively according to silica solubility,
- phosphate flux is controlled by the corresponding sequestering or reductive remobilization of surface iron oxides, and
- ammonium has a strong upward flux which appears to undergo quantitative nitrification in spring.

None of the measured flux rates would have a major impact on the nutrient budget for the local estuary, Delaware Bay.

Introduction

The traditional ecological approach to salt marsh nutrient dynamics involves determining the exchange of water and nutrients between the marsh as a whole ecosystem and some parent body of water. While more recent flume studies (Wolaver et al. 1983) greatly reduce the inherent large degree of uncertainty in such mass-balance approaches (Nixon 1980), they inadequately address the specific biogeochemical processes and pathways which contribute to the observed net fluxes. The objective of this study was to apply a traditional *geochemical* approach to examine the diagenesis of salt marsh sediments and the consequential regeneration of primary nutrients.

Such an approach, which has found previous wide-spread application in sub-tidal marine sediments, utilizes two differing but complementary experimental designs. The first, more theoretical in nature, utilizes pore water concentration gradients to calculate potential sedimentary fluxes based on a modified diffusion model. The second approach empirically measures flux rates directly, employing "bell jar" flux chambers deployed on the marsh surface. By comparing the "predicted" fluxes to the "measured" values, one can evaluate the relative importance of surface and sub-surface processes in regulating sedimentary nutrient fluxes.

Recognizing the quantitative limitations inherent with this approach in accurately predicting actual fluxes, the objectives of this study are:

- to resolve the direction and relative magnitude of nutrient fluxes at one representative salt marsh site on a seasonal basis; and
- to identify the biogeochemical process which may play important roles in governing nutrient transformations and exchange in these sediments at this site.

Site description

The area chosen for this study was a typical saline, high marsh site in the Great Marsh, bordering the Delaware Estuary (Fig. 1). Due to logistical constraints, our study site was located about 100 m. upstream from the site reported in Lord & Church (1983). Overall, this marsh emcompasses an area of approximately $2 \times 10^6 m^2$, and the study site is occupied by the short form of *Spartina alterniflora* Loisel. Complete inundation of the marsh surface occurs only during spring tides and tidal storm surges, when tidal amplitude exceeds 5.0 feet. Coring and flux chamber experiments were conducted approximately 15 m. from the nearest creekbank. The surface sediments (0–20 cm) at this site are predominantly composed of a dense, fibrous root mat, and appear to remain saturated even at low tides. There is no visual evidence of bioturbation in these sediments, nor does ^{210}-Pb geochronology (Church et al. 1981) reveal any indication of significant biological reworking at the marsh surface.

Methods

Sediment pore water

Four seasonal cores were obtained at the same study site in January, April, July, and November 1980, subsequently referred to as winter (marsh surface frozen), spring (emergence of *Spartina* shoots), summer (full *Spartina* growth), and fall (*Spartina* senescence), respectively. The cores were extrac-

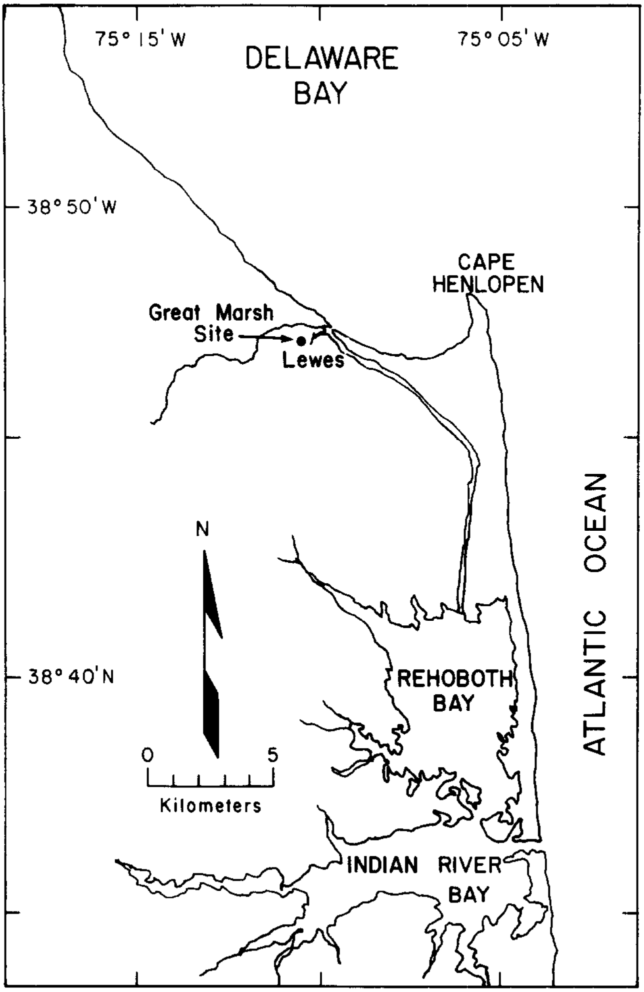

Fig. 1. Location of study site in the Great Marsh, Lewes, Delaware.

ted hermetically according to previously established procedures (Lord 1980). In a glove box, the cores were extruded and subsectioned into 2 – 3 cm sections; the pore water was expressed and filtered (0.4 μm Nuclepore) directly into 30 ml plastic syringes, using a pneumatic sediment squeezing technique (Reeburgh 1967). To prevent chemical artifacts which result from changes in temperature and the introduction of atmospheric 0_2 (Bischoff et al. 1970; Fanning & Pilson 1971; Bray et al. 1973; Hurd & Spielvogel 1975; Loder et al. 1978), all operations were carried out at near-in situ temperatures and under a positive nitrogen atmosphere. To facilitate chemical analyses, the dilutions, chemical pre-treatments and analytical methods outlined in Table 1 were employed. Analyses were performed in triplicate, including method and reagent blanks.

Table 1. Analytical chemistry of salt marsh sediments pore water analyses.

Parameter	Dilution	Analytical method [Uncertainty]	Pretreatment
PO_4^{-3}	1:10	Murphy & Riley (1962) [±5%]	0.2 mls Q-HCl purge with N_2 (to remove H_2S)
NH_4^+	1:100	Solorzano (1969) [±10%]	purge with N_2
NO_3^-	1:100	Strickland & Parsons (1972) [NO_2^- ± 3%; NO_3^- ± 6%; Si (OH) 4 ± 5%]	purge with N_2 ; allow sample to stand at room temp. 24 h after thawing before Si $(OH)_4$ analyses
NO_2^-	1:100		
$Si(OH)_4$	1:100		
Cl^-	1:10	Strickland & Parsons (1972) (Mohr titration) [±1%]	
POC		Holme & McIntyre (1971) Allen 1978 [±16%]	

In contrast to subtidal marine sediments, salt marshes are only periodically inundated, so that diffusive transport across the sediment/water interface must be modeled assuming pseudo-steady-state behavior. The potential nutrient exchange rates between the sediments and flooding water can be estimated using a modified form of Fick's first law of diffusion, i.e.,

$$J = \Phi \cdot D' \cdot \frac{\partial c}{\partial z}$$

where J is the calculated flux rate, Φ the porosity of the sediment, $\partial c/\partial z$ the slope of the concentration gradient at the sediment/water interface, and D' is the effective diffusion coefficient.

The effective diffusion coefficient (D') is related to the bulk solution diffusion coefficient (D°) in seawater by D°/t^2 (Li & Gregory 1974; VanBrakel & Heertjes 1974), where t is the tortuosity of the sediment. Based on the harmonic diffusion model of Lord & Church (1983), the estimated ratio of D'/D° for local salt marsh sediments is 0.7, and the average porosity is $0.85\,cm^3\ H_2O \cdot cm^{-3}$ sed.. The bulk solution diffusion coefficients employed in making our calculations were literature values, adjusted for ambient seasonal temperatures (Wollast & Garrels 1971; Li & Gregory 1974; Krom & Berner 1980). For the sake of simplicity, we have assumed that the porosity and effective diffusion coefficients are seasonally and vertically constant within each core. Though evidence suggests these terms may vary by as much as 30% at the sediment surface (Lord & Church 1983), the use of mean annual constants is justified in making such first-order estimations of potential flux rates.

Surface flux chamber experiments

To determine the actual nutrient fluxes across the sediment/water interface, flux chambers were deployed on the marsh surface in conjunction with the winter and summer coring activities. These chambers are of a closed system design, consisting of cylindrical plexiglas enclosures (20 cm. diam. × 30 cm. high) containing septum ports for sampling and mixing via gas dispersion.

The experiments were initiated by carefully inserting the chambers into the marsh approximately 10 cm, then rinsing and filling them with open ocean (Sargasso Sea) water. Where the marsh acts as a nutrient *source*, use of water initially low in nutrients maximizes the sediment/water concentration gradient and hence, the resultant chemical flux. If the marsh acts as a *sink*, the gradient and flux would be minimized. The chambers were run under ambient light conditions, and an effort was made to include a typical standing stock of marsh macrophytes, so that naturally occurring processes such as plant uptake or leaching from aboveground plant tissue would be included in the observed net flux rate.

During the winter experiment, two chambers were run concurrently in differing modes:

- oxically, (achieved by gently mixing the chamber water by bubbling compressed air, yet minimizing the disturbance of the sediment surface), and
- anoxically, (accomplished by similarly mixing with nitrogen).

The purpose of the anoxic chamber was to examine the redox sensitivity of surface oxide veneer, while the oxic chambers more realistically mimic natural conditions. For the summer experiments, both chambers were maintained oxically, in duplicate, to examine the on-site variability. The objective of such aeration was not only to produce a homogenous and controlled oxygen regime, but also to minimize the establishment of an artifically stagnant chemical gradient above the sediment/water interface. In all cases, the gas was prefiltered with an in-line filter (0.1 μm Nuclepore) and introduced into the chamber water column via an air dispersion tube.

At regular intervals (about every 3 hours), over a period encompassing up to 4 tidal cycles, 100 ml aliquots were withdrawn with a plastic syringe via the sampling port, and filtered in the field by means of a pre-combusted 25 mm inline prefilter (Whatman GF/C). At the laboratory, the samples were flash frozen over dry ice within an hour of collection, for subsequent analyses. Based on the duplicate chambers results, the standard error associated with the flux chamber measurements (Table 3) was less than 20%.

Creek sampling

In conjunction with the flux chamber sampling (i.e., at 3 hour intervals), the adjacent tidal creek was sampled at mid-depth, and in mid-stream. As with the flux chamber samples, the creek water was filtered (Whatman GF/C), and the filtrate flash frozen within the hour for later analyses. The purpose for this sampling was to determine tidal trends relative to sedimentary fluxes, and to quantify the concentration of the chemical constituents in the flooding tidal water (which determines the upper boundary for calculating diffusive fluxes). While the creek water nutrient concentrations exhibit intra-tidal and seasonal variability, when compared to the pore water concentrations, such deviations are relatively small and exert little influence in establishing the chemical gradients. The creek water concentrations measured at high flood tide were employed as representative of water flooding the marsh.

Results

Depth profiles for nutrient concentrations in pore water are presented in Figs. 2–8, and resultant seasonal and yearly intergrated calculated fluxes are given in Table 2. All depth intervals have been corrected to account for compaction during sampling (Lebel et al. 1982) and assumes such effects are linearly constant over the length of the core. The observed chemical gradients (dashed line), in many instances, are the result from a simple least mean squares fit of the depth gradient. In other cases, (e.g., spring nitrate profile), such a linear gradient does not extrapolate to the measured flooding creek water concentration (as indicated by arrows on the concentration axis, winter and summer cores only) due to the occurrence of a sub-surface concentration maximum. In these cases, it was necessary to project a chemical gradient which more accurately reflects the chemical differential at the sediment/water interface. Thus, the flooding water concentration and near-surface data points are most critically weighted.

Due to the limited spatial resolution in our experimental design, our observations regarding the direction, relative magnitude and processes mediating nutrient fluxes can only be applied with certainty to our study site. However, the consistancy in the organic carbon, chloride and iron profiles between this study and those reported for a nearby site over a ten year period (Lord & Church 1983; Luther et al. 1986; Luther & Church 1988) indicate general areal homogeneity of this marsh system. Furthermore, the temporal variability observed at our site far outweighs the relatively small degree (< 20%) of spatial variability we have observed between sites. Thus, while

Table 2. Predicted diffusive fluxes of nutrients from sediments at a a Delaware salt marsh site.

Parameter	Calculated Flux Rate (n moles cm^{-2} d^{-1})				Annual integrated flux rate (m moles m^{-2} yr^{-1})
	Winter	Spring	Summer	Fall	
$Si(OH)_4$	+4.6	+3.2	+119.5	+18.7	+166
NH_4^+	+24.2	+13.5	+494.0	+12.3	+631
PO_4^{-3}	+0.3	+0.2	+0.6	+14.2	+14
NO_3^-	−4.4	+14.1	+11.8	−14.4	+12

(Positive values imply marsh source, while negative values a marsh sink)

our interpretations of the data are bound by the limits imposed by the size of our sampling site, we feel there is sufficient evidence to suggest they are at least qualitatively applicable to the entire high marsh regime in the Great Marsh.

Carbon

The ultimate "driving force" which fuels the major diagenetic processes in salt marsh sediments is the breakdown of buried organic carbon. In fact, it has been clearly demonstrated that the rates of microbial activity resulting in sulfate reduction (Westrich & Berner 1984) and denitrification (Kaplan et al. 1979) are directly proportional to the organic carbon content of the sediment.

The profile of sedimentary organic carbon content shown in Fig. 2 is a composite representing the average of the four seasonal cores, as analyzed by two independent studies at our laboratory. This profile is in close agreement with that reported by Lord & Church (1983) for a nearby study area. For comparison, the organic content of these Great Marsh sediments is about twice that of Sapelo Island marshes, and about a factor of four less than the Great Sippewissett Marsh (Giblin & Howarth 1984). Though it is difficult to differentiate between living and dead biomass, the observed distribution reflects an enrichment of reactive, labile organic carbon at the surface of the marsh (above 20 cm). Below 20 cm the organic content decreases to an asymptotic concentration of ~ 100 mg/g, which presumably represents the buried "refractory" carbon such as cellulose and lignin derivatives.

Chloride

Pore water chloride represents a conservative (not biologically or chemically reactive) tracer in sediments. The behavior of interstital chloride in salt

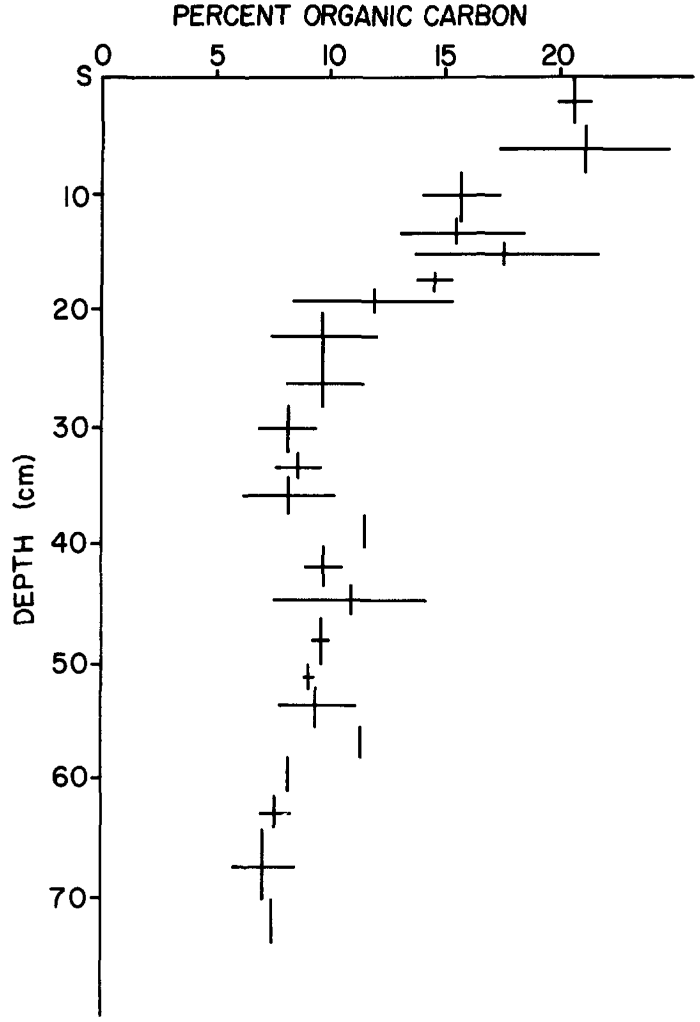

Fig. 2. Seasonal composite sedimentary organic carbon profile versus depth in the Great Marsh, Delaware.

marsh sediments (Fig. 3) has been previously described by Lord & Church (1983), in which profiles converged at depth to net evaporative concentrations and were modeled accordingly. These profiles are interpreted to be the result of the physical processes of dessication, diffusion, and dilution, which operate in accord with a seasonal harmonic diffusion model.

In the present study, the seasonal oscillations at the surface converge at depth to a time-averaged mean (26 ± 3 g/l) except in the spring core (~ 20 g/l), which perhaps represents the degree of spatial heterogeneity at this sampling site. While the hydrologic regime of the Great Marsh has not been

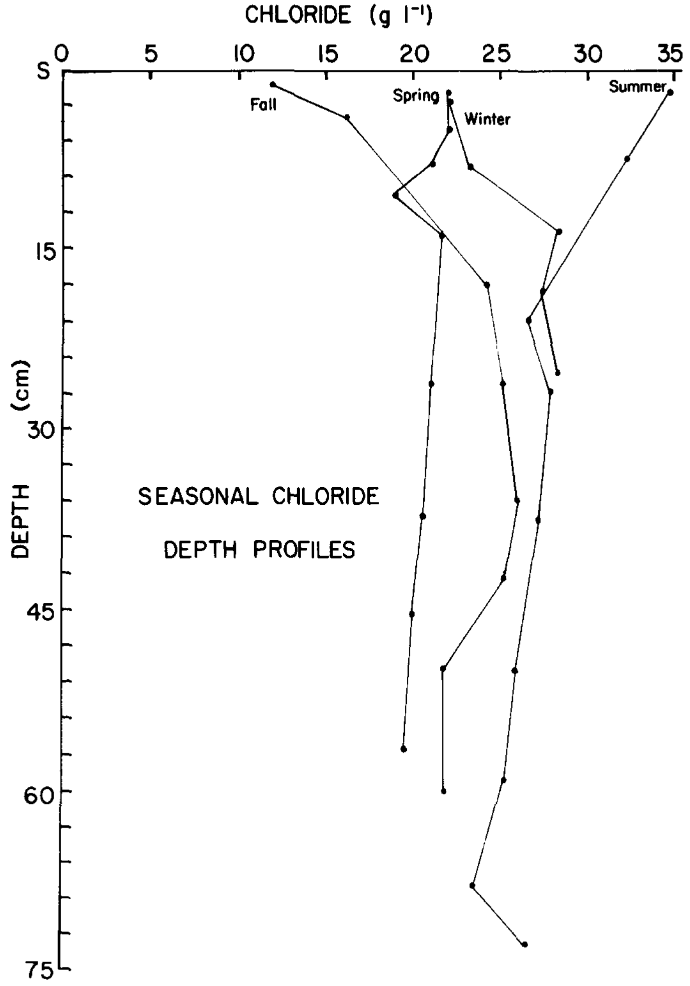

Fig. 3. Seasonal sedimentary pore water profiles of dissolved chloride (g/l) versus depth in the Great Marsh, Delaware.

well-characterized, there is no evidence of significant tidal advective exchange of pore water constituents such as observed with the Great Sippewissett Marsh (Hemond & Fifield 1982). Furthermore, more recent hydrological studies in Chesapeake Bay and South Carolina marshes (Jordan & Correll 1985; Agosta 1985) concur that significant tidal infiltration is limited to within several meters of the creekbank. Thus, tidal exchange of dissovled nutrients at our high marsh site appears to be dominated by sedimentary diffusion rather than other tidal advective processes. With the exception of the spring core, chloride concentration at depth is consistent with results previously obtained by Lord & Church (1983) in a nearby study area. This salinity is significantly above that of tidal waters (~ 16 g/l), and confirms the large degree of net desiccation and evapotranspiration which occurs in salt marsh sediments (Dacey & Howes 1984).

Silicate

As with sub-tidal marine sediments, the distribution of pore water silicate in inter-tidal sediments can be explained by a dynamic balance of two processes:

- Dissolution reactions involving amorphous biogenic silicate derived from the tests of edaphic diatoms, marsh vegetation, and from imported detrital material.
- Reprecipitation and adsorption/desorption reactions between dissolved silicate and authigenic silica phases (Mackenzie et al. 1967; Hurd 1972; Schink et al. 1975; Sayles & Mangelsdorf 1977).

In the surface sediments, the variable gradient at the upper part of the concentration maximum (Fig. 4) reflects the kinetic balance between dissolution and precipitation rates in response to sediment temperature (Lerman 1979). In fact, the steady-state silicate concentration at depth (0.4–0.9 mM) is significantly lower than the solubility of amorphous silica at the same temperature ($\sim$ 1.8 mM; Wollast 1974), implying lower solubility for authigenic mineral phases.

With both seasonal experiments, the measured chamber fluxes are in disaccord with the calculated estimates (Table 3). In the winter, the larger measured fluxes may reflect the increased release (via dissolution and /or disaggregation) of solid phase silicate resulting from the partial thawing of the marsh surface upon filling the chambers; an analagous process may occur naturally when the frozen marsh is flooded by tidal action. In the summer, the reverse trend is evident, where the calculated silicate flux is about twice the observed flux. In this instance, a strong silicate flux may be partially co-precipitated at the sediment surface along with iron and phosphate under oxic conditions in the chambers (Loder et al. 1978), or may be consumed by edaphic diatoms (as is subsequently discussd). The somewhat larger silicate fluxes under anoxic conditions in the winter chamber experiments supports this theory, as do the phosphate data (as subsequently discussed). Overall, the silicate fluxes measured in summer are 4–5 times greater than in winter, which agrees quantitatively with reported silicate solubility/temperature relationships (Alexander et al. 1954).

Nitrogen species

In contrast to the predominantly geochemical behavior of chloride and silicate, the distribution and speciation of nitrogen in salt marsh soils

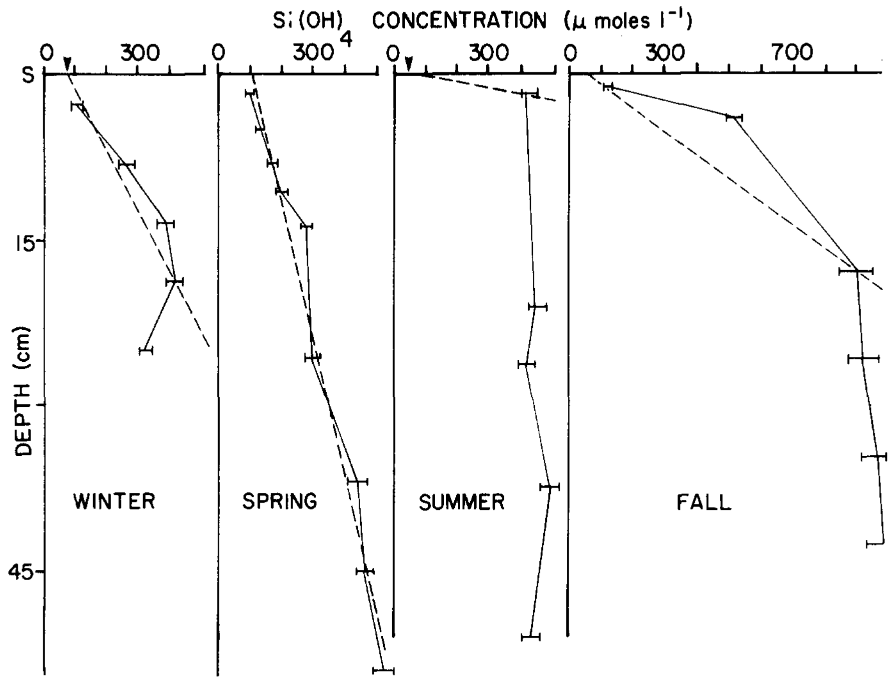

Fig. 4. Seasonal sedimentary pore water profiles of dissolved silicate (μ moles.l^{-1}) versus depth in the Great Marsh, Delaware.

Table 3. Calculated diffusive fluxes versus observed fluxes of nutrients from a Delaware salt marsh sediment.

Parameter	Calculated flux (n moles. cm^{-2}. day^{-1})	Observed flux	
		Chamber bubbling	
		Air	N_2
	Winter		
Si(OH)4	+4.6	+6.8	+7.4
NH_4^+	+24.2	−7.2	+4.2
PO_4^{-3}	+0.3	0	+4.1
NO_3^-	−4.4	+9.1	0
	Summer		
$Si(OH)_4$	+119.5	+63.4	
NH_4^+	+494	+42.3	
PO_4^{-3}	+0.6	−1.9	
NO_3^-	+11.8	0	

(Positive values imply a marsh source, while negative values indicate a marsh sink) appears to be dictated by biochemical processes. The seasonal depth profiles obtained for ammonium and nitrate (Figs. 5, 6) indicate that several metabolic processes, acting to variable degrees both spatially and seasonally, contribute to the interstitial nitrogen cycle at our sampling site.

Maximum ammonium concentrations are encountered during the summer months, as a consequence of production via sulfate and nitrate reduction, by nitrogen fixation (Valiela & Teal 1979), and due to temperature-regulated partitioning between pore water ammonium and adsorption onto clay minerals. Isotope dilution experiments by Bowden (1984) indicate that sediment temperature and substrate type, rather than end-product inhibition, are the dominant factors in ammonium production. Competing with these ammonium-producing processes are assimilation by *Spartina*, and nitrification (Haines et al. 1977; Teal et al. 1979; Dicker & Smith 1980). The nitrate profiles for our Delaware marsh site suggest that in spring, massive net nitrification is occurring in the surface marsh sediments. Nitrification is made possible in soils having low redox potentials due to various possible modes of oxic ventilation which create aerobic microzones around the roots (Teal & Kanwisher 1966). In spring, when a large subsurface maximum of

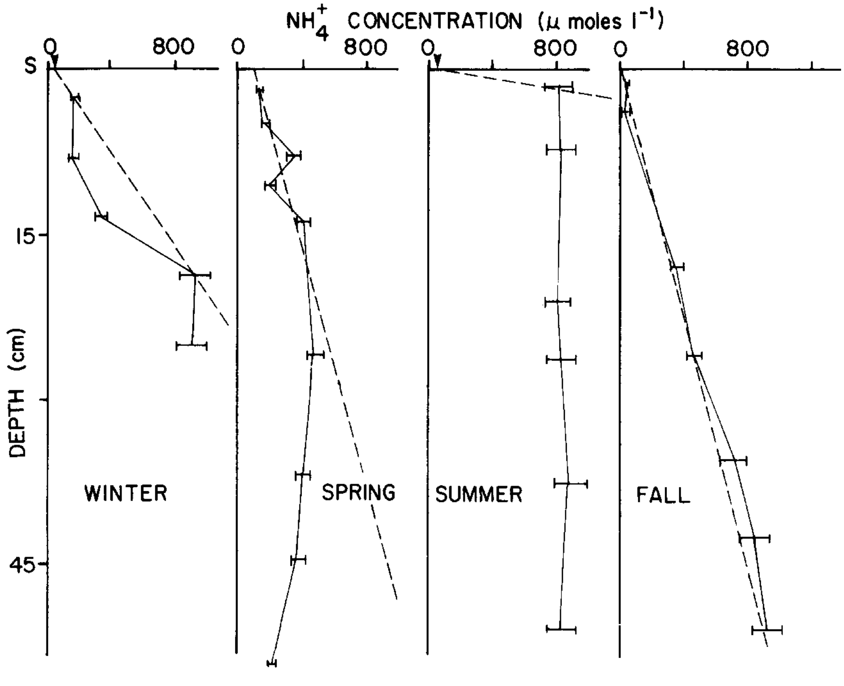

Fig. 5. Seasonal sedimentary pore water profiles of dissolved ammonium (μ moles.l^{-1}) versus depth in the Great Marsh, Delaware.

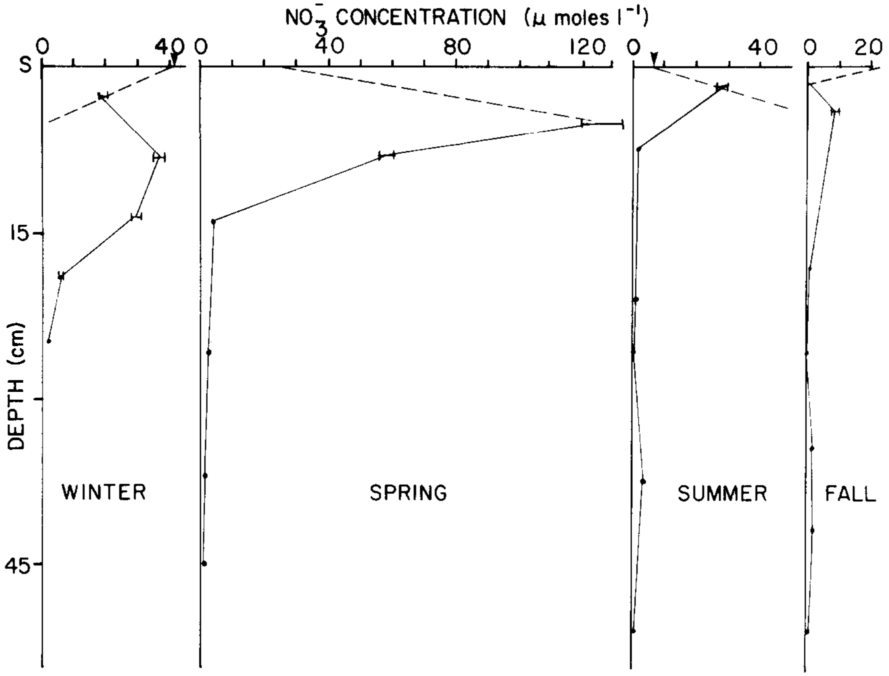

Fig. 6. Seasonal sedimentary pore water profiles of dissolved nitrate (μ moles.l^{-1}) versus depth in the Great Marsh, Delaware.

nitrate is observed, the rate of nitrification may temporarily exceed plant uptake. However, in summer, when nitrate levels have decreased, the rate of nitrification may be in competition with plant uptake or denitrification (Kaplan et al. 1979). Consistent with our observed pore water nitrate levels, Daiber & Gooch (1968), working in a near-by study area, present evidence of maximum nitrification rates in spring.

When the predicted diffusive fluxes are compared with those measured directly (Table 3), there are significant differences in both seasonal experiments. In the winter, when the sedimentary profiles predict a nitrate sink, we observe a comparatively large positive flux under ambient (oxic) conditions. In the summer, the pore water gradient dictates a diffusive nitrate source, which our direct flux measurements fail to account for. Here, the rapid turnover and consumption of nitrate (including denitrification and plant uptake) appears to dominate the cycling of nitrogen in marsh sediments. The concurrent stream concentration measurements for nitrate support our flux chamber results, with winter nitrate levels a factor of five greater than summer measurements (41 vs. 8 μM). This seasonal trend has been observed also in the nearby Canary Creek marsh (Aurand & Daiber 1973). For ammonium, observed stream concentrations are also greater in winter (2–

3 ×), despite our prediction of a maximum diffusive flux during summer. In this instance, the difference between potential and realized export might be attributable to a more rapid turnover of the nitrogen pool within tidal creeks during summer months.

Overall, these observed fluxes and trends are consistent with our general understanding of nitrogen redox chemistry. Under anoxic conditions, a positive ammonium flux and corresponding consumption of nitrate is observed. In the presense of dissolved oxygen (e.g., spring), there is a net release of nitrate, while the marsh surface serves as a ammonium sink. Quantitatively, even without plant uptake, the loss in ammonium can account for the gain in nitrate, suggesting a nitrification pathway. For comparison, the direct flux of inorganic nitrogen (nitrate plus ammonium) from atmospheric wet deposition is about 0.1 moleN $\cdot$ $m^{-2}yr^{-1}$ (Church et al. 1982), of which about 2/3 is in the form of nitrate. Even excluding a potentially significant contribution from dry deposition, the rate of atmospheric input is comparable to the maximum (summer) measured flux of inorganic nitrogen from salt marsh sediments.

Phosphate

The behavior of phosphate in salt marsh sediments is unique in that it can behave both as a geochemical, as well as biochemical species. However, this and previous studies (Eastman & Church 1984) indicate that its mobility in the salt marsh seems to be dominated by its geochemical reactivity, including particle desorption during tidal mixing. During the period from winter through summer, phosphate pore water profiles exhibit "pseudo-conservative" behavior, with low surface concentrations increasing uniformly with depth (Fig. 7). By fall, a radically different picture emerges which we believe may be in response to the well-documented coupling between phosphate and iron geochemistries.

In the salt marsh, the sedimentary iron cycle is characterized by dynamic seasonal transformations (Lord 1980; Giblin & Howarth 1984; Luther & Church 1988). During the summer, when oxidation rates in the near-surface (< 10 cm) sediments are sufficiently high to titrate the alkalinity produced via sulfate reduction, we have noted a substantial decrease in the pore water pH (Luther et al. 1986; Luther & Church 1988). Thus, oxidized iron minerals and presumably any associated bound phosphate are resolubilized, as reflected in the seasonal pore water profiles (Figs. 7, 8). However, at the sediment/air interface the diffusive flux of phosphate appears to be reprecipitated along with $Fe(OH)_3$ and sequestered in the surface oxide veneer. Such a co-precipitation mechanism of soluble phosphate (and silicate) by iron

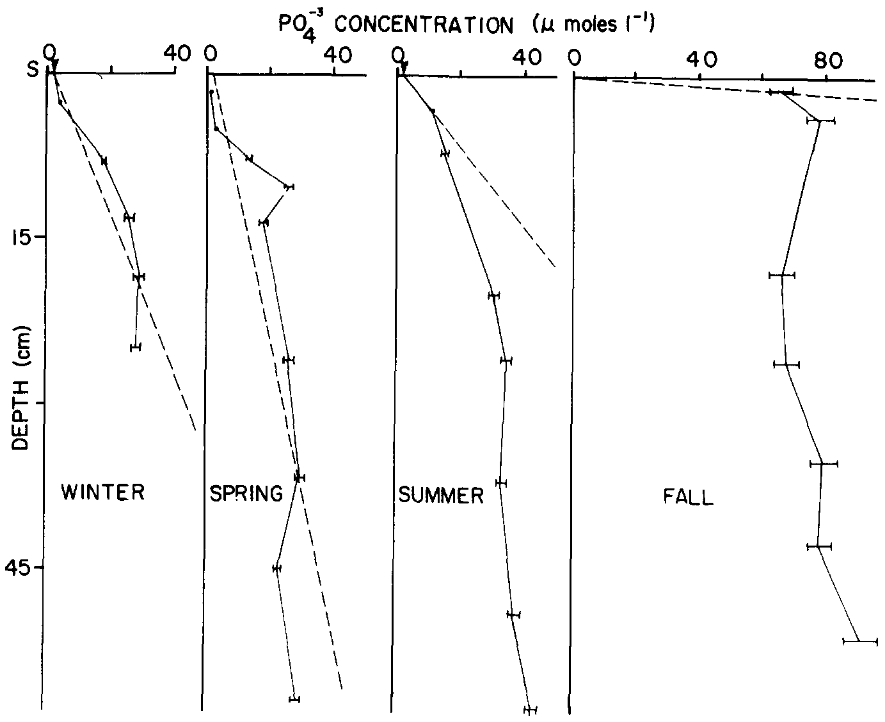

Fig. 7. Seasonal sedimentary pore water profiles of dissolved phosphate (μ moles.l^{-1}) versus depth in the Great Marsh, Delaware.

oxy-hydroxides is well established, and has been postulated as the controlling mechanism in many sub-tidal sediments (Stumm & Leckie 1970; Callender et al. 1982).

By fall, when oxidation rates decrease and the rate of sulfate reduction is at a maximum (Howarth & Teal 1979; Howarth & Giblin 1983), the zone of net sulfate reduction migrates upwards in response (Lord 1980). In the Great Marsh, this reducing zone probably succeeds in breaking through the sediment surface, by reductive dissolution of the surficial iron oxide veneer. In fact, the pore water profile for fall (Fig. 8) indicates elevated levels of soluble iron, a trend previously reported for this study area (Lord 1980) and the Great Sippewissett Marsh (Giblin & Howarth 1984). As with the summer core, this reduction of iron oxy-hydroxides would serve to resolubilize the bound phosphate, resulting in the dramatic increase in pore water phosphate evident in Fig. 7.

The concurrent flux chamber data also support our proposed link between surface processes controlling the flux of phosphate (Table 3). In winter, our calculations predict a small positive diffusive flux of dissolved

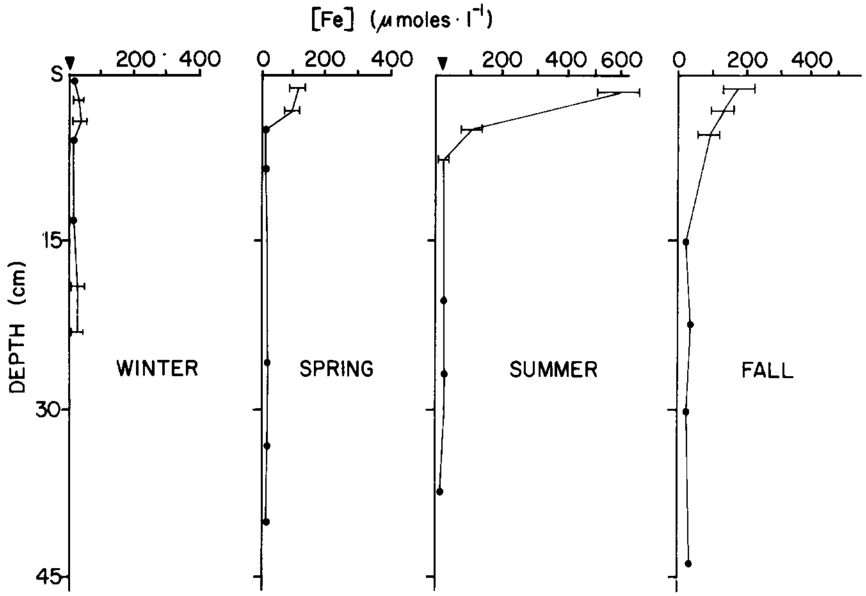

Fig. 8. Seasonal sedimentary pore water profiles of dissolved iron (μ moles.l^{-1}) versus depth in the Great Marsh, Delaware.

phosphate. Under anoxic conditions, the actual rate we observe is thirty-fold greater, presumably resulting rom the resolubilization of the surface oxide veneer. In an oxygenated chamber environment, net consumption of dissolved phosphate results from its co-precipitation with oxidized iron, a mechanism previously postulated by Patrick & Khalid (1974) for soils of Louisiana salt marshes.

In summer a somewhat higher diffusive phosphate flux is predicted, though under representative ambient conditions (oxic chamber), we measure a net sink for phosphate. This consumption of phosphate may reflect plant uptake in addition to the co-precipitation mechanism. We see no evidence in our chamber data to support a *Spartina* phosphate "pump" mechanism (Reimold 1972), in which phosphate is proposed to be actively translocated from the sediments to the flooding water through the plant leaves.

Discussion

Perhaps the best way to view the predicted flux calculations (Table 2) is in terms of the sedimentary "potential," that is, the maximum rate of diffusion the sediments will support in the absense of additional production or consumption processes at the marsh surface. On this basis alone, we would predict a positive flux of all measured nutrients at our high marsh site. The discrepancies between the predicted flux and observed rates (Table 3) reflect the importance of biogeochemical processes at the marsh surface, not only in regulating diffusive fluxes, but also contributing directly to essential trace element cycling and sustained fertility in salt marsh soils. For the Great Marsh the "active zone" of such transformations extends to about 20 cm depth, as determined by the porosity and extent of the rhizosphere.

For example, the diffusion of both silicate and phosphate will be directly mediated by the activity of edaphic diatoms (Sullivan 1971; Gallagher & Daiber 1974; Moll 1977). Such biogenic processes will influence not only the near-surface pore water profiles, but potentially, can mediate the net sediment exchange rates observed in the flux chambers. While we are not able to gauge the importance of such effects to this study, identical flux chamber experiments by Lord (1980), in which the light/dark regime was varied, reveal a strong diel periodicity for alkalinity, pH and iron flux, presumably in response to autotrophic metabolism. It is likely that silicate and phosphate solubility behavior responds to similar processes, both directly (via phytoplankton uptake) and indirectly (via pH mediated iron solubility/coprecipitation reactivity). On a seasonal time scale, phytoplankton activity could play a major role in regulating net nutrient exchange rates, particularly during bloom episodes.

Although the high marsh area of this study is submerged only periodically, the calculated and measured flux estimates (Tables 2, 3) represent constant inundation. Though the actual diffusive fluxes from the marsh are probably somewhat less than these estimates, episodic meteorological events, such as rain showers and coastal storms, may play a dominant role in controlling marsh nutrient exchange, not accounted for by considering tidal exchange alone.

For example, in the case of phosphate, if our iron co-precipitation hypothesis is valid, the build-up of the surface oxidized layer through the summer might act as a geochemical reservoir for the upward diffusion of phosphate from the marsh. When subjected to the acidic conditions of local precipitation (pH of local summer rain events range from 3.2 to 4.5 (Church et al. 1982) or inundation due to wind-driven tidal surges during storms, the oxide veneer may be periodically mobilized to release phosphate for tidal export. There is evidence (Lotrich et al. 1979) that such meteorological events are not only important in governing phosphate export from the marsh, but also prevail in the control of trace metal (Church 1983) and carbon exchange (Roman 1981; Chalmers et al. 1985).

While our experimental design limits any rigourous quantitative interpretation, part of the rationale behind this study is to assess the potential impact of indigenous salt marshes on the nutrient budget for the parent Delaware Estuary. Overall, even when assumptions are made to maximize our flux estimates, our experiments indicate that for the high marsh study area of the Great Marsh, the sediments may potentially provide ony minimal fluxes of ammonium and silicate. In the case of phosphate, we estimate a minor sedimentary diffusive flux, except when the surface oxidized layer may be mobilized by a seasonal peak in sulfate reduction or meteorological episodes. For nitrate, the marsh sediments do not appear to provide an ecologically significant source to the estuary, particularly when compared to the large input of nitrate from the Delaware River (Pennock 1987). Differences between potential and realized export suggest that these nutrients are predominantly recycled within the marsh, allowing for sustained high levels of productivity.

Acknowledgements

We wish to express our gratitude to Drs. David Smith, Jack Gallagher, Frank Daiber, Ted Callender, Stewart LeCato and three anonymous reviewers for valuable comments on the manuscript. We also thank Jack Tramontano for assistance with field sampling and dissolved iron analyses, and Sandra Slates for providing duplicate organic carbon content assays.

Support for this research was provided under grant No. NA80AA-D-00106 from the NOAA National Sea Grant College Program Office, US Deptartment of Commerce.

References

Agosta K (1985) The effect of tidally induced changes in the creekbank water table on pore water chemistry. Estuarine Coastal and Shelf Science 21: 389–400

Allen EA (1978) Petrology and stratigraphy of holocene coastal-marsh deposits along the western shore of Delaware Bay. Ph.D. thesis, University of Delaware, 287pp

Alexander GB, Heston WM & Iler RK (1954) The solubility of amorphous silica in water. Physical Chemistry 58: 453–455

Aurand DV & Daiber FL (1973) Nitrate and nitrite in the surface waters of two Delaware salt marshes. Chesapeake Science 14: 105–111

Bischoff JL, Greer RE & Luistro AO (1970) Composition of interstitial waters of marine sediments: Temperature of squeezing effect. Science 16: 1245–1246

Bowden WB (1984) A nitrogen-15 isotope dilution study of ammonium production and consumption in a marsh sediment. Limnology and Oceanography 29: 1004–1015

Bray JT, Bricker OP & Troup BN (1973) Phosphate in interstitial waters of anoxic sediments: oxidation effects during sampling procedure. Science 180: 1362–1364

Callender ED (1982) Benthic phosphorus regeneration in the Potomac River Estuary. Hydrobiologia 92: 431–446

Chalmers AG, Wiegert RG & Wolf PL (1985) Carbon balance in a salt marsh: interactions of diffusive export, tidal depostion and rainfall - caused erosion. Estuarine Coastal and Shelf Science 21: 757–771

Church TM, Galloway JN, Jickells TD & Knap AH (1982) The chemistry of western Atlantic precipitation at the mid-Atlantic coast and on Bermuda. Journal of Geophysical Research 87: 11013–11018

Church TM, Lord CJ III & Somayajulu BLK (1981) Uranium, thorium, and lead nuclides in a Delaware salt marsh system. Estuarine Coastal and Shelf Science 13: 267–275

Church TM (1983) The geochemistry of intertidal sediments. Proceedings of The International Union of Geodesy and Geophysics, Hamburg, Germany, August, 1983: 2: 898

Dacey JWH & Howes BL (1984) Water uptake by roots controls water table movement and sediment oxidation in short *Spartina* marsh. Science 224: 487–489

Daiber FC & Gooch EL (1968) Production and release of nutrients from the sediments of the tidal marshes of Delaware. Annual Pittman-Robertson Report to the Delaware Board of Game and Fish Commissioners for 1967–1968, 93pp

Dicker HJ & Smith DW (1980) Acetylene reduction (nitrogen fixation) in a Delaware salt marsh. Marine Biology 6: 161–171

Eastman KW & Church TM (1984) Behavior of iron, manganese, phosphate, and humic acid during mixing in a Delaware salt marsh creek. Estuarine Coastal and Shelf Science 18: 447–458

Fanning KA & Schink DR (1969) Interaction of marine sediements with dissolved silica. Limnology and Oceanography 14: 59–68

Fanning KA & Pilson MEQ (1971) Interstitial silica and pH in marine sediments: some effects of sampling procedures. Science 173: 1228–1231

Fanning KA & Pilson MEQ (1974) The diffusion of dissolved silica out of deep-sea sediments. Journal of Geophysical Research 79: 12931297

Gallagher JL & Daiber FC (1974) Primary production of edaphic algal communities in a Delaware salt marsh. Limnology and Oceanography 19: 390–395

Giblin AE & Howarth RW (1984) Pore water evidence for a dynamic sedimentary iron cycle in salt marshes. Limnology and Oceanography 29: 47–63

Haines E, Chalmers A, Hanson R & Sherr B (1977) Nitrogen pools and fluxes in a Georgia Salt Marsh In: Wiley M (Ed) Estuarine Processes, Vol 2 (pp 241–254) Academic Press

Hemond HF & Fifield JL (1982) Subsurface flow in salt marsh peat: A model and field study. Limnology and Oceanography 27: 126–136

Holme N & Mcintyre A (1971) Methods for the study of marine benthos. Blackwell

Howarth RW & Giblin A (1983) Sulfate reduction in the salt marshes at Sapelo Island, Georgia. Limnology and Oceanography 28: 70–82

Howarth RW & Teal JM (1979) Sulfate reduction in a New England salt marsh. Limnology and Oceanography 24: 999–1013

Hurd DC (1972) Factors affecting dissolution rate of biogenic opal in seawater. Earth and Planetary Science Letters 15: 411–417

Hurd DC & Spielvogel LQ (1975) Changes in the concentration of dissolved silica in stored sediments as a function of time: A theoretical model. Journal of Geophysical Research 80: 4975–4977

Jordan TE & Correll DL (1985) Nutrient chemistry and hyrology of interstitial water in brackish tidal marshes of Chesapeake Bay. Estuarine Coastal and Shelf Science 21: 45–55

Kaplan W, Valiela I & Teal JM (1979) Denitrification in a salt marsh ecosystem. Limnology and Oceanography 24: 726–734

Kato K & Kitano Y (1968) Solubility and dissolution rate of amorphous silica in distilled and seawater at 20 °C Journal of the Oceanographic Society of Japan 24: 147–152

Krom MD & Berner RA (1980) The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments. limnology and Oceanography 25: 327–337

Lebel J, Silverberg N & Sundby B (1982) Gravity core shortening and pore water chemical gradients. Deep-sea Research 29: 1365–1372

Lerman A (1979) Geochemical Processes: Water and Sediment Environments. Wiley-Interscience, New York

Li YH & Gregory S (1974) Diffusion of ions in seawater and in deep sea sediments. Geochimica et Cosmochimica Acta 38: 703–714

Loder TC, Lyons WB, Murray S & McGuinness HD (1978) Silicate in anoxic pore waters and oxidation effects during sampling. Nature 273: 373–374

Lord CJ (1980) The chemistry and cycling of iron, manganese, and sulfur in salt marsh sediments. Ph.D. thesis, University of Delaware, 177 pp

Lord CJ III & Church TM (1983) The geochemistry of salt marshes: sedimentary diffusion, sulfate reduction, and pyritization. Geochimica et Cosmochimica Acta 47: 1381–1391

Lotrich VA, Meredith WH, Weisberg SB, Hurd LE & Daiber FC (1979) Dissolved and particulate nutrient fluxes via tidal exchange between a salt marsh and lower Delaware Bay. The 5th Biennial International Estuarine Research Conference Abstracts, Jeckyll Island, Georgia 7–12 October

Luther GW III, Cosman M, Church TM & Scudlark JR (1986) Cycling between inorganic and organic sulfur in salt marsh pore waters: evidence for both abiotic and biotic transformations. Science 232: 746–749

Luther GW III & Church TM (1988) Seasonal cycling of sulfur and iron in porewaters of a Delaware Salt Marsh. Marine Chemistry 23: 295–309

Mackenzie FJ, Garrells RM, Bricker OP & Bickley F (1967) Silica in seawater: control silicate minerals. Science 155: 1404–1406

Moll RA (1977) Phytoplankton in a temperate-zone salt marsh: net production and exchanges with coastal waters. Marine Biology 42: 109–118

Murphy J & Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal. Chem. Acta 27: 31–36

Nixon SW (1980) Between coastal marshes and coastal waters – a review of twenty years of speculation and research on the role of salt marshes in estuarine productivity and water chemistry. In: Hamilton P & MacDonald KB (eds), Estuarine and Wetland Processes, Plenum (pp 437–525)

Patrick WH & Khalid RA (1974) Phosphate release and sorption by soils and sediments: Effect of aerobic and anerobic conditions. Science 186: 53–55

Pennock JR (1987) Temporal and spatial variability in phytoplankton ammonium and nitrate uptake in the Delaware Estuary. Estuarine, Coastal and Shelf Science 24: 841–857

Reeburgh WS (1967) An improved interstitial water sampler. Limnology and Oceanography 12: 163–165

Reimold RJ (1972) The movement of phosphorus through the salt marsh cord grass *Spartina altiniflora*Loisel. Limnology and Oceanography 17: 606–611

Roman CT (1981) Detrital exchange processes of a Delaware salt marsh. Ph.D. Thesis. University of Delaware, 144 pp

Sayles FL & Mangelsdorf PL (1977) The equilibrium of clay minerals with seawater: exchange reactions. Geochimica et Cosmochimica Acta 41: 951–960

Schink DR, Guinasso NL & Fanning KA (1975) Processes affecting the concentration of silica at the sediment-water interface of the Atlantic Ocean J Geophy. Res. 80: 3013–3031

Siever R (1968) Establishment of equilibrium between clays and seawater. Earth and Planetary Science Letters 5: 106–110

Solorzano L (1969) Determination of ammonia in natural waters by the phenol-hypochlorite method. Limnology and Oceanography 14: 799–801

Strickland JDH & Parsons TR (1972) A Practical Handbook of Seawater Analysis. 2nd edn. Bulletin of the Fisheries Research Board of Canada, 310 pp

Stumm W & Leckie JO (1970) Phosphate exchange with sediments: its role in the productivity of surface waters. In: Advances in Water Pollution Research, Vol 2 (pp 2611–2616) Pergamon

Sullivan MJ (1971) Distribution and ecology of edaphic diatoms in the Canary Creek salt marsh. M.S. thesis, Univ. of Delaware, 95 pp.

Teal JM & Kanwisher JW (1966) Gas transport in the marsh grass, *Spartina alterniflora*. Journal of Experimental Botany 17: 355–361

Teal JM, Valiela I & Berlo D (1979) Nitrogen fixation by rhizosphere and free living bacteria in salt marsh sediments. Limnology and Oceanography 24: 126–132

Valiela I & Teal JM (1979) The nitrogen budget of a salt marsh ecosystem. Nature 280: 652–656

VanBrakel J & Heertjes PM (1974) Analysis of diffusion in macroporous media in terms of a porosity, a tortuosity and a constricitivity factor. International Journal of Heat and Mass Transfer 17: 1093–1103

Westrich JT & Berner RH (1984) The role of sedimentary organic matter in bacterial sulfate reduction: the G model tested. Limnology and Oceanography 29: 236–249

Wolaver TG, Zieman JC, Wetzel R & Webb KL (1983) Tidal exchange of nitrogen and phosphorus between a mesohaline vegetated marsh and the surrounding estuary in the lower Chesapeake Bay. Estuarine Coastal and Shelf Science 16: 321–332

Wollast R & Garrels RM (1971) Diffusion coefficient of silica in seawater. Nature Physical Science 229: 94