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# BENTHIC NUTRIENT FLUX IN A SMALL ESTUARY IN NORTHWESTERN FLORIDA (USA)

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*ABSTRACT* Benthic nutrient fluxes of ammonium (NH<sub>4</sub><sup>+</sup>), nitrite/nitrate (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>), phosphate (PO<sub>4</sub><sup>-3</sup>), and dissolved silica (DSi) were measured in Escambia Bay, an estuary within the larger Pensacola Bay system of northwestern Florida (USA). Our study occurred during a severe drought which reduced riverine inputs to Escambia Bay. Laboratory incubations of field-collected cores were conducted on 8 dates between June and October 2000 to estimate nutrient flux, and cores were collected from locations exhibiting a range of sediment organic matter content. NH<sub>4</sub><sup>+</sup> flux ranged from – 48.1 to 110.4 µmol m<sup>-2</sup> h<sup>-1</sup>, but the mean flux was 14.6 µmol m<sup>-2</sup> h<sup>-1</sup>. Dissolved silica (DSi) fluxes were also variable (-109. 3 to 145.3 µmol m<sup>-2</sup> h<sup>-1</sup>), but the mean net flux (9.3 µmol m<sup>-2</sup> h<sup>-1</sup>) was from the sediment to the water column. Bay sediment fluxes for NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>-3</sup> were less variable during this period (– 7.93 to 28.73 and – 1.74 to 3.29 µmol m<sup>-2</sup> h<sup>-1</sup> for NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>-3</sup>, respectively). Low NH<sub>4</sub><sup>+</sup> fluxes were similar to published estimates from lagoonal Gulf of Mexico (GOM) estuaries, possibly due to the reduced freshwater input. Diminished regeneration of phosphate relative to inorganic nitrogen observed during the study period was consistent with previous research in Pensacola Bay suggesting phytoplankton phosphorus limitation. Finally, the estimated residence time of Escambia Bay and the mean turnover times for NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> suggested that benthic flux significantly influenced nitrogen concentrations in overlying water.

#### INTRODUCTION

Fluxes of nutrients across the sediment-water interface represent an important link between benthic and pelagic environments (Boynton et al. 1980, Sullivan et al. 1991, Caffrey et al. 1996, Cowan and Boynton 1996), especially in shallow estuarine systems (Kemp et al. 1992, 1998). The benthos can either sequester nutrients from or contribute nutrients to the water column thereby affecting estuarine primary production (Fisher et al. 1982). The environmental and biological factors that regulate benthic nutrient fluxes operate over a variety of temporal and spatial scales (Twilley et al. 1999). For instance, many coastal systems exhibit a seasonal pattern of sediment fluxes, with high summer and low winter fluxes of inorganic nutrients (Kemp and Boynton 1984, Kemp et al. 1998, Cowan et al. 1996). Sediment organic matter (Twilley et al. 1999) and resident benthic fauna (Blackburn and Henrikson 1983, Yamamuro and Koike 1993, Mayer et al. 1995, Gilbert et al. 1998), which can vary over small spatial scales, also influence nutrient fluxes.

Conceptual models of estuarine dynamics, including benthic nutrient fluxes, have emerged from extensive study of temperate estuaries such as San Francisco Bay, Chesapeake Bay, and Narragansett Bay. The 39 estuaries adjacent to the Gulf of Mexico (GOM) differ from temperate estuaries in many ways. For instance, GOM estuaries are generally warmer with less seasonably variable water temperatures, compared to the strong seasonal temperature dynamics of higher latitude systems (Twilley et al. 1999). Furthermore, GOM estuaries have relatively low tidal energy. Tides range up to 1 m in GOM estuaries; however, most systems show tidal ranges from 0.5 to 0.7 m (Solis and Powell 1999). In lieu of reduced tidal influences, the primary forcing function for many GOM estuaries is freshwater input, and GOM estuaries demonstrate a considerable range of freshwater input. River-dominated estuaries include the Atchafalaya/Mississippi River complex (Teague et al. 1988, Solis and Powell 1999), Mobile Bay (Cowan et al. 1996), and Apalachicola Bay (Mortazavi et al. 2000). At the other extreme are the lagoonal estuaries of south Texas, where freshwater input is negligible and evaporation greatly exceeds precipitation and runoff (Flint 1985, Solis and Powell 1999). Furthermore, within a particular system, seasonal or interannual variability in river input will influence the relative role of benthic nutrient flux in estuarine dynamics (Flint 1985, Cowan et al. 1996, Mortazavi et al. 2000). Studies of benthic flux in GOM estuaries over a wide range of physical and ecological conditions will lead to general models of benthic nutrient flux in these systems (Twilley et al. 1999).

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Research on benthic nutrient fluxes in GOM estuaries will also inform studies of coastal eutrophication in the region. Symptoms of eutrophication, including frequent hypoxia/anoxia, loss of submerged aquatic vegetation (SAV), and altered food webs, are prominent in many GOM estuaries (Bricker et al. 1999, Livingston 2001). Benthic flux is an integral component of estuarine nutrient dynamics and thus a potentially strong determinant of coastal eutrophication. For instance, Cowan et al. (1996) found that sediments in Mobile Bay, AL, at times contributed up to 94% of the nitrogen and 83% of the phosphorus required by phytoplankton.

The location for this study was Escambia Bay, FL, a northern GOM estuary. Escambia Bay is part of the Pensacola Bay system, a moderately sized (8800 ha) estuary in northwestern Florida (Figure 1). Escambia Bay, a micro-tidal, partially stratified, drowned river valley estuarine system (Schroeder and Wiseman 1999), has a mean depth of 2.5 m and an approximate tidal range of 0.3 m (Olinger et al. 1975). The primary freshwater input is the Escambia River, with annual flows averaging ca. 195 m<sup>3</sup>s<sup>-1</sup> (Alexander et al. 1996, Solis and Powell 1999). About 80% of the freshwater flow into Pensacola Bay comes from the Escambia River (Olinger et al. 1975). Other freshwater inputs include the Blackwater, Yellow, and East rivers, which empty into the East Bay region. Exchange with the GOM occurs through a narrow, deep pass at the western end of Pensacola Bay and Santa Rosa Sound. The mean water residence time for the entire system is ca. 25 d (Solis and Powell 1999), but the residence time for Escambia Bay



Figure 1. Map of Escambia Bay and the larger Pensacola Bay System. Sampling locations for this study are denoted by the dots and labeled with the following codes: GPS = Gull Point Shallow, GPD = Gull Point Deep, TB = Trout Bayou, MB = Mackie Bay, MT = Mulat Bayou, and GN = Garcon Point.

is between 4 and 8 d (Olinger et al. 1975). Symptoms of eutrophication, including hypoxia and loss of SAV (Olinger et al. 1975, Bricker et al. 1999), have been and are still prominent in this estuary (Livingston 2001). The primary objective of this research was to quantify benthic fluxes of inorganic nutrients ( $NH_4^+$ ,  $NO_2^- + NO_3^-$ ,  $PO_4^{-3}$ , and DSi) in Escambia Bay. In addition to nutrient flux measurements, we estimated the relative importance of benthic nutrient flux to overlying water column concentrations in Escambia Bay by estimating turnover times.

#### MATERIALS AND METHODS

#### **Field Collection and Laboratory Methods**

Nutrient flux measurements were made 8 times between June and October 2000 (Table 1) using diver-collected cores incubated in the laboratory under flowthrough conditions (Miller-Way et al. 1994, Miller-Way and Twilley 1996). Collection sites were all unvegetated, and sediment organic matter content ranged between 0.44% and 8.21% (Table 1). Core cylinders (15 cm i.d.) were 30 cm high, and cylinders were pressed into the sediments to a depth of 15 to 20 cm. The top of each core cylinder was sealed to create a vacuum, and cores were carefully removed from the sediment. To prevent sediment slumping, a plastic plate with the same diameter as the cylinder was placed under the sediment plug. Following collection, the bottom of each core was sealed with a PVC cap fitted with an O-ring gasket. Tops were placed on the cores for transport in insulated coolers to the laboratory. Water (100 L) was collected from each site using a

diaphragm pump, filtered through an 80-µm mesh, and stored in 20-L polyethylene carboys (Nalgene<sup>®</sup>). On the first 2 collection dates, water was collected from the top 0.5 m, but on the remaining dates water was collected from the bottom 0.5 m. Standard hydrographic parameters (temperature, dissolved oxygen, pH, and salinity) were measured at the surface and bottom of each site with a HydroLab<sup>®</sup>.

In the lab, overlying water in the cores was drained and replaced with site water. Cores were then sealed, placed in a water bath, and incubated in the dark. Water bath temperature was adjusted over the study to mimic ambient field temperatures  $(\pm 1 \, ^{\circ}\text{C})$  measured on station. Site water was delivered at a controlled rate via a peristaltic pump (MasterFlex<sup>®</sup>) to each core chamber through Tygon<sup>®</sup> tubing. Preliminary experiments demonstrated that flow rates ca. 10 mL min<sup>-1</sup> were suitable for estimating nutrient fluxes. Water entered each core through an inflow port in the lid via a cannula fitted with a rubber stopper and drained out a separate port in the lid. Gentle internal stirring was maintained using a floating stir bar (Nalgene<sup>®</sup>) mounted to the chamber top and propelled by a magnetic stirrer. Stirring was intended to minimize the development of chemical gradients within experimental chambers (Miller-Way 1994).

Nutrient concentrations from inflow and outflow water were used to calculate flux. Outflow water was sampled directly from each core; inflow nutrient concentrations were determined from the source water (Miller-Way 1994, Miller-Way and Twilley 1996). Samples were collected in acid-washed glass bottles at 2.5–3.5 h intervals

#### TABLE 1

Sample dates and physical/chemical characteristics of sampling sites in Escambia Bay, FL. For study sites, Gull Point SH and DP indicate shallow and deep sites, respectively, near Gull Point. <sup>1</sup>determined as weight loss on ignition, <sup>2</sup>measured using an Elementar Vario EL without acidification, <sup>3</sup>molar ratio, <sup>4</sup>no data.

		Depth	Temp	DO	Sal	%				NH4 <sup>+</sup>	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup>	PO4-3	DSi
Date	Site	( <b>m</b> )	(°C)	(mg L <sup>-1</sup> )	(PSU)	organic <sup>1</sup>	%C <sup>2</sup>	%N <sup>2</sup>	C:N <sup>3</sup>	(µM)	(µM)	(µM)	(µM)
6/6/2000	Gull Point SH	1.0	27.6	7.8	17.3	0.50	0.12	0.01	14.23	0.07	0.02	0.11	56.05
	Gull Point DP	2.0	27.8	7.3	19.1	6.95	1.70	0.14	14.36	0.27	0.03	0.11	56.85
6/20/2000	Trout Bayou	2.0	29.4	5.0	17.5	0.44	0.08	0.02	6.72	0.79	0.56	0.01	47.52
7/12/2000	Mackey Bay	1.0	31.3	5.3	17.3	0.61	0.13	0.02	9.66	3.01	0.16	1.00	67.60
7/26/2000	Mulat Bayou	1.0	29.7	n.d. <sup>4</sup>	19.1	2.27	0.71	0.08	10.54	1.38	0.21	0.74	58.80
8/29/2000	Gull Point SH	1.0	31.0	3.2	26.6	0.44	n.d.	n.d.	n.d.	0.15	0.64	0.67	40.00
	Gull Point DP	2.0	30.9	3.5	25.1	8.21	2.43	0.22	13.01	- 3.15	0.64	0.67	49.20
9/19/2000	Mackey Bay	0.8	25.3	5.2	19.3	0.59	0.23	0.04	8.61	4.49	2.97	0.30	53.63
10/16/2000	Garcon Point	1.6	21.9	5.6	31.2	0.60	0.13	0.03	6.69	1.98	0	0.08	7.93
10/30/2000	Gull Point SH	0.7	23.1	7.1	23.9	0.55	0.13	0.02	7.57	4.20	0.20	0.15	01.40
	Gull Point DP	2.0	23.1	7.1	24.0	7.99	2.19	0.20	12.50	- 4.32	0.29	0.15	21.42

and stored on ice until processing within 1 h. Samples were filtered through a pre-combusted Whatman® GF/F filter, and the filtrate was collected in HDPE bottles and frozen at -70 °C until nutrient analyses. Experiments lasted 10-12 h, during which time 5 serial samples were collected from each core (only 4 time points were sampled on the first date). At the conclusion of each experiment, 1-2 cores from each site were selected for sediment analysis. Three sediment subsamples, taken from the top 5 cm using an open-ended 60 mL syringe, were pooled and stored at 4 °C. Small amounts (2–5 g) were dried and combusted at 500 °C for 4 h to determine % organic matter [determined as weight loss on ignition (WLOI)]. In addition, sediment %carbon (C) and %nitrogen (N) were measured on samples without acidification using an Elementar® vario EL Analyzer.

All nutrient analyses were conducted on an Astoria Pacific<sup>®</sup> analyzer following US EPA standard methods (US EPA 1984). NH<sub>4</sub><sup>+</sup> was analyzed using the indolphenol blue method. NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were analyzed together by the cadmium reduction method, and throughout this paper both oxidized forms of nitrogen are referred to collectively as NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>. PO<sub>4</sub><sup>-3</sup> was analyzed as orthophosphate using the molybdenum method, and DSi was measured via  $\beta$ -molybdosilicate formation.

#### Flux Calculations and Statistical Analyses

Fluxes were calculated for each nutrient using the formula:

$$Flux = F(C_0 - C_i) / A_i$$

where F = flow rate (L h<sup>-1</sup>),  $C_o =$  outflow concentration ( $\mu$ M),  $C_i =$  inflow concentration ( $\mu$ M), and A = benthic surface area (m<sup>2</sup>). Flux ( $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>) was calculated for each nutrient at each sampling interval. Sediment disturbance was minimized, but as a rule initial flux estimates (i.e., determined from initial  $C_o$  and  $C_i$  values) were excluded from analyses. Flux for each nutrient was calculated as the mean of the individual core time point estimates. By convention, a positive flux value represents nutrient efflux from the sediment, while a negative flux denotes influx into the sediment. The overall mean flux rate for a parameter was calculated as the mean of all measurements.

To examine local variability in fluxes, cores were collected from 2 depths at Gull Point (Table 1, Figure 1) on 3 dates (6 June, 29 August, and 30 October). Sediment at the shallower Gull Point site was similar to other sampled shallow habitats, but the deeper site was representative of the muddy habitat that comprises ca. 75% of Escambia Bay (Olinger et al. 1975). To test whether fluxes were significantly different across depth, data from these experiments were analyzed using repeated measures ANOVA (rmANOVA, Potvin et al. 1990, Von Ende 1993). The rmANOVA followed a split-plot single factor design, with depth and time representing the between- and within-subject factors, respectively (Potvin et al. 1990). The assumptions of normality and homoscedasticity were tested, and log-transformations were used to correct significant heteroscedasticity. If data could not be made homoscedastic, a nonparametric test of the overall treatment effect was done using a Wilcoxon two-sample test (Potvin et al. 1990). All analyses were done using SAS (SAS 1989).

Pearson product-moment coefficients were calculated to examine the relationships among mean nutrient fluxes, water column nutrient concentrations, and hydrographic and sediment characteristics [temperature, dissolved oxygen (DO), pH, salinity, sediment %organic matter, sediment %C content, sediment %N content, sediment C:N molar ratios].

Nutrient turnover times were used to evaluate the overall importance of the benthos as a source or sink of dissolved nutrients for this shallow estuary. Turnover time (d) was calculated using overlying water column concentrations, water depth, and sediment flux estimates (Warnken et al. 2000); these estimates were compared to the residence time reported for Escambia Bay (Olinger et al. 1975).

#### RESULTS

Water temperature over the survey period followed a typical seasonal pattern, ranging from 31 °C in July and August to 22 °C in October (Table 1). On all sampling dates, DO was high (> 5 mg L<sup>-1</sup>), with the exception of 29 August, when it was nearly 3 mg L<sup>-1</sup>. The high salinity (> 17 PSU) was atypical and reflected the extreme drought and consequent reduced freshwater input from the Escambia River during this period. Sediments demonstrated variable particle size distributions, from very coarse sands to fine silts and muds, and the organic content of the sediments (determined as WLOI) ranged from less than 1% up to ca. 8%. The deeper site off Gull Point consistently had the highest sediment organic matter. Sediment C:N molar ratios ranged from 6.7 at Garcon Point to 14.4 at the deeper Gull Point site (Table 1).

NH<sub>4</sub><sup>+</sup> flux estimates ranged from – 48.1 to 110.4  $\mu$ mol m<sup>-2</sup> h<sup>-1</sup> (Table 2), and the mean flux indicated overall efflux of NH<sub>4</sub><sup>+</sup> (14.6  $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>). The highest NH<sub>4</sub><sup>+</sup> fluxes were observed on 26 July and 29 August (at the deep station). On the final 3 sampling dates, however, results indicated NH<sub>4</sub><sup>+</sup> influx to the sediment (Figure 2).



Figure 2. Nutrient fluxes (µmol m-2 h-1) as measured 8 times between June and October, 2000, in Escambia Bay, FL. Bars are means of replicate cores, and error bars are ±1 SE. Experiments on 6 June, 29 August, and 30 October at Gull Point were done at shallow (open bars) and deep (gray bars) locations.

Over the study, NH<sub>4</sub><sup>+</sup> flux was positively correlated with water temperature (P = 0.0063, Table 3); the influx of NH<sub>4</sub><sup>+</sup> into the sediments occurred only late in the season when water temperatures fell to 25 °C and below. When a direct comparison was made between the shallow sandy and deep muddy Gull Point sites, NH<sub>4</sub><sup>+</sup> flux was typically higher at the muddy site. There was a marginal statistical difference (rmANOVA, P = 0.058, Figure 2) between NH<sub>4</sub><sup>+</sup> fluxes at the 2 depths in the 6 June experiment. A significant Time × Treatment interaction (P < 0.01) indi-

cated a difference across depth for  $NH_4^+$  flux on the 29 August experiment. On the final sampling date, though,  $NH_4^+$  flux estimates were similar at both depths.

The pattern of  $NO_2^- + NO_3^-$  flux differed from  $NH_4^+$ .  $NO_2^- + NO_3^-$  fluxes were low in Escambia Bay over the survey period, ranging from – 7.9 to 28.7 µmol m<sup>-2</sup> h<sup>-1</sup>, with a mean flux of 2.7 µmol m<sup>-2</sup> h<sup>-1</sup> (Table 2).  $NO_2^-$  +  $NO_3^-$  fluxes into sediments were apparent on 20 June, on 29 August at both depths, and 19 September.  $NO_2^-$ +  $NO_3^-$  efflux into the water column occurred on 6 June

#### TABLE 2

Mean (S.E.) nutrient fluxes from locations in Escambia Bay, FL, measured from intact core incubations during Summer/Fall, 2000. Rates given in  $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>.

Date	Site	Ν	N	$H_4^+$	NO <sub>2</sub>	+NO <sub>3</sub> -	Р	O4 <sup>-3</sup>	Ι	DSi
6/6/2000	Gull Point SH	3	13.0	(9.4)	6.4	(3.0)	0.1	(0.4)	27.5	(41.1)
	Gull Point DP	3	50.7	(11.1)	0.9	(1.2)	-0.3	(0.4)	145.3	(26.9)
6/20/2000	Trout Bayou	4	5.0	(7.1)	-5.4	(2.4)	-0.2	(0.2)	1.3	(9.9)
7/12/2000	Mackey Bay	4	19.5	(11.3)	1.9	(1.2)	-1.0	(1.7)	-74.8	(32.0)
7/26/2000	Mulat Bayou	4	73.4	(5.0)	0.5	(1.2)	0.1	(0.1)	67.5	(10.8)
8/29/2000	Gull Point SH	2	35.7	(16.2)	-1.2	(0.6)	0.2	(0.0)	-109.3	(134.3)
	Gull Point DP	4	110.4	(25.4)	-3.5	(0.9)	3.3	(0.4)	39.8	(39.8)
9/19/2000	Mackey Bay	3	-40.9	(3.9)	-7.9	(2.4)	-1.7	(0.1)	-49.3	(21.0)
10/16/2000	Garcon Point	4	-12.0	(1.8)	0.0	(0.0)	0.8	(0.3)	8.7	(11.7)
10/30/2000	Gull Point SH	4	-45.7	(11.7)	28.7	(4.8)	0.6	(0.3)	21.1	(28.2)
	Gull Point DP	4	-48.1	(7.2)	8.9	(1.8)	0.5	(0.1)	24.1	(16.6)
	Average		14	4.6	2	2.7	(	0.2	ç	9.3

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#### TABLE 3

Pearson product-moment correlation coefficients between benthic fluxes and environmental parameters. Temp,
pH, DO, and Sal are all environmental parameters, while %organic, %C, %N, and C:N refer to various sediment
characteristics. [Nutrient] refers to the nutrient concentration in the overlying water. $N = 11$ for all pairs, except
%C, %N, and C:N, where <i>N</i> = 10. ** <i>P</i> < 0.01, *0.05 > <i>P</i> > 0.10

	NH4 <sup>+</sup> Flux	NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> Flux	PO <sub>4</sub> -3 Flux	DSi Flux
Temp	0.763**	-0.468	0.067	- 0.19
pН	- 0.169	0.586*	0.328	- 0.036
DO	-0.486	0.569*	-0.266	0.587*
Sal	- 0.11	0.16	0.544*	-0.212
%organic	0.361	-0.047	0.541*	0.580*
%C	0.421	- 0.096	0.594*	0.516
%N	0.408	-0.127	0.602*	0.47
C:N	0.464	-0.037	0.231	0.550*
[NH4]	-0.449	0.276	0.029	- 0.503
[NO <sub>2</sub> +NO <sub>3</sub> ]	- 0.273	- 0.403	- 0.389	-0.382
[PO <sub>4</sub> ]	0.536*	-0.221	0.063	-0.408
[Si]	0.541*	- 0.449	- 0.321	-0.059

and 30 October (Figure 2).  $NO_2^- + NO_3^-$  efflux on 30 October corresponded to the significant influx of  $NH_4^+$  during that experiment, implying that  $NH_4^+$  influx provided substrate for nitrification at this time. With respect to environmental characteristics, there was a weak relationship between  $NO_2^- + NO_3^-$  flux and DO (P = 0.086, Table 3).

Like NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>, fluxes of PO<sub>4</sub><sup>-3</sup> in Escambia Bay were generally low (– 1.7 to 3.3 µmol m<sup>-2</sup> h<sup>-1</sup>; Table 2). PO<sub>4</sub><sup>-3</sup> flux estimates were negligible in all measurements through July. On 29 August there was a significant PO<sub>4</sub><sup>-3</sup> efflux at both depths, and flux at the deeper site was significantly higher (rmANOVA, P < 0.01) than at the shallow location. PO<sub>4</sub><sup>-3</sup> fluxed into the sediment during the 19 September experiment but fluxed out in both October tests (Table 2, Figure 2). On average, Escambia Bay sediments showed a positive net flux (0.2 µmol m<sup>-2</sup> h<sup>-1</sup>). Statistical analyses suggested relationships between PO<sub>4</sub><sup>-3</sup> flux and sediment %C, sediment %N, %organic, and salinity (Table 3).

#### TABLE 4

Turnover times (d) of nutrients in Escambia Bay, FL, calculated from flux data, overlying water nutrient concentrations, and water depth.

	$\mathbf{NH4}^{+}$	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup>	PO4 <sup>-3</sup>	DSi
Average	3.9	4.3	77.6	273.6
Range	0.4-3.1	0.2-16.2	7.1–271.1	29.6-3018.6

Dissolved silica fluxes were variable (– 109.3 to 145.3 µmol m<sup>-2</sup> h<sup>-1</sup>), and mean DSi flux over this survey was positive (9.3 µmol m<sup>-2</sup> h<sup>-1</sup>, Table 2). The highest DSi flux was observed on 6 June at the deep site, and there was also a strong positive flux on 26 July (Table 2, Figure 2). A silica influx was detected at the Mackey Bay site on 12 July (– 74.8 µmol m<sup>-2</sup> h<sup>-1</sup>) and 19 September (– 49.3 µmol m<sup>-2</sup> h<sup>-1</sup>). All other DSi fluxes were indistinguishable from 0. Marginal correlations existed between DSi flux and % organic matter (P = 0.062), sediment C:N ratio (P = 0.0992), and DO (P = 0.075; Table 3).

Nutrient turnover times in Escambia Bay ranged from < 1 d up to 13 d for NH<sub>4</sub><sup>+</sup> and < 1 d up to 16 d for NO<sub>2</sub><sup>-</sup>  $+ NO_3^{-}$  (Table 4). The mean turnover time was 3.9 d for  $NH_4^+$  and 4.3 d for  $NO_2^- + NO_3^-$ . Mean turnover times for the other nutrients were much longer (PO4-3:78 d; DSi: 274 d). Olinger et al. (1975) reported a 4-8 d residence time for Escambia Bay, depending on the freshwater input. US Geological Survey (USGS) streamflow data collected from the Escambia River at Century, FL (http://water.usgs.gov/nwis/discharge) demonstrated that Escambia River discharge was severely reduced during 2000 (Figure 3). In fact, the discharge was the lowest recorded in 65 years. Because of the extremely low freshwater input during summer 2000, it is highly likely that a 4-8 d residence time underestimates the residence time during the study period. If that were correct, then water residence time was likely greater than the turnover times for inorganic nitrogen, but still shorter than those of PO4-3 and DSi.



Figure 3. Hydrograph for the Escambia River discharge  $(m^3 s^{-1})$ . The solid line shows the discharge from 2000, whereas the dashed line shows the historical mean weekly flow averages. The horizontal bar indicates the period during which benthic flux studies occurred.

#### DISCUSSION

In general, estuaries of the GOM are river-dominated, that is, freshwater input is the dominant forcing function in these systems (Twilley et al. 1999). During the period of this study, though, the major source of freshwater input for Escambia Bay was only ca. 15% of its 65-year average. During this low-flow period, the benthic fluxes for many of the parameters resembled those witnessed in GOM lagoonal and other low input systems, rather than the typical river-dominated estuaries.

NH<sub>4</sub><sup>+</sup> fluxes observed in this study demonstrated a larger range of variation (– 48.1 to 110.4 µmol m<sup>-2</sup> h<sup>-1</sup>) than previously studied Texas lagoons (Trinity-San Jacinto, – 3.9 to 45.2 µmol m<sup>-2</sup> h<sup>-1</sup>; Nueces, 0.6 to 7.0 µmol m<sup>-2</sup> h<sup>-1</sup>). However, the mean NH<sub>4</sub><sup>+</sup> flux in Escambia Bay (14.6 µmol m<sup>-2</sup> h<sup>-1</sup>) was more similar to estimates from the Trinity-San Jacinto (11.7 µmol m<sup>-2</sup> h<sup>-1</sup>, Zimmerman and Benner 1994), Nueces estuaries (2.9 µmol m<sup>-2</sup> h<sup>-1</sup>, Yoon and Benner 1992), and Ochlockonee Bay (1.3 µmol m<sup>-2</sup> h<sup>-1</sup>, Seitzinger 1987), a small riverine system in Florida, compared to the larger river-dominated

systems of Apalachicola Bay, Mobile Bay, and Fourleague Bay (NH<sub>4</sub><sup>+</sup> fluxes of 38.0, 62.8 and 141.7  $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>, respectively; Twilley et al. 1999). These latter systems are characterized by freshwater input of nearly an order of magnitude higher than other GOM systems (Solis and Powell 1999). Higher freshwater input delivers more inorganic nutrients fueling primary production; subsequent decomposition in the sediment often leads to higher NH<sub>4</sub><sup>+</sup> fluxes. During the extended period of drought and reduced freshwater input, NH<sub>4</sub><sup>+</sup> fluxes measured in Escambia Bay resembled the lagoonal and smaller input GOM systems.

Reduced freshwater input may have influenced NH4<sup>+</sup> fluxes, but many other factors, like temperature, sediment organic content, and macroinvertebrate assemblages, also impact sediment NH4<sup>+</sup> flux. Temperature influenced NH4<sup>+</sup> flux, as suggested by the strong positive correlation between these variables (Table 3), and this is a common result from other studies (e.g., Teague et al. 1988). Our data did not indicate a general relationship between NH4<sup>+</sup> flux and sediment organic matter content seen in other systems (e.g., Cowan et al. 1996). However, data collected from shallow and deep Gull Point sites often showed higher NH4<sup>+</sup> (and other nutrient) fluxes at the deeper, more organic-rich location (Table 2, Figure 2). Higher organic matter content provides substrate for higher remineralization rates. Flux differences were not evident in all Gull Point comparisons, however, and this suggests that localized factors, for instance benthic invertebrate assemblages, further modified nutrient fluxes. Benthic macroinvertebrates can impact fluxes directly by excreting NH4<sup>+</sup> (Yamomura and Koike 1993) or indirectly via bioturbation (Miller-Way 1994). Macroinvertebrate communities in Escambia Bay vary with sediment type (Olinger et al. 1975). One sediment core from both the shallow and deeper locations collected on 6 June was sieved following the test. At the deeper, high-organic matter site, polychaetes (e.g., Mediomastus sp.) were more abundant than at the lower organic matter site (1500 vs. 556 m<sup>-2</sup>, respectively). Polychaetes influence sediment nitrification and denitrification (Pelegri and Blackburn 1995), and community differences across different sediment types were likely contributors to nutrient flux variability (Twilley et al. 1999).

Benthic NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> fluxes in Escambia Bay averaged 2.7 µmol m<sup>-2</sup> h<sup>-1</sup> and were similar to NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> fluxes in Ochlockonee Bay (1.1 µmol m<sup>-2</sup> h<sup>-1</sup>, Seitzinger 1987) and the Trinity-San Jacinto system (– 2.7 µmol m<sup>-2</sup> h<sup>-1</sup>, Zimmerman and Benner 1994). In the present study, there was no apparent relationship between NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> flux and its concentration in the bottom-water. Sediments are thought to act as NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> sinks when ambient concentrations are high (Boynton et al. 1980, Teague et al. 1988, Jensen et al. 1990, Cowan and Boynton 1996, Trimmer et al. 1998). The low mean NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> concentrations (0.6 µM, Table 1) in Escambia Bay during this study would be unlikely to drive NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> dynamics at the sediment-water interface.

Other factors, including nitrification in the sediments, will regulate  $NO_2^- + NO_3^-$  flux. The potential for sediment nitrification depends on sediment NH4+ concentration and local fauna (Mayer et al. 1995). We did not measure porewater nutrient concentrations, but the significant influx of NH<sub>4</sub><sup>+</sup> measured during the final 3 collection dates could have provided the necessary substrate for high nitrification rates. The strong net efflux of  $NO_2^- + NO_3^-$  on 30 October corresponded to a strong influx of NH<sub>4</sub><sup>+</sup> (Table 2, Figure 2), implying that NH<sub>4</sub><sup>+</sup> uptake may have driven significant nitrification in this system. Additionally, during incubations showing significant NH4<sup>+</sup> influx, the results did not reveal an equivalent molar efflux of  $NO_2^- + NO_3^-$  (Table 2), suggesting that some nitrogen may have been lost from the system via denitrification. We did not measure denitrification in Escambia Bay, but previous research suggested potential denitrification rates could be very high (Flemer et

al. 1998). Denitrification has been documented as a sink for nitrogen in other GOM estuaries (Seitzinger 1987, Yoon and Benner 1992, Zimmerman and Benner 1994). Denitrifying organisms utilize nitrate in the overlying water, but they also rely on nitrification in the sediment to produce  $NO_3^-$  for denitrification (Gardner et al. 1987, Yoon and Benner 1992). Denitrification in this system could be fueled in part by sediment  $NH_4^+$  uptake.

Elderfield et al. (1981), Boynton et al. (1991), and Cowan and Boynton (1996) reported high benthic PO4-3 fluxes in northeastern US estuaries, but PO<sub>4</sub>-3 fluxes in GOM estuaries are typically low (Twilley et al. 1999). Mean benthic PO<sub>4</sub><sup>-3</sup> flux (0.2 µmol m<sup>-2</sup> h<sup>-1</sup>) in Escambia Bay was similar to that from the Trinity-San Jacinto estuary (0.6 µmol m<sup>-2</sup> h<sup>-1</sup>, Zimmerman and Benner 1994). Furthermore, the range of PO<sub>4</sub>-<sup>3</sup> flux in Escambia Bay  $(-1.7 \text{ to } 3.3 \text{ }\mu\text{mol } \text{m}^{-2} \text{ }h^{-1})$  is similar to that of the Trinity-San Jacinto (- 2.6 to 3.5 µmol m<sup>-2</sup> h<sup>-1</sup>, Zimmerman and Benner 1994) and much less variable than most other GOM systems (Twilley et al. 1999). In the Guadalupe and Nueces estuaries, the sediments tend to be PO<sub>4</sub>-<sup>3</sup> sinks (Twillev et al. 1999), whereas Mobile Bay and Mississippi River Bight sediments are PO4-3 sources (3.9 and 17.5 µmol m<sup>-2</sup> h<sup>-1</sup>, respectively). PO<sub>4</sub><sup>-3</sup> efflux often accompanies reduced DO, and Cowan et al. (1996) hypothesized that this is associated not only with DO concentration but also with the duration that sediments are exposed to hypoxic/anoxic conditions. The highest PO<sub>4</sub>-<sup>3</sup> efflux in our study coincided with a period of lower DO in the bottom waters (< 3.5 mg  $L^{-1}$ , Table 1).

Relative fluxes of nitrogen and phosphorus from this study indicate another important aspect of benthic flux dynamics in Escambia Bay. Assuming that organic matter deposited to the sediments follows the Redfield ratio of 16:1 N:P and that this material is the primary substrate for remineralization, we would expect that the total fluxes of DIN and DIP will approximate Redfield. However, the mean DIN:DIP ratio calculated from our results (86.5) far exceeded the Redfield ratio, suggesting that sediments were retaining phosphorus. Sediment phosphorus binding appeared to be important, if temporally variable, in Mobile Bay (Cowan et al. 1996), and Caffrey et al. (1996) argued that phosphorus binding might be occurring in San Francisco Bay sediments as well.

The implications of reduced phosphorus regeneration in Escambia Bay extend to local phytoplankton dynamics. A previous study in Pensacola Bay using nutrient bioassays found phosphorus-limited phytoplankton growth, especially during summer (Murrell et al. 2002). N:P ratios of material arriving via the Escambia River often exceed 16 (Alexander et al. 1996), and low PO4<sup>-3</sup> remineralization from the sediments may contribute to or even exacerbate phosphorus limitation within Pensacola Bay. In contrast, Cowan and Boynton (1996) argued that sediment fluxes were consistent with a model of phytoplankton limitation in the Chesapeake Bay system: the phytoplankton was nitrogen-limited in the summer when benthic fluxes showed increased regeneration of phosphorus relative to nitrogen.

DSi fluxes were variable in our study (Table 2, Figure 2), and similar variability (342 to -15  $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>) was observed in Mobile Bay by Cowan et al. (1996). Many factors influence silica fluxes, including temperature, sediment character, and benthic flora and fauna (Sundbäck et al. 1991, Cowan et al. 1996, Sigmon and Cahoon 1997). With respect to sediment character, our results suggested a weak relationship between DSi flux and %organic matter (P = 0.0616, Table 3), a finding consistent with the results of Sigmon and Cahoon (1997). We did not estimate benthic algal biomass, but benthic diatoms can act as silica sinks under both dark and light conditions (Sundbäck et al. 1991, Sigmon and Cahoon 1997). Benthic invertebrates, like polychaetes, can also impact DSi fluxes (Marinelli 1992). As previously noted, polychaetes were more abundant at the deeper site, where silica flux was higher than at the shallow location on 6 June. Such quantitative differences between invertebrate communities across the depth gradient may have influenced silica dynamics at that time.

These results also suggest that benthic flux can represent a strong link between the benthic and pelagic habitats of Escambia Bay, FL, as ascertained from nutrient turnover times. Both  $NH_4^+$  and  $NO_2^- + NO_3^-$  showed turnover times (Table 4) equal to or less than the residence time of the Bay (4-8 d), implying that benthic exchange processes can affect the overlying nitrogen concentrations before water is advected. This is common in shallow estuarine systems (Kemp et al. 1998, Warnken et al. 2000). The estimated turnover times of PO4-3 and DSi were much longer (78 and 274 days, respectively, Table 4), and thus the influence of benthic processes on water column concentrations of PO4-3 and DSi is likely more limited. Further study of benthic fluxes in this estuary will provide estimates of turnover time under a wider variety of environmental conditions. Turnover time is calculated from water column concentrations, sediment flux rates, and water depth (Warnken et al. 2000). Water depth is relatively static, but flux rates and water column concentrations will change with varying freshwater input. Continued research in Escambia Bay has documented the dynamic distribution of inorganic nutrients with changing freshwater input (pers. comm., M.C. Murrell, US EPA, Gulf Breeze, FL).

Another goal of continued research on benthic flux in this system will be estimating the relative contributions of nutrients from benthic and riverine sources. In some systems, the benthic contribution to estuarine nutrient pools can equal or exceed the supply from riverine or other external sources (Nixon 1981, Fisher et al. 1982). For example, Flint (1985) reported that sediment NH4<sup>+</sup> flux in Corpus Christi Bay, TX, provided greater than 90% of the nitrogen necessary for primary production. Similarly, Mortazavi et al. (2000) showed that, during low-flow summer periods (May-September), benthic flux in Apalachicola Bay supplied nitrogen (in the form of NH4<sup>+</sup>) to the water at about the same rate as the Apalachicola River. This finding of Mortazavi et al. (2000) also implies that the benthic contribution to estuarine nutrient levels may change over longer temporal scales. Seasonal dynamics (low-flow summer, high-flow spring) are overlain by regional climactic events, like droughts, that introduce variability over longer periods. The mean summer discharge from the Escambia River is 138 m<sup>3</sup> s<sup>-1</sup>. Discharge during 2000 was dramatically lower than the 65-year mean (Figure 3). From these data it is difficult to extrapolate a system-wide nutrient budget for Escambia Bay; the spatial and temporal distribution was limited and the study occurred during a unique period. Only continued research on this topic can quantify the relative contributions of nutrient sources in this system.

Our study of benthic nutrient flux in Escambia Bay, a northern GOM estuary, occurred during a period of regional drought and low freshwater input. The mean daily flow of the Escambia River during our study was the lowest ever recorded and only 15% of the long-term mean summer daily flows. Low riverine input, and consequent low nutrient loading, is associated with reduced benthic nutrient fluxes in GOM estuaries (Twilley et al. 1999). Our NH4<sup>+</sup> flux data from Escambia Bay were consistent with that general observation. Flux of PO4<sup>-3</sup> was also very low, a condition typical of GOM estuaries (Twilley et al. 1999). More importantly with respect to system dynamics, PO<sub>4</sub>-3 may not be remineralized from the benthos to the water column at the rate it is supplied. Previous observations in Pensacola Bay showed phytoplankton phosphorus-limitation, and reduced sediment PO4-3 flux likely contributed to this condition. Further research is necessary to quantify the contribution of benthic flux to Escambia Bay nutrient dynamics over a wider range of freshwater inputs.

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