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Seasonal dissolved inorganic nitrogen and phosphorus budgets for two sub-tropical estuaries in south Florida, USA

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Abstract. Interactions among geomorphology, circulation, and biogeochemical cycling determine estuary responses to external nutrient loading. In order to better manage watershed nutrient inputs, the goal of this study was to develop seasonal dissolved inorganic nitrogen (DIN) and phosphorus (DIP) budgets for the two estuaries in south Florida, the Caloosahatchee River estuary (CRE) and the St. Lucie Estuary (SLE), from 2002 to 2008. The Land-Ocean Interactions in the Coastal Zone (LOICZ) approach was used to generate water, salt, and DIN and DIP budgets. Results suggested that internal DIN production increases with increased DIN loading to the CRE in the wet season. There were hydrodynamic effects as water column concentrations and ecosystem nutrient processing stabilized in both estuaries as flushing time increased to > 10 d. The CRE demonstrated heterotrophy (net ecosystem metabolism or NEM < 0.0) across all wet and dry season budgets. While the SLE was sensitive to DIN loading, system autotrophy (NEM > 0.0) increased significantly with external DIP loading. This included DIP consumption and a bloom of a cyanobacterium (Microcystis aeruginosa) following hurricane-induced discharge to the SLE in 2005. Additionally, while denitrification provided a microbiallymediated N loss pathway for the CRE, this potential was not evident for the SLE where N₂ fixation was favored. Disparities between total and inorganic loading ratios suggested that the role of dissolved organic nitrogen (DON) should be assessed for both estuaries. Nutrient budgets indicated that net internal production or consumption of DIN and DIP fluctuated with inter- and intra-annual variations in freshwater inflow, hydrodynamic flushing, and primary production. The results of this study should be included in watershed management plans in order to maintain favorable conditions of external loading relative to internal material cycling in both dry and wet seasons.

1 Introduction

Estuaries modulate the inputs of water and materials from the watershed to the coastal ocean through intense internal biogeochemical cycling. Water column concentrations of carbon (C), nitrogen (N), and phosphorus (P) vary with interactions among external inputs and exports, circulation, sedimentwater exchanges, and biological processes. Eutrophication disturbs these integrated processes as allochthonous and autochthonous organic carbon inputs increase in excess of balanced consumption (Nixon, 1995). This imbalance is often stimulated by loading of dissolved inorganic nutrients from the watershed (Cloern, 2001). While this model of coastal fertilization is generally applicable, estuaries have differential capacities to accommodate introduced nutrients through a variety of factors including latitude, geomorphology, and flushing time (Dettmann, 2001; Smith et al., 2003). In particular, sub-tropical estuaries such as those in south Florida have experienced alterations including manipulation of freshwater inflows to meet municipal, agricultural, and environmental demands. Discharge to these estuaries introduces pulses of watershed materials that vary on synoptic to inter-annual timescales depending upon weather, climate, and watershed management (Childers et al., 2006; Dennison, 2008; SFWMD, 2012a, b).

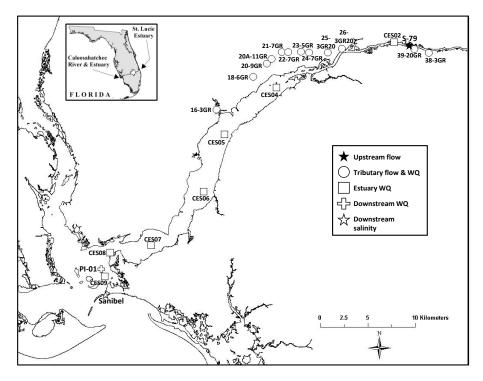


Fig. 1. Map depicting the Caloosahatchee River estuary. See Table 1 and Sect. 2.2 for details of data sources and integration into the nutrient budgets. Included is the upstream boundary site of gauged freshwater inflow (S-79; filled star), 12 locations of tributary water quality data (open circles), 7 locations of estuary water quality data (open squares), the location of downstream water quality data (PI-01; open cross), and the downstream boundary location for salinity (Sanibel; open star).

Baseline quantification of material inputs, flushing time, downstream export, and the potential for internal production or consumption of C, N, and P (CNP) is essential to better understand estuarine system metabolism (Gordon et al., 1996; Smith et la., 2005; Giordani et al., 2008). This is particularly true for coastal water bodies with heavily managed freshwater inflow subject to both short- and long-term fluctuations in discharge (Brock, 2001). In fact, sensitivity to both reduced inflows (loss of freshwater and estuarine habitats) and increased inorganic nutrient loading (symptoms of eutrophication) offers an apparent contradiction for estuarine management (Flemer and Champ, 2006). The amount of water and dissolved materials required to maintain optimal system metabolism with regard to CNP production and consumption should be quantified and factored into management plans for coastal watersheds.

In 1993 the International Geosphere-Biosphere Program (IGBP) and the International Human Dimensions Program on Global Environmental Change (IHDP; http://www.loicz. org/; http://nest.su.se/mnode/) initiated a project to investigate biogeochemistry of the coastal zone (Gordon et al., 1996; Smith et al., 2005; Swaney et al., 2011). The Land–Ocean Interactions in the Coastal Zone (LOICZ) included a spreadsheet tool designed to quantify internal C, N, and P sources and sinks in estuaries (Giordani et al., 2008). LOICZ also has been useful in socio-economic-political assessments

of human dimensions in the coastal zone (Talaue-McManus et al., 2003; Swaney et al., 2011). The approach has been used to investigate CNP cycling in hundreds of coastal environments (Smith et al., 2005; Giordani et al., 2008; Yamamoto et al., 2008; Liu et al., 2009; Swaney et al., 2011. The spreadsheets are customizable depending upon the quality and quantity of data and can be applied to any estuary without the need for detailed rate process information.

In order to explore internal biogeochemical mechanisms, the overall goal of this study was to generate wet and dry season DIN (dissolved inorganic nitrogen) and DIP (dissolved inorganic phosphorus) budgets for both the Caloosahatchee River and St. Lucie estuaries (CRE and SLE, respectively) from 2002 to 2008. This time period was derived based on data availability and consideration for the range of climatic conditions. The specific objectives were to estimate DIN and DIP loading via atmospheric, groundwater, and surface inputs; to quantify seasonal changes in estuarine salinity and flushing time; to assess seasonal patterns of estuarine DIN and DIP concentrations; and to explore, compare, and contrast relationships between loading, flushing, concentrations, and ecosystem-scale CNP cycling within and between the CRE and SLE.

2 Methods

2.1 Study sites

The CRE is located in southwest Florida and has been altered by human activities starting in the 1880s when the river was straightened and deepened (Fig. 1; Antonini et al., 2002). The first water control structures at Lake Okeechobee (S-77) and Ortona (S-78) were completed in the 1930s with the last installed in 1966 at Olga (S-79; Antonini et al., 2002). The Franklin Lock at S-79 represents the head of the CRE that extends \sim 42 km downstream to Shell Point where it empties into the Gulf of Mexico. The meso- and poly-haline estuary downstream of S-79 has also experienced anthropogenic impacts (Chamberlain and Doering, 1998). Early descriptions of the CRE characterize it as barely navigable due to extensive shoals and oyster bars near the estuary's mouth (Sackett, 1888). A navigation channel was dredged with a causeway built across the mouth of San Carlos Bay in the 1960s. Historic oyster bars immediately upstream were mined for road construction.

Located in southeast Florida, the SLE comprises a major tributary to the ecologically and commercially valuable Indian River lagoon (Sime, 2005; Ji et al., 2007; Fig. 2). Historically, the SLE was a freshwater system that was temporarily exposed to the coastal ocean only through ephemeral inlets (United States Army, 1915). The St. Lucie Inlet was permanently opened in 1892 to provide a connection between the SLE and coastal ocean resulting in a partially mixed estuary with semi-diurnal tidal amplitude of ~ 0.4 m. The past several decades have seen the SLE watershed altered from a system of natural sloughs and wetlands into a series of sub-basins affected by agriculture and urbanization. The SLE has a large watershed : estuary surface area ratio of 150 : 1 (Tampa Bay, 5.5:1). Watershed changes and periodic highvolume water releases from Lake Okeechobee have altered historical wet season and dry season patterns of nutrient loading. These changes in flow, salinity, and water quality are associated with increased prevalence of phytoplankton blooms, accumulation of muck-like sediments, and the loss of seagrass and oyster habitats (Sime, 2005; SFWMD, 2012a).

2.2 Application of the LOICZ approach to the Caloosahatchee and St. Lucie estuaries

Application of the LOICZ approach results in water, salt, DIN, and DIP budgets for the estuary of interest (Gordon et al., 1996; Smith et al., 2005; Giordani et al., 2008; Swaney et al., 2011; the reader is encouraged to refer to these published efforts for conceptual and mathematical details of the LOICZ approach). It was designed to isolate internal, nonconservative production or consumption of dissolved CNP from conservative exchanges for a spatially homogeneous layer, segment, or estuarine water body.

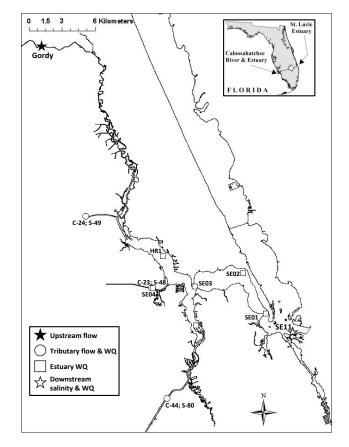


Fig. 2. Map depicting the St. Lucie Estuary. See Table 1 and Sect. 2.2 for details of data sources and integration into the nutrient budgets. Included is the upstream boundary for freshwater inflow (Gordy Rd.; filled star), three locations of tributary water quality and inflow data (open circles), six locations of estuary water quality data (open squares), and the downstream boundary location for water quality and salinity (SE-11; open star).

The approach assumes a steady state condition that balances the sum of physical inputs against the sum of physical outputs (Wosten et al., 2003; Swaney et al., 2011). In general, salinity (S) differences between the estuary and the downstream oceanic boundary are used to define net flows, residual exchange, and flushing time (T_f) . The water budget and hydrodynamic exchange attributes are used to predict internal production or consumption of dissolved inorganic C, N, and P. This study generated budgets in order to evaluate net internal production or consumption of DIN (Δ DIN; g $Nm^{-2}d^{-1}$) and DIP (Δ DIP; g $Pm^{-2}d^{-1}$) at the seasonal scale (dry vs. wet seasons). Dry and wet seasons for south Florida were defined using the months of December-May and June-November, respectively. Negative and positive values denote net internal consumption or production, respectively, by the estuarine system. LOICZ relies upon the molar stoichiometry of the photosynthesis-respiration equation to link C, N, and P cycles (Gordon et al., 1996; Smith et al., 2005; Swaney et al., 2011).

Abbreviation	Definition	Unit	CRE	SLE
V _{rain}	Rain to estuary surface	$10^6 \mathrm{m}^3 \mathrm{d}^{-1}$	Nexrad	Nexrad
$V_{\mathbf{Q}}$	Freshwater discharge	$10^6 \mathrm{m}^3 \mathrm{d}^{-1}$	DBHydro S-79	DBHydro S484980 + Gordy
VOFW	Tributaries + groundwater	$10^6 \mathrm{m}^3 \mathrm{d}^{-1}$	Tidal basin model	30% of total Q
Ve	Estuary volume	$10^{6} \mathrm{m}^{3}$	Interpolated bathymetry	Interpolated bathymetry
Se	Estuary salinity		DBHydro CES stations	DBHydro SE stations
So	Downstream bound salinity		Shell Point daily model	DBHydro station SE-11
DIP _{rain}	DIP in rain	${ m gm^{-3}}$	DBHydro averages	DBHydro averages
DIP _{Oc}	DIP in discharge	$\mathrm{g}\mathrm{m}^{-3}$	Lee County Stations	DBHydro S-484980
DIPOFW	DIP in tributaries + gw	${ m gm^{-3}}$	Lee County Stations	DBHydro S-484980
DIP _e	DIP in estuary	$\mathrm{g}\mathrm{m}^{-3}$	DBHydro CES stations	DBHydro SE stations
DIPo	DIP in downstream bound	${ m gm^{-3}}$	Lee County Stn. PI-01	DBHydro station SE-11
DIN _{rain}	DIN in rain	$\mathrm{g}\mathrm{m}^{-3}$	NADP St. Petersburg, FL	NADP St. Petersburg, FL
DIN _{Oc}	DIN in discharge	$\mathrm{g}\mathrm{m}^{-3}$	DBHydro station S-79	DBHydro S-484980
DINOFW	DIN in tributaries + gw	$g m^{-3}$	Lee County Stations	DBHydro S-484980
DINe	DIN in estuary	$g m^{-3}$	DBHydro CES stations	DBHydro SE stations
DINo	DIN in downstream bound	$g m^{-3}$	Lee County Stn. PI-01	DBHydro station SE-11

Table 1. Sources of input data for seasonal DIN and DIP budgets for CRE and SLE. Please see Sect. 2.2 for explanation and details and Figs. 1 and 2 for water quantity and quality monitoring locations.

The budgets required DIN and DIP concentrations in rain (DIN_{rain} and DIP_{rain}), surface discharge (DIN_{Qc} and DIP_{Qc}), other freshwater sources (DIN_{OFW} and DIN_{OFW}), the estuary (DIN_e and DIP_e), and the oceanic boundary (DIN_o and DIP_o). Seasonal hydrological inputs via the atmosphere, groundwater, and surface inflow; salinity; and DIN and DIP concentrations in the upstream, tributaries and ground water, main water body; and downstream oceanic boundary from 2002 to 2008 were assembled for each estuary (Table 1).

Since DIP does not have an air-sea conversion term it is assumed to be in stoichiometric balance with dissolved inorganic carbon (DIC) mass in the estuarine volume. Using straightforward Redfield stoichiometry (molar C:N:P=106:16:1), \triangle DIP can be converted to net ecosystem metabolism (NEM; g $C m^{-2} d^{-1}$) with NEM defined as a positive number (autotrophic) when the system consumes DIP internally (Yamamoto et al., 2008). In contrast, there is net exchange of DIN between the water and atmosphere through microbially mediated N cycling that confounds direct inter-conversion through stoichiometry. The LOICZ budgets are used to calculate the actual Δ DIN from differences in DIN imports and exports, and, the expected $\Delta DIN~(\Delta DIN_{exp})$ from $\Delta~DIP$ and the N:P ratio of particulate matter ($N: P_{part} = 16$). The difference between the two values represents the relative difference between N2 fixation and denitrification ($N_{fix}D > 0.0 = \text{net } N_2$ fixation; Yamamoto et al., 2008; Swaney et al., 2011).

Each estuarine water body was bounded and assumed to represent a homogenous volume to assess system-level internal cycling of CNP. While splitting each estuary spatially into multiple segments and vertically into multiple layers can be desirable (Webster et al., 2000), treating each estuary as a single box was optimal for initial assessments. The CRE was assumed to extend from the Franklin Lock (S-79) to Shell Point (CES09) approximately 40 km downstream (Fig. 1). Estuarine surface area for the CRE is 56.9 km^2 (569000000 m^2) with an average depth of 2.4 m (Buzzelli et al, 2013b). In contrast, the SLE has multiple upstream points of freshwater inflow (Fig. 2). Three water control structures (S-49, S-48, S-80) provided upstream boundaries for the SLE. The final upstream bound was the St. Lucie Blvd. Bridge in the North Fork, which was assumed to possess flow indicative of a gated structure located farther upstream (Gordy Rd.; Fig. 2). The downstream boundary was the St. Lucie Inlet. Estuarine surface area for the SLE is 22.0 km^2 ($22\,000\,000\,\text{m}^2$) with an average depth of 2.7 m (Buzzelli et al., 2013b).

Average monthly rainfall $(m^3 d^{-1})$ directly to the water surfaces of the CRE and SLE was queried from NEXRAD data available through the South Florida Water Management District (SFWMD) publicly accessible database (DBHydro; http://www.sfwmd.gov/dbhydroplsql/show_dbkey_info.main_menu). Seasonal rainfall amounts for the CRE and SLE were summed from the time series of monthly averages. Daily freshwater inflow rate to the CRE at S-79 $(m^3 d^{-1})$ available through DBHydro was averaged over each dry and wet season. Other freshwater inflow $(m^3 d^{-1})$ representative of combined tributary and ground water input to the CRE was derived using a tidal basin watershed model presently in development at the SFWMD (Y. Wan, unpublished data; Table 2).

Total daily freshwater discharge to the SLE from DBHydro was estimated by summing daily inflow measurements at structures S-48, S-49, S-80, and Gordy Rd and then averaged over each season. By contrast, the sum of freshwater inflow

Table 2. Inputs for seasonal DIN and DIP budgets for the CRE. Values are seasonal averages from 2002 to 2008 for water, salt, DIN, and DIP budgets. The wet season consisted of months 6–11 (June–November) within each year. The dry season consisted of month 12 (December) from the preceding year followed by the first 5 months (January–May) of the next year. Abbreviations and units shown for average daily input of rain (V_{rain} ; 10⁶ m³ d⁻¹), upstream flow or discharge (V_Q ; 10⁶ m³ d⁻¹), and other freshwater sources (V_{OFW} ; 10⁶ m³ d⁻¹); salinity in the estuary (S_e) and downstream or ocean boundary (S_o); and concentrations of DIN and DIP in rainfall (DIN_{rain} and DIP_{rain}), discharge (DIN_{Qc} and DIP_{Qc}), the estuary (DIN_e and DIP_e), and the ocean boundary (DIN_o and DIP_o). All concentrations are in g m⁻³. DIN and DIP in other freshwater sources (DIN_{OFW} and DIP_{OFW}) were assumed to be equal to DIN_{Qc} and DIP_{Qc}. See text for specifics and sources of input data for budget development. CRE volume was assumed to be constant ($V_{CRE} = 140 \times 10^6$ m³).

			Water		S	alt		DIF	•			DIN	1	
year	season	V _{rain}	V_{Q}	$V_{\rm OFW}$	Se	$S_{\rm o}$	DIP _{rain}	DIP _{Qc}	DIPe	DIPo	DIN _{rain}	DIN _{Qc}	DINe	DIN ₀
2002	Dry	0.1	2.2	0.4	12.6	30.2	0.04	0.16	0.06	0.05	0.75	0.27	0.10	0.04
	Wet	0.5	8.1	0.9	7.9	18.8	0.08	0.09	0.11	0.07	0.96	0.15	0.16	0.15
2003	Dry	0.1	4.6	0.5	8.4	21.7	0.04	0.05	0.05	0.02	0.82	0.15	0.11	0.04
	Wet	0.4	15.4	2.7	8.2	12.5	0.08	0.08	0.06	0.04	0.78	0.14	0.23	0.11
2004	Dry	0.1	4.5	0.4	10.6	24.1	0.04	0.04	0.04	0.02	0.45	0.12	0.12	0.06
	Wet	0.4	13.3	9.3	6.5	17.1	0.08	0.06	0.07	0.03	0.73	0.14	0.18	0.13
2005	Dry	0.2	7.2	0.5	6.2	20.8	0.04	0.03	0.05	0.02	0.74	0.13	0.35	0.12
	Wet	0.5	19.6	2.2	1.6	9.5	0.08	0.05	0.08	0.06	0.58	0.12	0.30	0.19
2006	Dry	0.1	2.2	0.4	1.9	22.6	0.04	0.03	0.05	0.02	1.19	0.15	0.25	0.12
	Wet	0.4	4.2	1.9	7.4	23.1	0.08	0.07	0.11	0.06	0.68	0.14	0.20	0.09
2007	Dry	0.1	0.2	0.3	19.4	33.1	0.04	0.07	0.06	0.02	1.22	0.12	0.16	0.04
	Wet	0.3	0.4	0.8	15.7	31.2	0.08	0.08	0.11	0.01	0.84	0.17	0.10	0.07
2008	Dry	0.1	0.4	0.4	20.0	34.0	0.04	0.07	0.05	0.01	0.77	0.18	0.08	0.03
	Wet	0.5	6.1	2.5	9.1	22.1	0.08	0.08	0.11	0.04	0.77	0.19	0.13	0.05

from four gauged input canals (C-44, C-23, C-24, and North Fork) is approximately 70% of the total freshwater input to the SLE (Ji et al., 2007). Thus, other freshwater input to the SLE was added as 30% of the total summed daily discharge of surface water (Table 3).

S in the CRE was based on an average of seven midchannel stations (CES02, CES04, CES05, CES06, CES07, CES08, CES09; Fig. 1; Table 2). Similarly, average seasonal S in the SLE was calculated using monitoring data from five stations (SE01, SE02, SE03, SE04, HR1; Fig. 2; Table 3). Daily S predicted at the Sanibel Bridge using a 3-D hydrodynamic model provided the downstream boundary for the CRE water budgets (Fig. 1; D. Sun and Y. Wan, unpublished data; Table 2). S values at the oceanic boundary of the SLE were from observational data at the most downstream station (SE-11; Fig. 2; Table 3).

Seasonally varying concentrations of DIP in rain $(DIP_{rain}; g Pm^{-3})$ from 2002 to 2008 were from data available in DBHydro (Table 2). Seasonally varying concentrations of DIN in rain (DIN_{rain}; g Nm^{-3}) was calculated by summing NO₂⁻ + NO₃⁻ + NH₄⁺ concentrations from St. Petersburg, FL, as part of the National Atmospheric Deposition Program (NADP; http://nadp.sws.uiuc.edu/data/ntndata.aspx). Atmospheric concentrations were assumed to be representative of the south Florida region so the same seasonal time series of DIP_{rain} and DIN_{rain} were applied to both estuaries. Lee County in southwest Florida maintains a water quality database for the CRE and its

tributaries (available at http://www.lee-county.com/gov/dept/ naturalresources/WaterQuality/Pages/default.aspx). DIN and DIP concentrations (g N m⁻³; g P m⁻³) from 12 tributary stations were averaged by season for use as DIP_{OFW} and DIN_{OFW} for the CRE (Fig. 1). Concentrations from the two upstream stations (38-3GR and 39-20GR) were used for DIP_{Qc} and DIN_{Qc} in order to calculate DIP and DIN loading at S-79 (DIP_Q and DIN_Q; g d⁻¹; Table 2). The concentrations of DIP (DIP_e; g P m⁻³) and DIN (DIN_e; g N m⁻³) in the main body of the CRE were derived from monthly monitoring at the seven mid-estuary stations (CES02-CES09). Finally, data from the Lee County station PI-01 were the source of DIP and DIN concentrations at the oceanic boundary of the CRE (DIP_o and DIN_o; Table 2).

Seasonally averaged concentrations of DIP (g P m⁻³) and DIN (g N m⁻³) observed at S-49, S-48, and S-80 provided DIP_{Qc} and DIN_{Qc} to estimate surface loadings to the SLE (DIP_Q and DIN_Q; g d⁻¹; Table 3). DIP_{OFW} and DIN_{OFW} concentrations were assumed to be equal to DIP_{Qc} and DIN_{Qc}. DIP (DIP_e; g P m⁻³) and DIN (DIN_e; g N m⁻³) concentrations in the main body of the SLE were derived from monthly monitoring at the five mid-estuary stations (Fig. 2; Table 3). Nutrient concentrations observed at SE11 provided the condition at the oceanic boundary (DIP_o and DIN_o; g m⁻³).

LOICZ water, salt, and nutrient budgets were generated using MS Excel spreadsheets and macros for two different time periods (dry vs. wet seasons). Annual spreadsheets were created for each of the 7 yr (2002–2008) for both the CRE

Table 3. Inputs for seasonal DIN and DIP budgets for the SLE. Values are seasonal averages from 2002 to 2008 for water, salt, DIN, and DIP budgets. The wet season consisted of months 6–11 (June–November) within each year. The dry season consisted of month 12 (December) from the preceding year followed by the first 5 months (January–May) of the next year. Abbreviations and units shown for average daily input of rain (V_{rain} ; 10⁶ m³ d⁻¹), upstream flow or discharge (V_Q ; 10⁶ m³ d⁻¹), and other freshwater sources (V_{OFW} ; 10⁶ m³ d⁻¹); salinity in the estuary (S_e) and downstream or ocean boundary (S_o); and concentrations of DIN and DIP in rainfall (DIN_{rain} and DIP_{rain}), discharge (DIN_{Qc} and DIP_{Qc}), the estuary (DIN_e and DIP_e), and the ocean boundary (DIN_o and DIP_o). All concentrations are in g m⁻³. DIN and DIP in other freshwater sources (DIN_{OFW} and DIP_{OFW}) were assumed to be equal to DIN_{Qc} and DIP_{Qc}. See text for specifics and sources of input data for budget development. SLE volume was assumed to be constant ($V_{SLE} = 53 \times 10^6$ m³).

			Water	ſ	Sa	alt		DIF)			DIN	1	
year	season	V _{rain}	V_{Q}	$V_{\rm OFW}$	$S_{\rm e}$	$S_{\rm o}$	DIP _{rain}	DIP _{Qc}	DIPe	DIPo	DIN _{rain}	DIN _{Qc}	DINe	DINo
2002	Dry	0.03	0.5	0.2	20.3	33.2	0.04	0.10	0.08	0.02	0.75	0.16	0.09	0.06
	Wet	0.06	3.7	1.1	14.2	26.7	0.08	0.12	0.18	0.09	0.96	0.19	0.19	0.15
2003	Dry	0.04	2.9	0.9	17.7	30.6	0.04	0.16	0.08	0.02	0.82	0.19	0.11	0.05
	Wet	0.07	6.2	1.9	5.9	18.0	0.08	0.09	0.18	0.09	0.78	0.23	0.18	0.17
2004	Dry	0.03	2.0	0.6	17.2	30.4	0.04	0.09	0.06	0.02	0.45	0.20	0.07	0.04
	Wet	0.90	7.8	2.4	11.2	25.9	0.08	0.29	0.21	0.1	0.73	0.34	0.36	0.24
2005	Dry	0.05	2.8	0.8	13.8	28.5	0.04	0.38	0.06	0.02	0.74	0.39	0.19	0.04
	Wet	0.10	9.9	3.0	2.3	17.4	0.08	0.70	0.20	0.14	0.58	0.21	0.26	0.21
2006	Dry	0.02	2.2	0.7	14.1	30.8	0.04	0.41	0.07	0.03	1.19	0.33	0.20	0.05
	Wet	0.05	1.0	0.3	19.5	31.9	0.08	0.41	0.18	0.04	0.68	0.70	0.18	0.04
2007	Dry	0.02	0.2	0.1	27.7	35.9	0.04	0.17	0.07	0.01	1.22	0.19	0.02	0.02
	Wet	0.10	1.7	0.5	16.2	33.3	0.08	0.68	0.17	0.02	0.84	0.25	0.16	0.03
2008	Dry	0.04	0.4	0.1	20.2	34.0	0.04	0.23	0.07	0.01	0.77	0.18	0.06	0.02
	Wet	0.10	2.7	0.8	9.4	24.8	0.08	0.87	0.12	0.05	0.77	0.19	0.17	0.11

and SLE (14 total spreadsheets). Each annual spreadsheet had input and result pages for both the dry and wet seasons with each result page including both DIN and DIP budget values. Data assembly and entry for budget calculations was the most time intensive and important part of budget development (Tables 2, 3). Results from the LOICZ budgets were collated within each estuary with results for the CRE and SLE combined for graphical and tabular presentation.

3 Results

3.1 Caloosahatchee River estuary

Rainfall directly to the surface of the CRE ranged 0.1– 0.15 × 10⁶ m³ d⁻¹ and 0.35–0.45 × 10⁶ m³ d⁻¹ in the dry and wet seasons, respectively (Fig. 3a). Total rainfall varied inter-annually for both the dry and wet seasons of 2002– 2008. Freshwater discharge to the CRE revealed long-term variability with maximum values of $15–20 \times 10^6$ m³ d⁻¹ in the wet seasons of 2003–2005 followed by minimal inflow for both seasons beginning in 2006 (Fig. 3b). Freshwater input from the tidal basin downstream of S-79 generally reflected patterns of surface flow except for the extreme peak in the wet season of 2005 (~9 × 10⁶ m³ d⁻¹; Fig. 3c).

Salinity in the CRE was inverse to freshwater discharge ranging from 7 to 13 in both wet and dry seasons of 2002-2004 before values < 2.0 in the wet season of 2005 and dry season of 2006 (Fig. 4a). The salinity of the CRE de-

creased from 20 to < 5 with increased freshwater inflow over all seasonal water budgets of 2002-2008 (Fig. 5a). Average salinity increased to ≥ 20.0 in the dry seasons of 2007 and 2008 when discharge was lowest and the $T_{\rm f}$ of the CRE approached 50 and 70 days, respectively (Fig. 6a). Estuarywide, average DIN concentrations exhibited inter-annual climatic fluctuations similar to patterns of inflow from 2002 to 2008 (Fig. 4b). DIN ranged from 0.1 to 0.25 g m^{-3} from 2002 to 2005 before reaching 0.35 g m^{-3} in 2005. Average DIN concentrations decreased in both dry and wet seasons of 2006–2008. Over all seasonal budgets, the concentration of DIN in the CRE ranged from 0 to 0.35 g m^{-3} and exhibited a modest increase with external loading of DIN up to $0.06 \text{ g N m}^{-2} \text{ d}^{-1}$ (Fig. 5b). The relationship between flushing time and DIN concentrations were unclear although DIN was reduced ($\sim 0.1 \text{ g m}^{-3}$) when $T_f = 50 \text{ d}$ (Fig. 6b). In contrast to DIN, DIP concentrations in the CRE were remarkably consistent ranging from 0.03 to 0.12 across all seasons and years (Fig. 4c). In fact, there was no obvious relationship between either the external loading of DIP (0.0-0.025 g Pm⁻² d⁻¹), or $T_{\rm f}$ and internal DIP concentrations in the CRE $(0.025-0.10 \text{ g m}^{-3}; \text{ Figs. 5c, 6c})$. DIP concentrations declined ($< 0.075 \text{ g m}^{-3}$) when inflow was greatest from 2004 to 2005 (Fig. 5c).

The LOICZ budgets indicated that DIN was produced within the CRE (Δ DIN > 0.0) in wet season of 2003, the wet season of 2004, and both seasons in 2005 (Fig. 7a). Aside from these instances, Δ DIN was near zero for a

Table 4. Rates of internal dissolved CNP turnover resulting from seasonal DIN and DIP budgets of CRE and SLE from 2002 to 2008. Net internal production or consumption of DIN and DIP were derived through a budgeting process that incorporates water, salt, and input concentrations (ΔN , g N m⁻² d⁻¹; ΔP , g P m⁻² d⁻¹; Swaney et al., 2011). The DIP rate was converted to net ecosystem metabolism (NEM; g C m⁻² d⁻¹). Average values were calculated across all dry and all wet seasons, respectively.

			C	RE			SI	LE	
year	season	ΔN	ΔP	NEM	N _{fix} D	ΔN	ΔP	NEM	N _{fix} D
		${ m g~Nm^{-2}d^{-1}}$	${\rm g}{\rm P}{\rm m}^{-2}{\rm d}^{-1}$	${\rm g}{\rm C}{\rm m}^{-2}{\rm d}^{-1}$	$g N m^{-2} d^{-1}$	${\rm g}{\rm N}{\rm m}^{-2}{\rm d}^{-1}$	${\rm g}{\rm P}{\rm m}^{-2}{\rm d}^{-1}$	${\rm g}{\rm C}{\rm m}^{-2}{\rm d}^{-1}$	$g N m^{-2} d^{-1}$
2002	Dry	0.006	-0.004	0.16	0.03	-0.002	0.003	-0.11	-0.02
	Wet	-0.001	0.009	-0.37	-0.07	0.011	0.034	-1.39	-0.23
2003	Dry	-0.001	0.004	-0.16	-0.03	-0.002	-0.0005	0.02	0.002
	Wet	0.259	0.021	-0.84	0.11	-0.017	0.052	-2.12	-0.39
2004	Dry	0.003	0.001	-0.06	-0.01	-0.010	0.004	-0.15	-0.04
	Wet	0.028	0.010	-0.59	-0.08	0.056	0.021	-0.85	-0.09
2005	Dry	0.044	0.004	-0.17	0.01	-0.010	-0.048	1.97	0.34
	Wet	0.078	0.010	-0.58	-0.02	0.027	-0.287	11.8	2.10
2006	Dry	0.004	0.001	-0.05	-0.005	-0.001	-0.068	2.79	0.49
	Wet	0.010	0.008	-0.33	-0.05	-0.018	-0.002	0.07	-0.01
2007	Dry	0.001	0.001	-0.03	-0.005	0.001	0.002	-0.07	-0.01
	Wet	-0.004	0.005	-0.19	-0.04	0.002	-0.034	1.37	0.24
2008	Dry	-0.001	0.001	-0.04	-0.008	-0.002	-0.001	0.04	0.01
	Wet	-0.002	0.015	-0.40	-0.11	0.0004	-0.112	3.07	0.81
Average	Dry	0.006	0.001	-0.050	-0.003	-0.004	-0.016	0.639	0.109
e	Wet	0.052	0.012	-0.471	-0.036	0.009	-0.047	1.703	0.347

majority of the 2002-2008 budgets averaging 0.006 and $0.052 \text{ g N m}^{-2} \text{ d}^{-1}$ for the dry and wet seasons, respectively (Table 4). Internal DIN production did not dramatically increase with the loading of external DIN to the CRE despite a maximum input rate of $0.25 \text{ g N m}^{-2} \text{ d}^{-1}$ in the wet season of 2003 (Fig. 8a). There was no apparent net DIN production or consumption (~0.0 g N m⁻² d⁻¹) by the CRE when $T_{\rm f}$ > 10 d (Fig. 9a). Similar to Δ DIN, internal Δ DIP was positive averaging 0.001 and 0.012 g $Pm^{-2}d^{-1}$ suggesting that the CRE was heterotrophic $(-0.05 \text{ to } -0.47 \text{ g Cm}^{-2} \text{ d}^{-1})$ across all seasonal budgets (Table 4, Fig. 7c). There was no discernible relationship between Δ DIP and DIP loading or flushing time (Figs. 8b, 9b). NEM of the CRE signified a balance between internal production and consumption of primary production over all seasonal budgets. Moreover, average seasonal $N_{fix}D$ was negative in both the dry (-0.003 g $Nm^{-2}d^{-1}$) and wet (-0.036 g $Nm^{-2}d^{-1}$) seasons indicating net denitrification with an order of magnitude more occurring in the wet season (Table 4). $N_{fix}D$ did not fluctuate with NEM in the CRE (Fig. 10a).

3.2 St. Lucie Estuary

Rainfall directly to the surface of the SLE ranged from 0.05 to $0.9 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ across all seasonal budgets (Fig. 3a). Except for the extreme value of $0.9 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ in the wet season of 2004, total seasonal rainfall was $\leq 0.1 \times 10^6 \text{ m}^3 \text{ d}^{-1}$. Freshwater discharge to the SLE was variable with maximum values of $\sim 10 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ in the wet seasons of 2003–2005 followed by low inflow for both dry and wet seasons beginning in 2006 (Fig. 3b). Surface water inflow was very low from 2007 to 2008. Basin inflow was proportional to surface discharge across all seasons (Fig. 3c).

Salinity in the SLE was inverse to freshwater discharge ranging from 6 to 20 in both wet and dry seasons of 2002-2004 after which values decreased to < 2.0 in the wet season of 2005 (Fig. 4a). The salinity of the SLE decreased from $27.0 \text{ to} < 2.0 \text{ with increased freshwater inflow across all wa$ ter budgets from 2002 to 2008 (Fig. 5a). Average salinity increased to 27.0 in the dry season of 2007 when discharge was least and $T_{\rm f} = 40$ days (Fig. 6a). Estuary-wide, average DIN concentrations exhibited inter-annual fluctuations similar to patterns of inflow from 2002 to 2008 (Fig. 4b). DIN_e ranged $0.09-0.20 \text{ g m}^{-3}$ from 2002 to 2005 before increasing to 0.35 g m^{-3} in wet season of 2004. Seasonally averaged DIN concentrations decreased in both dry and wet seasons from 2006 to 2008. Over all seasonal budgets, the concentration of DIN in the SLE increased linearly from 0.0 to 0.38 g m^{-3} as external loading approached $0.20 \text{ g N m}^{-2} \text{ d}^{-1}$ $(r^2 = 0.85;$ Fig. 5b). The relationship between flushing time and DIN suggested that concentrations in the SLE declined hyperbolically reaching a minimum of $0.1 \,\mathrm{g \, m^{-3}}$ when $T_{\rm f}$ > 10 d (Fig. 6b). Wet season DIP concentrations were generally 2.5 times greater than in the dry seasons of 2002-2008 (Fig. 4c, Table 4). DIPe concentration reached an apparent saturation at $0.20 \,\mathrm{g}\,\mathrm{m}^{-3}$ with increased external DIP loading (DIP_O) ranging up to $0.4 \text{ g N m}^{-2} \text{ d}^{-1}$ (Fig. 5c). The hyperbolic relationship for DIP_e was inverted when T_f served as the independent variable with concentrations declining as flushing time was > 10 d (Fig. 6c).

DIN was produced within the SLE (Δ DIN > 0.0) in the 2002, 2004 and 2005 wet seasons (Fig. 7a). DIN was consumed (Δ DIN < 0.0) by the estuary in the wet seasons of 2003 and 2006 and the dry seasons of 2004 and 2005 (Table 4). Internal DIN production increased slightly with

Table 5. Comparisons among attributes of CRE and SLE. Rate values were averaged across all DIP and DIN budgets derived for each estuary (2002–2008). Shown are estuary surface area, flushing time ($T_{\rm f}$), freshwater discharge (Q), daily DIP and DIN loading (DIP_Q and DIN_Q), internal production (+) or consumption (–) of DIP and DIN (Δ DIP and Δ DIN), net ecosystem metabolism (NEM), and the relative difference between nitrogen fixation and denitrification ($N_{\rm fix}$ D > 0.0 = net N₂ fixation; N_{fix}D < 0.0 = net denitrification). The final row provides the trophic status in terms of production vs. respiration (+NEM = p > r = autotrophic; -NEM = p < r = heterotrophic). The final column provides the ratio of values between the estuaries (CRE : SLE) in terms of surface area, $T_{\rm f}$, Q, and DIP_Q and DIN_Q.

Attribute	Unit	CRE	SLE	CRE: SLE
Surface Area	km ²	56	22	2.5
T_{f}	d	18.4	11.4	1.6
Q	$10^6 \mathrm{m}^3 \mathrm{d}^{-1}$	6.3	3.1	2.0
DIPO	$g P m^{-2} d^{-1}$	0.003	0.005	0.6
DINQ	$g N m^{-2} d^{-1}$	0.005	0.007	0.7
ΔDIP	$g P m^{-2} d^{-1}$	0.014	-0.031	
ΔDIN	${ m g~Nm^{-2}d^{-1}}$	0.055	0.002	
NEM	$g C m^{-2} d^{-1}$	-0.544	1.171	
N _{fix} D	${ m g~Nm^{-2}d^{-1}}$	-0.043	0.228	
Trophic Status	<i>p</i> vs. <i>r</i>	heterotrophic	autotrophic	

Table 6. Summary of average DIP and DIN loadings (DIP_Q and DIN_Q) and system DIP (Δ DIP) and DIN (Δ DIN) production (+) or consumption (-) from several studies using the LOICZ methods. Similar units were derived among the studies for loadings (moles m⁻² yr⁻¹) and production/consumption (mmol m⁻² yr⁻¹). Studies with daily rates were multiplied by 182.5 days to calculate seasonal values that were summed to derive annual estimates. Studies reporting a single daily rate were multiplied by 365 days to derive annual estimates.

				DIPQ	ΔDIP	DINQ	ΔDIN
Reference	Estuary	Size (km ²)	$T_{\rm f}$ (days)	$ m molm^{-2}yr^{-1}$	$ m mmolm^{-2}yr^{-1}$	$ m molm^{-2}yr^{-1}$	$\rm mmolm^{-2}yr^{-1}$
Que et al., 2003	Lake Illawarra, Australia ^a	35					
	LIA, 1995				1.37		26.5
	Miller, 1998		56		7.43		-119.9
	Qu, 2001		33		12.43		-85.8
Hung and Huang, 2005	Tsengwen Estuary, Taiwan	2,3,4 ^b	150, 4.5, 1 ^b		-83.0		-4484.6
Gazeau et al., 2005	Randers Fjord, Denmark	23	13		65.7		
Boonphakdee and Fujiwara, 2008	Bangakong Estuary, Thailand	~ 23	15.2		109.5		930.8
Giordani et al,. 2008	LOICZ and Italian lagoons ^c						
	$LOICZ_1 (n = 94)$	< 2500		0.31	146.5	5.3	2423.0
	$LOICZ_2 (n = 61)$			0.11	35.3	2.4	-813.0
	LaguNet $(n = 17)$		2 d to 3 yr ^c	0.04	-13.7	1.2	-761.0
Noriega and Araujo, 2011	Barra da Jangandas Estuary, Brazil	13	8-16	0.11	2190.5	0.03	-1292.8
This Study							
	CRE	57	18.4	0.08	159.6	0.41	1429.9
	SLE	22	11.3	0.65	-367.2	0.97	63.0

The entreformation of tailing large the LOCZ budgeting includes to the Lake mawara estuary in Australia. The received in stuary includes dry, were and nood seasons with unrecent values not estuary size and nusling time. LOICZ metrics for a network of tailing lagoons. (LaguNet) were compared to those derived for a group of estuaries that were $<2500 \text{ km}^2$ in size (LOICZ₁; n = 94) and a sub-set of smaller estuaries (LOICZ₂; n = 61). T_f estimates varied greatly among the 17 Italian lagoons.

external DIN_Q up to a maximum loading rate of 0.18 g N m⁻² d⁻¹ in the wet season of 2004 (Fig. 8a). Net estuarine DIN production/consumption hovered near 0.0 g N m⁻² d⁻¹ when $T_{\rm f} \ge 10$ d (Fig. 9a).

ΔDIP within the SLE was more variable and revealing than Δ DIN. The SLE generally produced DIP (ΔDIP > 0.0) in the wet seasons of 2002–2004 (Fig. 7b; Table 4). However, DIP was consumed (ΔDIP < 0.0) at rates of −0.05 to −0.30 g P m⁻² d⁻¹ in 2005 and the dry season of 2006. Internal DIP consumption became more negative as DIP_Q increased to 0.4 g P m⁻² d⁻¹ (Fig. 8b). Similar to DIN dynamics, Δ DIP was near zero when *T*_f ≥ 10 d (Fig. 9b). NEM was inverse to internal DIP consumption with maximum values of 1.0–12.0 g C m⁻² d⁻¹ (Fig. 7c) that increased linearly with the external DIP load (Fig. 8c). Thus, both Δ DIP and NEM approached 0.0 when $T_{\rm f} \ge 10$ d (Fig. 9b, c). The average relative difference between N₂ fixation and denitrification (N_{fix}D) was positive in both dry (0.109 g N m⁻² d⁻¹) and wet seasons (0.347 g N m⁻² d⁻¹) in the SLE (Table 4). The proportion of N₂ fixation (N_{fix}D > 0.0) increased linearly with NEM, which increased with external DIP loading (Fig. 10a). Closer inspection revealed that SLE ecosystem metabolism may be sensitive to the DIN : DIP loading ratio as NEM (g C m⁻² d⁻¹) and relative N₂ fixation (g N m⁻² d⁻¹) decreased to < 0.0 when the molar ratio of externally supplied nutrients was 3 : 1 (Fig. 10b, c). The wet season of

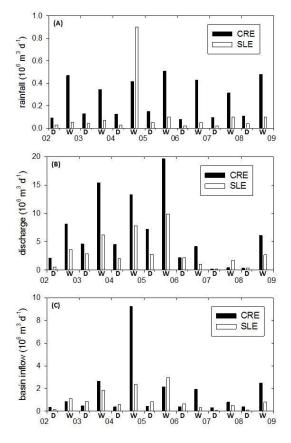


Fig. 3. Comparative seasonal time series of water budget components for CRE and SLE. CRE (filled) and SLE (open) bars are paired seasonally with the first pair of each year representing the dry season. All values are in $10^6 \text{ m}^3 \text{ d}^{-1}$. (A) Rainfall; (B) discharge; (C) basin inflow = tributaries + ground water.

2005 had the lowest DIN : DIP loading ratio (~ 1.0), the most NEM (~ 12 g C m⁻² d⁻¹), and the greatest relative N fixation (~ 2.2 g N m⁻² d⁻¹).

4 Discussion

The Caloosahatchee and St. Lucie estuaries on opposite sides of Florida are small, sub-tropical water bodies with highly modified watersheds (Barnes, 2005; Sime, 2005). While natural variations in freshwater inflow and associated salinity changes are part of estuarine dynamics, anthropogenic modification of water delivery to afford flood protection and public safety can create unstable salinity distributions that adversely affect estuarine biota. The direct physical consequences of high flow events in the wet season can lead to low salinity throughout both of these estuaries. Rapid decreases in salinity can make it difficult for benthic organisms such as oysters and seagrass to survive (Buzzellli et al., 2012, 2013a). Conversely, periods with low freshwater input indicative of the dry season permits upstream in-

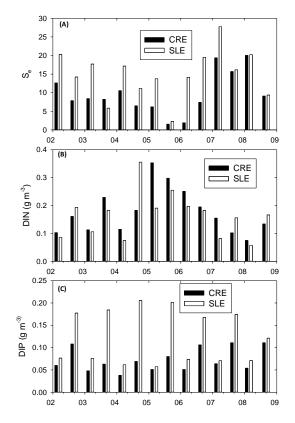


Fig. 4. Comparative seasonal time series of water budget components for CRE and SLE. CRE (filled) and SLE (open) bars are paired seasonally with the first pair of each year representing the dry season. (A) Salinity; (B) DIN $(g m^{-3})$; (C) DIP $(g m^{-3})$.

trusion of saltier water that endangers estuarine organisms with freshwater-dependent life cycles (Adams et al., 2009; Tolley et al., 2010; Simpfendorfer et al., 2011). Although both coastal water bodies possess similar watershed patterns of agriculture and urbanization and ranges in flushing time, these two estuaries have very different biogeochemical attributes (Table 5).

This study demonstrated that the CRE responded to external DIN loading by producing internal DIN at an average rate of 1429 mmol m⁻² yr⁻¹ (Table 6). A similar result was reported for the 23 km^2 , sub-tropical Bangakong Estuary in Thailand (930.8 mmol m⁻² yr⁻¹), which has a flushing time of 15.2 d (Table 6; Boonphakdee and Fujiwara, 2008). It is likely that the increased concentration of DIN in the CRE during the wet season was due to heightened rates of remineralization and denitrification in response to increased DIN loading and primary production. In contrast, estuaries in Australia (Lake Illawarra), Taiwan (Tsesngwen Estuary), and Italy (several lagoons) responded to DIN loading by consuming DIN on annual timescales (Que et al., 2003; Hung and Huang, 2005; Giordani et al., 2008, Noriega and Araujo, 2011).

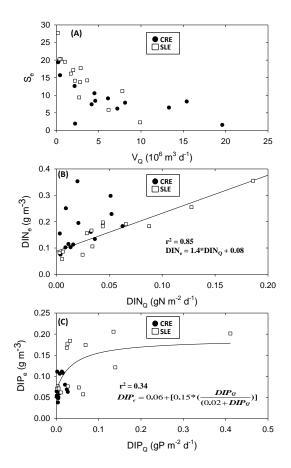


Fig. 5. Scatter plots from seasonal DIN and DIP budgets for CRE and SLE from 2002 to 2008. (**A**) Freshwater discharge (V_Q) vs. estuary salinity; (**B**) external DIN load (g N m⁻² d⁻¹) vs. estuary DIN concentration (g m⁻³); (**C**) external DIP load (g P m⁻² d⁻¹) vs. estuary DIP concentration (g m⁻³). Regression lines, r^2 values, and equations provided for the SLE points only.

Compared to the CRE, the response of the SLE to DIN loading was less clear with N₂ fixation in excess of denitrification for all seasonal budgets. Empirical measurements of denitrification from both estuaries reinforced the notion that denitrification is an important sink for nitrogen in the CRE but not the SLE (Table 5; Howes et al., 2008, b). It is suspected that biogeochemical feedbacks including coupling of nitrification-denitrification at the sediment-water interface could account for the observed differences between the CRE and SLE (Kemp et al., 2005). The water column is more isolated from the benthos in the SLE due to the presence of muck-like sediments and considerably reduced light penetration across the estuary (Sime, 2005; Buzzelli et al., 2013b). Since LOICZ results are dependent upon stoichiometric assumptions and DIP dynamics, it is possible that DIN budgets are confounded in benthic-dominated estuaries with low DIN concentrations and significant denitrification (Swaney et al., 2011). This could be the case for the CRE.

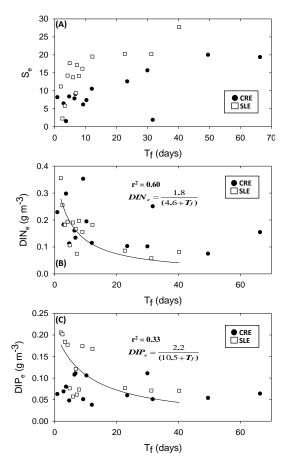


Fig. 6. Scatter plots from seasonal DIN and DIP budgets for CRE and SLE from 2002 to 2008. Estimated flushing time (T_f ; days) provided the independent variable vs. (**A**) salinity; (**B**) estuary DIN concentration (g m⁻³); (**C**) estuary DIP concentration (g m⁻³). Regression lines, r^2 values, and equations provided for the SLE points only.

The budgets revealed that the internal production of C, N, and P was more influenced by external loading to the SLE than the CRE. While the CRE is 2.5 times larger and receives twice the freshwater inflow, spatially normalized DIP and DIN loadings are only 60-70% of those to the SLE (Table 5). Water column DIP concentrations, DIP consumption, and system autotrophy increased with external DIP loading to the SLE. A similar positive relationship between DIP loading and net primary production has been reported for an estuary in Taiwan and several eutrophied Italian lagoons (Table 6; Hung and Huang, 2005; Giordani et al., 2008). In contrast, annual estimates of ΔDIP were positive in estuaries such as Randers Fjord, Denmark $(65.7 \text{ mmol m}^{-2} \text{ yr}^{-1}; \text{ Gazeau et al., 2005}); \text{ Bangakong Es-}$ tuary, Thailand (109.5 mmol $m^{-2} yr^{-1}$; Boonphakdee and Fujiwara, 2008); and the CRE $(159.6 \text{ mmol m}^{-2} \text{ yr}^{-1}; \text{ this})$ study). Although drainage and discharge typically deliver much of the P required for primary production in south

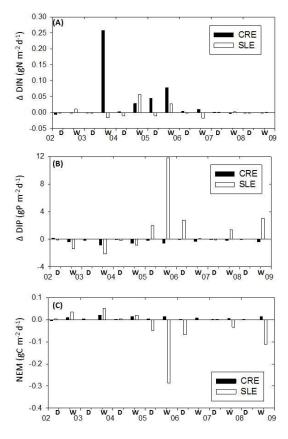


Fig. 7. Comparative seasonal time series of internal CNP source/sink processing for CRE and SLE. CRE (filled) and SLE (open) bars are paired seasonally with the first pair of each year representing the dry season. (**A**) Δ DIN (g N m⁻² d⁻¹); (**B**) Δ DIP (g P m⁻² d⁻¹); (**C**) NEM (g C m⁻² d⁻¹).

Florida estuaries (Koch et al., 2011), there is additional potential for eutrophication of the SLE through combined water column and benthic regeneration of DIP that fuels primary production (Buzzelli et al., 2013b).

The magnitude of freshwater, DIN, and DIP inputs relative to the flushing time provide the setting for interesting biogeochemical dynamics in the SLE (Dettman 2001; Sheldon and Alber, 2006). In the absence of freshwater inflow, the flushing time of the SLE is approximately 20 d solely through tidal exchange (Y. Wan and D. Sun, unpublished data). Nutrient budget results suggested that both the concentrations and internal utilization of DIP and DIN stabilized with flushing times greater than 10d. Longer water residence times allow for increased grazing and sedimentation to respond to primary production and balance system metabolism (Buzzelli et al., 2007; Lucas et al., 2009; Phlips et al., 2011; Swaney et al., 2011). In fact, it appears that the negative relationship between flushing time and NEM observed in this study is a common attribute of many estuaries (Fig. 11). If T_f in the SLE is < 10 d as it is much of the time (Ji et al., 2007), then the inputs of freshwater and nu-

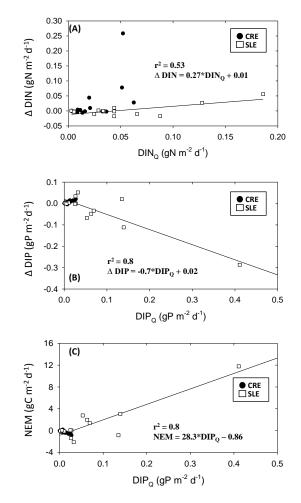


Fig. 8. Scatter plots from seasonal DIN and DIP budgets for CRE and SLE from 2002 to 2008. (A) Δ DIN (g N m⁻² d⁻¹); (B) Δ DIP (g P m⁻² d⁻¹); (C) NEM (g C m⁻² d⁻¹). External DIN load (g N m⁻² d⁻¹) or DIP load (g P m⁻² d⁻¹) provided the independent variable. Regression lines, r^2 values, and equations provided for the SLE points only.

trients result in rapid DIP consumption, a spike in autotrophy, increased N₂ fixation, and the potential for DIN export to the coastal ocean. For example, rates of estuarine DIP consumption ($-3.0 \text{ g Pm}^{-2} \text{ d}^{-1}$), NEM ($12 \text{ g Cm}^{-2} \text{ d}^{-1}$), and N_{fix}D ($2.3 \text{ g Nm}^{-2} \text{ d}^{-1}$) were all maximized in the wet season of 2005. In the case of extreme freshwater inflows and rapid flushing ($T_{\text{f}} < 1 \text{ d}$), both allochthonous and autochthonous materials are transported from the estuary to the coastal ocean (Doering et al., 2006; Murrell et al., 2007; Phlips et al., 2011). Reliable estimates of freshwater inflow and nutrients along with knowledge of flushing time offer a platform to quantify and link external loading to internal ecosystem metabolism (Fig. 11; Dettmann, 2001; Sheldon and Alber, 2006; Swaney et al., 2011).

Nitrogen limitation of phytoplankton in controlled bioassays on daily timescales suggested that reductions in

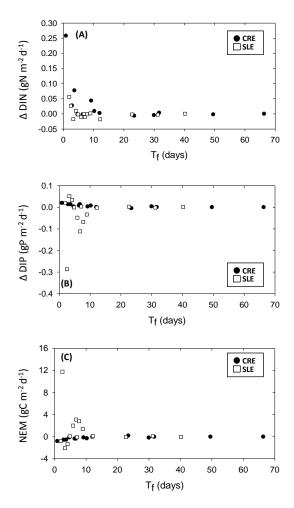


Fig. 9. Scatter plots from seasonal DIN and DIP budgets for CRE and SLE from 2002 to 2008. Estimated flushing time (T_f ; days) provided the independent variable vs. (**A**) Δ DIN (g N m⁻² d⁻¹); (**B**) Δ DIP (g P m⁻² d⁻¹); (**C**) NEM (g C m⁻² d⁻¹).

N loading could decrease primary production in the SLE (Phlips et al., 2011). This result is reasonable given that N has been emphasized as the dominant limiting nutrient in estuaries (Howarth and Marino, 2006). However, the extrapolation of knowledge gained from fine-scale experiments to the seasonal estuary scale may not be appropriate because of feedbacks related to internal biogeochemical cycling (Kemp et al., 2005; Wulff et al., 2011). This may be particularly true for N and P recycling within the SLE where there is surplus DIN produced under increased DIP loading. While increased freshwater inflow could provide the DIP required for N2 fixation, it is possible that benthic nitrogen fixation may be inhibited by lack of light penetration in the SLE (Howarth and Marino, 2006; Buzzelli et al., 2013b). Despite the result that N₂ fixation exceeded denitrification in the SLE, it is possible that N₂ fixation may be negligible since the phytoplankton community is composed of diatoms and dinoflagellates (Millie et al., 2004; Phlips et al., 2011). Smith (1990) hy-

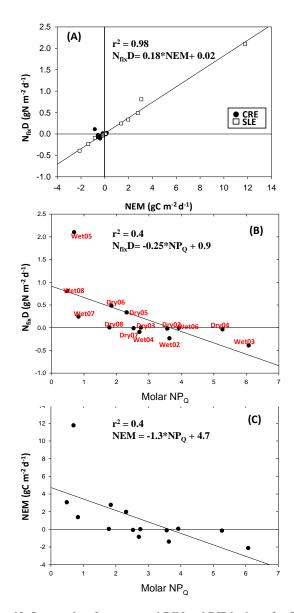


Fig. 10. Scatter plots from seasonal DIN and DIP budgets for CRE and SLE from 2002 to 2008. (**A**) Both the CRE (filled circles) and the SLE (open squares) presented with net ecosystem metabolism (NEM) vs. the difference between N₂ fixation and denitrification (N_{fix}D). Regression lines, r^2 values, and equations provided for the SLE points only. (**B**) Scatter plots of seasonal values from the SLE from 2002 to 2008. Relationship between the DIN : DIP ratio of loading (independent) and N_{fix}D (dependent). (**C**) Relationship between the DIN : DIP ratio of loading as the independent variable and NEM as the dependent variable.

pothesized that when DIN supply is great, non-heterocystous phytoplankton can proliferate if provided with adequate P supply. This appears to be the case as the SLE experienced a huge bloom of the toxic, non-heterocystous cyanobacterium *Microcystis aeruginosa* with the extreme inputs of freshwater and nutrients in 2005 (Phlips et al., 2011).

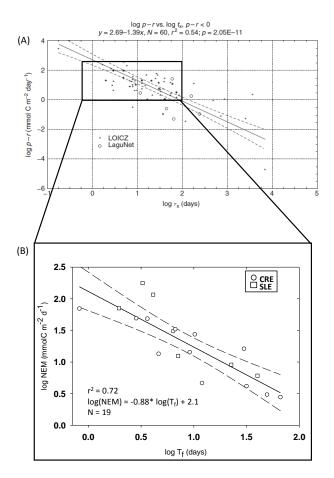


Fig. 11. Integrated results demonstrating the relationship between flushing time (T_f ; days) and NEM (mmol C m⁻² d⁻¹). (**A**) Plot of estuaries from the LOICZ database with negative NEM, adopted with permission from Swaney et al. (2011). (**B**) Similar results from the CRE and SLE confined to seasonal budgets with negative NEM (N_{CRE} = 13; N_{SLE} = 6). Values resulted from log transformation of the absolute values of NEM in each of the 19 cases. Provided are the linear regression information and 95 % confidence intervals (dashed lines).

The recognition that sub-tropical estuaries have the potential to respond to both N and P inputs is an important step to establish nutrient load limits (Smith et al., 2006; Howarth and Marino, 2006; Wulff et al., 2011). However, merely setting criteria for either total or dissolved nutrient loading based on their correlation to water column concentrations fails to appreciate the complexity and uncertainty of estuarine biogeochemical cycling (Dodds, 2003). In both the discharge and the receiving basin, the DIN: DIP ratios are often very different than the TN: TP ratios due to the differential composition and reactivity of dissolved organic N and P (DON and DOP; Smith et al., 2005). The assessment of particulate and dissolved organic fractions of the TN and TP pools requires a modification of the existing LOICZ protocol (Hung and Huang, 2005).

Freshwater inflow to the SLE has a comparatively high TN: TP ratio ($\sim 14:1$), but a much reduced DIN: DIP ratio (\sim 3.0; Doering 1996; SFWMD 2012a). While most of the TP is available as DIP (DIP : TP = 0.7), most of the TN is in the form of DON with DIN comprising only 30% of TN. It is possible that autochthonous DOP production and contribution to NEM could confound LOICZ results in some estuaries (Gazeau et al., 2005). DON is a potentially important component in CNP cycling in CRE, which possesses comparatively low concentrations of water column N (Hung and Huang, 2005; Eyre et al., 2011). Like many estuaries, there is limited understanding about the effects of DOP and DON cycling on primary production and system metabolism in the SLE and CRE (Smith and Hollibaugh, 2006; Loh, 2008). Future studies should examine the partitioning and reactivity of TP and TN external loading and internal concentrations including dissolved and particulate organic and inorganic fractions. Knowledge of the role and reactivity of TN and TP constituents would support the contention that the regulation of both nutrients should be considered (Smith, 2006; Paerl, 2009; Conley et al., 2009).

LOICZ was designed to estimate carbon metabolism for estuaries around the world where salinity and inorganic nutrient concentrations, and not biogeochemical rate processes, provided a bulk of the available data (Swaney et al., 2011). The approach assumes that estuaries can be represented as well-mixed, homogeneous boxes. This assumption creates the potential for errors if an estuary possesses spatial and/or vertical variability in conservative (salinity) and nonconservative (CNP) properties (Webster et al., 2000). While the CRE and the SLE are often well-mixed over depth, there can be horizontal gradients between the headwaters and the oceanic boundary during some inflow conditions (Buzzelli et al., 2013b). A modification that could improve the reliability of the LOICZ approach would be to split each estuary into segments based upon predominant salinity and nutrient gradients in the dry and wet seasons. To further refine the approach, in situ rates of dissolved CNP exchanges across the sediment-water interface for different years could be introduced to improve system-level calculations and estimates (Buzzelli et al., 2013b).

It is possible that generating LOICZ budgets using annually averaged data could increase the error inherent in the calculations (Webster et al., 2000). This potential source of error is mitigated in the present study due to the availability of intra-seasonal and intra-annual data used to develop the LOICZ nutrient budgets. Overall, estimates of external nutrient loading, estuarine flushing, and internal CNP cycling derived in this study should be viewed as highly reliable given the quantity and quality of the monitoring data and the predictable relationships between system physical attributes and biogeochemical signatures (Smith et al., 2005; Swaney et al., 2011). The observed relationship between flushing time and NEM is in agreement with that determined for a large number of estuaries where LOICZ was applied (Fig. 11).

Smaller estuaries such as the CRE and SLE that are subjected to high material loading and fast flushing are very important components in biogeochemical cycling at the local, regional, and global scales (Smith et al., 2005). The LOICZ approach to estuarine nutrient budgets offers a highly transferrable method to link watershed inputs to biogeochemical responses for a variety of coastal embayments (Swaney et al., 2011). While the LOICZ approach has been applied to hundreds of coastal water bodies, its value to coastal management is dependent upon the quality of input data, the reliability of the steady-state and stoichiometric assumptions, and the connectivity between the watersheds and the estuaries (Smith et al., 2005; Swaney et al., 2011). This study provided an improved understanding of the relationships among seasonal variations in watershed N and P loading, hydrodynamic flushing time, nutrient cycling, and ecosystem metabolism for sub-tropical estuaries with heavily modified watersheds (Millie et al., 2004; Phlips et al., 2011; Eyre et al., 2011).

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