

# SEASONAL NUTRIENT FLUXES IN THE OGEECHEE RIVER ESTUARY

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**Abstract.** Seasonal distribution and inventories of nutrients (organic and inorganic N & P), dissolved organic carbon (DOC), and chlorophyll were obtained from seven survey transects of the Ogeechee River from August, 2015, to April, 2016. Riverine freshwater residence times ranged from ~45 days in the late summer to ~5 days in the winter. A box model approach was used to estimate the export and internal cycling of individual constituents. Riverine inflows of all constituents were primarily a function of river discharge and were an order of magnitude greater during the high flow winter/spring period than the low flow summer/fall period. Exports of most constituents were proportional to inputs (i.e., greater during high flow periods), but were strongly modified by internal cycling processes within the estuary. In particular, net import of phytoplankton biomass from the coastal ocean and subsequent degradation of the particulate carbon, nitrogen, and phosphorus were major contributors to the net exports of dissolved nutrients from the estuary.

## INTRODUCTION

The balance between import fluxes at the riverine endmember and export fluxes at the marine endmember represents the sum of all internal biogeochemical transformations within an estuary. Simple flux balance approaches provide limited information about the locations of nutrient transformations or of the chemical or biological intermediates involved in them, but, given the dearth of fundamental information about nutrient concentrations and nutrient cycling in Georgia estuaries, even simple approaches can advance our understanding of material processing at the land/sea interface.

We used a simple box modeling approach (Officer 1979, Kaul and Froelich 1984) to estimate the seasonal and annual fluxes of multiple constituents in the Ogeechee river estuary based on the results of seasonal survey transects along the estuarine axis. Export of most dissolved constituents at the estuary mouth was greater than their riverine import at the head of the estuary. Comparison of dissolved exports with particulate imports (as chlorophyll a) suggests that the additional export flux could be supported almost entirely by import of phytoplankton biomass from the coastal ocean.

## METHODS

Seven seasonal transects from the mouth of the Ogeechee River (31.83N, -81.02W) to freshwater (< 0.1 PSU) were undertaken to assess the concentrations and fluxes of nutrients and other water column properties within the estuary. Surveys were timed to sample the estuary low and high river flows and during times of both low and high water temperatures (Figure 1). All surveys began at or just before a neap low tide at the estuary mouth and proceeded upriver at ~ 8 knots, or approximately the rate of propagation of the incoming tidal wave upriver, thus allowing all sampling along the tidal axis to be undertaken at the same tidal stage. A flow-through underway sampling system (Savidge et al. 2016) was used to sample surface waters continuously while underway. The flow through instrumentation consisted of a Hummingbird 797 C25 depth finder and GPS unit, a Seabird SBE-21 CTD, a YSI 600 OMS oxygen sonde, a Wetlabs FLNTU chlorophyll and turbidity sonde, a Wetlabs FLCD organic matter fluorescence (fDOM) sensor, and a S::CAN “spectro::lyzer” scanning absorbance spectrometer. All instruments sampled continuously while underway to generate a high-resolution map of property distributions along the estuarine axis.

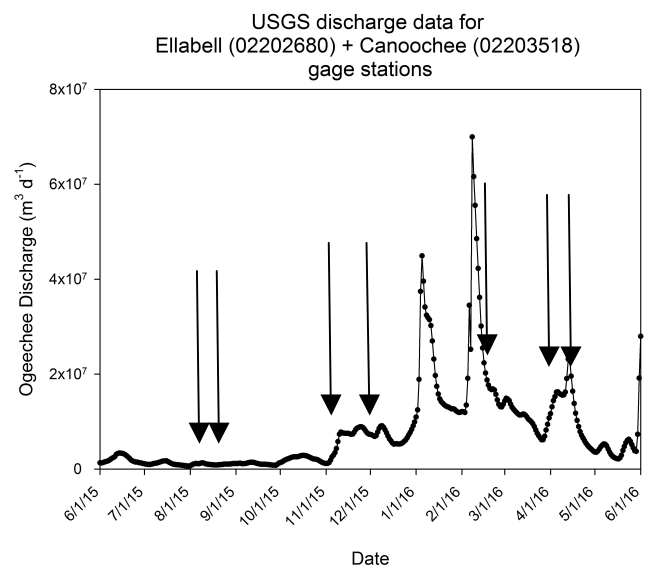


Figure 1. Ogeechee River discharge and sampling dates (arrows).

At ~3 PSU intervals, bottle samples were collected for analysis of nutrients and chlorophyll. 50 ml samples for analysis of nutrients were syringe filtered through a 0.2 um Target filter into 60 ml Nalgene bottles while underway, and the filtrates were stored on ice. All nutrients samples were express shipped for analysis to the JBL Analytical Services lab at the University of Georgia the following day. DOC and TDN were analyzed on a Shimadzu TOC-V with a TN unit. NO<sub>2</sub> was quantified according to the procedures outlined in Bendschneider and Robinson (1952). Total NO<sub>x</sub> was measured as NO on an Antek detector and NO<sub>3</sub> was calculated by difference. Ammonium was also quantified, but the data were compromised by blanks in excess of field values, and were discarded.

During each transect, chlorophyll samples were vacuum filtered under a shroud to shield them from ambient light. Samples were collected as triplicate 40 ml aliquots. Particulates collected onto an ashed 25 mm GF/F filters were stored on ice in the field and were analyzed within 48 hours at the Skidaway Institute of Oceanography. Filters were extracted with 90% acetone for 4-6 hours at -20°C in darkness, sonicated, and then re-extracted for an additional hour. Centrifuged extracts were analyzed for chlorophyll content on a Turner AU-10 fluorometer using standard protocols (Strickland and Parsons 1972).

Low tide river volumes were obtained for two km sections of the river from Mike Robinson at Skidaway Institute. Average values for constituent concentrations were calculated for each section. For continuous sonde data, all individual sonde readings from within the section were averaged. Nutrient station data were collected at greater than 2 km intervals, so the data were first linearly interpolated between stations, and then the averages for the 2 km interpolated sections were calculated.

To obtain fluxes, averaged salinity and nutrient data were refit to smoothed piecewise hermite (PCHIP) splines interpolated to 0.1 km intervals. Derivatives of spline curves were obtained numerically. At any point within the estuary, the seaward flux of constituents can be calculated as:

$$(1) \text{ Flux} = R \times (C - S_{\%} * (\delta C / \delta S_{\%})) = R \times C^*$$

Where R is the riverine water flux (m<sup>3</sup> d<sup>-1</sup>), C is the constituent concentration, S<sub>%</sub> is the salinity at that location, and δC/δS<sub>%</sub> is the gradient in the constituent with respect to salinity (Officer 1979; Kaul and Froelich 1984). The quantity C\* represents the riverine endmember concentration that would be required to support the concentration at any point if that constituent behaved conservatively. At any point, if C\* > C<sub>S=0‰</sub>, then there must be a net addition of C upstream. Conversely, if C\* < C<sub>S=0‰</sub>, there must be net removal. C\* at the seaward endmember represents the

net flux of C out of the estuary, and the sum of all internal addition and removal processes within the estuary can be represented as C<sub>sw</sub>\* - C<sub>0</sub>.

For each of the seven sampling dates R\*C<sub>0</sub> and R\*C<sub>sw</sub>\* were calculated, and the internal estuarine fluxes were obtained by difference. To estimate annualized fluxes, the 9-month sampling period of this study was augmented by two “phantom” dates (July 1 and August 4, 2016) to extend the time series through the low-flow time period at the beginning of the summer. Numerical values for all constituents for the phantom dates were set to the same values as the initial summer data point of August 4, 2015. A PCHIP spline was used to interpolate daily fluxes between the sampling cruises. The addition of the phantom point of July 1, 2016, was used to force the curves to respond more quickly to the attenuation of river flows during the summer months. Total annualized fluxes were calculated as the summation of the modeled daily fluxes.

## RESULTS

Nitrate fluxes through the Ogeechee River estuary were dominated by high discharges in the winter and spring (February-April) (Figure 2). In the summer, when riverine freshwater fluxes were lower, the magnitudes of the fluxes of nitrate were an order of magnitude lower than during the high flow season. During the low-flow months the estuary removed ~90% of the riverborne nitrate. In contrast, in February, 2016, the estuary removed only 30% of the nitrogen inflow, although the rate of NO<sub>3</sub> removed during estuarine transit during the February 2016 sampling was greater than during the summer (4.9 x 10<sup>4</sup> moles d<sup>-1</sup> vs 1.6 x 10<sup>4</sup> moles d<sup>-1</sup>). During the second fall transect (12/6/2015) and the first spring transect (4/4/2016) the estuary was a net source of NO<sub>3</sub>, with exports exceeding imports by 157% and 25% respectively. On an annualized basis, the estuary removed ~16% of riverine nitrate inflows.

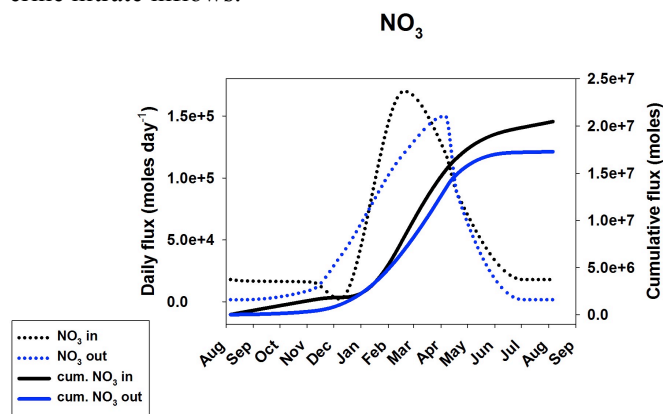


Figure 2: Daily and cumulative nitrate fluxes.

Riverine nitrite inputs into the estuary were more than an order of magnitude smaller than for nitrate. In contrast to nitrate, internal consumption of nitrite within the estuary greatly exceeded inflows, and there was consequently a net import of nitrite into the estuary from the coastal ocean for most of the year. Nitrite fluxes were highly variable, with fluxes oscillating between net import and net export at the mouth of the estuary over the year. Import of  $\text{NO}_2$  from the ocean was greater during the summer than the winter.

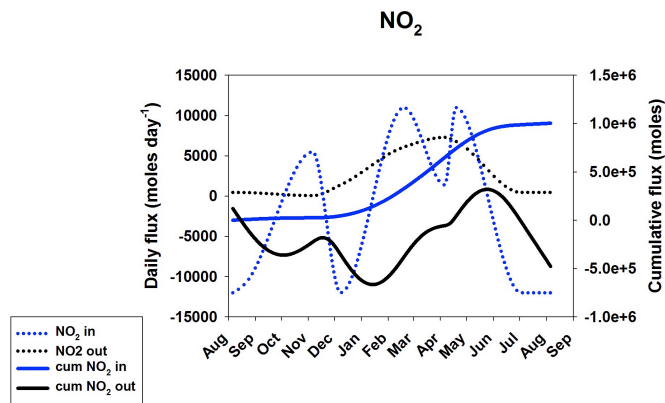


Figure 3: daily and cumulative fluxes of nitrite.

Dissolved organic nitrogen (DON) fluxes exceeded  $\text{NO}_3$  fluxes by an order of magnitude (Figure 4). On 6/7 sampling dates, the calculated export of DON from the estuary was greater than the riverine influx. Only on the first spring sampling date (4/4/2016) did there appear to be any consumption of DON within the estuary. On an annualized basis, DON exports at the mouth of the estuary were 50% greater than imports at the freshwater endmember.

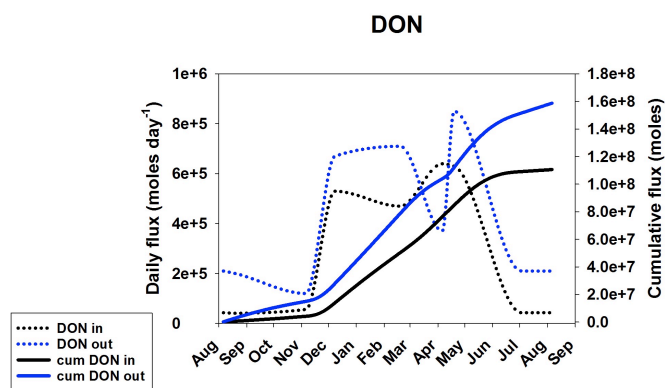


Figure 4: Daily and cumulative DON fluxes

Seasonal dissolved organic carbon (DOC) fluxes were very similar to those of DON with the exception that the very high DON fluxes observed in December, 2015,

were not seen for DOC. Annualized exports were 39% greater than annualized imports.

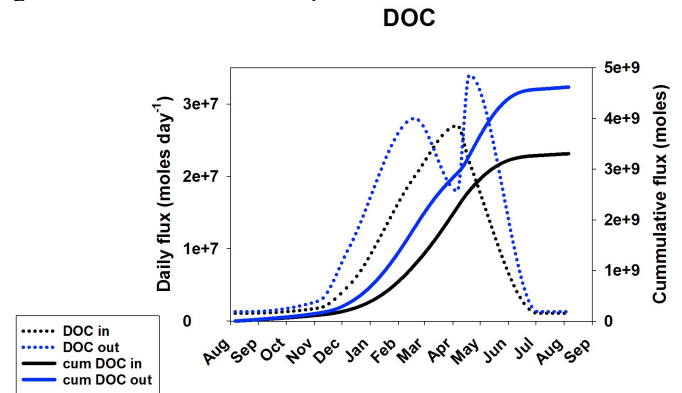


Figure 5: daily and cumulative fluxes of DOC

For the fDOM component of dissolved organic matter, exports modestly exceeded imports for most of the year (Figure 6). However, because of a large apparent influx of fDOM into the estuary during the first fall sampling, the annual net flux out of the estuary is almost identical to the flux in ( $1.8 \times 10^8$  quinine sulfate equivalents (QSEs) exported and  $1.7 \times 10^8$  QSEs imported).

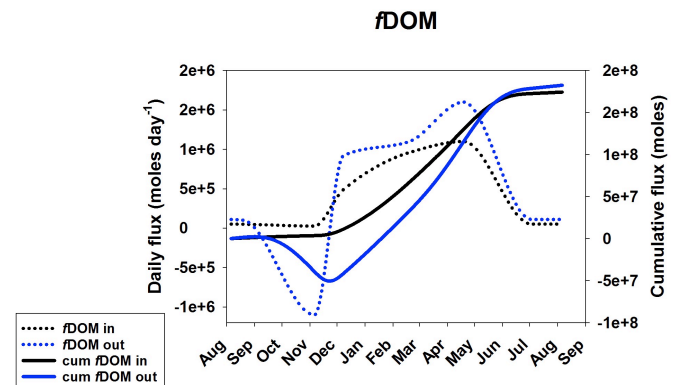


Figure 6: Daily and cumulative fluxes of fDOM

Phosphate fluxes were dominated by large exports in the fall after near zero exports during the summer (Figure 7). Net phosphate consumption in the estuary (exports < imports) were observed in the winter and spring sampling cruises.

Seasonal chlorophyll fluxes were dominated by large imports from the coastal ocean for most of the year (Figure 8). The exception was in the spring, when an apparent spring bloom within the estuary led to a net export of chlorophyll from the estuary.

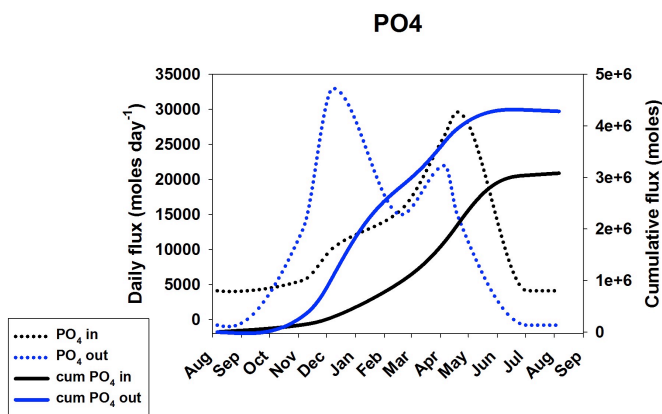


Figure 7: Daily and cumulative phosphate fluxes

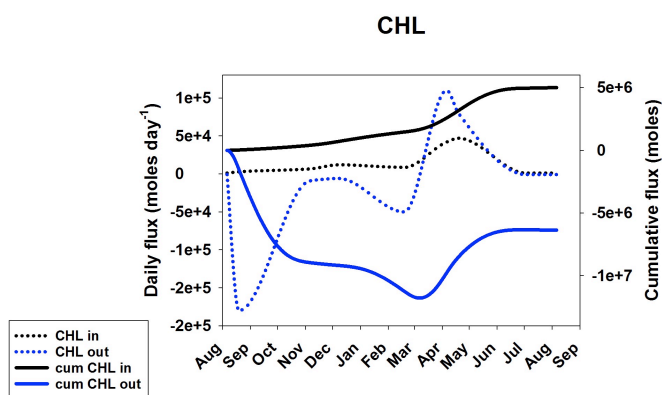


Figure 8: Daily and cumulative chlorophyll fluxes

### DISCUSSION

The results of this study must be interpreted conservatively because the conditions of this study depart from ideal conditions for the application of the box modeling technique. The data here are not tidally averaged, nor can the assumption of steady-state river flows be met, particularly for the winter/spring period when discharges were dominated by flood pulses. In addition, the summation of our sparse daily data into annualized totals should be regarded as an assessment of relative abundance and order of magnitude rather than as precise quantification of realized deliveries of constituents to the estuary and to the coastal ocean. Nevertheless, the trends reported here provide valuable insights into the mechanisms and timing of nutrient processing in the Ogeechee river estuary.

The most remarkable overall feature of the data set is the evidence for large within-estuary sources for DON, DOC and phosphate. For all three constituents, the estimated annualized exports from the estuary were ~40% greater than the riverine inputs. In contrast to these other constituents, nitrate showed a small (~15%) net consumption within the estuary when summed over an annual cycle. The discrepancy is likely to result from denitrification losses within the estuary that counter the diagenetic pro-

cesses for the other constituents that are contributing to the net export of those compounds. The estuary's capacity for denitrification can be crudely estimated. The similarity in net estuarine additions to riverine fluxes for DOC, DON and especially PO<sub>4</sub> (i.e., ~40% of riverine inputs) suggests a common source or contributing process. If the same process is assumed to be supplying NO<sub>3</sub> to the estuary, the potential resulting export of NO<sub>3</sub> should also be ~140% of its riverine input. From the simple model, it was estimated that annual riverine imports amounted to 2x10<sup>7</sup> moles NO<sub>3</sub>. A 40% increase over that flux would be 2.8x10<sup>7</sup> moles. Calculated export fluxes were 1.7x10<sup>7</sup> moles. The magnitude of that flux deficit indicates that approximately 40% of estuarine NO<sub>3</sub> from all sources is denitrified in the estuary and does not contribute to export to the coastal zone. Denitrification losses are greatest in the summer when temperatures are high and water residence time in the estuary is > 40 days.

The source of the excess export of nutrients is the importation of particulate matter into the estuary as phytoplankton chlorophyll. The Ogeechee estuary is consuming all the chlorophyll that enters it via the river, and it is consuming an equal flux of chlorophyll from the coastal ocean. On an annual basis, the estuary is a sink for ~1.1x10<sup>7</sup> grams of chlorophyll. If an average carbon:chlorophyll ratio of 200 is assumed, and a Redfield C:N:P ratio of 106:16:1 is applied, then the estuary consumes 1.9x10<sup>8</sup> moles of phytoplankton carbon, 2.9x10<sup>7</sup> moles of phytoplankton nitrogen, and 1.8x10<sup>6</sup> moles of phytoplankton phosphorus. These totals amount to 15% of the excess DOC flux and 60% of the excess DON flux. Moreover, the imported phytoplankton N is equal to 150% of the annualized river import and 170% of the annualized export of NO<sub>3</sub>. It is equivalent to 150% of the excess PO<sub>4</sub> flux and 40% of the total PO<sub>4</sub> export from the estuary.

In summary, this analysis of seasonal nutrient fluxes through the Ogeechee River estuary indicate that the riverborne nutrients entering the estuary contribute little to the estuary itself but pass through the estuary to fertilize the coastal ocean. There, aided by a more favorable light regime and an extended residence time, these nutrients produce a crop of phytoplankton that is then re-imported into the estuary by tidal exchange and other wind driven processes (e.g., Di Iorio and Castelao 2013). The particulate matter is quickly scavenged by the estuary – both by grazing and sedimentation onto the marsh surface -- and remineralized, after which it contributes to an enhanced export of dissolved constituents.

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