

# Phytoplankton Production and Nutrient Distributions in a Subtropical Estuary: Importance of Freshwater Flow

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**ABSTRACT:** The relationships between phytoplankton productivity, nutrient distributions, and freshwater flow were examined in a seasonal study conducted in Escambia Bay, Florida, USA, located in the northeastern Gulf of Mexico. Five sites oriented along the salinity gradient were sampled 24 times over the 28-mo period from 1999 to 2001. Water column profiles of temperature and salinity were measured along with surface chlorophyll and surface inorganic nutrient concentrations. Primary productivity was measured at 2 sites on 11 dates, and estimated for the remaining dates and sites using an empirical regression model relating phytoplankton net production to the product of chlorophyll, euphotic zone depth, and daily solar insolation. Freshwater flow into the system varied markedly over the study period with record low flow during 2000, a flood event in March 2001, and subsequent resumption of normal flow. Flushing times ranged from 1 d during the flood to 20 d during the drought. Freshwater input strongly affected surface salinity distributions, nutrient flux, chlorophyll, and primary productivity. The flood caused high turbidity and rapid flushing, severely reducing phytoplankton production and biomass accumulation. Following the flood, phytoplankton biomass and productivity sharply increased. Analysis of nutrient distributions suggested Escambia Bay phytoplankton alternated between phosphorus limitation during normal flow and nitrogen limitation during low flow periods. This study found that Escambia Bay is a moderately productive estuary, with an average annual integrated phytoplankton production rate of  $290 \text{ g C m}^{-2} \text{ yr}^{-1}$ .

## Introduction

Human activities have altered the flux of materials at the land-sea interface in most regions of the world, resulting in a net increase of nutrient loading to estuarine receiving waters (Nixon 1995; NRC 2000; Cloern 2001). In general, increased nutrient loading stimulates primary production (i.e., eutrophication), which contributes to environmental problems such as hypoxia, harmful or nuisance algal blooms, and changes in food web structure (NRC 2000). Our understanding of estuarine dynamics has been advanced by sustained research in temperate systems such as Chesapeake Bay (Boynton et al. 1982; Harding 1994; Kemp et al. 2005), San Francisco Bay (review: Cloern 1996), and the Baltic Sea (Granéli et al. 1990; Conley 2000). Subtropical estuaries have received comparatively less study, but are also experiencing noticeable anthropogenic alterations (Zhang et al. 1995; Eyre 1997; Turner and Rabalais 2003; Brodie and Mitchell 2005). As a class, subtropical estuaries exhibit extreme diversity in physiography, hydrology, and biogeochemistry (Bianchi et al. 1999; Eyre 2000; Roy et al. 2001). Generalizations drawn from the extensive study of temperate systems may not always hold for subtropical estuaries. This diversity, or unpredictability, in system responses has frustrated

resource managers in developing uniform standards and criteria to reduce the negative effects of excess nutrient loading to estuaries (USEPA 2001).

The Gulf of Mexico coastal zone includes about 35 estuarine systems that vary widely in physical regime from highly-stratified, river-dominated systems to well-mixed, marine-dominated systems (Bianchi et al. 1999). Gulf of Mexico estuaries share important characteristics, including low tidal energy, high solar radiation, high water temperatures, and shallow depth. The northern Gulf of Mexico, where this study was conducted, experiences high rainfall and high freshwater runoff per estuarine volume (Turner 2001). While most northern Gulf of Mexico estuaries have relatively low river-borne nutrient inputs (Bricker et al. 1999; USEPA 2001), rapid human population growth along the United States coastline will continue to place pressures on adjacent estuarine systems (Culliton et al. 1990). Hypoxia is frequently observed during summers in Pensacola Bay (Hagy and Murrell In press) and other shallow stratified estuaries in the region (Rabalais et al. 1985).

This study was conducted in Escambia Bay, Florida, a river dominated estuary in the northern Gulf of Mexico. We examine the relationship between freshwater flow, nutrient distributions, and phytoplankton productivity. One goal of this study was to compare and contrast the observed

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estuarine responses in this Gulf of Mexico subtropical estuary with better studied temperate and subtropical systems. This is part of an ongoing research effort, focused largely on Escambia and Pensacola Bays, to examine aspects of system function, including bacterial productivity (Murrell 2003), phytoplankton and zooplankton seasonal dynamics (Lores et al. 2002; Murrell and Lores 2004), microzooplankton grazing interactions (Murrell et al. 2002a; Juhl and Murrell 2005), and nutrient limitation of phytoplankton growth (Murrell et al. 2002b). The results from these and related studies are being incorporated into guidance documents to aid resource managers in developing regional-specific nutrient criteria for U.S. estuaries.

#### STUDY SITE

Escambia Bay is a subestuary of the Pensacola Bay system located in northeastern Gulf of Mexico (Fig. 1). Escambia Bay is a river-dominated, moderately-sized (75 km<sup>2</sup>), shallow (mean depth 2 m) system. Like all Gulf of Mexico estuaries, Escambia Bay experiences very low tidal amplitudes ranging from 15 to 65 cm (NOAA unpublished data). The Escambia River is the main freshwater source with an annual mean discharge rate of 180 m<sup>3</sup> s<sup>-1</sup> (<http://waterdata.usgs.gov/nwis>). The seasonal patterns in river flow are similar to temperate systems with the highest flows occurring during spring (February to April) and lowest flows occurring during summer and fall (June to November). Annual rainfall in this region of the Gulf of Mexico averages 160 cm distributed throughout the year, though peak rainfall occurs during summer, accounting for about 50% of the annual total. The Escambia River watershed area is 11,000 km<sup>2</sup> draining a landscape of forests (77%), croplands (12%), pastures (7%), and urbanized lands (2%). Monthly nutrient data for the Escambia River from 1973 to 1994 (Alexander et al. 1996) shows an increasing trend in total nitrogen (TN) but not total phosphorus (TP). TN and TP concentrations averaged  $40 \pm 18$  and  $1.2 \pm 0.6 \mu\text{M}$  ( $\pm$  standard deviation), respectively, with an average TN:TP of 34. Chlorophyll concentrations in Pensacola Bay average  $5.4 \pm 4.8 \mu\text{g l}^{-1}$  (mean  $\pm$  standard deviation), based on a 5-yr quarterly survey from 1996 to 2000 (Macauley et al. 2005).

#### Materials and Methods

##### FIELD SAMPLING

Water sampling occurred on 24 dates during a 28-mo period from June 1999 to November 2001 at 5 sites oriented along the salinity gradient in Escambia Bay (Fig. 1). Hydrographic data were collected using a Hydrolab H2O multimeter, measuring

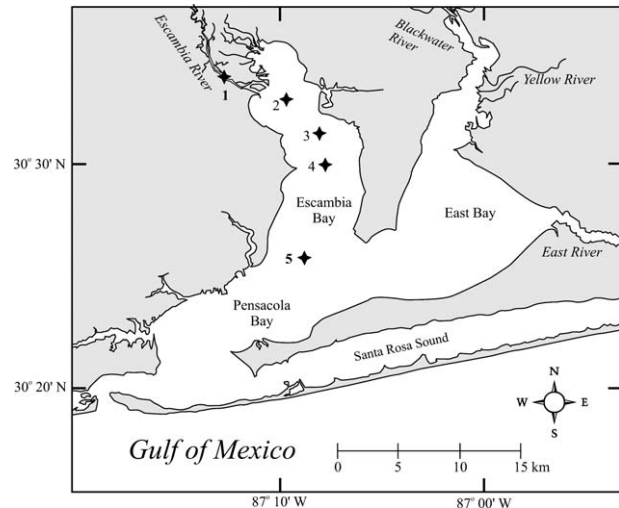


Fig. 1. Map showing sampling locations in the Pensacola Bay system.

temperature and salinity at 0.5 to 1 m depth intervals. Photosynthetically active radiation (PAR, 400 to 700 nm) was measured at 0.5 to 1 m intervals using a LICOR LI-192 underwater 2 pi quantum sensor. The air PAR data were corrected for surface reflectance using a constant of 0.23 empirically derived from paired air-underwater observations. Secchi disk depth was also recorded at each station. Light attenuation coefficients were calculated as the least-squares regression slope of the natural log of PAR versus depth. On some dates, PAR data were not collected, so Secchi depth was used to calculate the light attenuation coefficient with an empirically-derived relationship of  $1.57/\text{Secchi disk depth}$ . Surface water samples were collected with a Van Dorn bottle, transferred to acid-cleaned polyethylene bottles, and processed at the laboratory within 2 to 3 h. Water samples were filtered through a GF/F filter; the filters were frozen for chlorophyll *a* (chl *a*) analysis and the filtrate was collected and frozen for nutrient analyses. The Chl *a* samples were extracted in methanol, sonicated, and analyzed fluorometrically (Jeffrey et al. 1997). Nutrients ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{2-}$ ,  $\text{SiO}_2$ ) were analyzed using standard methods (APHA 1989); dissolved inorganic nitrogen (DIN) denotes the sum of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and dissolved inorganic phosphorus (DIP) denotes  $\text{PO}_4^{2-}$  concentration. The chlorophyll data were originally reported in Murrell and Lores (2004), which contains further details of sample collection and analysis.

##### FRESHWATER FLOW AND FLUSHING TIMES

Daily freshwater flow records were obtained for the Escambia River from the U.S. Geological Survey gauging station at Century, Florida (hydrologic unit

# 03140305, site # 02375500 <http://waterdata.usgs.gov/nwis>). Freshwater flushing times were calculated using a fraction of freshwater method (Dyer 1973). Baywide average salinity was calculated from salinity profile data at the 5 stations, which were volume-weighted using a three-dimensional spatial model of Escambia Bay (Hagy unpublished data). Lateral salinity variations were ignored, and the vertical salinity contours were assumed to be laterally uniform. Freshwater flushing times were calculated by summing the daily discharges prior to the sampling date until the volume of freshwater in the estuary was equaled (Eyre 2000). From baywide average salinity, the fraction of freshwater was calculated. Instead of using typical oceanic salinity end members, we used the bottom water salinity from station 5 to represent the seaward end member of the water mass mixing into Escambia Bay.

#### NUTRIENT FLUXES AND DISTRIBUTION PATTERNS

River nutrient fluxes were calculated for each sampling date as the product of the Escambia River nutrient concentrations (station 1) and the river flow for each sampling date, and normalized to the area of Escambia Bay (75 km<sup>2</sup>).

The nutrient-salinity distributions were examined by calculating the percent departure from the conservative mixing line. This value was calculated as:  $(A_e - A_o)/A_o$ , where  $A_e$  is the area under the conservative mixing line and  $A_o$  is the area under the curve defined by the observed nutrient distributions (Eyre and Twigg 1997).

To examine system-wide relationships among variables, the weighted mean concentrations of DIN, DIP, chlorophyll, and phytoplankton production were calculated using the width of the bay (as a weighting factor) at each site orthogonal to the estuarine axis. Vertical and lateral variations in constituent concentrations were ignored.

#### PRIMARY PRODUCTION

Phytoplankton primary productivity was measured by the incorporation of NaH<sup>14</sup>CO<sub>3</sub> into particulate organic matter (Parsons et al. 1984) on 11 dates from August 2000 to November 2001 at 2 sites chosen from among the 5 fixed sites to sample contrasting salinity zones. Triplicate 50-ml samples were placed into 100-ml Whirlpak bags with 0.44 MBq (0.2 µCi) NaH<sup>14</sup>CO<sub>3</sub> and placed in an outdoor running seawater incubator at the laboratory with varying layers of neutral density screening to produce treatments at 93%, 45%, 24%, 14%, and 0% of ambient PAR. PAR insolation was measured using a LiCor 190SA meter deployed at the laboratory dock (30°20.3'N, 87°09.5'W). After the

24-h incubation, the samples were filtered onto 0.45-µm pore size Millipore HA filters and placed into 7-ml scintillation vials. The filters were acidified (1N HCl, 100 µl) to degas inorganic carbon before adding scintillation cocktail (Packard Filter Count), and assayed using a Packard TR 2500 liquid scintillation analyzer with transformed spectral-index quench correction.

To scale <sup>14</sup>C activity to net organic carbon production, dissolved inorganic carbon (DIC) concentrations were calculated using a simple mixing model with seawater and freshwater end members. The seawater end member DIC (26.4 mg C l<sup>-1</sup>) was calculated assuming a salinity of 35 as in Parsons et al. (1984). The freshwater end member was calculated using historical water quality data from the Escambia River (Alexander et al. 1996), using an empirically-derived relationship:

$$\text{DIC} = 29.2 \times Q^{-0.37}, \quad (r^2 = 0.68, n = 146),$$

where DIC is total CO<sub>2</sub> concentration (mg C l<sup>-1</sup>) and  $Q$  is freshwater flow rate (m<sup>3</sup> s<sup>-1</sup>). Based on this relationship, freshwater DIC concentrations ranged from 2.0 to 10.7 mg C l<sup>-1</sup> (average: 6.2 mg C l<sup>-1</sup>) during this study.

The production-irradiance curves were fitted with the hyperbolic tangent model (Platt and Jassby 1976) using an iterative nonlinear regression technique (SAS NLIN), yielding parameter estimates of the assimilation number ( $\alpha$ ) and the maximum rate of photosynthesis normalized to chlorophyll ( $P_m^B$ ). Volumetric phytoplankton production rates were integrated at 0.1 m steps through the water column to generate daily integrated primary production rates. PAR at each depth step was calculated from field measurements of the light attenuation coefficient ( $K_d$ ).

Daily integrated primary production rates were regressed against the composite variable  $B \times Z_p \times I_o$ , the product of chlorophyll concentration ( $B$ ), the depth of euphotic zone ( $Z_p$ ), and daily PAR insolation ( $I_o$ ), as in Cole and Cloern (1987). The regression model was used to estimate primary production on all dates at all stations sampled.

## Results

#### FRESHWATER FLOW AND SALINITY DISTRIBUTIONS

During this 28-mo study, Escambia river flow varied by > 2 orders of magnitude from 13 to over 1500 m<sup>3</sup> s<sup>-1</sup> (Fig. 2). While broadly consistent with normal seasonal patterns, this study spanned periods of extreme drought and extreme flood. The time series began with a short-term flow pulse (380 m<sup>3</sup> s<sup>-1</sup>) in June 1999 followed by below average flow in winter-spring 2000. Drought conditions intensified through the remainder of 2000, result-



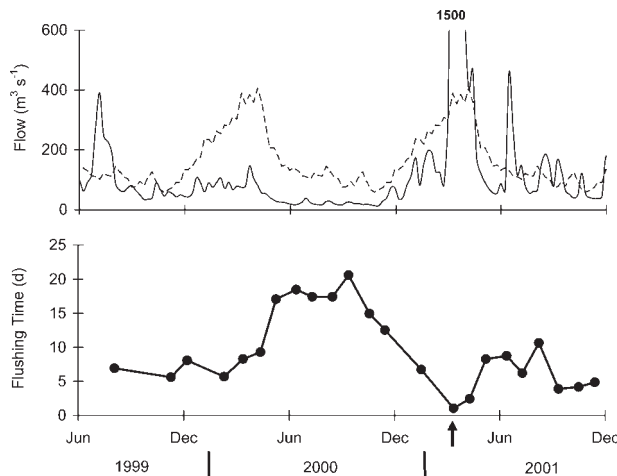


Fig. 2. Time series of: freshwater flow from the Escambia River (solid line) during study time compared to the 65 year average (dashed line), and the flushing time of Escambia Bay calculated by the fraction of freshwater method. The arrow marks the flood in March 2001.

ing in the lowest flows in the 67-yr record. The annual average flow for 2000 was  $47 \text{ m}^3 \text{ s}^{-1}$ , by far the lowest on record (cf.,  $62 \text{ m}^3 \text{ s}^{-1}$  in 1968). A series of rain events broke the drought in early 2001 generating flows greater than  $1000 \text{ m}^3 \text{ s}^{-1}$  for 15 d. The peak flow of  $1702 \text{ m}^3 \text{ s}^{-1}$  recorded on March 10, ranked in the 99.8th percentile of the long-term daily flow record. By summer 2001, flow resumed more normal levels. This freshwater flow regime had a dominating effect on flushing times for Escambia Bay, which ranged from  $< 1 \text{ d}$  during the flood to over  $20 \text{ d}$  during the drought. Over the study, flushing times averaged  $9.5 \pm 5.6 \text{ d}$  (Fig. 2).

The effects of river flow were clearly reflected in the salinity distributions in Escambia Bay (Fig. 3). Baywide average salinity ranged from 2 during the flood to over 25 during the drought, and was strongly correlated with the daily river flow ( $r = -0.67$ ,  $p < 0.01$ ). The flood depressed baywide salinity for about 2 mo, after which salinity returned to the preflood distribution. The time series of DIN and DIP distributions along the estuary generally showed higher concentrations in the upper estuary decreasing along the estuarine gradient. Chlorophyll concentrations were elevated during summers 1999 and 2001 but not during drought in 2000.

#### NUTRIENT CONCENTRATIONS AND NUTRIENT LOADING

Freshwater DIN concentrations averaged  $19.3 \pm 7.5 \text{ mmol m}^{-3}$ , and varied seasonally by fivefold, from a peak of  $36 \text{ mmol m}^{-3}$  during December 1999 to a minimum of  $5.9 \text{ mmol m}^{-3}$  during the flood (Fig. 4). Freshwater DIP concentrations averaged  $0.40 \pm 0.28 \text{ mmol m}^{-3}$  and, in contrast to DIN,

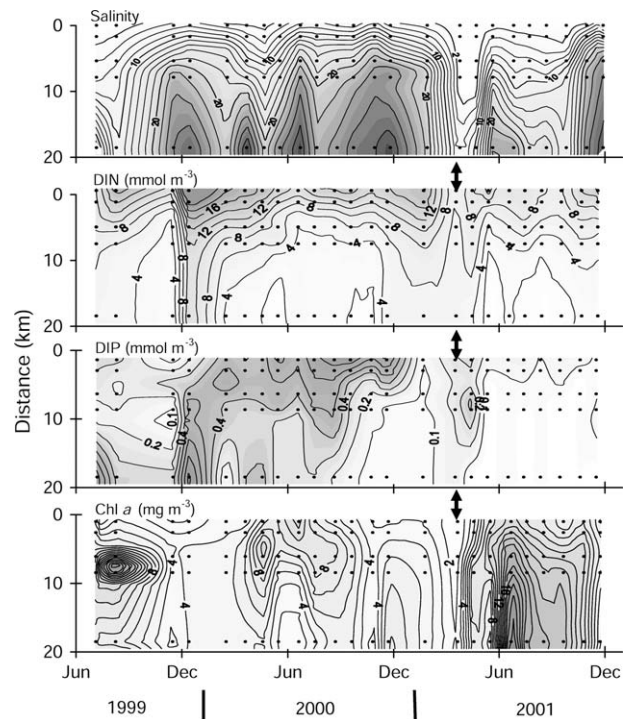


Fig. 3. Space-time contour plots of: surface salinity with contour intervals of 2 psu, DIN with contour intervals of  $2 \text{ mmol m}^{-3}$ , and DIP with contour intervals of  $0.1 \text{ mmol m}^{-3}$ . The arrows mark the flood in March 2001. The contours were drawn using a two-step linear interpolation process, first by spatially interpolating along the bay axis at 1-km intervals, then by temporally interpolating each 1-km node at 10-d intervals.

were highest during the summer drought ( $0.8 \text{ mmol m}^{-3}$ ) and lowest during the summer following the flood ( $0.2 \text{ mmol m}^{-3}$ ). Freshwater DIN concentrations were negatively correlated with river flow ( $r = -0.56$ ,  $p = 0.0046$ ,  $n = 24$ ), a pattern not evident with DIP ( $r = -0.17$ ,  $p = 0.43$ ,  $n = 24$ ). DIN:DIP ratios of river water (and consequently nutrient fluxes) were consistently above the Redfield ratio of 16, with a geometric mean of 62. The only exception was during the flood when the DIN:DIP ratio was near the Redfield ratio at 20.

Freshwater flow strongly influenced the flux of DIN and DIP into Escambia Bay (Fig. 4). During nonflood conditions DIN and DIP fluxes (scaled to the area of Escambia Bay) were relatively stable, averaging  $1.4 \pm 0.67$  and  $0.02 \pm 0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$ , respectively. During the flood, DIN and DIP fluxes increased by 10 to 20 fold over this baseline. Baywide average DIN and DIP concentrations were less variable than fluxes.

#### NUTRIENT-SALINITY DISTRIBUTIONS

DIN distributions in Escambia Bay showed coherent seasonal patterns. During summers, DIN had

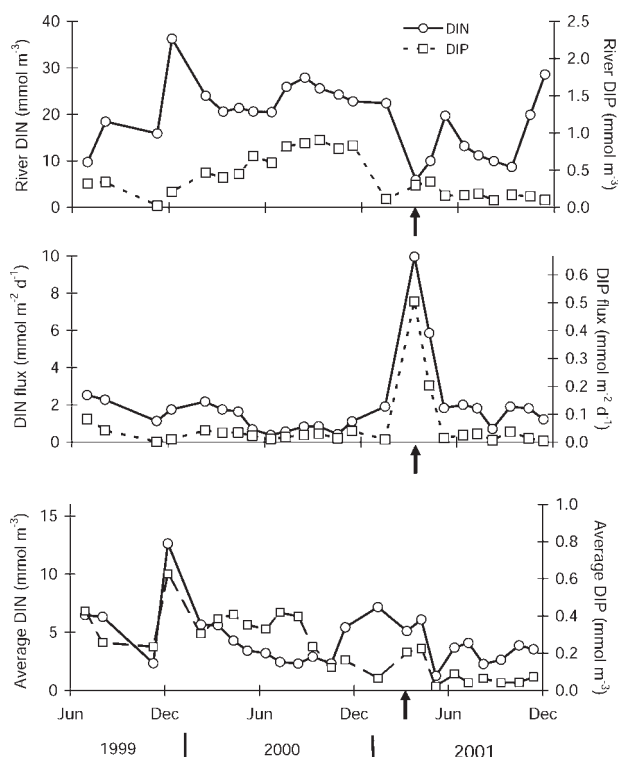


Fig. 4. Time series plots of: DIN and DIP concentrations in river water, DIN and DIP flux from the Escambia River scaled to the area of Escambia Bay ( $75 \text{ km}^2$ ), and DIN and DIP baywide average concentrations. Baywide averages were calculated as the mean of the 5 sampling sites, weighted by the width of the bay orthogonal to the estuarine axis at each site. The arrows mark the flood in March 2001. The axis ranges for DIN and DIP are scaled to Redfield proportions (16N:1P).

sharp spatial gradients in the upper bay, which were particularly sharp during the drought in 2000 (Fig. 3). The DIP distribution patterns were predominately interannual, with higher concentrations during the drought year (2000) and lower concentrations during normal flow years (1999 and 2001). During 2000, DIP gradients were shallower in winter and spring months (January to April) and sharper during summer and fall months (May to November).

The seasonal and interannual patterns in DIN and DIP distributions were more noticeable when represented as the percent departure from conservative mixing (Fig. 5). DIN uptake was strongest during summer and weakest (nearly conservative) during winter and spring. During the 2000 drought, uptake was first evident in March, whereas in 2001, uptake was delayed until May, 2 mo following the flood. During summer 2001, DIN uptake remained strong except for one sampling date in July. Examination of this mixing diagram indicated complex dynamics with a net DIN release in the

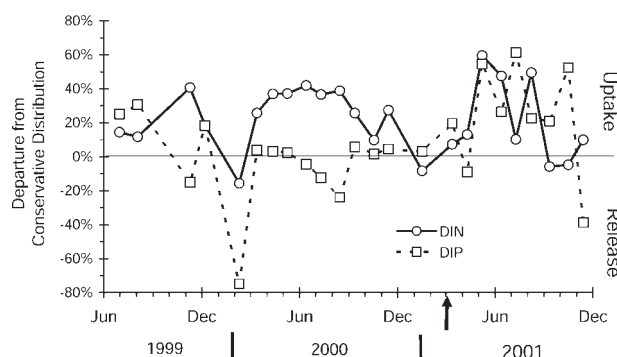


Fig. 5. Time series plot of the percent departure from conservative mixing for DIN and DIP. The arrow marks the flood in March 2001. The horizontal line depicts conservative mixing. The percent departure from conservative mixing was calculated as:  $(A_c - A_o)/A_c$ , where  $A_c$  is area under the conservative mixing line and  $A_o$  is the area under the curve defined by the observed nutrient-salinity distributions.

upper estuary (station 2) and strong removal in the lower estuary (data not shown). DIP departures had interannual and seasonal patterns. DIP uptake occurred during summer 1999 followed by near conservative distributions that remained from fall 1999 extending through 2000 drought. A large DIP release was observed on a single date in February 2000 when the DIP mixing curve was inverted, indicating a DIP source originating from outside of the system. In 2001, strong uptake of DIP was evident from May to October.

The relationship between flushing time and percent departures from conservative mixing shows a complex pattern (Fig. 6). When flushing times were very rapid (1 d) or very long (20 d), nutrients tended to be more conservatively distributed than during periods of moderate flushing (5 to 10 d). The effect of phytoplankton uptake on nutrient departures was clearly evident, with strongest uptake coinciding with highest productivity. Departures from conservative mixing appeared more strongly influenced by phytoplankton uptake (or factors that covaried with phytoplankton uptake) than by flushing characteristics.

#### PRIMARY PRODUCTION AND CHLOROPHYLL

The results of the primary productivity measurements are summarized in Table 1. Photosynthetic efficiency ( $\alpha$ ) averaged  $5.7 \pm 2.3 \text{ mg C}(\text{mg chl } a)^{-1}(\text{E m}^{-2})^{-1}$ , whereas the maximum photosynthetic rate ( $P_m^B$ ) averaged  $51.5 \pm 23.3 \text{ mg C}(\text{mg chl } a \text{ d})^{-1}$ . Neither parameter exhibited strong spatial or temporal patterns. Water column integrated daily production ( $P_{wc}$ ) varied by over 2 orders of magnitude, ranging from 10 (March 2001, upper bay) to  $2166 \text{ mg C m}^{-2} \text{ d}^{-1}$  (June 2001, lower bay).

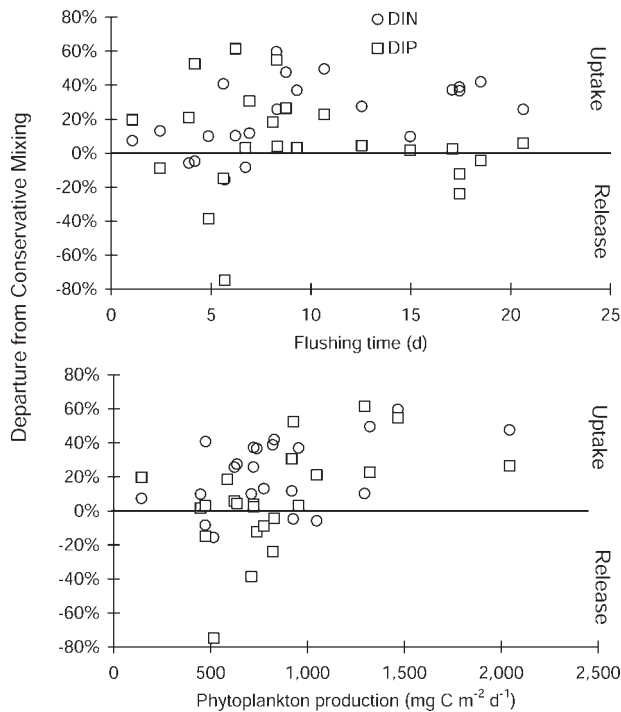


Fig. 6. The percent departure from conservative mixing plotted as a function of flushing time and phytoplankton production. The horizontal line depicts conservative mixing.

Spatially, water column primary production ( $P_{wc}$ ) tended to be higher at the lower bay site than the upper bay site (871 versus 721  $\text{mg C m}^{-2} \text{d}^{-1}$ ), which was largely attributable to the differences in

euphotic zone depth, because volumetric primary production rates ( $P_{1m}$ ) had the reverse pattern (431 versus 497  $\text{mg C m}^{-3} \text{d}^{-1}$ ).

Measurements of pelagic primary production were related to the composite variable,  $B \times Z_p \times I_0$ , the product of chlorophyll biomass ( $B$ ), photic depth ( $Z_p$ ), and daily PAR insolation ( $I_0$ ). The regression,  $P_{wc} = 0.59B \times Z_p \times I_0 + 124$ , explained 77% of the variability in productivity data, and data from upper and lower Escambia Bay were similar (Fig. 7). This regression was used to estimate primary production for the 28-mo study using site-specific measurements of chlorophyll and euphotic zone depth using the BZI model. The estimated productivity for the 5 sites was converted into a single baywide weighted average for each date (Fig. 8). The time series of baywide estimated productivity shows relatively little seasonal variability in productivity throughout 1999 and 2000 ranging from 500 to 1000  $\text{mg C m}^{-2} \text{d}^{-1}$ . Productivity declined during the flood to a minimum of 140  $\text{mg C m}^{-2} \text{d}^{-1}$ , and strongly increased after the flood subsided to reach a peak in June 2001 at 2042  $\text{mg C m}^{-2} \text{d}^{-1}$ . Following the peak, productivity declined for several months, approaching pre-flood values in the fall.

Chlorophyll concentrations generally tracked productivity patterns, with higher concentrations occurring during summer and lower concentrations occurring during winter and spring (Figs. 3 and 8). Chlorophyll was lowest (1  $\text{mg m}^{-3}$ ) during and immediately after the March flood, then sharply

TABLE 1. Summary of primary production and key parameters from Pensacola Bay. PAR:  $\text{E} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ ; Chl  $a$ :  $\text{mg} \cdot \text{m}^{-3}$ ;  $K_d$ :  $\text{m}^{-1}$ ;  $Z_p$ : m;  $\alpha$ :  $\text{mg C}(\text{mg chl } a \text{ d})^{-1}(\text{E} \cdot \text{m}^{-2} \cdot \text{d}^{-1})^{-1}$ ;  $P_m^B$ :  $\text{mg C}(\text{mg chl } a)^{-1} \cdot \text{d}^{-1}$ ;  $P_{wc}$ :  $\text{mg C m}^{-2} \cdot \text{d}^{-1}$ ;  $P_{1m}$ :  $\text{mg C m}^{-3} \cdot \text{d}^{-1}$ .

Date	Station	PAR	Chl $a$	$K_d$	$Z_p$	$\alpha$	$P_m^B$	$P_{wc}$	$P_{1m}$
Upper Bay									
15 August 2000	2	38.5	11.5	1.5	3.1	9.2	63	1138	764
12 September 2000	2	36.3	7.8	1.7	2.7	8.0	83	774	607
18 October 2000	2	29.3	4.3	0.9	5.2	12.9	100	819	458
13 March 2001	4	25.5	1.3	5.2	0.9	2.6	17	10	10
10 April 2001	4	38.9	11.3	2.7	1.7	2.3	24	215	200
8 May 2001	2	40.9	13.2	1.5	3.1	6.7	31	744	446
13 June 2001	3	43.5	15.1	1.6	3.0	6.0	40	976	650
8 August 2001	3	21.1	14.6	1.6	2.9	6.4	43	742	573
11 September 2001	3	31.2	16.5	1.7	2.7	8.8	60	1287	975
16 October 2001	2	26.5	15.6	3.1	1.5	6.4	29	395	370
13 November 2001	2	19.2	8.5	0.8	6.0	12.7	44	827	408
Lower Bay									
15 August 2000	4	38.5	7.0	1.2	4.0	4.8	51	646	372
12 September 2000	4	36.3	5.6	1.2	3.9	8.8	81	829	476
18 October 2000	4	29.3	2.5	1.1	4.2	11.3	92	433	238
13 March 2001	5	25.5	2.0	5.2	0.9	7.9	53	48	48
10 April 2001	5	38.9	7.3	0.9	5.4	5.7	63	1086	488
8 May 2001	5	40.9	4.9	0.5	9.4	6.2	54	1127	292
13 June 2001	5	43.5	24.3	1.2	3.7	5.0	48	2166	1238
8 August 2001	5	21.1	15.7	1.0	4.8	3.3	27	757	417
11 September 2001	5	31.2	12.8	1.2	4.0	7.8	64	1489	850
16 October 2001	5	26.5	9.7	1.6	2.8	7.5	16	311	170
13 November 2001	5	19.2	3.2	0.4	10.7	12.6	45	684	157

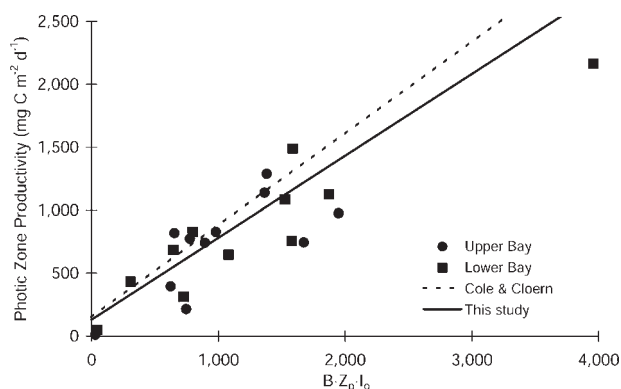


Fig. 7. Daily water column integrated phytoplankton production plotted as a function of the composite parameter  $B \cdot Z_p \cdot I_0$ . The dashed line denotes the consensus regression from four estuarine systems (Cole and Cloern 1987). The solid line is the Model II regression fit of data from this study in Escambia Bay, combining both upper bay (circles) and lower bay (squares) sites.

increased baywide, peaking at  $21 \text{ mg m}^{-3}$  in June, and remained elevated through the summer.

## Discussion

### SEASONAL AND ANNUAL PRODUCTIVITY

Based on this study, annual phytoplankton production in Escambia Bay is ca.  $290 \text{ g C m}^{-2}$  (Table 2), which is similar to nearby Gulf of Mexico systems (Bianchi et al. 1999) and other mesotrophic estuaries worldwide (Boynton et al. 1982). Although annual averages are similar to many temperate estuaries, the interseasonal variation in productivity is comparatively low, even when taking into account the flood-induced peak in productivity. Common to many subtropical estuaries, Escambia Bay experiences relatively high light ( $20 \text{ E m}^{-2} \text{ d}^{-1}$ ) and temperatures (minimum  $10^\circ\text{C}$ ) during winter when compared to higher latitude systems, resulting in

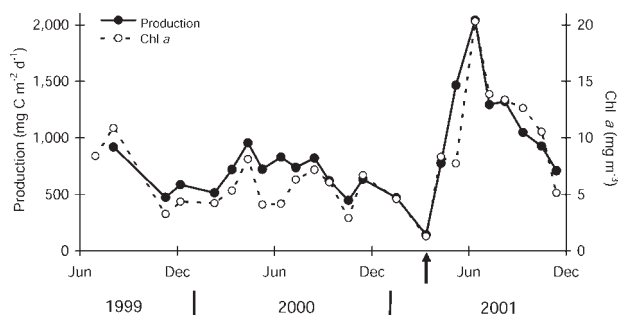


Fig. 8. The time series of the baywide averages of chlorophyll and the modeled phytoplankton production. The arrow marks the flood in March 2001. Baywide averages were calculated as the mean of the 5 sampling sites, weighted by the width of the bay orthogonal to the estuarine axis at each site.

TABLE 2. Seasonally-averaged daily primary production ( $\pm$  standard deviation) derived from direct measurements and calculated from the BZI model.

	mg C m <sup>-2</sup> d <sup>-1</sup>	Measured	Modeled
Winter			524 (58)
Spring		539 (512)	797 (427)
Summer		1071 (565)	1138 (462)
Fall		785 (375)	695 (222)
Average		798 (850)	789 (670)
Annualized average (g C m <sup>-2</sup> yr <sup>-1</sup> )		291 (310)	288 (244)

winter productivities of about  $500 \text{ mg C m}^{-2} \text{ d}^{-1}$  only about twofold lower than summer averages. Mid Atlantic estuaries receive about half the winter solar radiation ( $10 \text{ E m}^{-2} \text{ d}^{-1}$ ) and much lower water temperatures (near  $0^\circ\text{C}$ ), resulting in ca. fivefold interseasonal variation in primary productivity (Pennock and Sharp 1986).

### FRESHWATER FLOW, FLUSHING TIME, AND PHYTOPLANKTON RESPONSE

This study spanned one of the highest and the lowest freshwater flows recorded for the Escambia River. The extremes in freshwater flow affected the timing and magnitude of the ecosystem responses, which is reflected in nutrient distributions, phytoplankton biomass, and phytoplankton production. Flushing times in Escambia Bay varied from 1 to 21 d, representing the long-term extremes for this system. Eyre and Twigg (1997) compiled minimum and maximum flushing times for 17 estuaries, ranging from very rapid to very slow flushing times, representing the worldwide extremes. The mid-range flushing times of this group of estuaries varied from  $< 1$  d in the Don estuary (Scotland) to 123 d in the Neuse River Estuary (U.S.). In this context, Escambia Bay, with a median flushing time 8.3 d, is on the lower end of the worldwide range, but similar to other river-dominated subtropical estuaries (Eyre 2000). During normal flow periods, flushing times were remarkably stable varying between 5 to 10 d, suggesting that the basin morphology and the mixing characteristics of Escambia Bay modulated the freshwater flow by about fivefold; freshwater flows varied by 100 fold whereas flushing times varied by 20 fold.

As this study was conducted during a period of high flow variability, it also likely captured extremes in phytoplankton responses. Daily phytoplankton production rates varied by over 2 orders of magnitude, and showed clear responses to the freshwater flow and flushing times. The drought in 2000 had little effect on productivity, which appeared more strongly influenced by the return of normal freshwater flows. Productivity decreased



TABLE 3. Seasonal baywide averages of DIN, DIP, and the DIN:DIP ratio for Escambia Bay.

	DIN ( $\text{mmol m}^{-3}$ )			DIP ( $\text{mmol m}^{-3}$ )			DIN:DIP		
	1999	2000	2001	1999	2000	2001	1999	2000	2001
Winter		9.1	7.2		0.47	0.06		19.4	110.8
Spring		4.4	4.1		0.38	0.15		11.6	36.3
Summer	6.4	2.7	3.3	0.34	0.38	0.07	19.9	7.1	58.3
Fall		3.5	3.3		0.17	0.05		21.4	67.4
Annual		4.9	4.5		0.35	0.08		14.9	68.2

during the flood in 2001 when flushing times were rapid (1 d), and the waters were turbid ( $Z_p < 1$  m). After the flood, phytoplankton productivity increased strongly for the next several months, then gradually returned to preflood conditions by the fall. Similar lagged responses have been observed at a variety of estuaries (Eyre and Twigg 1997; Hubertz and Cahoon 1999; Pennock et al. 1999; Eyre 2000; Caffrey et al. 2007), floods can be important drivers of phytoplankton dynamics. While such floods are not annual occurrences in Escambia Bay, they do recur every 3 to 4 years in response to large spring rains or summer-fall tropical storms.

#### NUTRIENT LIMITATION OF PHYTOPLANKTON GROWTH

It is often difficult to predict whether N or P limits phytoplankton productivity based solely on nutrient data (Howarth 1988; Fisher et al. 1995), but a noteworthy interannual pattern was evident from this study, suggesting that phytoplankton production in Escambia Bay alternated between N limitation during the drought and P limitation during normal flow periods. The baywide average DIN:DIP ratios were consistently below Redfield during the drought and consistently above Redfield in normal flow years (Fig. 4). This was most pronounced between the summers 2000 and 2001, when DIN:DIP ratios averaged 7.1 and 58.3, respectively (Table 3). The DIN:DIP ratio during summer 2001 was much higher than comparable ratios compiled by Boynton et al. (1982) from multiple estuaries, further suggesting that P limitation was likely (Table 4).

DIN and DIP uptake patterns exhibited distinct response modes during drought and normal flow years. During 2000, DIN and DIP departures were out of phase; strong DIN uptake coincided with weak DIP uptake (actually some DIP release). The lack of net DIP uptake and relatively high average DIP concentrations ( $0.4 \text{ mmol m}^{-3}$ ) suggest that phytoplankton were N limited during the drought. During 1999 and 2001, strong uptake of both DIN and DIP was evident (Fig. 5). DIP concentrations during the phytoplankton bloom in 2001 were especially low and well below the half saturation concentration of about 0.1 to 0.2  $\text{mmol m}^{-3}$  re-

quired for phytoplankton uptake (Fisher et al. 1995). Seasonal and spatial alternation between N and P limitation has been reported in a variety of temperate and subtropical systems; examples include the Baltic Sea (Graneli et al. 1990), Chesapeake Bay (Fisher et al. 1992, 1999), Louisiana Bight (Smith and Hitchcock 1994), Cape Fear Estuary (Mallin et al. 1999), York River Estuary (Sin et al. 1999), and Pearl River Estuary (Yin et al. 2001). Higher prevalence of P limitation is observed in upper reaches of estuaries switching to N limitation in the lower reaches of estuaries. As this study was geographically fixed, the variation in flow characteristics caused the conditions in Escambia Bay to shift from N to P limitation in a predictable and consistent manner.

The temporal alternation between N and P limitation, as indicated by nutrient ratios and uptake patterns, is generally consistent with spatial patterns in nutrient limitation observed in Pensacola Bay from two different bioassay studies. Murrell et al. (2002b) consistently found P limitation in Escambia and upper Pensacola Bay, whereas Juhl (unpublished data) consistently found N limitation in Santa Rosa Sound in the lower reaches of the Pensacola Bay.

It should be noted that the above interpretation partly depends on the analysis of conservative nutrient-salinity mixing diagrams. Simple linear mixing diagrams assume that end-member constituent concentrations vary on time scales similar to the estuarine flushing time. When this steady-state assumption is met, the conservative mixing line is a straight line drawn between the two end members, and departures from this line provide a measure of net uptake or removal processes in the estuary. When variations in end-member concentrations occur at time scales markedly different from estuarine mixing time, the resulting conservative mixing line is curved. Several studies have evaluated the importance of (e.g., Loder and Reichard 1981; Officer and Lynch 1981) and corrected for (e.g., Eyre 2000) this potential artifact using high frequency data and flow-weighted modeling. As there are currently no high-frequency nutrient data for the Escambia Bay or Escambia River system, our



TABLE 4. Summary of seasonal mean ratios of dissolved inorganic nitrogen to dissolved inorganic phosphorus (DIN:DIP) from a variety of estuaries. Included are DIN:DIP ratios at time of maximum productivity, annual range in seasonal average DIN:DIP ratios, and the DIN and DIP concentrations at the time of maximum productivity. Reproduced from Howarth (1988), original graphic in Boynton et al. (1982). Data from current study are added at the bottom for comparison.

Estuary	DIN:DIP Ratio at Time of Maximum Productivity	Annual Range in DIN:DIP Ratio	DIN mmol m <sup>-3</sup>	DIP mmol m <sup>-3</sup>
Pamlico River, North Carolina	0.2	0–3	1.5	8.0
Roskeeda Bay, Ireland	0.3	0–1	0.4	2.2
Narragansett Bay, Rhode Island	0.5	0.5–14	0.6	1.6
Bedford Basin, Nova Scotia	0.8	0.5–8	0.6	0.5
Beaufort Sound, North Carolina	1.0	0.5–16	0.5	0.5
Chincoteague Bay, Maryland	1.2	1–10	3.2	2.5
Western Wadden Sea, Netherlands	1.3	1.3–120	3.0	2.0
Eastern Wadden Sea, Netherlands	1.5	1.5–56	4.0	2.5
Peconic Bay, New York	1.5	1–4	1.9	1.3
Mid-Patuxent River, Maryland	1.8	1.8–53	4.2	2.3
S. E. Kaneohe Bay, Hawaii	2.0	not reported	1.0	0.5
St. Margarets Bay, Nova Scotia	2.2	1–7	1.1	0.5
Central Kaneohe Bay, Hawaii	2.8	not reported	0.8	0.3
Long Island Sound, New York	3.9	1–6	1.5	0.5
Lower San Francisco Bay, California	6.0	4.5–8.5	20.6	3.8
Upper San Francisco Bay, California	6.0	0.5–16	11.5	2.0
Barataria Bay, Louisiana	6.2	6–16	4.6	0.8
Victoria Harbor, B.C.	6.2	6–15	11.5	2.0
Mid-Chesapeake Bay, Maryland	7.6	7–225	4.5	0.6
Duwamish River, Washington	8.5	8–16	5.0	0.6
Upper Patuxent River, Maryland	9.2	9–61	10.0	2.0
Baltic Sea	15	not reported	1.3	0.1
Loch Etive, Scotland	18	12–125	1.1	0.06
Hudson River, New York	20	16–30	60.0	3.0
Vostock Bay, USSR (sic) Russia	20	5–22	1.0	0.05
Apalachicola Bay, Florida	31	8–62	5.0	0.16
High Venice Lagoon, Italy	48	48–190	2.4	0.05
Escambia Bay, Florida (drought)	7.1		2.7	0.38
Escambia Bay, Florida (nondrought)	58	7–111	3.3	0.07

calculation of nutrient departures with simple mixing diagrams may include artifacts. The consistent seasonal and interannual patterns between nutrient departures, flushing times, and phytoplankton productivity imply that this artifact was relatively small.

#### NUTRIENT RECYCLING

The interacting factors of phytoplankton production, nutrient availability, and flushing characteristics were synthesized into a recycling index, as follows. Baywide average phytoplankton carbon production rates (from Fig. 8) were converted into their equivalent DIN and DIP demand via Redfield scaling (106C:16N:1P). The nutrient demand was divided by the baywide average nutrient concentration (from Fig. 4) to yield DIN and DIP turnover rates. The nutrient turnover rates were multiplied by the flushing time (from Fig. 2). This index normalizes phytoplankton nutrient demand to nutrient flushing, and can be viewed as proportional to the number of times DIN and DIP are recycled by phytoplankton before being lost from the system. Values near one indicate phytoplankton uptake and flushing are equally important

nutrient sinks, and that phytoplankton nutrient demand is largely met by available nutrient pools. Values below one indicate that flushing dominates the nutrient fluxes and that phytoplankton nutrient demand is relatively unimportant. Values above one indicate that phytoplankton production is supported by active recycling, and that flushing is relatively unimportant. The results (Fig. 9) show that the flood sharply reduced the recycling index for both DIN and DIP to values of 0.2 and 0.3, respectively, reflecting the dominance of flushing over phytoplankton uptake. Apart from the flood, there was a coherent seasonal trend in the recycling index for DIN and DIP, being smaller during winter and spring and larger during summers. This presentation further illustrates the reversal in DIN and DIP cycling among drought and normal years. During the drought, DIN recycling was larger than DIP suggesting that DIN was more likely limiting. During 2001, this pattern was reversed, suggesting that DIP was more likely limiting.

This analysis also suggests that, even during winter months, phytoplankton rely on nutrient recycling to support growth, requiring the available

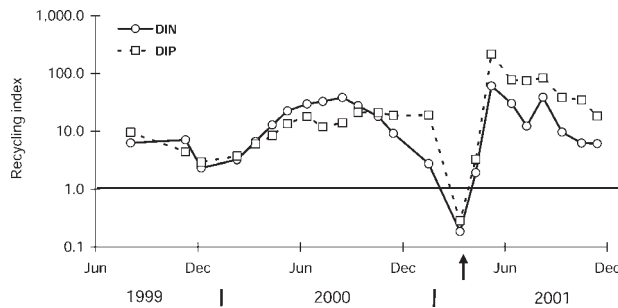


Fig. 9. The time series of the recycling index for DIN and DIP. The horizontal line shows where nutrient recycling and nutrient flushing are equally important sinks for DIN and DIP.

nutrient pools to be used several times. This is consistent with the evidence that the Pensacola Bay phytoplankton community is frequently nutrient limited (Murrell et al. 2002b; Juhl and Murrell 2005), in contrast to many temperate estuaries that alternate between light and nutrient limitation (Pennock and Sharp 1994; Cloern 1999; Mallin et al. 1999).

#### COMPARISONS TO OTHER SUBTROPICAL ESTUARIES

As a group, Gulf of Mexico estuaries are relatively poorly studied (see Bianchi et al. 1999), making explicit comparisons among Gulf of Mexico systems difficult. Yet river-dominated Gulf of Mexico estuaries share several important characteristics, including high solar insolation, shallow bathymetry, low tidal energy, high freshwater flow relative to estuarine volume, and low nutrient concentrations in river waters. Of subtropical estuaries worldwide, the best studied are located in southeastern Australia, which provides a useful comparison to Gulf of Mexico estuaries.

The Gulf of Mexico and southeastern Australia regions are of similar latitudes with similar seasonal cycles of temperature and solar insolation. Both regions experience episodic floods that cause similar sequence of events in the adjacent estuaries, namely system washout followed by a recovery phase and resumption of active nutrient recycling. This sequence has been well documented in river-dominated Australian estuaries (e.g., Eyre and Twigg 1997; Eyre 1998, 2000; Ferguson et al. 2004; Eyre and Ferguson 2006). While this sort of flood-response dynamic is not unique to subtropical estuaries (e.g., Hubertz and Cahoon 1999; Caffrey et al. 2007), the magnitude and frequency of floods is a generally more intense in subtropical systems.

Despite these similarities, there are noteworthy differences in estuarine character between these two regions. Gulf of Mexico estuaries are generally

larger than their Australian counterparts. For example, Escambia Bay is a 75 km<sup>2</sup> subestuary of the Pensacola Bay estuary, which is 370 km<sup>2</sup>. While moderately-sized compared to other Gulf of Mexico estuaries (Bianchi et al. 1999), Pensacola Bay is one or more orders of magnitude larger than most Australian estuaries (Eyre 2000; Roy et al. 2001). In river-dominated Gulf of Mexico estuaries, rainfall and freshwater flows occur year-round as opposed to the alternating dry and wet seasons typical of Australian estuaries (Eyre 2000). In this sense, the so called river-dominated estuaries of southeast Australia (Eyre 2000) are more similar to the lagoonal estuaries in Texas and the Yucatan peninsula (Bianchi et al. 1999). The river-dominated Gulf of Mexico estuaries have a larger base flow, which modulates nutrient pulses and likely explains why the nutrient concentrations observed in Escambia River waters were relatively low and constant throughout this study. During the 2001 flood, Escambia River DIN concentrations were lower than all other points in the time series (Fig. 4). This stands in stark contrast to Australian rivers that deliver high nutrient concentrations to the estuaries during flood events. Gulf of Mexico estuaries are microtidal (amplitude ca. 0.5 m), which combined with the relatively high freshwater flow leads to persistent stratification in most Gulf of Mexico estuaries. This stratification tends to physically decouple benthic and pelagic nutrient processes and also leads to hypoxic or anoxic bottom waters during warm summer months (May 1973; Rabalais et al. 2002; Hagy and Murrell In press). River-dominated Australian estuaries typically have 1 to 2 m tidal range and stratification is only transiently observed immediately following flood events (Eyre and Twigg 1997; Eyre and Ferguson 2006). As a result, Australian systems do not experience hypoxic or anoxic conditions.

While not an exhaustive comparison, these similarities and differences in estuarine character merely serve to exemplify the unique aspects of Gulf of Mexico systems relative to the better-studied subtropical estuaries. Future intercomparison studies among Gulf of Mexico estuaries and with other subtropical estuaries (e.g., Pearl River estuary, Dai et al. 2006) will improve our understanding of how these estuaries respond to natural and anthropogenic perturbations.

#### Conclusions

In this study we examined the relationship between freshwater flow, nutrient loading, and phytoplankton productivity in Escambia Bay; which is the first such study in any Gulf of Mexico estuary, and one of few such studies in any microtidal

subtropical estuary. Flushing times ranged from 1 to 20 d in Escambia Bay, similar to other river-dominated subtropical estuaries but rapid compared to temperate systems. Similar to temperate estuaries, the phytoplankton biomass and light field variables reasonably predicted phytoplankton production, validating this approach for estimating productivity in nutrient-limited subtropical estuaries. The nutrient distributions suggest that Escambia Bay alternated between N limitation drought conditions (higher salinity) and P limitation during normal flow conditions (lower salinity). This alternation between N and P limitation along salinity gradients is similar to that observed in estuaries worldwide. The interseasonal variability in phytoplankton production was lower than in temperate estuaries, which is attributable to relatively high winter productivity. Winter phytoplankton production is supported by relatively high light and active nutrient recycling. Episodic freshwater flow events appear to be an important driver of phytoplankton dynamics, having an initial inhibitory effect and a lagged stimulatory effect on productivity.

A persistent challenge to resource managers is the ability to accurately predict how changes in land use practices manifest at the estuarine margins, yet such predictions are necessary to make informed decisions. The moderate annual productivity observed is consistent with the relatively low ambient nutrient concentrations and indicates that Escambia Bay is not currently in an advanced state of cultural eutrophication. Like many Gulf of Mexico estuaries, Escambia Bay suffers symptoms of eutrophication such as yearly summertime hypoxia (Bricker et al. 1999; Macauley et al. 2005; Hagy and Murrell In press) and seagrass loss (Lewis unpublished data). The lack of seasonal light limitation and active nutrient cycling suggest that these systems will be very sensitive to future increases in nutrient loading. Future research needs to be focused on better understanding and ultimately predicting how episodic freshwater discharges, a common feature in Gulf of Mexico and other subtropical estuaries, affect phytoplankton and nutrient recycling processes.

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