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# Surface and Pore Water Mixing in Estuarine Sediments: Implications for Nutrient and Si Cycling

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## ABSTRACT

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## INTRODUCTION

Water flow into estuaries is one of the primary controls on the quantities and distributions of dissolved constituents including pollutants and nutrients (e.g., D'ELIA *et al.*, 1985; SIMMONS, 1992; GALLAGHER *et al.*, 1996). Flow paths for water and associated constituents that can be easily quantified for estuaries include surface water runoff, atmospheric deposition, and evapotranspiration (MACINTYRE *et al.*, 1995; SIGUA *et al.*, 2000). One additional and potentially significant source of water that is more difficult to quantify is the submarine discharge of ground water (SGD). Previously, this term has been defined to include both marine and terrestrially derived ground water components, but the magnitude of this SGD has been poorly defined because of difficulties associated with locating and measuring the flow (e.g., CABLE *et al.*, 1996a, 1996b, 1997a; BURNETT *et al.*, 2003) and perhaps by uncertainties about its composition.

Based on discrepancies between water balances and coastal measurements, recent studies have recognized that the measured volumes of SGD include both terrestrial and marine components (LI *et al.*, 1999; BURNETT *et al.*, 2003; CABLE *et al.*, 2004; MARTIN *et al.*, 2004). For example, MOORE (1996) used <sup>226</sup>Ra to estimate that ground water discharge to the South Atlantic Bight was as great as 40% of river inputs. Subsequently, modeling by LI *et al.* (1999) suggests that 4% of this SGD to the Atlantic continental shelf recognized by MOORE (1996) originates from the underlying Floridan aquifer, with the remainder derived from the overlying water column. MARTIN *et al.* (2004) reached similar conclusions in the Ba-

nana River Lagoon, Florida, where the conservative solute, Cl<sup>-</sup>, in shallow pore water was found to have composition identical to that of surface water and that these pore water compositions tracked the temporal variations of the surface water. These observations indicated that a large fraction of SGD may be composed of lagoon water that circulates through shallow estuarine sediments (CABLE *et al.*, 2004; MARTIN *et al.*, 2004). This circulation could originate through pumping mechanisms, such as wave action (e.g., SHUM, 1992, 1993; HUETTEL *et al.*, 1996; HUETTEL and WEBSTER, 2001; LI *et al.*, 1999) and bioirrigation (e.g., EMERSON *et al.*, 1984). The contributions of SGD to the water and nutrient budgets, including the role that ventilation of the sediment has on nutrient cycling, has not been determined.

The marine component of SGD represents an important flux of water across the sediment-water interface (CABLE *et al.*, 2004; MARTIN *et al.*, 2004). Processes that drive recirculation of seawater through sediments, or the marine SGD, and create a subterranean mixing zone also set up a critical boundary zone for diagenetic reactions (ALLER, 1980; SLOMP and VAN CAPELLEN, 2004). In particular, ventilation of the sediment by oxygenated surface water may influence redox conditions of sediment and pore water, organic matter and contaminant degradation, and dissolution of biogenic compounds (CaCO<sub>3</sub> and SiO<sub>2</sub>). The redox reactions in the sediments, coupled with pore water exchange, should alter profiles of dissolved components in the pore waters and may enhance nutrient fluxes through increases in dissolved N and P concentrations following organic matter degradation (e.g., MARTIN *et al.*, 2004; SLOMP and VAN CAPELLEN, 2004). The need to quantify these effects has led to the development of various numerical models that predict vertical mixing of particulate sediment and diagenetic reactions (BERNER, 1980; WHEATCROFT *et al.*, 1990) and characterize the geochemistry

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of the ventilated sediments (BOUDREAU, 1984; EMERSON *et al.*, 1984; SANDNES *et al.*, 2000). Depending on the rate of exchange of water across the sediment–water interface and the nutrient concentrations, fluxes caused by pore water mixing may represent a greater source of nutrients to the estuary water than diffusive processes.

In this paper, we demonstrate that the source of submarine ground water discharge in the Banana River Lagoon is surface water recirculation, estimate nutrient loading from this recirculation process, and trace the movement of pore water at two sites in the Banana River Lagoon, Florida. An analytical advection–diffusion–reaction model applied to Si concentration data suggests that mixing in the shallow sediment is an important transport mechanism in the area. We estimate the nutrient fluxes across the sediment–water interface using a mass balance approach based on water flow, sedimentation rate, and concentrations of nutrients in the water and sediment. These results indicate that ventilation of the sediments is an important process and may limit the burial rate of nutrients into the sediment by enhancing their dissolved benthic flux to the water column.

## STUDY AREA AND SAMPLE LOCATIONS

The Indian River Lagoon estuary system extends about 250 km along Florida's central Atlantic coast, from north of Cape Canaveral in Brevard County to as far south as St. Lucie Inlet in Martin County (Figure 1). Three estuaries make up the system, including the Indian River Lagoon, Banana River Lagoon, and the Mosquito Lagoon. The Mosquito Lagoon extends to New Smyrna Beach, approximately 30 km north of the northern end of the Indian River Lagoon, and the Banana River Lagoon is separated from the northern Indian River Lagoon by Merritt Island, thus marking the eastern edge of the Indian River Lagoon. As part of a larger project, pore water data and seepage rate measurements were collected from two locations in the Banana River Lagoon in summer (May and August) and winter (December) 2000 (MARTIN *et al.*, 2004). Subsequently, sediment cores were collected from the same two locations in November 2001. The locations are designated BRL2 and BRL6 and are separated by approximately 3 km (Figure 1).

## METHODS AND ANALYSES

Coring was done using vibracoring techniques with an internal aluminum pipe diameter of ~7.5 cm (SMITH, 1984). The lengths of the recovered cores were 1.57 m and 1.62 m sediment from BRL2 and BRL6, respectively. Compaction for both cores was ~16%, which was calculated by comparing the depth of penetration of the core tube to the length of the recovered sediment. This calculation assumes no sediment is lost when the cores are retrieved.

The cores were cut into ~50-cm-long sections in the field and returned to the laboratory at the Department of Geological Sciences, University of Florida in an upright position where they were split lengthwise and photographed. The  $\gamma$ -ray (GRA) bulk density of the cores was measured using a Geotek® Multisensor Core Logger (MSCL), and high-resolution digital images were collected using the corresponding

Geoscan® II imaging system. The bulk density measurements were calibrated using a standard aluminum density calibration piece (WEBER *et al.*, 1997). Subsamples of approximately 30 g were collected at 2-cm intervals over the entire length of the split cores. These samples were used to measure porosity, total carbon (TC) including organic as well as carbonate phases, total organic matter (OM), total nitrogen (TN), total phosphorus (TP), and reactive silica (SiO<sub>2</sub>), which is presumed to be the biogenic fraction of silica. We assume there are no N- or P-bearing minerals in the sediments and thus assume that the measured values of TN and TP represent the organic fractions. Organic matter concentrations were measured using the loss on ignition method (DEAN, 1974; BENGTSOON and ENELL, 1986). The organic carbon fraction was determined by subtracting TN and TP from the total organic matter. Total carbon and TN were measured using a Carlo Erba NA 1500 analyzer at the Department of Geological Sciences, University of Florida, following combustion at 1000C. Total phosphorus (TP) was analyzed using a Bran-Luebbe Autoanalyzer, following digestion of freeze-dried sediment with H<sub>2</sub>SO<sub>4</sub> and potassium persulfate. Biogenic SiO<sub>2</sub> was also analyzed using the Bran-Luebbe Autoanalyzer by digestion with Na<sub>2</sub>CO<sub>3</sub> and HCl. Analytical precision was estimated by measuring duplicates every 10th sample and calculating the relative percentage difference (RPD) of the duplicates (Table 1). Porosities were calculated from the bulk density.

Pore waters were collected using multilevel piezometers ("multisamplers"; MARTIN *et al.*, 2003) especially designed for this project. The multisamplers consist of eight ports screened with 250- $\mu$ m mesh built into a 2-in.-diameter, 230-cm-long schedule 80 PVC pipe (MARTIN *et al.*, 2003). The ports are glued to PVC tubing that extends up the interior of the PVC pipe to the surface. The pipe is pounded into the sediments, and the tubing led to the surface and hooked to a peristaltic pump located in a small boat. Pore water is pumped from the depths of the ports and collected, filtered, and preserved in HDPE bottles. The multisamplers do not always penetrate their entire length into the sediment, and not all ports always yield water. At BRL2, all eight ports yielded water to the maximum depth of 230 cm. At BRL6, however, the multisampler extended only to about 80 cm, and only the four uppermost ports in the sediment pumped water. Previous work on some of these samples has been reported by LINDENBERG (2001), MARTIN *et al.* (2003, 2004), and CABLE *et al.* (2004). Here we report on the Si concentrations of these pore water samples (Table 2).

## RESULTS

### Physical Characteristics of Cores

Several changes in sediment characteristics can be observed in the core recovered from BRL2 (Figure 2a). The upper 20 cm of BRL2 consists of fine-grained, light siliceous sand, interspersed with large (~1.5 cm) calcareous shells. The shells were mostly of molluscs (bivalves and gastropods), and most of them were well preserved and intact. The sediment composition and texture changes between 20 and 30 cm depth to include a greater fraction of dark muddy sand than

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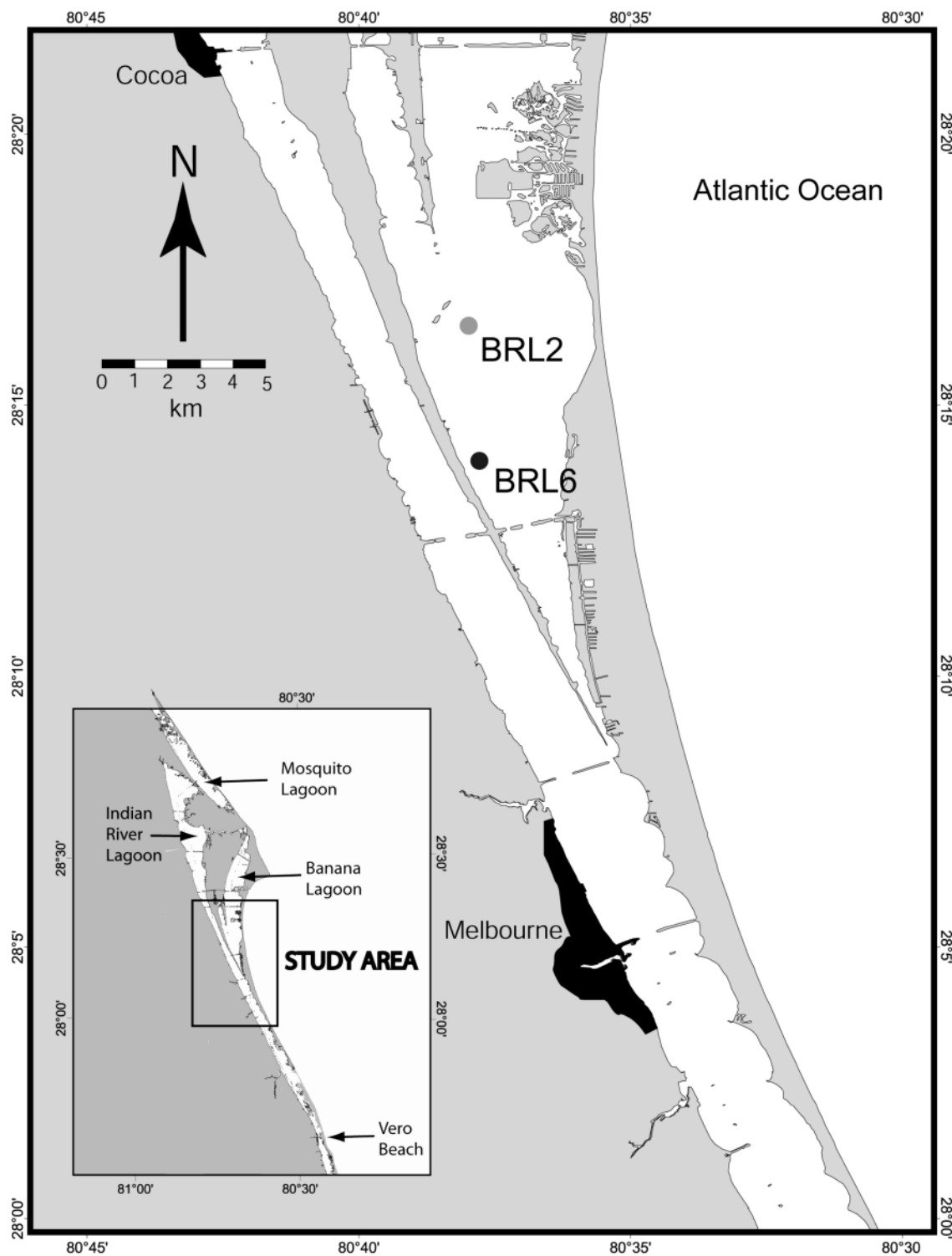


Figure 1. Location map of the study area.

Bhadha *et al.*Table 1. *Data precision.\**

Analyses	Precision (%)	Precision (%)
	BRL2	BRL6
TC	4.4	4.4
TN	4.1	4.1
TP	2.5	2.2
SiO <sub>2</sub>	1.4	0.8

\* Precision, RPD =  $(|x_1 - x_2|)/x_{\text{mean}}$ .

the layers above. The sand is interlayered with greenish clay lenses. Between 40 and 50 cm depth the composition of the sediment remains predominantly muddy sand but lacks clay lenses. Around 50 cm depth, the sediment becomes a dark siliceous sand interspersed with small (~0.4 cm) calcareous shell fragments, which extends to depths of ~140 cm. Over this interval, numerous vertical burrows, observed using x-ray imaging, occur as dark striations. Between 140 and 157 cm, the bottom 17 cm of the core is composed of light, fine-grained siliceous sand devoid of any shells. Over the entire core, bulk density values range between 1.70 and 2.15 g/cm<sup>3</sup> (Figure 3a). These density values convert to porosities ranging between 33% and 66%, with an average of about 42% ( $\pm 3.3$ , 1 $\sigma$ ; Figure 4a). Two zones exhibit higher porosity than the rest of the core, the first at 20 to 30 cm, and the other at 110 to 120 cm depth, which correspond to clay layers. The highest density in the sediment core occurs at depth of approximately 18 cm below the sediment-water interface, which reflects an interval of concentrated calcareous shells.

Variations in sediment composition also occur in the core from BRL6 (Figure 2b). The arrangements of the different sediment types are similar between the two sites, but their thicknesses are different (Figure 2). The upper 30 cm of the BRL6 core is composed of light siliceous sand, shell fragments, small burrows, and fresh plant debris such as weeds and roots in the upper 10 cm of the core. A thin layer of about 5 cm thickness, between 30 and 35 cm depth, consists predominantly of calcareous shell fragments. The concentration of the shell fragments decreases to a depth of 55 cm simultaneously with an increase in muddy sand. Between 55 and 80 cm depth the sediments are composed almost entirely of dark muddy sand, with only few scattered fragments of calcareous shell. From 80 to 110 cm depth, the core consists almost entirely of a dark clay layer. A horizon of dark muddy sand completely lacking shell fragments occurs at 110 to 135 cm depth. Between 135 and 162 cm depth, the bottom 27 cm shows a gradual transition from dark muddy sand to light siliceous sand. The bulk density values are fairly consistent, ranging from 1.80 to 1.90 g/cm<sup>3</sup> except between the depths of 80 to 110 cm, where the values drop to as low as 1.58 g/cm<sup>3</sup> (Figure 3b). These bulk density values indicate porosity ranges between 41% and 63%, with an average value of about 50% ( $\pm 5.4$ , 1 $\sigma$ ; Figure 4b). The low-bulk-density interval from 80 to 110 cm corresponds to a clay layer, which also has the highest porosity of the core of about 63%.

### Chemical Analyses of Sediments and Pore Waters

Assuming all of the TN and TP fraction are organic, sediments from both BRL2 and BRL6 are characterized by low

Table 2. *Pore water chemistry data.*

Depth in sediments (cm)	May 2000			August 2000			December 2000		
	TN mg/L	TP mg/L	SiO <sub>2</sub> mg/L	TN mg/L	TP mg/L	SiO <sub>2</sub> mg/L	TN mg/L	TP mg/L	SiO <sub>2</sub> mg/L
BRL2									
10	0.295	0.02	2.5	0.66	0.04	3.9	0.81	0.02	2.44
30	0.861	0.05	3.4	0.79	0.07	3.8	1.08	0.06	4.05
50	0.861	0.06	4.5	1.09	0.11	4.8	1.57	0.08	4.9
80	—	—	—	1.15	0.10	7.8	1.70	0.07	5.34
110	0.293	0.11	7.8	1.12	0.34	10.3	1.74	0.16	7.32
150	1.072	0.08	6.6	0.97	0.38	10.6	1.64	0.26	7.38
190	1.001	0.12	6.5	1.35	0.31	9.9	1.69	0.29	6.67
230	1.302	0.15	6.8	1.24	0.33	7.4	1.77	0.26	6.14
BRL6									
10	0.865	0.07	3.3	0.83	0.05	4.5	0.96	0.06	3.06
30	1.039	0.08	3.6	1.17	0.09	4.5	1.23	0.07	3.59
50	0.898	0.05	5.4	1.21	0.09	4.9	1.74	0.08	4.19
80	1.078	0.09	10.3	1.11	0.07	5.7	1.45	0.08	5.21

From Lindenberg (2001).

concentrations of organic C, N, and P, although these concentrations are slightly greater at BRL6 than at BRL2 (Figures 5 and 6). On average the concentrations of N, P, C, and SiO<sub>2</sub> are 0.06 mg/g, 0.02 mg/g, 2.8 mg/g, and 5.5 mg/g, respectively, at BRL2, and 0.14 mg/g, 0.04 mg/g, 6.5 mg/g, and 4.7 mg/g, respectively, at BRL6 for the entire core. The low concentrations of the organic components represent a typical open lagoon sandy environment.

Biogenic silica concentrations of sediments from BRL2 show high variability with depth and range between about 3 and 10 mg/g with an average value of 5.5 mg/g. The biogenic silica concentrations at BRL6 are mostly lower than those at BRL2 with less variability. These BRL6 concentrations range from about 1 to 5 mg/g with an average of 4.7 mg/g except at the depth interval 80 to 110 cm below the seafloor within the dark clay layer. In this clay interval, the silica concentrations increase to between 10 and 14 mg/g. In 2000 three separate sampling trips were made to sites BRL2 and BRL6 in the months of May, August, and December to collect pore water from multisamplers installed at each site. At BRL2 and BRL6, concentrations of TN increase to a depth of 50 cm and then maintain an approximately constant concentration below this depth (Figures 7a and 8a). In contrast, TP at BRL2 has the largest increase at depths below 70 cm, and SiO<sub>2</sub> concentrations increase gradually to a depth of 110 cm, below which they are approximately constant with depth (Figures 7b and 8b,c).

## DISCUSSION

### Evidence for Mixing from Dissolved Si Profiles

Evidence for dissolution of silica phases in the shallow pore waters in the Banana River Lagoon is shown by increasing concentrations with depth of dissolved SiO<sub>2</sub> in sediment pore water at BRL2 (MARTIN *et al.*, 2002). Several models for the early diagenesis of SiO<sub>2</sub> have been proposed (*e.g.*, HURD, 1973; WOLLAST, 1974; SCHINK, 1975), with the most complete model treating dissolution in terms of "reactive" or soluble silica to

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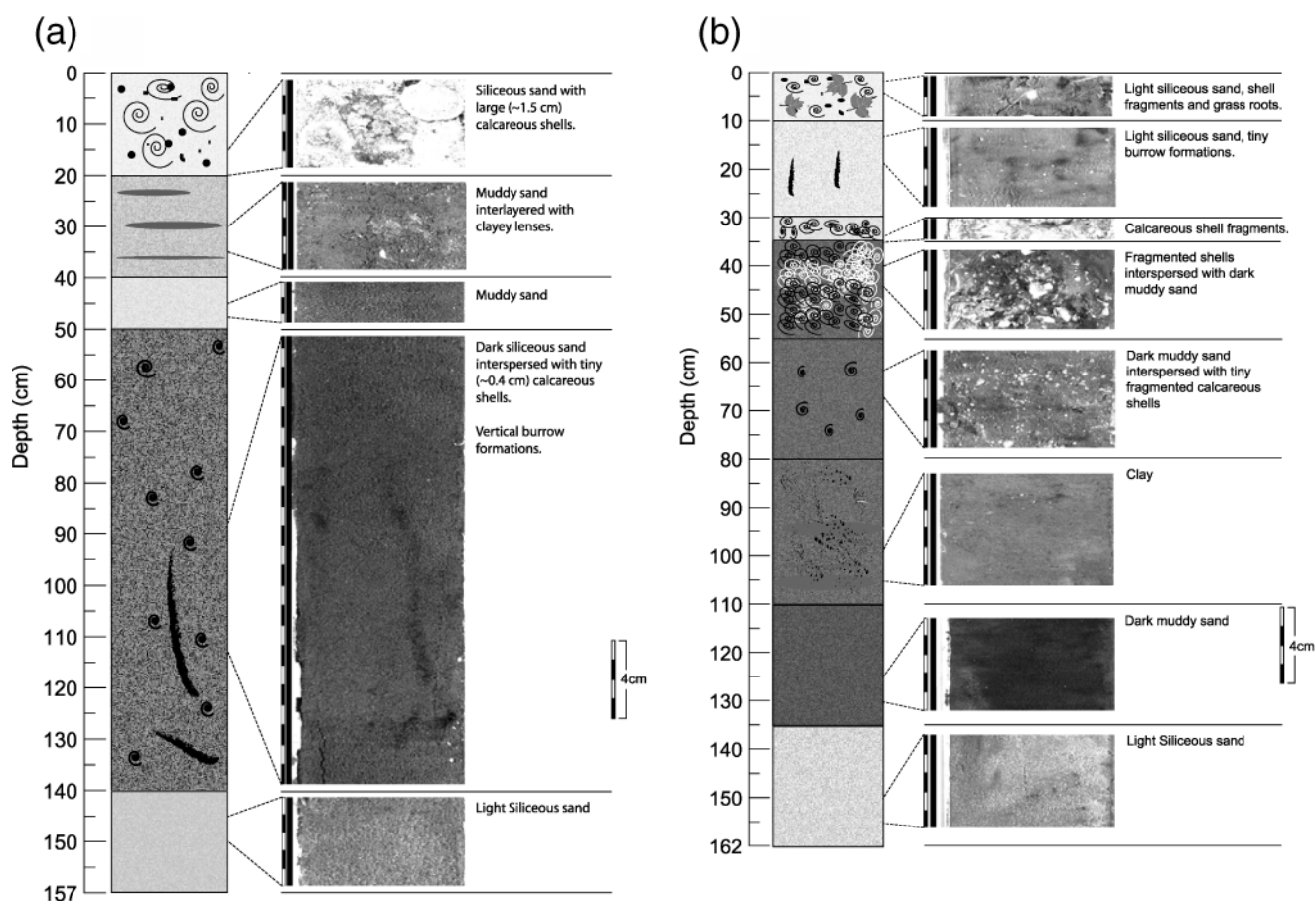


Figure 2. Sediment cores from BRL2 (a) and BRL6 (b). Images to the right are real photographic images of short sections of the core representing the five zones (a) or eight zones (b).

differentiate it from other less reactive forms such as crystalline silicate minerals (BERNER, 1980). Reactive  $\text{SiO}_2$  is presumed to be the opaline fraction of biogenic  $\text{SiO}_2$ , such as radiolarian and diatom tests, and hence, more soluble than the crystalline fraction. The rate of dissolution of freshly deposited siliceous plankton may vary, however, and as a result of incomplete dissolution, some opaline silica may accumulate in the sediments. Increasing Si concentrations with depth in the sediment likely relates to ventilation of the shallow sediments based on differences between the water column and pore water Si concentrations.

The recirculation mechanism is evaluated below using a one-dimensional model to describe the distribution of dissolved Si in the pore water as controlled by diffusion alone and by reaction and transport processes other than diffusion. The processes are included within a fitting parameter termed a nonlocal source term (IMBODEN, 1981). Mathematically the problem was formulated as a second-order partial differential equation:

$$\frac{\partial C}{\partial t} = K \frac{\partial^2 C}{\partial z^2} - \alpha \left( \frac{C - C_0}{\phi} \right) + R \quad (1)$$

(EMERSON *et al.*, 1984), where  $C$  is the concentration of a re-

active solute in the bulk sediment (in this case  $\text{SiO}_2$  concentration) at depth  $z$  and at time  $t$ ,  $K$  is the sediment diffusion coefficient,  $\alpha$  is the rate parameter used to evaluate the non-local source,  $C_0$  is the concentration of dissolved  $\text{SiO}_2$  in the overlying water,  $R$  is the reaction term including the rate of reaction. The value of  $K$  includes corrections to the diffusion coefficient,  $D$ , at infinite dilution (*e.g.*, LI, 1974) required by the tortuosity,  $\theta$ , of the sediments (BERNER, 1980), where

$$K = D/\theta^2 \quad (2)$$

Tortuosity is a difficult parameter to measure directly, and thus a variety of empirical relationships between tortuosity and porosity have been developed. The best fit to available data takes the form

$$\theta^2 = 1 - \ln(\phi^2) \quad (3)$$

(BOUDREAU, 1996). For the following calculations, the values of  $\theta^2$  and thus  $K$  are assumed to be constant with depth in the sediment because porosity varies by only a few percent over the depth of the sediments at BRL2 (Figure 4a).

Following the treatment in EMERSON *et al.* (1984), we assume Si concentrations in the pore water are at steady state, *i.e.*,  $\partial C/\partial t = 0$ , and the dissolution rate of solid silica phases

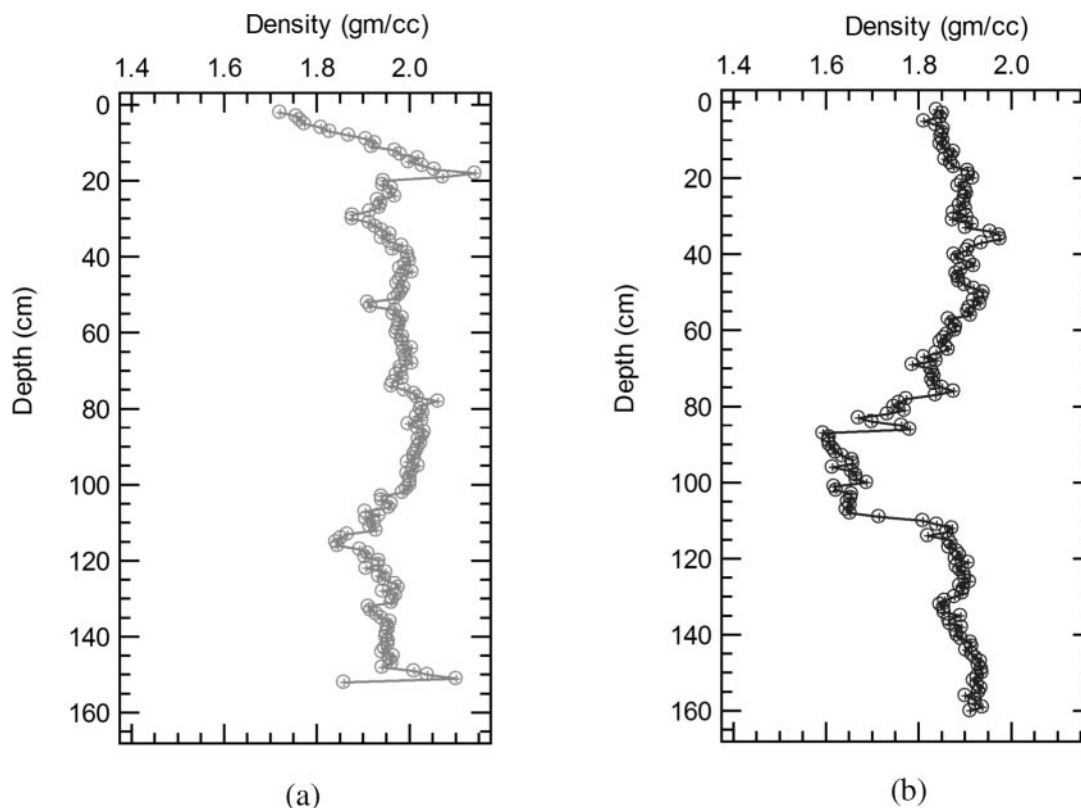
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Figure 3. Bulk density of sediments in (a) BRL2 and (b) BRL6.

is first order. With  $k$  as the first order rate constant (*i.e.*, the dissolution rate of opal), equation (1) becomes:

$$0 = K \frac{d^2[\text{Si}]}{dz^2} - \alpha \left( \frac{[\text{Si}] - [\text{Si}]_0}{\phi} \right) + k([\text{Si}]_a - [\text{Si}]) \quad (4)$$

where  $[\text{Si}]_0$  represents the local concentration of pore water at the sediment–water interface, and  $[\text{Si}]_a$  is the concentration of Si at some depth  $z$ , below which  $\text{SiO}_2$  concentrations remain unchanged. Rearranging equation 4 gives

$$0 = K \frac{d^2[\text{Si}]}{dz^2} - (k + \alpha)[\text{Si}] + k[\text{Si}]_a + \frac{\alpha[\text{Si}]_0}{\phi} \quad (5)$$

Boundary conditions are defined as follows:

$$\begin{aligned} [\text{Si}] &= [\text{Si}]_0/\phi \quad \text{at } z = 0 \\ \left. \frac{\partial[\text{Si}]}{\partial z} \right|_{z_1} &= G \quad \text{at } z = Z_1 \end{aligned} \quad (6)$$

where  $Z_1$  is the bottom boundary depth in the sediment, and  $G$  is the gradient in  $[\text{SiO}_2]$  at  $z = Z_1$ . Thus, following EMERSON *et al.* (1984), the analytical solution to equation 5 becomes:

$$\begin{aligned} [\text{Si}](z) &= \left( \frac{k[\text{Si}]_a + \alpha[\text{Si}]_0/\phi}{\beta} \right) (1 - e^{-\gamma z}) + \left( \frac{[\text{Si}]_0}{\phi} \right) e^{-\gamma z} + \frac{G \sinh(\gamma z)}{\cosh(\gamma Z_1)} \\ &+ \frac{e^{-\gamma(z+Z_1)} - e^{-\gamma(z-Z_1)}}{\cosh(\gamma Z_1)} \left( \frac{k[\text{Si}]_a + \alpha[\text{Si}]_0/\phi}{\beta} - \frac{[\text{Si}]_0}{\phi} \right) \end{aligned} \quad (7)$$

for boundary conditions, where  $\gamma = (\beta/K)^{1/2}$  and  $\beta = (k + \alpha)$ .

## Model Solution and Results

With equation (7) and various fitting parameters described in Table 3, three profiles were calculated and compared with the three observed Si concentrations. For these simulations, different values of  $K$  and  $\alpha$  were used in equation (7) to determine if diffusion alone could explain the observed Si profiles or if a nonlocal source parameter is required to fit the observed data. For this setting, a nonlocal source parameter is expected to be ventilation of the shallow pore water by lagoon water recirculation. One calculation uses  $K = 10^{-5} \text{ cm}^2/\text{s}$  and  $\alpha = 0$  in equation (7), thus assuming no ventilation. The other two calculations assume the pore waters are ventilated by setting  $\alpha = 4 \times 10^{-7}/\text{s}$  and allowing  $K$  to vary from  $10^{-3}$  to  $10^{-4} \text{ cm}^2/\text{s}$ . These two profiles can be used to estimate the control of the diffusion coefficient on the Si profiles when recirculation is included in the model.

The best model fits to the data are using the nonlocal source parameter in equation (7) (Figure 9), suggesting that nonlocal recirculation of the lagoon water is an important processes within the Banana River Lagoon Sediments. For all profiles, the Si concentrations are best reproduced by using diffusion rates of  $K = 10^{-3} \text{ cm}^2/\text{s}$  and a nonlocal source term of  $\alpha = 4 \times 10^{-7}/\text{s}$ . In May and December, the model results show nearly a perfect match with the observed data. The profile from August, however, shows some deviation between the model results and the observed data using these

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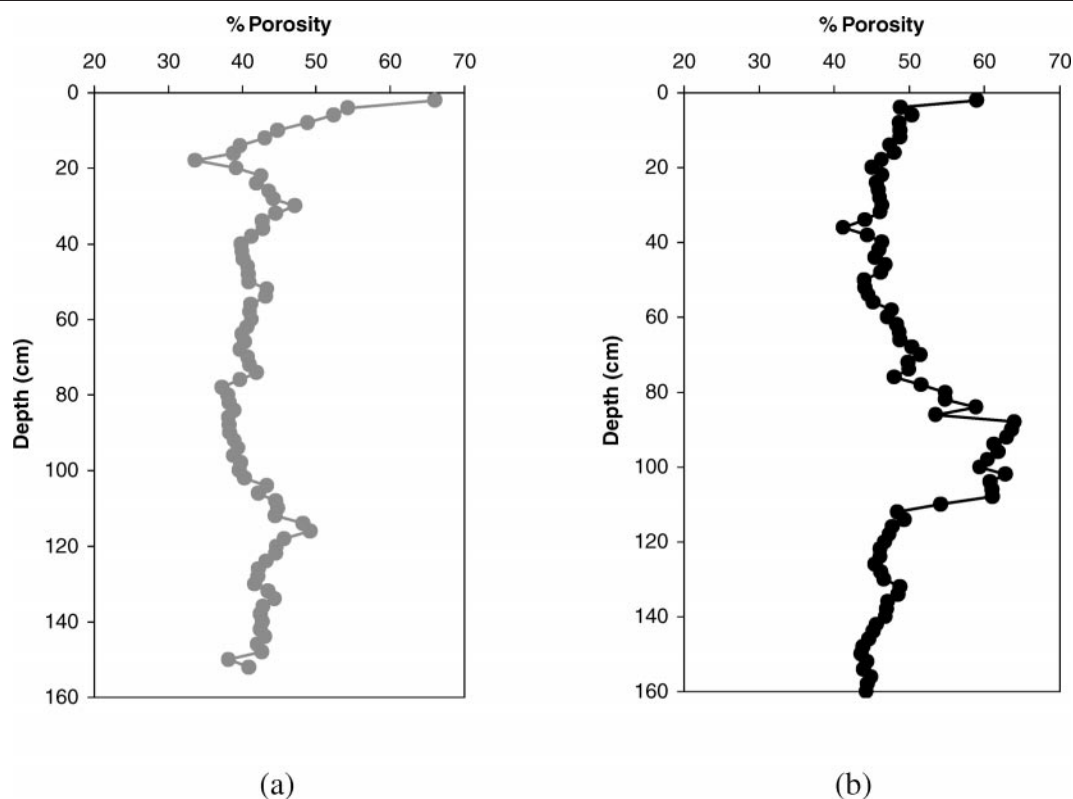


Figure 4. Porosity of sediments in (a) BRL2 and (b) BRL6.

parameters. The pore water Si concentrations indicate that diffusion and in situ reactions are not responsible for the profile shapes. An additional mechanism, represented by the nonlocal source term in the model, must control the pore water Si profiles. A likely explanation is ventilation of the shallow sediments by physical or biological forcing.

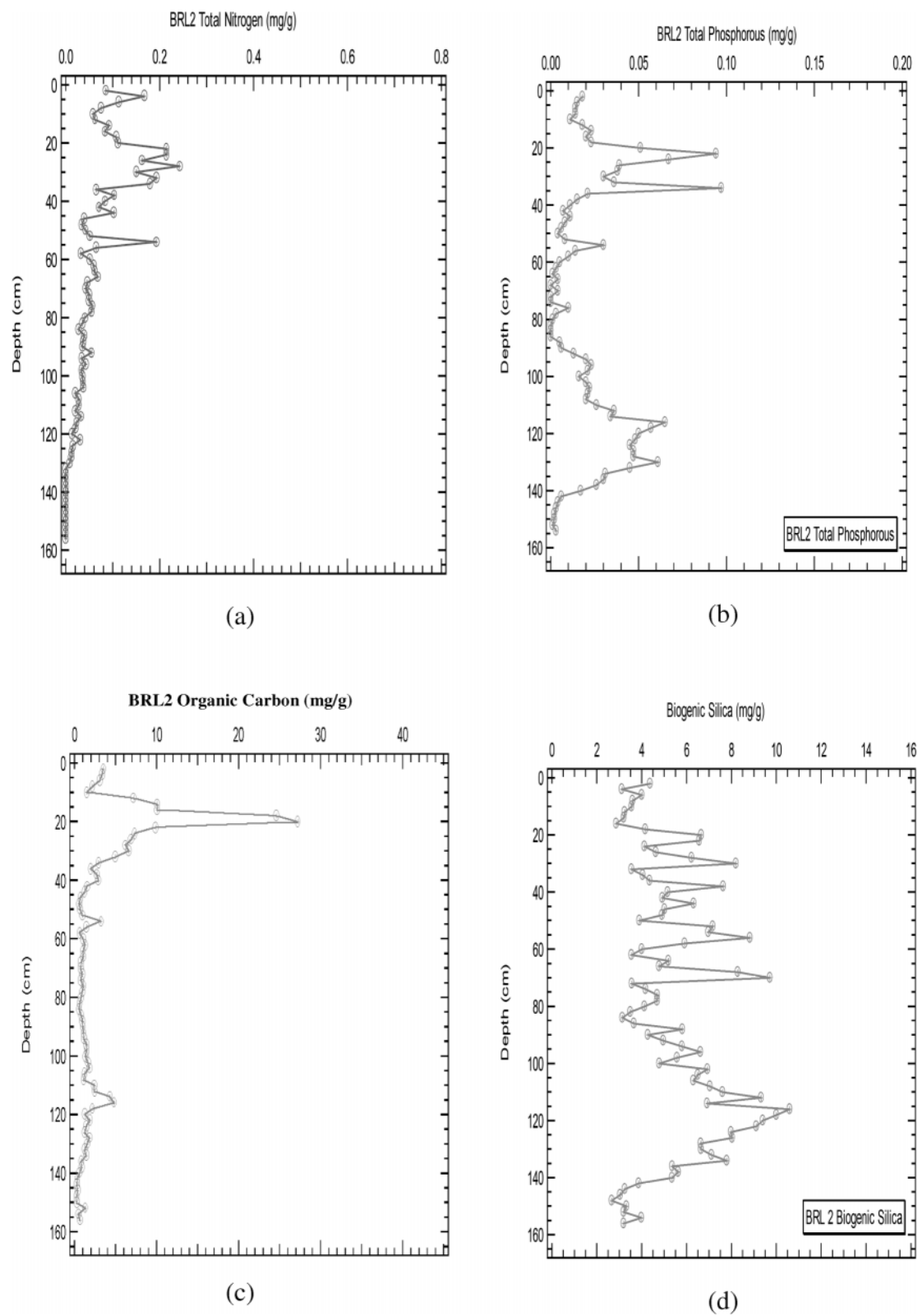
Although these data do not provide information on the rate of flow during ventilation or its primary mechanism, several possibilities for promoting lagoon water recirculation may exist. Prior work has suggested that a variety of processes could be responsible including bioirrigation (KOROSEC, 1979; EMERSON *et al.*, 1984; STAMHUIS and VIDELER, 1998) or physical pumping by waves and tides (SHUM, 1992, 1993; HEUTTEL *et al.*, 1996; LI *et al.*, 1999). Physical mechanisms for pumping water into and out of sediments usually have limited depth ranges (less than 20 to 30 cm) in sediments because of the increased friction of the pore network. HUETTEL *et al.* (1996) found that currents in a wave tank produce pore water exchange down to 30 cm for 3-cm-high ripple mounds. In contrast, sediment ventilation by burrowing shrimp, although generally episodic, has been shown to create pumping rates ranging from 340 to 2100 cm<sup>3</sup>/s through their tubes (KOIKE and MUKAI, 1983), and burrows may be as deep as 50 to 250 cm in the eastern coastal United States (GRIFFIS and SUCHANEK, 1991). Regardless of the mechanism, lagoon water recirculation may influence concentrations of reactive dissolved constituents in addition to the Si. Surface waters typically

contain dissolved oxygen from exchange with the atmosphere and photosynthesis, but pore waters lack oxygen. The loss of oxygen from the pore water could be caused by the oxidation of detrital organic matter in the sediment, and during this process, nutrients such as N and P would be remobilized. Changes in the pore water redox chemistry caused by pumping oxygenated water into the sediment are also likely to influence Fe and Mn solubility (CHARETTE and SHOLKOWITZ, 2002; TESTA *et al.*, 2002; SNYDER *et al.*, 2004).

#### Nutrient Mass Balance

The magnitude of the nutrient fluxes also depends on the source of nutrients. Some nutrients could originate from organic matter remineralization when oxygenated water flows through the sediment (*e.g.*, D'ANDREA *et al.*, 2002; DE BEER *et al.*, 2005) or could originate from meteoric water discharging from terrestrial aquifers (*e.g.*, TOBIAS *et al.*, 2001; SLOMP and VAN CAPELLEN, 2004). If little water originates from the terrestrial aquifers (CABLE *et al.*, 2004; MARTIN *et al.*, 2004), most nutrients must originate from remineralization of organic matter. Thus, this source will depend on the concentrations of labile organic N and P present in the sediment. The following calculations are designed to determine if the sedimentary flux of nutrients is sufficiently high to support estimates of nutrient fluxes to the water column.

The calculations described below compare estimates of the

Bhadha *et al.*Figure 5. BRL2 sediment concentrations of (a) TN, (b) TP, (c) OC, and (d)  $\text{SiO}_2$ .



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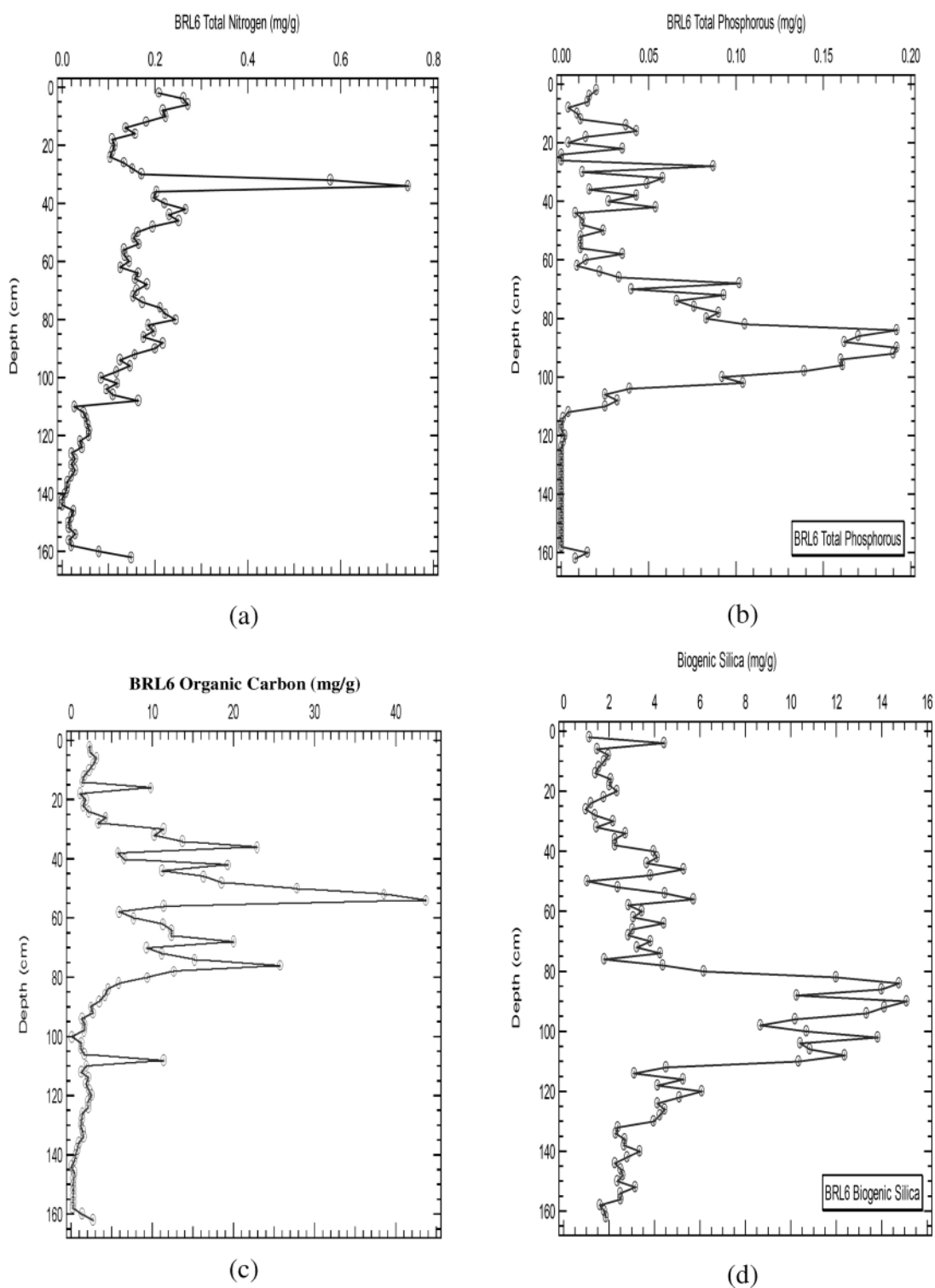


Figure 6. BRL6 sediment concentrations of (a) TN, (b) TP, (c) OC, and (d)  $\text{SiO}_2$ .

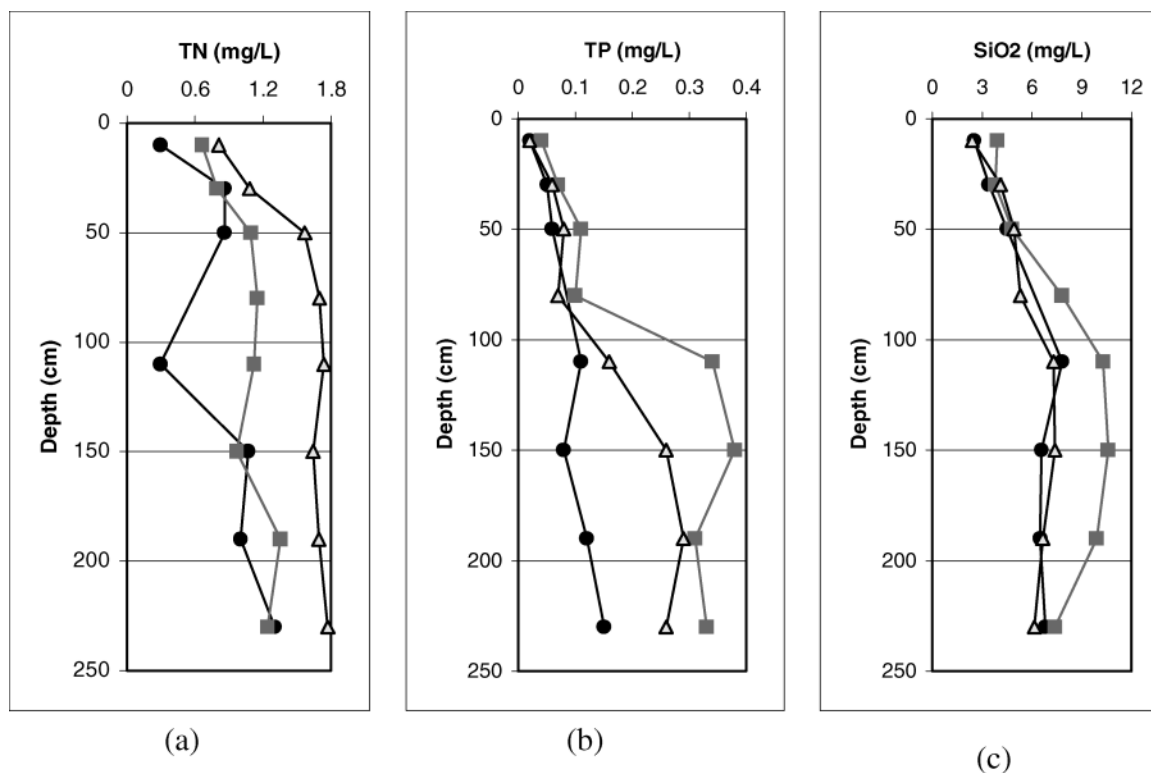
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Figure 7. Concentrations of (a) TN, (b) TP, and (c) SiO<sub>2</sub> versus depth for pore waters at BRL2. Circles represent samples collected in May 2000, squares represent samples collected in August 2000, and triangles represent samples collected in December 2000.

magnitudes of nutrient fluxes to and from the lagoon sediments. The magnitude of nutrient flux from the sediment was calculated by multiplying the N, P, and Si concentrations of the pore water by the magnitude of the SGD, following the approach used by GALLAGHER *et al.* (1996). The magnitude of SGD has been measured for BRL2 and BRL6 using seepage meters (LINDENBERG, 2001) and found to be  $44.5 \pm 12.0$  ml/m<sup>2</sup>/min ( $6.4 \pm 1.7$  cm/d) and  $18.7 \pm 12.6$  ml/m<sup>2</sup>/min ( $2.7 \pm 1.8$  cm/d), respectively. Seepage meters have a long history of use, and numerous field evaluations have been performed (*e.g.*, LEE, 1977; SHAW and PREPAS, 1989; CABLE *et al.*, 1997b; SHINN *et al.*, 2002). Calculated nutrient fluxes depend strongly on the measured seepage rates because, even if the seepage input is small, the significance of an advective pore water input can be large if the dissolved constituent concentrations are high. In an environment where the terrestrially derived ground water flux is likely small, recirculation of surface water through sediment pore waters can provide the delivery mechanism for these nutrients to the overlying water column. SLOMP and VAN CAPELLEN (2004) demonstrated in their review of controls on nutrient inputs via ground water discharge that the residence time of the mixing zone, and ultimately the available reaction time, are critical to evaluating the nitrogen and phosphorus inputs.

The flux of nutrients to the sediments was calculated by multiplying the average concentration of the chemical constituents within the sediment column by the rate of accu-

mulation of sediments (Table 4 and Table 5). The average concentrations were calculated only over the upper 80 cm of the sediment column, which are the depths where recirculation appears to be most prominent. Attempts to measure sedimentation rates using radioisotopic measurements failed because the coarse-grained sediments that make up the lagoon contained little to no isotopic signature. Consequently, sedimentation rates were estimated by partitioning the sediment mass input by area throughout the lagoon. Models based on topographic relief, basin area, and basin-averaged temperature allow the long-term flux of sediment from river basins to be predicted (MULDER and SYVITSKI, 1996; SYVITSKI and MOREHEAD, 1999; SYVITSKI *et al.*, 2003). The most recent model by SYVITSKI *et al.* (2003) is formulated as:

$$Q = \alpha_1 A^{\alpha_2} R^{\alpha_3} e^{kT} \quad (8)$$

where  $Q$  is the sediment load,  $R$  is the large-scale relief,  $A$  is the drainage area,  $T$  is average temperature,  $\alpha_1 = 0.31$ ,  $\alpha_2 = 0.40$ ,  $\alpha_3 = 0.66$ , and  $k = 0.1$  for northern (0–30°N) hemisphere tropical basins at a mean temperature of 25°C. The values of the  $\alpha$  parameters were derived from least-squares regression between the model and measured sediment fluxes from a global data set of 340 river basins. The predicted sediment delivery to the lagoon ranges from about 0.5 to 1.5 metric tons/y, and when evenly distributed over the submerged lagoonal area of about 1000 km<sup>2</sup>, the resulting mean sediment flux is 0.4 to 1.3 kg/m<sup>2</sup>/y. This flux converts to a

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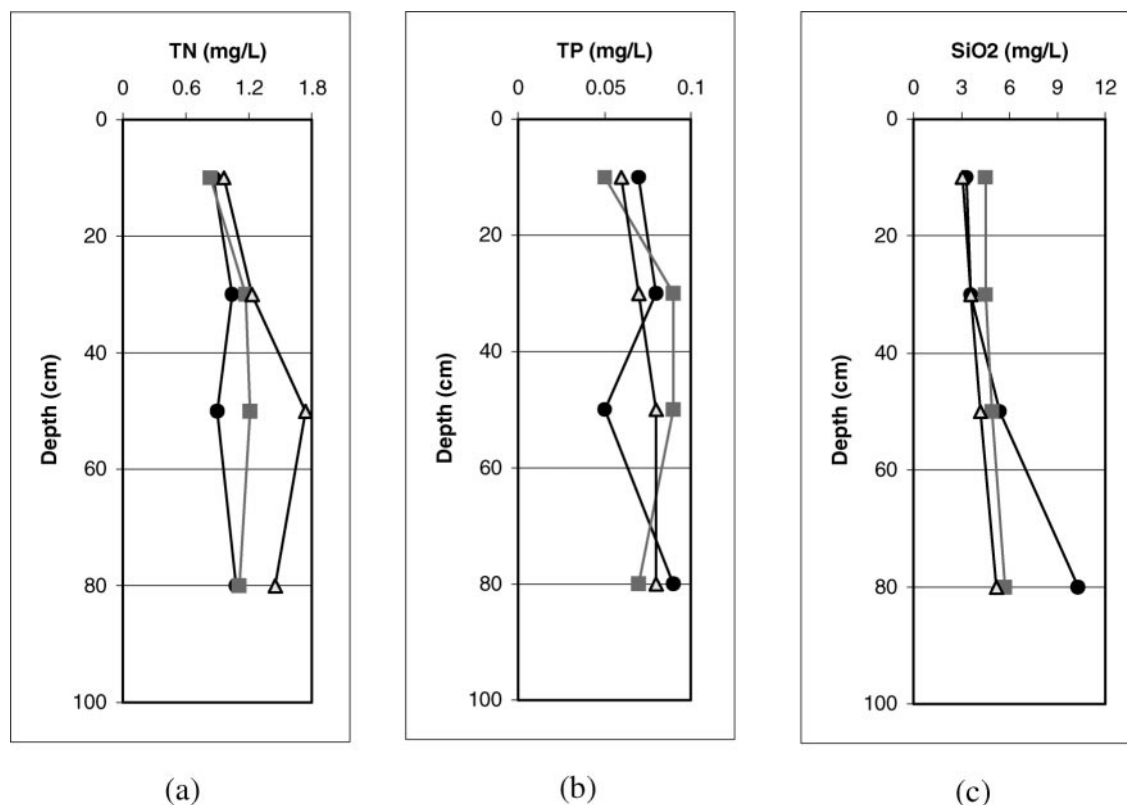


Figure 8. Concentrations of (a) TN, (b) TP, and (c) SiO<sub>2</sub> versus depth for pore waters at BRL6. Circles represent samples collected in May 2000, squares represent samples collected in August 2000, and triangles represent samples collected in December 2000.

sedimentation rate of about 0.2 to 0.7 mm/y given the average dry bulk density of 1500 to 1800 kg/m<sup>3</sup>. If the sediment input is assumed to be preferentially accumulating along the margins of the lagoon, thus reducing by half the submerged area receiving sediment, the mean sedimentation rate is about 0.5 to 1.0 mm/y (0.1 to 0.2 g/cm<sup>2</sup>/y). These rates are within a factor of 2 of the long-term rate of relative sea-level rise in the region and are similar to 14C-determined sedimentation

rates in the comparable sandy coastal plain of the Loxahatchee Estuary found just of the South of the Indian River Lagoon (WANLESS, 1984). With an average bulk density of about 1.85 g/cm<sup>3</sup> for both cores, the bulk sediment accumulation rates are about 100 to 200 mg/cm<sup>2</sup>/y at BRL2 and BRL6. From this bulk sediment accumulation rate, the accumulation rate of the N, P, and Si in BRL2 are estimated to be 9 to 17 μg/cm<sup>2</sup>/y, 2 to 4 μg/cm<sup>2</sup>/y, and 472 to 944 μg/cm<sup>2</sup>/y, and in BRL6

Table 3. Description and values of parameters used in the model for BRL2.

Parameter	Description	Value	Reference
$k$ (s <sup>-1</sup> )	Opal dissolution rate (given here for winter and summer conditions)	$5 \times 10^{-7}$ (at 10°C) $23 \times 10^{-7}$ (at 29°C)	Emerson et al. (1984)
$K$ (cm <sup>2</sup> /s)	Molecular diffusion coefficient	$10^{-5}$ (at 30°C)	Wollast et al. (1971)
	Coefficients for enhanced mixing	1. $10^{-3}$ (fast regime) 2. $10^{-4}$ (slow regime)	Emerson et al. (1984)
[Si] <sub>0</sub> (μM)	Bottom water silica concentration	16 (May) 45 (August) 22 (December)	Lindenberg (2001)
[Si] <sub>a</sub> (μM)	“Asymptotic pore” water concentration	130 (May) 172 (August) 122 (December)	Lindenberg (2001)
$\phi$	Porosity	0.42	This study
$Z_1$ (cm)	Lower sediment boundary (asymptotic depth)	110	Asymptotic depth
$G$	Slope of [Si] profile beyond the asymptotic depth	0	Assumption
$\alpha$ (s <sup>-1</sup> )	“Nonlocal” source parameter	0 (molecular diffusion) $4 \times 10^{-7}$ (enhanced mixing)	Emerson et al. (1984) Sandes et al. (2000)

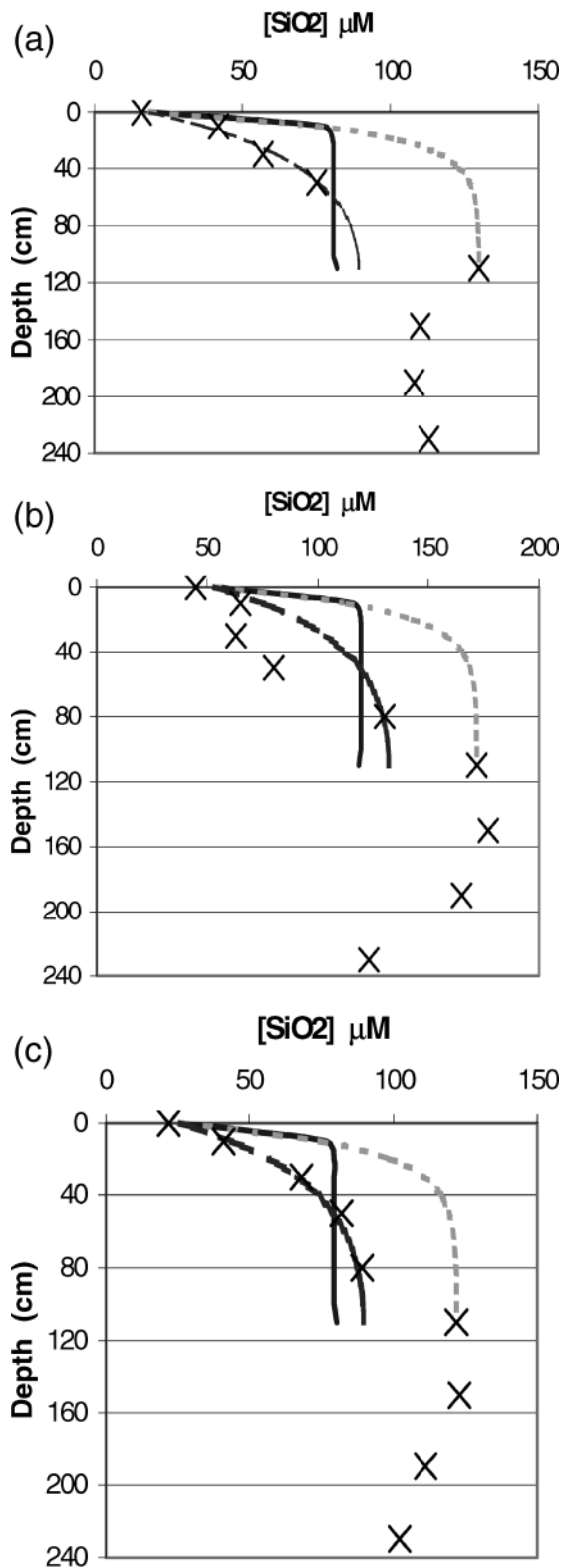
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Figure 9. Model solutions are overlain for the (a) May 2000, (b) August 2000, and (c) December 2000 depth distributions of silicate (X) for enhanced mixing ( $K = 10^{-4}$  cm<sup>2</sup>/s, long dash;  $K = 10^{-5}$ , short dash) with nonlocal transport ( $\alpha = 4 \times 10^{-7}$ /s) included, and molecular diffusion ( $K = 10^{-6}$  cm<sup>2</sup>/s,  $\alpha = 0$ , solid line).

Table 4. Average concentration of TN, TP, and SiO<sub>2</sub> up to 80 cm within the sediment at BRL2 and BRL6.

Site	TN mg/g	TP mg/g	SiO <sub>2</sub> mg/g
BRL2	0.09	0.02	5.1
BRL6	0.21	0.03	2.9

are estimated to be 19 to 38 µg/cm<sup>2</sup>/y, 3 to 6 µg/cm<sup>2</sup>/y, and 259 to 518 µg/cm<sup>2</sup>/y, respectively (Table 5).

At BRL6, the estimated flux of N, P, and Si to the sediment is greater than the return of these solutes to the water column through lagoon water recirculation, although the N flux to the sediment can only be about 30% greater than the return flux to the water column (Table 6). In contrast, the P flux to the sediment can be up to twice the flux from the sediment via recirculation processes, and the flux of Si to the sediment is about two to four times greater than the flux from the sediment. The differences in the fluxes to and from the sediment may depend on the rate of remineralization of the different elements, with Si being the most refractory and thus mostly likely to be buried during deposition without being remineralized. Regardless of the differences in the fraction of each element that is remineralized, the flux of nutrients to the sediment appears to be sufficient to support a benthic flux of nutrients from the sediment at this site. The similarity in the magnitudes of fluxes of these elements to the sediments during deposition and from the sediments via pore water exchange suggest that (1) recirculation of lagoon waters is the pore water source, not SGD, and (2) in estuaries where a large volume of recirculated surface water occurs, the sediments are unlikely to represent a significant sink for labile elements from the estuary water column.

Similar to BRL6, the Si depositional flux to the sediments at BRL2 is greater than the benthic flux of Si to the water column from pore water (Table 6). In contrast with BRL6, however, the mass balance calculations indicate that the estimated N flux to the lagoon water from pore water could be twice as greater as the estimated depositional flux to the lagoon sediments, and the estimated flux of P to the lagoon water from pore water is nearly half the estimated deposition flux to the lagoon sediments (Table 6). The differences in these fluxes are reflected in the lower overall concentrations of the elements in the sediments and the greater magnitude of pore water exchange at BRL2 than at BRL6. If nutrient fluxes associated with recirculated lagoon waters are derived primarily from remineralization of sedimentary N and P, then it is impossible for the depositional flux to the sediment to be less than the benthic flux to the water column. One possible explanation for this discrepancy is that much of the

Table 5. Net accumulation rates of TN, TP, and SiO<sub>2</sub> up to 80 cm within the sediment using a sedimentation rate of 0.5 to 1.0 mm/y.

Site	TN (µg/cm <sup>2</sup> /y)	TP (µg/cm <sup>2</sup> /y)	SiO <sub>2</sub> (µg/cm <sup>2</sup> /y)
BRL2	9–17	2–4	472–944
BRL6	19–38	3–6	259–518

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Table 6. Comparing input fluxes to the sediment versus output fluxes to the lagoon water of TN, TP, and SiO<sub>2</sub> at BRL2 and BRL6.

Nutrient	Source	BRL2		BRL6		
		Input flux (μg/cm <sup>2</sup> /y)	Output flux (μg/cm <sup>2</sup> /y)	Source	Input flux (μg/cm <sup>2</sup> /y)	Output flux (μg/cm <sup>2</sup> /y)
TN	benthic	9–17	38	burial	19–38	33
TP	benthic	2–4	5	burial	3–6	3
SiO <sub>2</sub>	burial	472–944	347	burial	259–518	142

N remineralization occurs at shallow burial depths, perhaps near the sediment–water interface and above the depth of the first sampling port of the multisamplers. Although downward flow during recirculation of the overlying lagoon water would carry some remineralized nutrients to the pore waters, some of the nutrients would also be flushed to the overlying water column without being sampled. All water venting from the sediment would be captured by the seepage meter and measured as SGD, but the nutrient concentrations of the sediments would be reduced.

## CONCLUSION

The origins of SGD are important to the fluxes and sources of nutrients to estuarine water. The results of dissolved Si profiles at one station in the Banana River Lagoon suggest that lagoon water circulates into the sediments, possibly to depths of around 110 cm below the sediment–water interface. This recirculation result is indicated by a lack of fit between observed pore water data and a diffusion–reaction model but a good fit when an advection–diffusion–reaction model is used. In this case, the advection is interpreted to be ventilation of the sediments caused by processes including bioirrigation and/or wave and tidal pumping. Regardless of the process responsible for ventilation, recirculation of oxygenated lagoon water across the sediment–water interface should enhance the remineralization of organic matter and increase N and P concentrations in the pore water. Increased concentrations of N and P would influence nutrient cycling within the estuary. Loading of the N, P, and Si to the sediments is greater at BRL6 on the basis of their average concentrations in the sediment and an estimate of the sedimentation rate of the lagoon sediments. Fluxes of N, P, and Si from the sediment at BRL6 are estimated to be approximately 33 μg/cm<sup>2</sup>/y, 3 μg/cm<sup>2</sup>/y, 142 μg/cm<sup>2</sup>/y, which were estimated from the pore water concentrations and seepage rates measured using seepage meters. In all but one case, more N and P were deposited in the sediment than were lost from the sediment by seepage, indicating that the deposition and burial of organic matter can support the internal cycling of nutrient through the sediment. For N concentrations at one of the stations, however, more discharge of N from the sediment occurred than deposition within the sediment. This discrepancy suggests that much of the remineralization may occur in the shallow sediments near the sediment–water interface.

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