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Dissolved organic nitrogen and nitrate in Apalachicola Bay, Florida: spatial distributions and monthly budgets

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ABSTRACT: Despite the quantitative importance of dissolved organic nitrogen (DON) in aquatic systems, information on the spatial and temporal distribution of DON in estuaries is lacking. We employed a combination of property-surface plots, hydrodynamic model results, and property-salinity plots to examine nitrate and DON distributions in Apalachicola Bay, Florida, USA, during Apalachicola River high-flow and low-flow conditions. DON enters Apalachicola Bay in river water and in seawater through several passes. DON concentrations in water at some stations within the estuary exceed end-member concentrations. Therefore, DON production by phytoplankton exceeds the combined effects of dilution plus DON processing by the food web at these stations. Depending on estuarine hydrodynamics, nitrate concentrations were influenced both by dilution with low-nitrate water entering the estuary from the passes and by biological processes. In contrast to DON, nitrate concentrations declined within the estuary as salinity increased. Budget calculations indicate that DON retention within the estuary was insignificant during all months sampled. Therefore, DON that is exported from Apalachicola Bay to the Gulf of Mexico (GOM) consists of DON that enters the estuary and is not utilized in this short residence-time estuary plus a fraction produced within the estuary by the food web. Nitrate and DON exported from the estuary comprise sources of new nitrogen for the northeastern GOM food web.

KEY WORDS: Dissolved Organic Nitrogen · Nitrate · Bar-built estuary · Residence time

INTRODUCTION

Rivers provide the major source of nitrogen, silicate, and phosphorus, which enter the ocean from terrigenous environments. Estimates of river nitrogen, silicate, and phosphorus input to the world ocean have been made by estimating river fluxes of these elements to the sea (Froelich et al. 1982, Meybeck 1982, Tréguer et al. 1995). However, estuaries, the interface between rivers and the sea, are active sites of biogeochemical processing where nutrients are transformed before reaching the ocean. A correction factor has been applied to river concentrations to account for processing of nitrogen and phosphorus within estuaries (Froelich et al. 1982, Nixon et al. 1995). While budgets have been prepared for inorganic nitrogen, silicate, and phosphorus input to the global ocean through rivers, dissolved organic matter transport from rivers into the global ocean is not as well understood (Ittekkot 1988).

Nitrogen input to near-shore marine environments is of increasing concern as the population in coastal areas increases and as instances of eutrophication are increasingly reported (Nixon 1995). Nitrogen input to estuaries occurs in particulate, inorganic, and organic forms. The particulate forms are considered less reactive, and are sequestered within the sediments after sedimentation (Pennock et al. 1999). Dissolved inorganic nitrogen (DIN) is readily utilizable by primary

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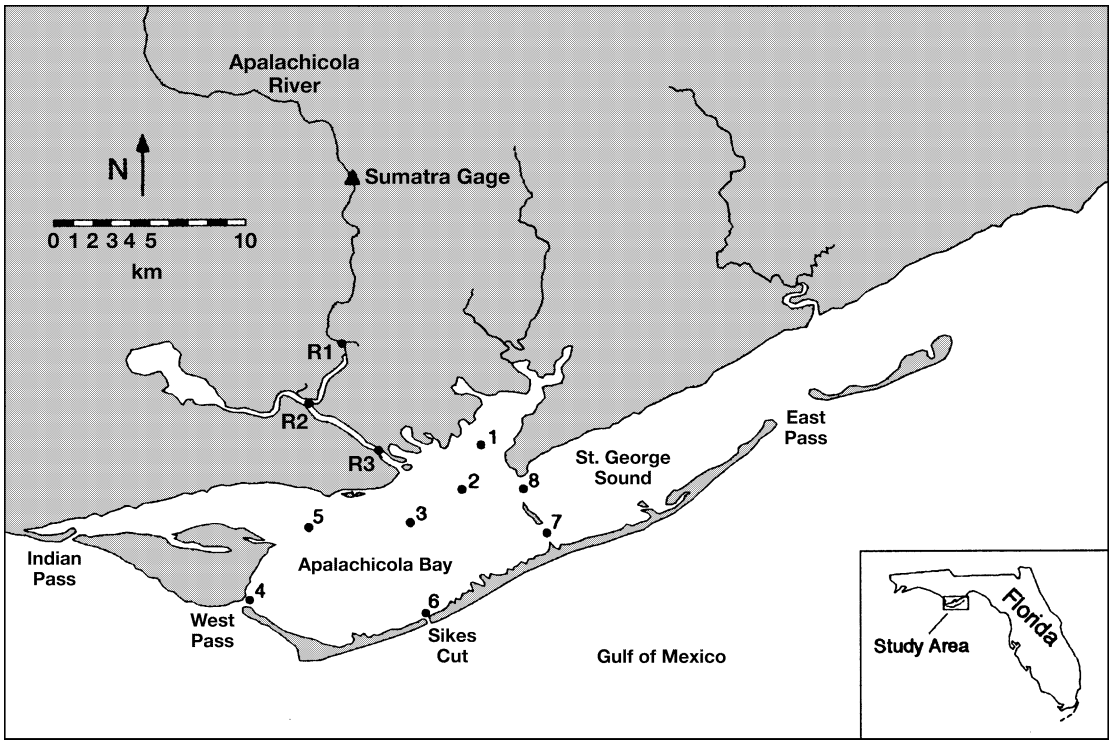

Fig. 1. Map of Apalachicola River and estuary. Apalachicola River flow was monitored at Sumatra Gage; 3 river samples (R1, R2, and R3) were sampled for nutrients; Apalachicola Bay surface and bottom samples were collected from Stns 1–8

producers, and frequently limits primary productivity in estuaries (Howarth 1988). Dissolved organic nitrogen (DON) represents a major fraction of the dissolved nitrogen pool in river water and of the nitrogen input to coastal oceans (Meybeck 1993). A fraction of riverine DON can be utilized by the estuarine bacterial community and regenerated to DIN to support phytoplankton production (Seitzinger & Sanders 1997, Jørgensen et al. 1999), while the rest is available for export to the bordering sea (Ittekkot 1988). The preferential use of DON as a nitrogen source has been implicated in harmful algal bloom developments (Berg et al. 1997, Laroche et al. 1997).

DON in estuarine waters consists of a mixture of compounds supplied by river water and DON originating from phytoplankton and released to the water column by food-web processes (Lampert 1978, Suttle et al. 1990, Pujo-Pay et al. 1997, Hasegawa et al. 2000). A significant fraction of DIN taken up by phytoplankton is released as DON (Bronk & Glibert 1991, Bronk & Glibert 1993a) and can be rapidly recycled by the heterotrophic and autotrophic communities (Bronk & Glibert 1993b). On a seasonal time scale, DON can serve as an intermediate nitrogen pool during the transition from autotrophy to heterotrophy in estuaries (Bronk et al. 1998).

The importance of DON in the dissolved nitrogen pools of river water (Meybeck 1993) and seawater (Sharp 1983) is understood. However, information concerning the temporal and spatial distribution of DON in estuaries is limited. We coupled nitrate and DON concentration measurements with outputs from a 3-dimensional numerical circulation model for Apalachicola Bay, a bar-built estuary in the northeastern Gulf of Mexico (GOM). Our objectives were (1) to report nitrate and DON spatial concentration distributions during high- and low- Apalachicola River flow conditions into Apalachicola Bay, and (2) to develop budget calculations to determine the relative importance of the passes in exchanging water, nitrate and DON with the GOM during high and low river-flow conditions.

METHODS

Field sample collection. Bar-built estuaries represent the most common morphologic features along the North American and the GOM coastline (NOAA 1997a,b). On a global scale, 13% of the coastlines lie behind barrier-type spits or barrier island formations (Seibold & Berger 1993). Our study site, Apalachicola Bay, a bar-built estuary with an area of 260 km^2 and a mean depth of 2.2 m, is situated in the northeastern GOM (Fig. 1). The estuary has a tidal range of 0.5 m

and is connected to the GOM by 3 natural passes and an artificial inlet. The Apalachicola River, with the third largest flow rate in the Northern GOM (Bianchi et al. 1999), is the estuary's freshwater source. The Apalachicola River drainage basin, with an area of 44 000 km^2 (Fu & Winchester 1994), is located in 3 US states. The Florida portion of the river is bordered by an extensive, forested flood plain. The average human population density (11 km^{-2}) throughout the Apalachicola portion of the watershed is low (Frick et al. 1996), and is considered one of the least polluted estuaries in the US (Livingston 1984). Mean daily river flow was obtained from the US Geological Survey's gage closest to the estuary at Sumatra, Florida, located 32 km upstream from the river mouth.

The monthly measurements of hydrographic and chemical variables reported here were made from November 1994 through November 1995 at 3 Apalachicola River locations and 8 bay stations (Fig. 1). Surface river-water samples were collected for nitrogen analysis with a non-metallic Kemmerer water sampler. Both surface and bottom estuarine-water samples were collected for nitrate, nitrite, ammonium (NH_4^+) and DON analyses. These samples were placed in acid-washed polyethylene bottles and kept on ice in the dark for transport to the laboratory. Water for DON analyses was immediately filtered through GF/F filters (combusted at 450°C for 4 h) and frozen for later analysis. Salinity was measured *in situ* with a YSI® salinometer.

Determination of chemical variables. DIN samples were analyzed within 24 h of sample collection. NH_4^+ was determined with the phenol-hypochlorite method as outlined in Strickland & Parsons (1972). Nitrate (NO_3^-) concentrations were determined with the chemiluminescence detector-based method for trace nitrite (NO_2^-) and NO_3^- in aqueous samples. The method was developed by Cox (1980) and applied to seawater analyses by Garside (1982). We used the modified version of Garside's method (Braman & Hendrix 1989). Nitrate and NO_2^- are rapidly reduced by vanadium (III) at 80 to 90°C to nitric oxide. Nitric oxide is then removed from the reaction solution by scrubbing with helium carrier gas and is detected with a Thermo Environmental® Model 42 chemiluminescence NO_x analyzer. Because NO_2^- is also reduced by this method, the procedure measures NO_3^- plus NO_2^-. Nitrite concentrations were measured colorimetrically (Strickland & Parsons 1972) and subtracted from the NO_3^- plus NO_2^- values to yield NO_3^- concentrations. The NO_3^- plus NO_2^- values determined with vanadium reduction were always higher than the NO_2^- concentrations.

Total dissolved nitrogen (TDN) concentrations were determined with the persulfate oxidation method. Briefly, 2.5 ml of a potassium persulfate oxidizing reagent (Pujo-Pay & Raimbault 1994) was added to 20 ml of filtered seawater and autoclaved at 120°C for 0.5 h. The digestions were carried out in acid-washed (10% HCl) Teflon bottles with screw caps. After cooling to room temperature nitrate was determined as described above. DON concentrations were determined by subtracting DIN from TDN concentrations.

Water export and residence-time calculations. Water export from the estuary to the GOM was determined with a 3-dimensional, time-dependent, numerical hydrodynamic model, which allowed velocity, temperature and salinity field calculations (Huang & Jones 1997). A Blumberg & Mellor (1980, 1987) model application to Apalachicola Bay used an explicit-in-horizontal, implicit-in-vertical, finite-difference format with freshwater inflow, tide, and wind-stress forcing. The model has been previously applied to Apalachicola Bay (Jones et al. 1994, Jones & Huang 1996) as well as to other estuaries such as Chesapeake Bay (Blumberg & Goodrich 1990) and Delaware Bay (Galperin & Mellor 1990). The set of governing equations is given by Blumberg & Herring (1987). The model solved a coupled system of prognostic differential equations describing conservation of mass, momentum, heat, and salinity at each of 930 horizontal grids and 5 vertical layers of the computational scheme. A horizontal, orthogonal, curvilinear coordinate system allowed representation of coastline irregularities. A sigma coordinate system allowed vertical stretching to simulate water-level changes in the estuary. A turbulence closure sub-model (Mellor & Yamada 1982, Galperin et al. 1988), which provides eddy viscosity and eddy diffusivity for vertical mixing, permitted variation in the forcing factors (Huang & Jones 1997).

The model was calibrated and verified with hydrographic data recorded at 0.5 h intervals from *in situ* instruments located throughout the estuary during a 6 mo period (Huang & Jones 1997). For simulations used in the present analysis, measured river discharge, winds, tides, temperature, and salinity were applied to the model as boundary conditions. The model was used to calculate water inflow and export at the passes. The estuarine-water residence time was calculated by dividing the estuary's volume by the sum of the total water imported into the estuary.

River-nutrient input was determined by multiplying average river-nutrient concentration by mean river flow for the 5 d prior to sampling. Nutrient exchange at the passes was determined by multiplying average surface and bottom nutrient concentrations at each pass by mean water exchange for the 5 d prior to sampling. Because only 2 samples were collected at West Pass, Indian Pass, and Bob Sikes Cut, the relative standard error at St. George Sound (n = 4) was applied to these passes. Error propagation, including the stan-

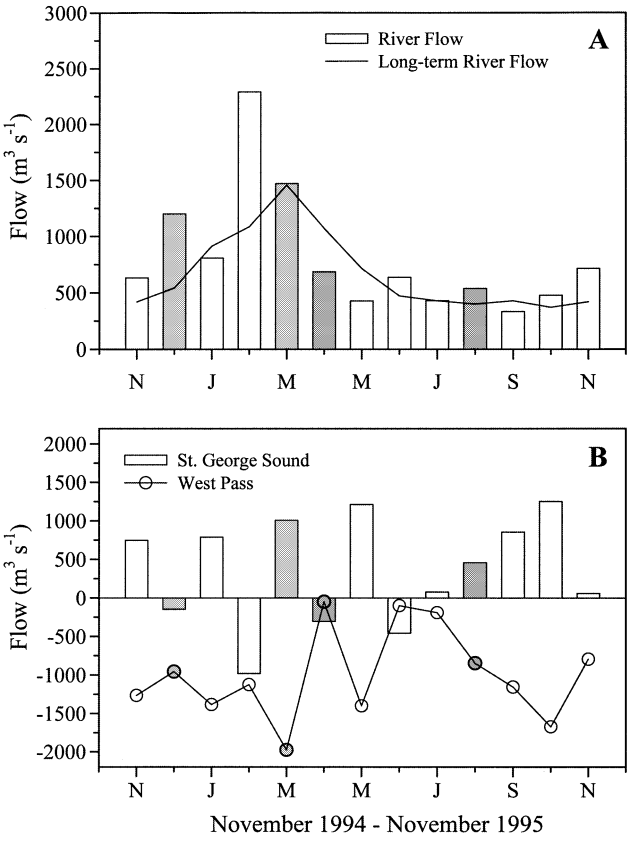

Fig. 2. (A) Apalachicola River discharge, long-term (1965 to 1989) monthly mean and discharge 5 d prior to sampling; shaded bars: months examined in this study. (B) Water exchange at St. George Sound and at West Pass averaged for 5 d prior to sampling; shaded bars and circles: months examined in this study

dard error for the river and passes, was applied to estimates of nutrient input to the estuary and export to the GOM for each month.

RESULTS

Hydrology

Apalachicola River discharge minima occur during the summer season, while the winter and early spring seasons are characterized by discharge maxima (Fig. 2A) in response to rainfall over the river drainage basin. Mean river discharge for the study period (November 1994 to November 1995) was 819 $m^3 s^{-1}$, slightly exceeding the long-term (1965 to 1989) Apalachicola River monthly mean discharge (710 $m^3 s^{-1}$) (Fu & Winchester 1994).

St. George Sound (Fig. 1) was the major source of GOM water to the estuary. Mean (±1 SE) seawater input to the estuary for the study period was 505 ± 136 $m^3 s^{-1}$. St. George Sound accounted for all the seawater input to the estuary, except in June 1995 when Indian Pass contributed 81 $m^3 s^{-1}$ of GOM water to the estuary. GOM water-inflow minima to the estuary occurred during high river-flow periods, except in March 1994 when there was a significant water inflow from the GOM concurrent with high river discharge (Fig. 2). GOM water-inflow maxima to the estuary occurred in low river-flow periods such as May (1212 $m^3 s^{-1}$) and October (1253 $m^3 s^{-1}$) 1995 and exceeded the long-term mean river flow for those months by 1.7 and 3.4 times, respectively (Fig. 2). On average, 69% of the water outflow from the estuary to the GOM occurred through West Pass (Fig. 1). However, in April and June 1995, St. George Sound was the major water outlet for the estuary and accounted for 66 and 76% of the total water outflow to the GOM, respectively.

Salinity, DIN, and DON distributions during river high-flow periods

In December 1994, freshwater input to the estuary from the Apalachicola River exceeded the long-term mean river flow into the estuary by a factor of 3 (Fig. 2A). Seawater input from the passes to the estuary was insignificant during this month (Fig. 2B). The average estuarine salinity in December 1995 was 13.5 ± 1.6 psu. The greater fraction of the total water export to the GOM occurred through West Pass at a salinity of 16.5 psu (Fig. 3A).

Average Apalachicola River nitrate concentration in December 1994 was 252.5 ± 2.2 µg N l^{-1}. Nitrate concentration in the estuary averaged 138.5 ± 14.5 and decreased with increasing salinity from the river mouth to reach minimal concentrations near the estuary-GOM boundary (Figs. 3B, 4A). Nitrate concentration at West Pass and St. George Sound were 127.0 (range: 123.4 to 130.7) and 72.5 ± 3.3 µg N l^{-1}, respectively.

In December 1994, the mean Apalachicola River DON concentration (201.6 ± 17.0 µg N l^{-1}) was similar to DON concentration exported from the estuary at St. George Sound (181.9 ± 6.2 µg N l^{-1}) and water exiting the estuary at West Pass (Fig. 4B). In contrast to nitrate concentrations that decreased with increasing distance from the river mouth, DON concentration maxima were observed at mid-salinity ranges in the estuary (Figs. 3C, 4B).

In March 1995, Apalachicola River flow had reached 1471 $m^3 s^{-1}$, a typical flow rate for this month (Fig. 2A). In contrast to December 1994, however, there was significant seawater input to the estuary from the GOM (Fig. 5A). The March 1995 mean estuarine salinity was 8.7 ± 2.0 psu. Water exported at West Pass at a salinity of 5.2 psu accounted for 82% of the total water

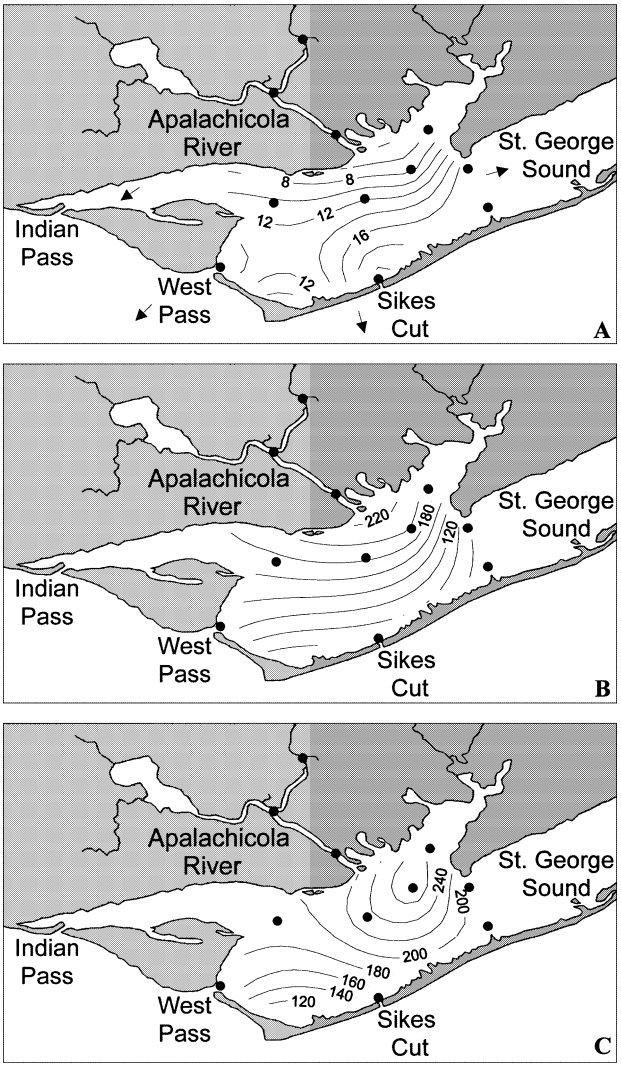

Fig. 3. Apalachicola Bay, December 1994. (A) Contour plots of mean salinity, psu (arrows indicate direction of water exchange at passes), (B) mean surface and bottom nitrate concentration (µg N l^{-1}), (C) mean surface and bottom DON concentration (µg N l^{-1})

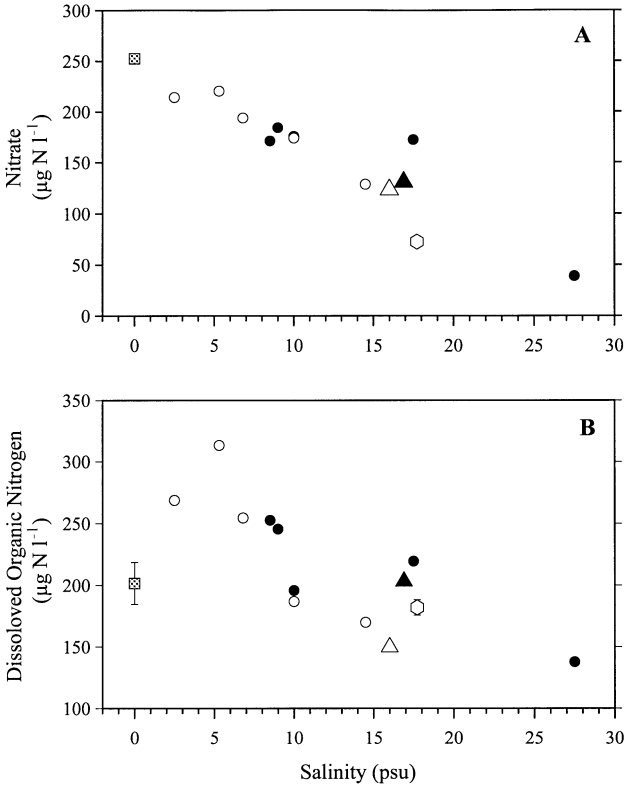

Fig. 4. Apalachicola River, December 1994, river and estuary nitrate (A) and DON (B) versus salinity. (⊠) river; (○,●) surface and bottom samples respectively; (△,▲) surface and bottom West Pass samples respectively; (⬡) mean concentration at St. George Sound; error bars in (B): ±1 SE; error bars for river and St. George Sound nitrate smaller than symbols

exported to the GOM, while 13% of the total water exported to the GOM was exported through Indian Pass at 2 psu (Fig. 5A).

In March 1995, the average Apalachicola River nitrate concentration (388.7 ± 5.5 µg N l^{-1}) exceeded the mean estuarine nitrate concentration (228.4 ± 30.3 µg N l^{-1}) (Fig. 6A). Nitrate concentrations decreased with increasing salinity within the estuary (Fig. 5B), reaching minimal values at the boundary with St. George Sound (61.8 ± 4.5 µg N l^{-1}) (Fig. 6A). The mean DON concentration at the St. George Sound boundary (156.8 ± 34.3 µg N l^{-1}) was similar in magnitude to river DON concentrations (Fig. 6B). In a fashion similar to the DON distribution in December 1994, DON concentrations increased from 130.7 ± 6.5 µg N l^{-1} in the river to reach maxima at low salinity ranges in the estuary during March 1995 (Figs. 5C, 6B). Water exported at West Pass had a DON concentration of 145.2 µg N l^{-1} (Fig. 6B).

Salinity, DIN, and DON distributions during river low-flow periods

The April 1995 Apalachicola River discharge (685 m^3 s^{-1}) was lower than the long-term river flow for that month (Fig. 2A). Mean Apalachicola Bay salinity in April 1995 was 16.0 ± 1.7 psu. During this month, water was exported to the GOM at all passes, with 66% exported through St. George Sound at 18 psu (Fig. 7A).

Mean Apalachicola River nitrate and DON concentrations in April 1995 were 449.8 ± 17.5 µg N l^{-1} and 199.2 ± 5.2 µg N l^{-1}, respectively (Fig. 8A,B). Mean nitrate concentration in the estuary (102.5 ± 22.2 µg N l^{-1}) was approximately 4 times lower than mean

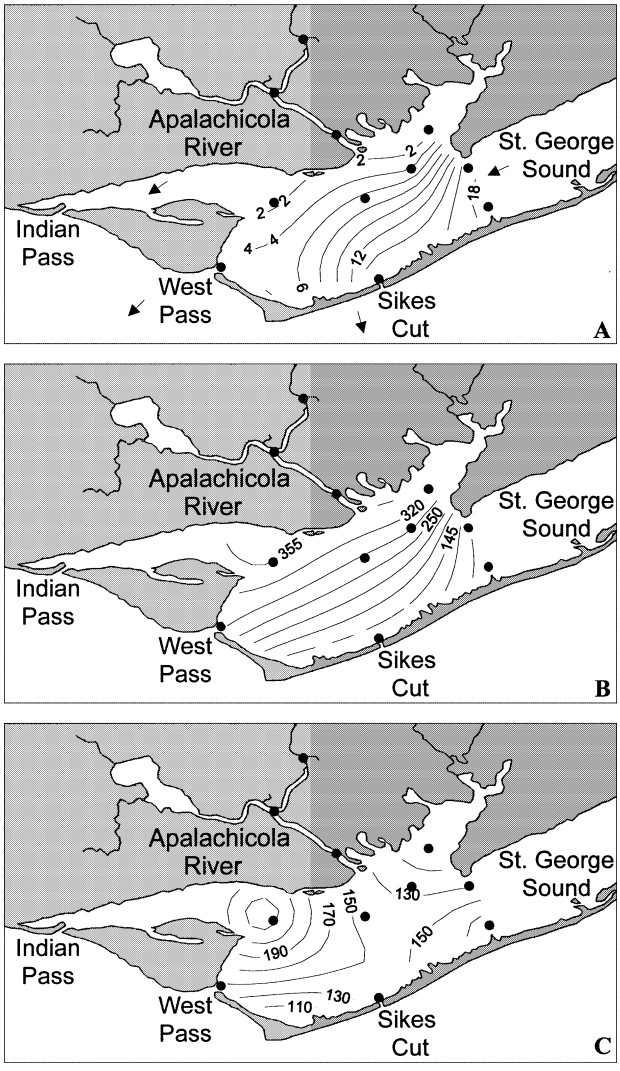

Fig. 5. Apalachicola Bay, March 1995. Contour plots of (A) mean salinity (arrows indicate the direction of water exchange at the passes), (B) mean surface and bottom nitrate concentration (µg N l^{-1}), (C) mean surface and bottom DON concentration (µg N l^{-1})

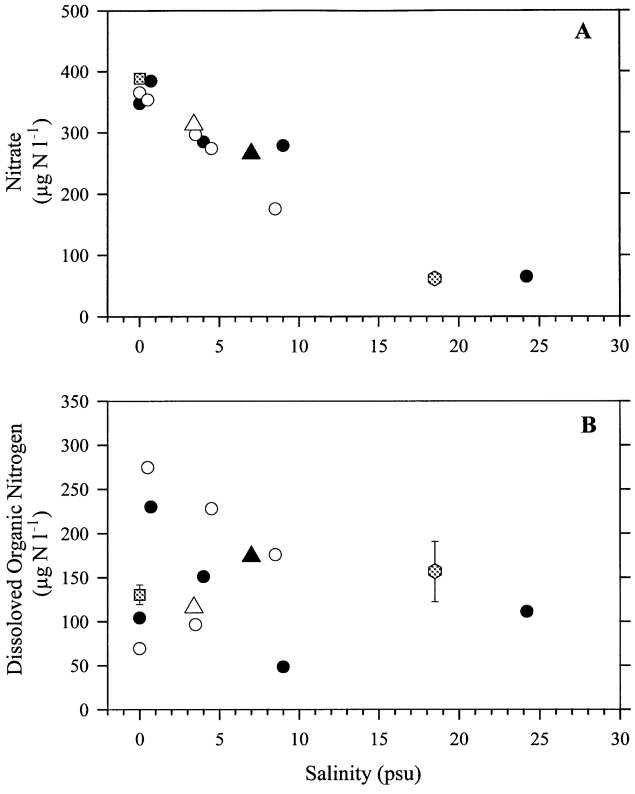

Fig. 6. Apalachicola River, March 1995, river and estuary nitrate (A) and DON (B) versus salinity. (⊠) river; (○,●) surface and bottom samples respectively; (△,▲) surface and bottom West Pass samples respectively; (⊛) mean concentration at St. George Sound which was a source of water to the estuary during this month; error bars in (B): ±1 SE; error bars for river and St. George Sound nitrate smaller than symbols

river DON concentration. Average estuarine DON concentration (183.7 ± 7.2) was similar to river DON concentration. In contrast to nitrate concentrations, which decreased with increasing distance from the river mouth (Figs. 7B, 8A), DON concentration maxima were observed at mid-salinity ranges (Figs. 7C, 8B).

In August 1995, freshwater input from the Apalachicola River was similar in magnitude to the long-term mean river flow (Fig. 2A). There was significant water inflow from the GOM through the passes during August, 1995 (Fig. 2B), when the average salinity in the estuary was 17.6 ± 1.5 psu. Eighty-five percent of water exported from the estuary was through West Pass at a salinity of 24 psu, while 12% of water exported from the estuary was through Indian Pass at 14 psu (Fig. 9A).

In August 1995, average Apalachicola River nitrate concentration was 188.6 ± 0.9 µg N m^{-3} decreasing to <1 µg N l^{-1} in the estuary (Figs. 9B, 10A). In contrast to the rapid decline in nitrate concentration from the mouth of the river to the estuary-GOM boundary, DON concentrations increased from the average river concentration of 181.5 ± 5.0 µg N l^{-1} to >260 µg N l^{-1} in the estuary at mid-salinity ranges (Figs. 9C, 10B).

Monthly budget calculations

Apalachicola Bay exchanges water with the GOM through 4 passes, depending on the prevailing winds and tides (Fig. 1). Therefore, each pass could act as a sink or source for the nitrate, complicating the interpretation of property-salinity plots.

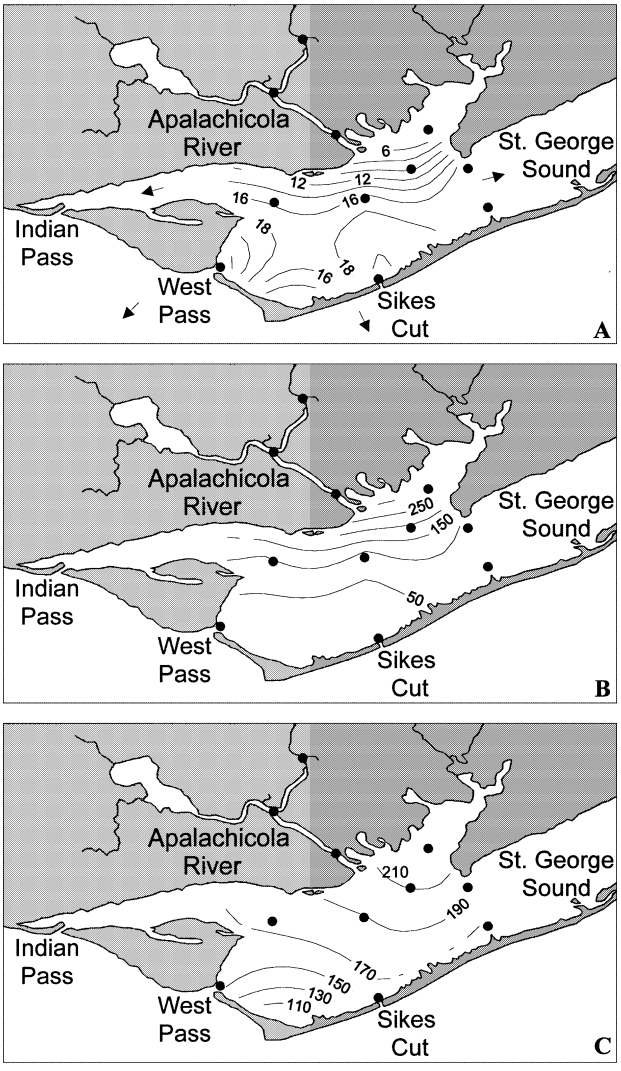

Fig. 7. Apalachicola Bay, April, 1995. Contour plots of (A) mean salinity, psu (arrows indicate the direction of water exchange at the passes); (B) mean surface and bottom nitrate concentration (µg N l^{-1}); (C) mean surface and bottom DON concentration (µg N l^{-1})

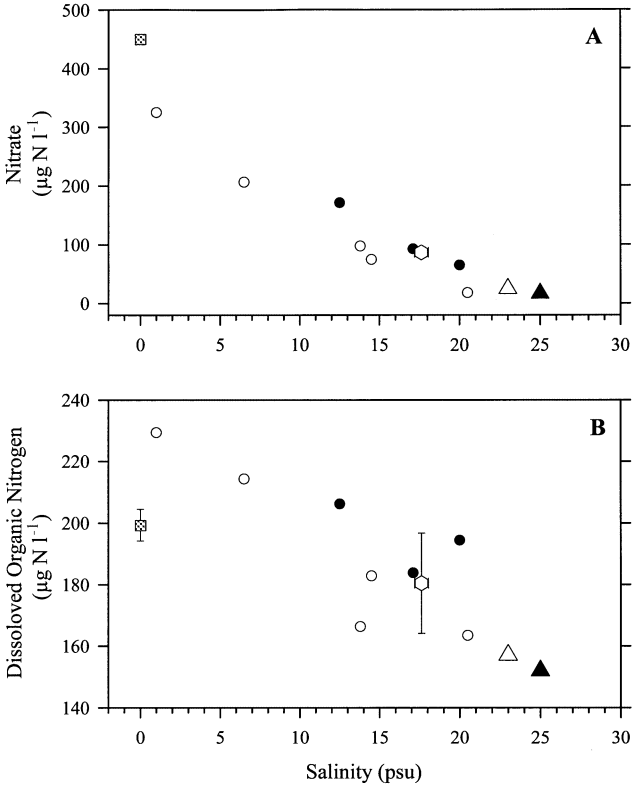

Fig. 8. Apalachicola River, April 1995, river and estuary nitrate (A) and DON (B) versus salinity. (○,●) surface and bottom samples respectively; (⊠) river; (△,▲) surface and bottom West Pass samples respectively; (⬡) mean concentration at St. George Sound; error bars in (B): ±1 SE; error bars for river and St. George Sound nitrate smaller than symbols

In December 1994, water was exported from the estuary to the GOM through West Pass at a flow rate of 957 m^3 s^{-1}, while a smaller fraction was exported at the other passes (Fig. 3A). Nitrate retention within the estuary is not apparent from examination of Fig. 3B or Fig. 4A. However, nitrate budget calculations indicate that there was a net nitrate retention of 13.1 ± 2.8 t N d^{-1} within the estuary, while a similar amount was exported to the GOM during December 1994 (Table 1).

In December 1994, Apalachicola River DON input to the estuary (20.9 ± 1.7 t N d^{-1}) was similar in magnitude to river nitrate input (Table 2). Examination of the surface plot suggests that DON was exported through all the passes during this month (Fig. 3C). The budget calculation results indicated that DON retention within the estuary (1.7 ± 1.9 t N d^{-1}) was insignificant for December 1994 (Table 2).

Apalachicola River flow in March 1995 had typical late-winter and early-spring values (Fig. 2A), with significant seawater inflow to the estuary from the GOM (Fig. 2B). This resulted in a very short freshwater residence-time of 2.8 d. During March 1995, nitrate input from the passes accounted for 12% of the total nitrate input to the estuary (Table 1). Budget calculations for March 1995 suggest that nitrate export to the GOM (60.7 ± 4.4 t N d^{-1}) and input to the estuary (54.6 ± 0.8 t N d^{-1}) were approximately balanced (Table 1). Despite the high level of nutrient input to the estuary, low salinity water (Fig. 5A) with high nitrate concentrations (Figs. 5B & 6A) was relatively rapidly flushed out of the estuary. Apalachicola River DON input to the estuary (16.6 ± 0.8 t N d^{-1}) in March 1995 was equivalent to DON input from the passes (13.7 ± 3.0 t N d^{-1}). DON was exported from Apalachicola Bay at a rate of 33.1 ± 7.2 t N d^{-1}, similar to the input rate (Table 2).

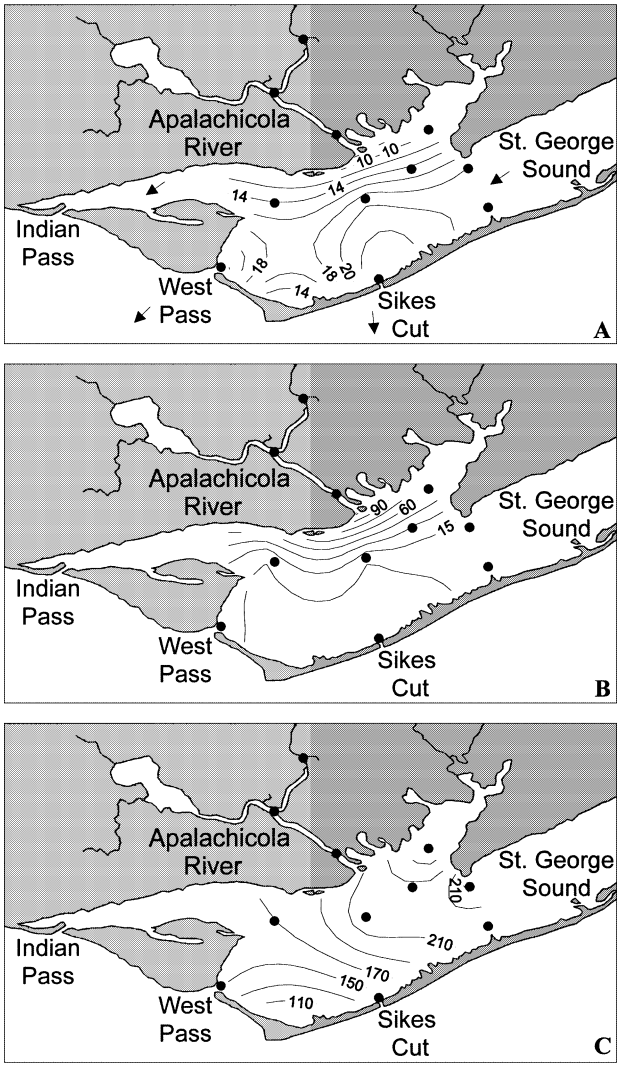

Fig. 9. Apalachicola Bay, August 1995. Contour plots of (A) mean salinity (arrows indicate the direction of water exchange at the passes); (B) mean surface and bottom nitrate concentration (µg N l^{-1}); (C) mean surface and bottom DON concentration (µg N l^{-1})

During April 1995, the Apalachicola River accounted for the entire nitrate input to the estuary (Table 1). The estuarine residence-time during this period was 9.6 d. Approximately 25% of nitrate input to the estuary was exported to the GOM at a rate equivalent to 3.0 ± 0.2 t N d^{-1}, while 9.2 ± 0.5 t N d^{-1} was retained in the estuary. DON export (7.0 ± 0.5 t N d^{-1}) from the estuary to the GOM (Table 2) exceeded nitrate export during this month (Table 1).

In August 1995, despite approximately equal seawater and freshwater inflow to the estuary, Apalachicola River accounted for 89% of the nitrate input to the estuary (Table 1). During this month, the water residence-time had reached 6.6 d and nitrate was rapidly removed within the estuary, as indicated both in the nitrate surface plot (Fig. 9B) and the nitrate-salinity (Fig. 10A) plots. The budget calculations suggest that nitrate was retained in the estuary at a rate equivalent to 8.7 ± 0.2 t N d^{-1} (Table 1).

In August 1995, DON input through the passes accounted for 49% of the total DON input to the estuary. Budget calculations for this month indicated that DON retention within the estuary was insignificant (3.4 ± 2.7 t N d^{-1}), with most of DON input to the estuary being exported to the GOM (13.3 ± 2.5 t N d^{-1}) (Table 2).

DISCUSSION

Hydrodynamics and nitrate and DON input to Apalachicola Bay

The general hydrodynamic circulation pattern in Apalachicola Bay is from the east to the west (Huang & Jones 1997). However, the magnitude and direction of

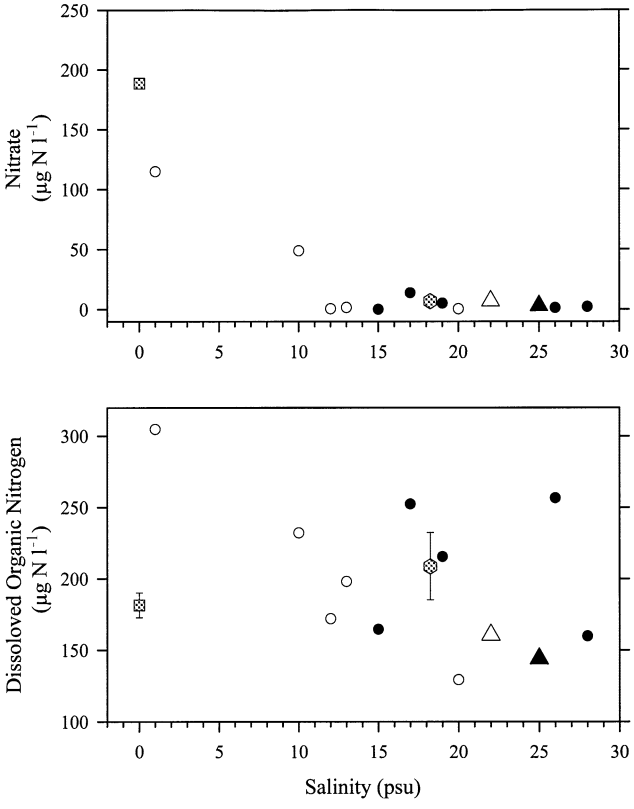

Fig. 10. Apalachicola River, August 1995, river and estuary nitrate (A) and DON (B) versus salinity; (⊠) river; (○,●) surface and bottom samples respectively; (△,▲) surface and bottom West Pass samples respectively; (⊗) mean concentration at St. George Sound, which was a source of water to the estuary;rror bars in (B): ±1 SE; error bars for river and St. George Sound nitrate smaller than symbols

Table 1. Nitrate input (t N d^{-1} ± 1 SE) to Apalachicola Bay in December 1994 and March, April and August 1995. On average, nitrate represented 76% of DIN exported during these 4 mo. Annual budget for period November 1994 to November 1995 (from Mortazavi et al. 2000a) is also shown. GOM: Gulf of Mexico

Month	River input (1)	Input from passes (2)	Export to GOM (3)	Retained (1 + 2) – (3)
December 1994	26.3 ± 2.8	0	13.2 ± 0.6	13.1 ± 2.8
March 1995	49.4 ± 0.7	5.2 ± 0.4	60.7 ± 4.4	−6.1 ± 4.5
April 1995	12.1 ± 0.5	0	3.0 ± 0.2	9.1 ± 0.5
August 1995	8.8 ± 0.1	0.3 ± 0.1	0.4 ± 0.2	8.7 ± 0.2
Annual DIN budget	27.0 ± 0.1	2.3 ± 0.2	19.5 ± 1.2	9.8 ± 1.7

water flow at the passes is variable (Fig. 2B) and depends on tidal current velocity and wind direction. During the river high- and low-flow months, St. George Sound acted either as an outlet (December 1994, April 1995) or as a significant source of water to the estuary (March and August 1995). Therefore, depending on water circulation patterns in the estuary, St. George Sound was a nitrogen source or sink for the estuary (Tables 1 & 2).

Under ordinary circumstances, GOM water enters St. George Sound from the east and is transported through the Sound into Apalachicola Bay. However, with a northwesterly wind, Apalachicola River water can exit the estuary into St. George Sound, remain within the Sound, and then again enter the estuary upon wind relaxation. This oscillation effect is apparent in the numerical simulation-model results of Huang & Jones (1997).

Nitrate accounts for 97% of the Apalachicola River DIN input to the estuary (Mortazavi et al. 2000b). During periods when St. George Sound was a water source for the estuary, St. George Sound nitrate input to the estuary was minor compared to Apalachicola River nitrate input (Table 1). In contrast, DON input rate through St. George Sound was approximately similar in magnitude to the Apalachicola River DON input rate to the estuary during 2 of 4 mo reported here (Table 2). On an annual time scale, however, the Apalachicola River is the main nitrogen source to the estuary, accounting for 92% of the total DIN input and 71% of the total DON input to the estuary (Mortazavi et al. 2000a).

Nitrate and DON concentrations related to salinity

Property-salinity plots have been used for determining element reactivity within estuaries (Boyle et al. 1974) and to infer the reactivity of dissolved organic matter (DOM) in coastal environments (Gardner & Stephens 1978, Mantoura & Woodward 1983). These plots have been used to construct nutrient budgets for Ocklockonee Bay (Kaul & Froelich 1984) and for the Ems estuary (van Beusekom & de Jonge 1998).

There are, however, limitations in the application of property-salinity plots to estuarine data. Officer (1979) showed that applications of these plots for use in quantitative calculations might not be appropriate in systems with complex hydrodynamics. Property-salinity plots are applicable to systems with 2 end-members, where the temporal variations in concentration of the constituent are less than the hydrodynamic residence-time of the estuary (Loder & Reichard 1981, Officer & Lynch 1981). A steady-state hydrodynamic condition must be assumed, which implies that the observed variations in the concentration of a constituent are governed only by biogeochemical processes (Regnier et al. 1998). The effective river concentration, which indi-

Table 2. DON input (t N d^{-1} ± 1 SE) to Apalachicola Bay in December 1994 and March, April and August 1995. Annual budget for period November 1994 to November 1995 (from Mortazavi et al. 2000a) is also shown

Month	River input (1)	Input from passes (2)	Export to GOM (3)	Retained (1 + 2) – (3)
December 1994	20.9 ± 1.7	0	19.2 ± 0.7	1.7 ± 1.9
March 1995	16.6 ± 0.8	13.7 ± 3.0	33.1 ± 7.2	−2.8 ± 7.9
April 1995	5.4 ± 0.1	0	7.0 ± 0.5	−1.6 ± 0.5
August 1995	8.4 ± 0.9	8.3 ± 0.9	13.3 ± 2.5	3.4 ± 2.7
Annual DON budget	17.4 ± 1.6	6.5 ± 0.5	23.4 ± 1.8	0.5 ± 2.5

cates the reactivity of an element in an estuary (Wen et al. 1999), is estimated by extrapolation from high-salinity concentrations to zero salinity. However, during times when there is a limited salinity range, this procedure can lead to a ±50% uncertainty at the 95% confidence interval (Yeats 1993). A bar-built, or barrier island estuary may exchange water and nutrients at more than 1 location if it has more than 1 opening to the sea. Therefore, application of property-salinity plots to data acquired from bar-built estuaries as a quantitative tool for estimating nutrient retention and export may violate the conditions defined by Officer & Lynch (1981). Despite these limitations, property-salinity plots are useful heuristic tools with which to draw inferences about nutrient distribution patterns in bar-built estuaries with multiple open passes.

The nitrate-salinity plots for Apalachicola Bay show the general patterns observed in tropical (Eyre & Balls 1999) and temperate-latitude (Pennock et al. 1999) coastal lagoons, with nitrate decreasing as salinity increases along a gradient through the estuary. However, the interpretation of the trend for data obtained during any sample period in Apalachicola Bay is not simple, but depends on hydrodynamics which are influenced by Apalachicola River flow rate, wind speed and direction, and tidal current speed and direction (Huang & Jones 1997). The nitrate concentration in St. George Sound water was always less than in Apalachicola River water (Figs. 4A, 6A, 8A, 10A). Therefore, water input from that source would be expected to affect the nitrate-salinity plot characteristics during months when water enters Apalachicola Bay from St. George Sound. This was the case during March (Fig. 5A) and during August (Fig. 9A) 1995, as indicated on the surface plots by arrows indicating water flow from St. George Sound into the estuary. Because nitrate concentrations in the estuary are affected by water exchange at multiple sources and by biological processes, it is not possible to calculate biological nitrate removal from nitrate-salinity plots within the estuary for those months from nitrate-salinity plots.

Property-salinity plots from a wide range of marine systems indicated that riverine DOM, which passed through estuaries and entered the sea was refractory (Georgia, USA, coastal waters, Gardner & Stephens 1978; Severn Estuary and Bristol Channel UK, Mantoura & Woodward 1983; and Zaire River estuary and plume, Cadée 1984). Considerable scatter was evident in a DON-salinity plot from the Laptev Sea, adjacent to the Lena River delta. However, a regression line for the data trend followed a dilution trend line expected for mixing Arctic surface water with Lena River delta water (Kattner et al. 1999), suggesting that DON was refractory or that biological processing of DON was occurring at very slow rates.

Meybeck (1993) computed global DON input from rivers to the ocean by multiplying DON concentration by flow rate for individual rivers where data were available. Our annual DON budget (Table 2) was prepared in a similar fashion, and indicates that the sum of river input and input from the passes is balanced by export from Apalachicola Bay to the GOM. However, DON concentrations within the estuary at some stations were greater than DON concentrations at the river or GOM end-member locations (Figs. 4B, 6B, 8B, 10B). DON export from the bay was greater than DON input to the bay during some months (Table 2). Therefore, DON must be produced within Apalachicola Bay as a result of various biogeochemical processes acting separately or in combination. The variability in DON-salinity plots is partly attributable to the effects of variable DON concentrations in waters entering the estuary from the river and the passes. This condition is most easily seen in data acquired during August 1995 (Figs. 9C & 10B). For this month, DON concentrations at the western boundary were similar to Apalachicola River DON concentrations. DON concentrations at some locations in the estuary that were less than concentrations in the river and in St. George Sound represent the effects of dilution and, most likely, food-web processing. For example, in the Gulf of Riga, Baltic Sea, on average 13% of total DON was assimilated within 7 or 8 d by the bacterial community (Jørgensen et al. 1999). This was less than the 40 to 72% total DON assimilated measured in Delaware and Hudson River estuaries by Seitzinger & Sanders (1997), and was attributed by Jørgensen et al. to a larger proportion of refractory organic matter and smaller amounts of anthropogenic compound input to the Gulf of Riga compared to the American estuaries.

Several processes may contribute to DON concentrations that frequently exceeded river and estuarine end-member DON concentrations in Apalachicola Bay (Figs. 4B, 6B, 8B, 10B). Photochemical release of nitrogen-containing compounds from DOM in coastal marine systems is a potential mechanism which may increase DON concentrations in estuarine surface waters (Bushaw et al. 1996). The experimental results of Bushaw-Newton & Moran (1999), however, suggest that in southeastern US coastal waters between 1 and 2% of equivalent river DON concentrations are converted to ammonium and primary amines. In Apalachicola Bay, DON concentrations were at times between 117 to 144 mg N m^{-3} greater than the end-member DON concentrations (Fig. 6B). Therefore, mechanisms other than photochemical formation of DON from DOM must contribute to the high DON concentrations observed in this estuary.

Benthic DON flux may potentially contribute to the high DON concentrations observed in an estuarine

water column. In the Parker River-Plum Island Sound estuary, located in Massachusetts, US, benthic DON fluxes were examined over an annual cycle (Hopkinson et al. 1999). With the exception of 1 occasion and at 1 station, however, DON was taken up and consumed by biochemical processes within the sediments (Hopkinson et al. 1999). Results of benthic nitrogen-flux studies in Chesapeake Bay also suggest that DON does not appear to be a major component of the nitrogen cycle (Cowan & Boynton 1996, Burdige & Zheng 1998). In Apalachicola Bay, surface DON concentrations were higher than benthic DON concentrations, except in April 1999 when bottom concentrations exceeded surface DON concentrations at locations that had salinities between 10 and 20 psu (Fig. 8B). Therefore, the DON concentration gradient in Apalachicola Bay does not indicate DON flux from the sediments as an important factor contributing to increased DON concentrations in the water column of that estuary.

Food-web processes, particularly those of phytoplankton, are important factors contributing to increased DON concentrations in estuarine waters. Collos (1992) demonstrated DIN uptake in excess of particulate nitrogen production, with DON export representing 75% of DIN uptake in early portions of unialgal batch-culture time-series. An inverse relation between nitrate and DON concentrations reported for the English Channel (Butler et al. 1979) and Chesapeake Bay (Bronk et al. 1998) suggests that phytoplankton DIN uptake was followed by DON release and accumulation in the water column. DON originating from phytoplankton can be released to the water column by excretion (Bronk & Glibert 1993a, Pujo-Pay et al. 1997), cell death and lysis or virus-induced lysis (Suttle et al. 1990), or by 'sloppy feeding' of herbivores (Lampert 1978, Bronk & Glibert 1993a, Hasegawa et al. 2000). This newly released DON, and a fraction of DON originating from river water, can be recycled by the microbial community (Wheeler & Kirchman 1986, Bronk & Glibert 1993b) and made available to primary producers.

Nitrate and DON budgets

Nutrient input to coastal plain estuaries has been estimated by adding diffuse and atmospheric input to the product of river flow-rate and nutrient concentration time-series, while export to seas bordering these estuary types has been estimated by subtracting internal losses from input rates (Kaul & Froelich 1984, Boynton et al. 1995). This approach, however, does not provide valid results when applied to bar-built estuaries with multiple passes such as Apalachicola Bay. In Apalachicola Bay, input from the passes during both high- and low-river-flow conditions can account for a large fraction of the total nitrate or DON input to the estuary. In March and August 1995, for example, St. George Sound was a significant nitrogen source to the estuary. Nitrate and DON input through St. George Sound accounted for as much as 10 and 50%, respectively, of the total dissolved nitrogen input to the estuary (Tables 1 & 2). Therefore, nutrient budget calculations for bar-built estuaries require a combination of hydrodynamic modeling results and measurements of nutrient concentrations at river and pass locations.

There is a significant difference in transfer of nitrogen through estuaries with long residence-times compared to estuaries with short residence-times. Chesapeake Bay is a long (mean = 256 d) residence-time estuary (Boynton et al. 1995). Approximately 30% of total nitrogen annually entering Chesapeake Bay is exported from the estuary (Boynton et al. 1995). However, there is net DON accumulation during the spring and net DON utilization during the summer-to-fall period in this estuary (Bronk et al. 1998). Therefore, in long residence time estuaries such as Chesapeake Bay, DON can serve as a nitrogen pool linking new nitrogen input from the river during the spring to a system based on regenerated productivity during the summer (Bronk et al. 1998).

Apalachicola Bay is a short (mean = 6 d) residence-time estuary. This condition results in rapid passage of water and dissolved substances through that estuary. The annual budgets indicate that 66% of nitrate input was exported from the estuary, while DON input to and export from the estuary to the GOM were in balance (Mortazavi et al. 2000a). On a monthly basis, nitrate retention within the estuary varied between 0 and 100% of the input (Table 1). In contrast, DON retention within the estuary was not statistically significant during those months (Table 2). River DON and DON transformed from DIN entering the estuary was less likely to have remained within Apalachicola Bay to serve as a substrate for bacterial utilization and remineralization (Seitzinger & Sanders 1997) than to be exported to the adjacent GOM. This was particularly true during March, a period when a seasonal phytoplankton bloom condition has been observed in GOM coastal waters by satellite imagery.

Nitrogen in water discharged from rivers along the Florida coast has been proposed as one of the alternate causal hypotheses for the recurring seasonal phytoplankton bloom in the northeastern GOM (Gilbes et al. 1996). The Apalachicola River dominates the freshwater discharge into the northeast GOM bloom region. Nitrate export from the estuary was 1821 t N during March 1995, while DON export was 993 t during that month. Applying the conversion range of 40 to 70% experimentally obtained by Seitzinger & Sanders (1997) to determine the fraction of DON that can be

remineralized to DIN, from 397 to 695 t N were available for use by the northeastern GOM food web during that month. This calculation yields a total of 2218 to 2516 t N available for conversion to phytoplankton chlorophyll on the northeast GOM shelf during March 1995, a period when a bloom occurred off Apalachicola Bay (del Castillo et al. 2000).

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