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#### CARBON, NITROGEN, AND PHOSPHORUS DISCHARGE FROM THE ALIAMAHA RIVER, GEORGIA

A Thesis

Presented to

The Faculty of the School of Marine Science The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements For The Degree of

Master of Arts

by

Frederick A. Hoffman

1989

#### APPROVAL SHEET

This thesis is submitted in partial fulfillment of the

requirements for the degree of

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## TABLE OF CONTENTS

ACKN	OWL	EDG	MEN	TS	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•	iv
LIST	OF	TA	BLF	S	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	v
LIST	OF	FI	GUR	ES	•	•	•	•	•	٠	٠	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	vi
ABST	RAC	г.	•••	•	•	•	•	•	٠	•	•	•	•	•	•	•	•	•	•	÷	•	٠	•	•	•	•	•	٠	•	viii
INTR	ODUC		ON.	•	•	•	٠	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	2
	Des	jec scr	ipt	ion		of	A]	Lta	ma	aha	1	Riv	vei	. a	and		5ta	,dy	7 S	511	te	•	•	•	•	•	•	•	•	5 6
METH	ODS	AN	D M	AT	ER	IAI	s	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	13
	Sar	npl	ing	l De	es:	igr	1.	٠	•	•	•	٠	•	•	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	٠	•	٠	•	٠	13
	Sar	mpl	e F	you,	œ	ຣຣງ	ing	J.	•	•	•		•	•	•	•	•	•	•	•	•	•	•	•		•	•	•	•	14
	Ana	alv	tic	al	Me	etł	100	İs		•	•		•					•									•	•		15
	Sta	ati	sti	ca	11	Pro	x	d	m	s	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	17
RESU	LITS	AN	DD	oiso	WS	551		1.	•	•	•	•	•		•		•	•	•	•	•	•	•	•	•	•	•	•	•	20
	Phy	/si	cal	α	ond	lit	ic	ons	5 I	ì	cir:	q	T	æ	St	ax	ły	Pe	eri	lo	1.	•		•	٠	•	•	•	•	20
	Nut	tri	ent	: Iı		its	s t	o	Tj	da	ป	Ē	res	shv	vat	e	Ē	201	ti	Lor	<b>1</b> (	of	T	e	R	ive	er			28
	Qua	ant	ita	tiv	<i>i</i> e	C	nar	ge	×s m	ir	ייי 1 1 1 יי	Nut	tri	er	nt Ial	2		er Ser		at	cio ar	ons Dr	s I	) Un	cir me	ŋg	۰f		-	
					211	70 Y	- 1			يرم							, T C	~	THC		- <b>L</b>	E			<i>A</i> E	5 (				40
	<u></u>					7	 	••••	•		•	÷	16	÷			- τ			÷.		·	<b>.</b>	÷.		•	٠	•	•	40
	Que	uic	ICA		/e		ΨC	)T (	a		: (	Л	NU		. те	410	- 1	٠vī		. La	2 1	.TC	<b>A</b> II	u	æ					07
			Aτ	Tar	nar	na	٠	•	•	•	٠	٠	٠	•	•	•	٠	•	•	•	•	•	•	٠	•	•	•	•	•	87
SUMM	ARY	•	••	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	97
LITE	RAT	JRE	CI	TEI	).	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	101
VITA.	•	•	•••	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	107

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## LIST OF TABLES

<u>Table</u>	<u>aqe</u>
1. Monthly averages of physical variables	27
2. Estimates of residence time of water in the tidal freshwater portion of the Altamaha	34-
3. Monthly average carbon concentrations at stations 10 and 11	35
4. Monthly average nitrogen and orthophosphate concentrations at stations 10 and 11	36
5. Nutrient concentrations in several larger rivers of the world	37
6. Pearson correlation of input concentration with riverflow	38
7. Pearson correlation of input concentration with water temperature	39
8. Regression analysis of nutrient concentration and river kilometer	42
9. Comparison of sources of organic carbon input to the coastal interface zone	88
10. Nitrogen demand by primary producers within the coastal interface zone	92
11. Nitrogen inputs to the coastal interface zone	94
12. Summary of physical and nutrient dynamics in the tidal portion of the Altamaha	100

## LIST OF FIGURES

Figure	Page
1. Altamaha river and station locations	9
2. Total monthly riverflow during the study period	22
3. Longitudinal distribution of salinity on October 11, 1983	24
4. Longitudinal distribution of salinity on March 12, 1983	26
5. Longitudinal distribution of total organic carbon on March 12, 1983	44
6. Longitudinal distribution of dissolved organic carbon on March 12, 1983	46
7. Longitudinal distribution of total organic carbon on October 11, 1983	48
8. Longitudinal distribution of dissolved organic carbon on October 11, 1983	50
9. Longitudinal distribution of SMW dissolved organic carbon on October 11, 1983	51
10. Longitudinal distribution of dissolved organic carbon on August 17, 1982	55
11. Longitudinal distribution of dissolved humic carbon on August 17, 1983	57
12. Longitudinal distribution of dissolved organic nitrogen on August 17, 1982	60
13. Longitudinal distribution of dissolved organic nitrogen on October 11, 1983	62
14. Longitudinal distribution of nitrate plus nitrite on March 9, 1983	65
15. Iongitudinal distribution of nitrate plus nitrite on May 26, 1982	67
16. Longitudinal distribution of nitrate plus nitrite on November 26, 1982	69

## LIST OF FIGURES (cont.)

Figure	Page
17. Longitudinal distribution of nitrate plus nitrite on June 3, 1983	71
18. Longitudinal distribution of ammonium on November 26, 1982 .	73
19. Longitudinal distribution of ammonium on June 3, 1983	76
20. Longitudinal distribution of ammonium on April 6, 1984	78
21. Longitudinal distribution of ammonium on July 15, 1983	80
22. Longitudinal distribution of orthophosphate on Nov. 26, 1982	82
23. Longitudinal distribution of orthophosphate on July 14, 1982	84
24. Longitudinal distribution of orthophosphate on June 3, 1983	86

#### ABSTRACT

Quantitative and qualitative aspects of the discharge of nutrients from the Altamaha River to the coastal interface zone (CIZ) of Georgia was examined over a two year period. Sampling for various forms of carbon (dissolved organic, particulate organic), nitrogen (dissolved organic, particulate organic, ammonium, nitrate plus nitrite) and phosphorus (dissolved orthophosphate) was carried out at eleven stations located throughout the tidal portion of the river.

Dissolved organic forms of carbon and nitrogen dominated the total annual discharge of these nutrients. Changes in the concentration of all dissolved nutrient forms occurred during passage of river water through the tidal freshwater portion of the river. Inorganic nutrients (ammonium, nitrate plus nitrate, dissolved orthophosphate) were decreased on several dates, while organic nutrients (dissolved organic carbon, dissolved organic nitrogen) were increased on several dates. These changes occurred during a wide range of physical conditions. Nutrient budgets indicate that riverine discharge of carbon was equal to appx. 10% of the total carbon available within the CIZ. Riverine discharge of nitrogen accounts for appx. 50% of the total new nitrogen available to the CIZ. This input of nitrogen from rivers is sufficient to supply appx. 10% of the annual needs of primary producers within the CIZ. CARBON, NITROGEN, AND PHOSPHOROUS DISCHARGE FROM THE ALITAMAHA RIVER, GEORGIA

#### INTRODUCTION

An understanding of ecosystem functioning requires knowledge of cross boundary fluxes as well as cycles within the ecosystem. For many coastal aquatic environments, riverine input is a major influence on chemical, physical, and biological processes. In the Apalachicola estuary, Sheridon and Livingston (1979) linked cyclic trophic relationships of fishes to inputs of organic matter from the Apalachicola River. Correlations between riverflow and commercial fishery catches have been found by Armstrong (1979), Copeland (1966), Turner et al. (1979), and Sutcliff (1972). In Louisiana, the productivity and nutrient dynamics of several coastal water bodies have been shown to be controlled by runoff from uplands (Hopkinson and Day, 1979). Phytoplankton dynamics of San Francisco Bay have been demonstrated to be controlled by the physical influence of river discharge (Cloern et al., 1983). Boynton et al. (1982) examined several published studies and found a significant relationship between phytoplankton productivity and nitrogen inputs. High fisheries productivity in waters off the mouth of the Mississippi have been attributed to nutrient discharges from Mississippi River (Ho and Barrett, 1977). These studies all indicate that riverine inputs are an important factor influencing the structure and function of coastal aquatic ecosystems.

-2-

In the coastal waters of Georgia, considerable ecological research has focused on community metabolism and nutrient cycling. Pomeroy and Wiegert (1981) have summarized twenty years of research in the salt marshes of this area. A dominant feature of this region is the highly productive salt marsh estuaries, which are situated between the mainland and a series of barrier islands located 7 km offshore.

In the nearshore region of the continental shelf, runoff from land forms a band of lower salinity water that extends out 20 km (Blanton, 1981). Comparisons of the rates of primary production and community respiration indicated that the near shore region was net heterotrophic and functionally coupled to adjacent estuaries (Hopkinson and Hoffman, 1984). The entire estuarine-nearshore system can be considered a coastal interface zone that is influenced by riverine discharge of organic and inorganic materials.

There has been little research evaluating the importance of river inputs of nutrients for the Georgia coastal zone. In a study of primary productivity off the mouth of the Altamaha River, Thomas (1966) concluded that the river flushes phosphorus-rich estuarine water off shore, where increased water clarity promotes high rates of primary productivity. Windom et al. (1975) showed that annual inputs of inorganic nitrogen and phosphorus from the nine major rivers that discharge into the Georgia bight were sufficient to supply all of the phosphorus and 20% of the nitrogen required for the annual growth of

-3-

<u>Spartina alterniflora</u> in the region. A shortcoming of these studies was a disregard for the quantitatively larger organic nitrogen fraction associated with riverine discharge.

However, examination of organic nitrogen concentrations in nearshore waters has suggested that riverine discharged nitrogen may not be readily utilized in the coastal waters (Haines and Dunstan, 1975; Gardner and Stephens, 1978). In an analysis of sources of organic carbon for food webs in Georgia estuaries, Haines (1977) suggested the potential importance of terrestrial inputs from rivers. Based on these studies, it is clear that riverine input may play an important role for the coastal interface zone of Georgia. Adding to the present understanding of the riverine input of mutrients to this coastal interface zone was the goal of this study.

#### **Objectives**

The objective of this study was to add to our understanding of land - margin coupling in the Georgia Bight and more specifically to examine nutrient discharge from a representative piedmont-coastal plain river, the Altamaha, to the coastal interface zone. Three specific aspects of riverine discharge of carbon, nitrogen, and phosphorus were examined over a two year period:

1. <u>Riverflow related temporal patterns and qualitative aspects of the</u> <u>carbon, nitrogen, and phosphorus input to the tidal portion of the</u> <u>Altamaha:</u> temporal patterns were examined by periodic sampling during different seasons and flow regimes. Several forms of each nutrient were quantified in order to determine the relative dominance of dissolved vs particulate and dissolved organic vs dissolved inorganic forms. The forms of nitrogen examined were ammonium ( $NH_4^+$ ), nitrate plus nitrite ( $NO_X^-$ ), particulate organic nitrogen (FN), and dissolved organic nitrogen (DON). Forms of carbon examined included particulate carbon (PC), dissolved organic carbon (DOC), small molecular weight dissolved organic carbon (IMWDOC), large molecular weight dissolved organic carbon (IMWDOC), and dissolved humic acid carbon (DHC). Dissolved orthophosphate ( $PO_4^{3-}$ ) was also examined.

- 2. Quantitative changes in nutrient concentration during passage through the tidal portion of the Altamaha River: it was expected that biogeochemical processes in the extensive tidal wetlands would affect concentrations of nutrients as water flowed downriver through the tidal portion of the river.
- 3. <u>Loadings of carbon and nitrogen from the Altamaha River to the</u> <u>coastal interface zone:</u> the relative importance of these loadings was examined by comparison to other terms in elemental mass budgets for the coastal interface zone.

#### Description of Altamaha River and Study Site

The Altamaha River empties into the Atlantic Ocean approximately 70 miles north of the Georgia-Florida border (Figure 1). The drainage basin encompasses  $37,632 \text{ km}^2$  and is the second largest on the Atlantic coast of the United States. The river is formed by the confluence of the Ocenee and Ocmulgee Rivers. The main tributary of the Altamaha proper is the Oheepee, a typical black water coastal plain river that drains 9% of the watershed. Of the total watershed, 40% lies within the Piedmont province and 60% is within the coastal plain. The floodplain averages 1-6 miles wide, encompassing 5% of the basin. Much of the floodplain is inundated for several months during spring (DNR, 1978).

Land usage within the basin is 68% woodland, 17% cropland, 17% pasture and 7% urban (U.S. Study Commission, 1963).

Sediments in the basin are composed of sands, limestones, stratified silts, and clay (DNR, 1972). The average discharge of the Altamaha is  $390 \text{ m}^3$ /sec (12 \*  $10^6 \text{ m}^3$ /year) (DNR 1978). Its hydroperiod is typical of large southeastern rivers and is controlled by the natural seasonal balance between rainfall, evaporation, and evapotranspiration in the watershed. Flow is minimum in the summer and fall, increases through the winter and reaches a maximum flow in the late winter/early spring.

Figure 1. Altamaha River and station locations.



The Altamaha is one of the least anthropogenically altered large rivers in the Southeast. Though there are hydroelectric dams on both the Oconee and Ohoopee, they have little influence on its hydroperiod. An average of 0.15 million  $m^3$  of effluent (municipal sewage and industrial waste) is discharged into Altamaha basin streams each year (DNR 1978). This is less than 1% of the annual riverflow and most of this waste has been secondarily treated. Major metropolitan effluents originate from the cities of Macon, Milledgeville, Athens, and Atlanta.

The largest single effluent comes from ITT Raynier, a chemical cellulose industry approximately 150 miles from the river mouth. Except for an approximate 18 mile length downstream from ITT Raynier, water quality throughout the river is generally excellent (DNR 1972). An 18 mile length below ITT Raynier is biologically impacted by effluents which stimulate algal and bacterial growth. The waters of the Altamaha have been described as "silicious, moderately hard, low in oxygen-demanding material, low in bacteria counts, near neutral in pH and high in dissolved oxygen concentration (near saturation). Turbidity is moderate and color (some derived from tannic acids leaching from the swamps) is moderate to high. Organic matter content is high and nutrient levels (total phosphorus, nitrate, and nitrite) are moderately high" (DNR, 1978). Like most Southern rivers, the basin is non-glaciated and therefore has a relatively low percent runoff and carries a high sediment load.

-10-

The coastal zone in Georgia is a low wave energy environment. A wide continental shelf dampens wave energy such that waves average 20-30 cm in height and rarely exceed 1.7 m (Helle, 1958). However, tidal energy on the coast is quite large with an average tidal range of about 2.4 m and spring tides exceeding 3 m (Howard and Frey, 1975). This relatively high tidal range, along with large sediment loads from rivers has created extensive salt marsh estuaries along the coast. The large tidal range also allows the formation of large areas of freshwater tidal marshes in the lower regions of large rivers such as the Altamaha.

In this study, sampling stations were established in the tidal portion of the Altamaha (Figure 1). The river has an anastomosing form typical of most southeastern rivers and is bordered by a floodplain about 6 miles wide. The floodplain is dominated by bottomland hardwood swamps and tidal marshes. Sediments in the main channel are composed of coarse sand while the smaller tributaries have a higher percentage of organic matter and fine silt. The normal upstream extent of tidal influence is about 50 Km upriver from the mouth (DNR, 1978) where Station 11 was established. The river between stations 11 and 6 is 100-200 m wide with mid-channel depths averaging 4-6 m at mid tide. Stations 7-8A are on a tidal tributary named Lewis Creek which drains an extensive bottomland and hardwood swamp forest. Lewis Creek is less than a meter wide at Station 8A and gradually widens to 75 m where it enters the mainstem Altamaha. Lewis Creek has a mid-channel depth of about 0.5 m at Station 8A and 2 m at Station 7.

-11-

The width of the river at Stations 2-4 is about 1 Km and the river widens to about 2.5 Km at its mouth. Mid-channel depth at Station 1 averages approximately 10 m.

The area between stations 1 and 4 is a partially mixed estuary. The water column here was usually moderately stratified with evidence of a salt wedge present on most sampling dates. Saltmarsh communities dominated by <u>Spartina alterniflora</u> cover the intertidal islands in the region of stations 1-2. Intertidal marshes in the area of stations 3-4 are dominated by <u>Spartina cynosuroides</u>. Fresh to brackish marsh communities flank the river around Stations 5-6. The vegetation of these communities is much more diverse and includes <u>Spartina</u> <u>cynosuroides</u>, <u>Zizaniopsis miliacea</u>, <u>Zizania aquatica</u>, <u>Pontederia</u> <u>cordata</u> and <u>Typha latifolia</u>, as well as other vegetation. Many of the islands in this area of the delta were diked and farmed for rice in the 1800's. Since the late 1800's, the dikes have deteriorated and natural plant communities have returned. The study area upriver from Station 6 is bordered by tidal freshwater swamps, freshwater marshes, and bottomland hardwood forest.

-12-

#### METHODS AND MATERIALS

#### Sampling Design

The sampling approach for this study was to characterize nutrient conditions within the tidal Altamaha both spatially and temporally. Sampling stations were established which cover the main river and a tidal tributary from the ocean outlet to the upper extent of tidal influence. Sampling was done once a month on selected dates over a two year period. The months were chosen to cover the full range of river discharge states and seasonal conditions. The most intensive sampling was during summer when biological processes were expected to be most active and water residence time was long enough to allow observable nutrient transformations.

In order to minimize variability due to diel rhythms or tidal stage, "slack water" sampling was conducted at slack before flood (SBF) tidal stage beginning at about the same time on each sampling date. The river has a progressive tidal wave with a six hour period required for the passage of the wave from Station 1 to Station 11 (personal observation). Time of SBF at Station 1 was determined from NOAA tide tables. Sampling began at Station 1 during SEF and progressed through upriver stations at a uniform rate such that Station 11 was sampled six hours later. All sampling dates were chosen so that sampling began between 0500 and 0900 EST.

-13-

At each station, two 500 ml brown polyethylene bottles and two 300 ml tape-wrapped glass bottles were filled with water from a depth of about 15 cm. Samples were drawn from mid-channel and the bottles were submerged inverted to avoid contamination from the water surface microlayer.

Surface temperature was determined with a mercury thermometer, salinity determined by a refractometer and light penetration was measured with a 25 cm diameter seechi disk. Water from approximately 50 cm above the sediment was sampled with a van Dorn water sampler. Bottom water samples were collected for nutrient analysis if stratification of the water column was indicated by a salinity difference greater than .5 ppt between surface and bottom water. Finally, the water samples were placed on ice and kept in darkness until return to the laboratory. All sample bottles had been previously washed with 10% HCL and were rinsed three times with river water before final filing.

#### Sample Processing

Processing of water samples began immediately upon return to the laboratory. All sample handling was done with acid washed glassware and filtering was done through pre-combusted glass fiber filters using a vacuum pressure of less than 254 mm Hg. Before sample filtration, the filters were rinsed with 200 ml of distilled/deionized water. Processing of water from individual stations proceeded as follows:

From each sample bottle 350 ml of water was filtered through a 47 mm diameter filter for suspended organic matter and suspended solids

-14-

analysis. Another 50 ml was filtered through a 25 mm diameter Gelman AE filter for particulate carbon and particulate nitrogen analysis. During the first five sampling dates, the filtrate from the two replicate bottles was pooled. Three subsamples were then withdrawn for dissolved organic nitrogen, nitrate plus nitrite, ammonium, dissolved orthophosphate, and dissolved organic carbon analysis. On the last five sampling dates, three subsamples from each replicate bottle were taken for these analyses. On all sampling dates, the polyethylene bottles were frozen for later analysis of humic acid carbon.

Ammonium analysis was conducted immediately. Nitrate plus nitrite, and dissolved orthophosphate samples were frozen for later analysis. Filters for suspended organic matter, particulate carbon, and particulate nitrogen determinations were dried at 60°C oven until dry. The following analytical methods were used:

#### Analytical Methods

<u>Nitrate Plus Nitrite</u>: An automated photometric method in which nitrate is reduced to nitrite by cadmium and then complexed into an azo dye (Grasshoff, 1976). Light absorbance of the dye is then measured at 540 nm wavelength.

<u>Ammonium:</u> A photometric method using phenol as described in Grasshoff (1976). In this method ammonium is chemically bound by indophenol blue and light absorbance is measured at 630 nm wave length.

<u>Dissolved organic nitrogen</u>: For this analysis, all organic nitrogen in the sample was oxidized to nitrate using an alkaline persulfate digestion procedure.

-15-

The sample was then analyzed for nitrate and the organic portion determined by subtracting the original nitrate and ammonium concentration (D'Elia, 1977).

Particulate carbon and particulate nitrogen: A Perkin-Elmer CHN analyzer was used to analyze particulate matter captured on a glass fiber filter. The filter was a 25 mm diameter, "AE" type, manufactured by Gelman Filters Inc. with a nominal pore size of 1.0 um.

Dissolved organic carbon: Carbon analysis on filtrate was preformed using the method of Menzel and Vaccaro (1964) in which organic carbon is converted to carbon dioxide using an alkaline persulfate digestion. Inorganic carbon is first purged by bubbling with nitrogen gas after addition of dilute phosphoric acid. Quantification of final carbon dioxide was conducted using an Oceanographic International carbon dioxide analyzer.

Small molecular weight organic carbon: The sample water was first filtered through a 1.0 um glass fiber filter. This filtrate was then passed through an Amicon micro filter having a pore size of 30,000 molecular weight. The final filtrate was then analyzed for dissolved organic carbon using the above method.

Large molecular weight dissolved organic carbon: The arithmetic difference between DOC and SMWDOC.

<u>Dissolved humic acid carbon:</u> Humic acid was precipitated by lowering the pH of the filtrate to 2 using concentrated sulfuric acid. Humic acid carbon was then determined as described for particulate carbon above.

-16-

Orthophosphate: This analysis used the photometric method of Grasshoff (1976). In this method, inorganic phosphate ions react to yield a phosphomolybdate complex. Light absorbance of the complex was measured at 880 nm.

<u>Suspended organic matter:</u> A gravimetric method after combustion at 500° for 5 hours.

Suspended Solids: A gravimetric method after drying at 60°C.

## Statistical Analysis

The first objective was to examine temporal patterns and qualitative aspects of the carbon, nitrogen, and phosphorus input to the tidal Altamaha from its watershed. For this analysis the nutrient inputs from above the fall line to the tidal river were assumed to be the average of concentrations observed at stations 10 and 11. These stations are at the upriver extent of tidal influence and upstream from the tidal wetlands. In order to determine if these concentrations were related to discharge, a Pearson correlation analysis was performed between concentration and riverflow on the day of sampling. A similar Pearson correlation analysis was performed between concentration and water temperature in order to determine if concentrations were related to season. Riverflow data was from USGS gauging station in Doctortown, approximately 25 miles upriver from station 11. Prior to this test all variables were examined for normality of distribution, and if necessary, a log<sub>10</sub> transformation was made. As riverflow possessed a non-normal distribution it was transformed for all correlations.

-17-

The second objective of this study was to determine quantitative changes in nutrient concentrations as river water flowed through the tidal freshwater portion of the Altamaha River. Quantitative changes in nutrients during passage through the tidal river were examined using regression analysis. In order to exclude any effects due to dilution by oceanic water, this analysis used only data from the fresh water section of the river and stations exhibiting salinities greater than 1 PSU were excluded. Linear changes were detected by conducting a separate regression analysis of concentration vs. river km for each nutrient on each date. A test for non-linear changes was performed through a regression of km vs. a  $\log_{10}$  transformation of concentration. The length of the tidal freshwater portion ranged from 32.1 to 50 km. This was due to differences in the extent of saltwater intrusion which was inversely related to riverflow.

The third objective was to examine the importance of loadings of carbon and nitrogen from the Altamaha River to the coastal interface zone (CIZ). For this analysis the annual riverine input of carbon and nitrogen was compared to other factors in nutrient budgets for the CIZ. The physical dimensions used for these budgets extends along the 400 km coastline of the Georgia Bight from Cape Hatteras to just south of the St. Johns River in Florida. Along this coastline, the CIZ consists of the 7 km wide estuary between the mainland and the barrier islands and a 10 km wide nearshore zone. Based on characterization of the estuaries along the Georgia coast (Pomeroy and Wiegert, 1981),

-18-

the estuary is assumed to be comprised of 80% marsh surface and 20% open water bodies. Total river input  $(5.8 * 10^{10} \text{ m}^3/\text{year})$  was calculated as the annual total discharge of water from the nine major rivers along the Georgia Bight (Pee Dee, Black, Santee, Cooper, Savannah, Ogeechee, Altamaha, Satilla, St. Johns). The nutrient concentration of this riverine input was assumed to be equal to the flow weighted average concentrations found in the Altamaha during this study. Biological nutrient utilization rates were taken from the available literature.

#### RESULTS AND DISCUSSION

#### Physical Conditions During The Study Period

The Altamaha estuary is classified as moderately statified during both high and low riverflow (NOAA, 1987). Figure 2 shows the average monthly riverflow (U.S.G.S.; 1982,1983,1984) during the study and blackened bars indicate months during which sampling occurred. Figure 3 shows the salinity distribution throughout the river on October 11, 1983 during the lowest riverflow month of this study. Salinity was 15.5 FSU in surface waters at the mouth and extended upriver to at least 13.5 km on both the surface and bottom. During the highest flow month of March, 1983, freshwater was present throughout the water column and extended to the river mouth (Figure 4). Water temperatures on sampled dates show a typical seasonal pattern and ranged from  $15.2^{\circ}C$  during March 1983 to  $30.1^{\circ}C$  during August 1983. Sampling occurred over a wide range of flow conditions with the lowest months discharge being .23 x  $10^{9}$  m<sup>3</sup> and the highest months riverflow being  $3.7 \times 10^{9}$  m<sup>3</sup>.

Monthly average values of physical variables during the study period are shown in Table 1. Secchi depth values ranged from 26 to 72 cm. Average suspended solid concentrations ranged from 16.8 to 60.9 mg/l during the study and suspended organic matter ranged from 3.5 to 23 mg/l.

-20-

Figure 2. Total monthly riverflow during the study period.

# **RIVER FLOW**



Figure 3. Longitudinal distribution of salinity on October 11, 1983.



-24-

Figure 4. Longitudinal distribution of salinity on March 12, 1983.



-26-

DATE	TEMP C≈	SECCHI (cm)	SS (mg/l)	SOM (mg/1)	%SOM(1)
26MAY82 11JUN82 14JUL82 17AUG82 26NOV82 09MAR83 03JUN83 15JUL83 31AUG83 110CT83 06APR84	26.5 27.05 226.50 18.00 15.00 30.9 24.0	26 52 50 62 72 63 72 63 37 48 51	60.9 24.2 22.1 18.2 36.0 16.8 19.1 33.7	26.2 7.3 8.5 5.6 10.9 5.5 7.9 15.3	39 38 41 32 30 57 57

Table 1. Monthly average of physical variables. Values are the average of all freshwater stations excluding Lewis Creek.

1)Percentage of suspended solids (SS) in organic form.
None of these typical measures of water clarity (Secchi, suspended solids, suspended organic matter) showed any statistically significant correlation with water temperature or river discharge. Estimates of residence times in the tidal freshwater portion of the river ranged from 0.7 to 3.5 days (Table 2). Assumptions and methods of calculation are given in the Table. These relatively large ranges of physical characteristics and residence times provided a wide selection of conditions in which to evaluate nutrient dynamics in the tidal fresh ecosystem of the Altamaha.

## Nutrient input to the tidal freshwater portion of the river Carbon:

Organic carbon concentrations in rivers are functions of net annual primary productivity, water residence times, and nutrient retention processes in the watershed (Mulholland and Watts, 1981). The concentration of total organic carbon in water entering the tidal Altamaha ranged from 7.2 to 17.6 mg/l (Table 3). The average over the study period was 11.1 mg/l (Table 5). Values in other large river systems range from 2.2 to 24.6 mg/l with a median of less than 5 mg/l (Table 5). High primary productivity and a relatively flat topography (resulting in longer residence times) may be why carbon concentrations are higher in the Altamaha than in many of these other rivers.

The temporal pattern of all forms of carbon showed no relation to riverflow (Table 6) or water temperature (Table 7).

Previous work has shown that in smaller rivers and streams, there are usually trends of increasing organic carbon concentrations during periods of increasing riverflow (Brinson, 1976; Naiman and Sibert, 1978; Darm, 1980). However, in larger rivers, this relationship is usually not as strong (Mulholland and Watts, 1981). There was no correlation of flow with carbon concentrations found in the Apalachicola (Elder and Mattraw, 1982) and only a weak positive correlation observed in the Mississippi (Malcolm and Durum, 1976). In a study of data on 82 major rivers, Mulholland and Watts (1981) found only a weak pattern of higher carbon concentrations during higher riverflows.

Dissolved organic carbon ranged from 4.9 - 11.7 mg/l (Table 3), and averaged 8.3 mg/l (Table 5). As in most natural waters, this dissolved form accounted for the majority (72%) of the carbon pool. This was even more pronounced during periods of high riverflow. Though the concentration of dissolved organic carbon was not correlated with riverflow, its percentage of the total carbon pool increased with increased riverflow (r=0.64, P<0.09). Also, the two months with the highest riverflow also showed the highest percentage of dissolved organic carbon (88% and 93% during March, 1983 and April, 1984 respectively). If concentrations are weighted by the total riverflow during each month, then the percentage in the dissolved form increases from 72% to 84% of the total organic carbon (Table 5).

Particulate carbon ranged from 1.0 - 8.0 mg/l (Table 3) and averaged 3.3 mg/l (Table 5).

-29-

Concentrations showed no relation to riverflow but as a percentage of total carbon it showed a decreasing trend with increasing riverflow (r=-0.62, P<0.10). This pattern of increased relative importance of dissolved carbon during high riverflow suggests that dissolved organic carbon may be leached from the river floodplain or watershed during the inundation accompanying times of high riverflow.

On the four dates that dissolved humic acid carbon was measured, concentrations ranged from 1.7 to 4.8 mg/l (Table 3). During the highest riverflow month of March 1983, dissolved humic acid carbon accounted for 49% of the dissolved organic carbon pool, while during the lowest riverflow month of October 1983, the dissolved humic acid carbon accounted for only 19% of the dissolved organic carbon pool. This suggests that much of the dissolved organic carbon exported from the watershed or floodplain during times of high riverflow is humic in origin.

### Nitrogen:

Total nitrogen concentrations of water entering the tidal Altamaha from its watershed ranged from 36.1 to 91.4 um (Table 4). Total nitrogen concentrations in other large rivers show a fairly large range of 20 - 300 um (Table 5). The average total nitrogen concentration in the Altamaha was 60 um and is quite close to the value of 54 um found in the lower Apalachicola river (Table 5). The Apalachicola is in the S.E. United States and has a drainage basin very similar in size and composition to the Altamaha. There was no relationship found between concentration of total nitrogen and riverflow or water temperature.

-30-

On all sampling dates, the largest fraction of nitrogen was in the organic form (range 52-84%, avg=68%). The majority of this organic nitrogen was in the dissolved form (Range=40-88%, avg=58%, Table 4). Over the study, dissolved organic nitrogen averaged 22.9 um while particulate nitrogen averaged only 17.1 um. None of the nitrogen forms measured had a statistically significant relationship with water temperature (Table 7).

Dissolved organic nitrogen was the nutrient form which showed the strongest relationship with riverflow with concentrations increasing during higher river discharge (r=0.63, P<0.09, Table 6). As was the case with carbon, the proportion of dissolved organic nitrogen relative to the total organic pool increased with increased riverflow. Dissolved organic nitrogen as a percent of total nitrogen also increased with increasing riverflow (r=0.90, P<0.007, Table 6). The raw data showed that dissolved organic nitrogen, on average comprised 40% of the total nitrogen, when the data were weighted according to total monthly riverflow the percentage increased to 60%.

For dissolved inorganic nitrogen, concentrations ranged from 6.9 to 30.3 um with an average of 19.3 um. Nitrite plus nitrate made up the majority of the inorganic nitrogen pool (range=44-95%, avg=82%). This is a nutrient which can be greatly altered by anthropogenic influences because of its widespread use as a fertilizer and its high solubility. This is reflected in Table 5 which shows a very wide range of nitrite plus nitrate concentrations with values as low as 3.05 um in the Amazon and as high as 294 um in the Rhine.

-31-

The concentration in the Altamaha was in the low end of this range at 15.1 um.

An earlier study in the lower Altamaha found nitrate plus nitrite concentrations of 6.3 um (Table 5). The higher concentrations found during the present study could be the result of increases due to anthropogenic influences or different sampling locations. It is not clear when or where this earlier study was conducted. If this earlier study sampled water within the estuary (i.e. where salinity>0.5 PSU), then the lower concentration is probably a result of the dilution of the river water by estuarine water with lower nutrient content.

A trend of high nitrate plus nitrite concentrations during high riverflows is often a sign of non-point source inputs of nitrogen from anthropogenic activities. It is caused by excess application of agricultural fertilizers as well as high nitrogen laden runoff from pastures and/or animal feedlots. In the Altamaha, there was no significant correlation between concentration and riverflow. However, there was a tendency for lower nitrate plus nitrite concentrations occurring during higher riverflows as indicated by the two lowest values observed during the two highest riverflow months. Another indication of lower concentrations during increased riverflow is that the amount of dissolved inorganic nitrogen as a percentage of total nitrogen decreased as riverflow increased (r=0.74, P=0.06). This is the opposite of what would be expected for highly impacted rivers and suggests that the Altamaha is not overly effected by cultural eutrophication.

-32-

Ammonium concentrations were considerably lower than nitrate plus nitrite, averaging only 4.3 um and were quite variable with a low of 0.8 um observed in April 1984 and a high of 20 um observed in July of 1982 (Table 4). The highest ammonium values were observed during warmer, low flow months (July 1982, July 1983, October 1983) presumably when organic matter decomposition and ammonification were highest. An earlier study in the lower Altamaha found ammonium concentrations of 1.1 um (Table 5). As with nitrate plus nitrite, the higher concentrations found during the present study could be the result of increases due to anthropogenic influences or different sampling locations.

#### Orthophosphate:

Orthophosphate concentrations ranged from 0.5 to 1.3 um (Table 4) and averaged 0.9 um. The earlier study by Windom et al. (1975) found orthophosphate concentrations of 0.3 um (Table 5). Again, the higher concentrations found during the present study could be the result of increases due to anthropogenic influences or different sampling locations. The concentration of orthophosphate in waters entering tidal portions of the Altamaha from its watershed was not significantly related to riverflow (Table 6) or water temperature (Table 7) during this study. Smith et al. (1982) examined phosphorus monitoring data from 300 U.S.G.S. monitoring stations throughout the United States. They found that for total phosphorus, 50% of the stations showed a positive correlation between concentration and riverflow while 20% of the stations showed a negative relationship.

-33-

Table 2. Estimates of residence times of water in the tidal freshwater portion of the Altamaha.

SAMPLING	RIVERFLOW	TIDAL FRESHWATER	RESIDENCE TIME
DATE	( m³/sec)	VOLUME ( mº#107)	(DAYS) (3)
26MAY82	229	2.65 (1)	1.3
11JUN82	435	2.65 (1)	0.7
14JUL82	203	2.65 (1)	1.5
17AUG82	246	2.65 (1)	1.4
26NOV82	131	2.65 (1)	2.3
12MAR83	1311	8.25 (2)	0.7
03JUN83	242	2.65 (1)	1.3
15JUL83	183	2.65 (1)	1.7
31AUG83	88	2.65 (1)	3.5
110CT83	98	2.65 (1)	3.1
06APR84	894	8.25 (2)	1.1

Notes: Riverflow is the average of the ten days preceeding the sampling date (USGS; 1982, 1983, 1984). Tidal freshwater volume was calculated from information in "National Estuarine Inventory Data Atlas, NDAA, 1985". This source lists the Altamaha estuary as having an average depth of 2.65 meters. It lists a 'tidal fresh zone' as having a surface area of 1.0\*10<sup>7</sup> m<sup>e</sup> and a 'mixing zone' as having a surface area of 2.1\*10<sup>7</sup> m<sup>e</sup>. On the two high flow sampling dates of this study (March 1983 and April 1984), what would normally be considered a 'mixing zone' was all freshwater. Therefore the volume of this 'mixing zone' was added to the volume of the 'tidal fresh zone' for these two dates. This is why the tidal freshwater volume is greater on these two dates. These residence times are only approximate because the suface areas given are at a mean high tide datum. Variability in tidal hight will change surface areas and volume. Details of calculations are as follows:

 Volume of tidal freshwater during all but high flow months (i.e. March 1983, April 1984): Assumed to be equal to the volume of the 'tidal fresh' zone.

Volume of 'tidal fresh' zone = Surface area of 'tidal fresh zone' # Avg depth of Altamaha estuary (1.0\*10' m²) \* (2.65 m) = 2.6#107 m³

2) Volume of tidal freshwater during high flow periods (i.e. March 1983, April 1984): Assumed to be sum of 'tidal fresh zone' volume plus 'mixing zone' volume.

Volume of 'mixing zone'= Surface area of 'mixing zone' = Avg depth of Altamaha estuary (2.1=10<sup>7</sup> m<sup>2</sup>) = (2.65 m) = 5.6=10<sup>7</sup> m<sup>3</sup>

Volume of 'tidal fresh zone' + Volume of 'mixing zone' =  $(2.65\pm107 \text{ m}^3) + (5.6\pm107 \text{ m}^3) = 8.2\pm107 \text{ m}^3$ 

3) Residence time: Volume/riverflow (freshwater volume m<sup>3</sup>)/((Riverflow m<sup>3</sup>/day)(86400 sec/day)) Table 3. Monthly average of carbon concentration at stations 10 and 11. All values are in units of mg/l.

DATE	DOC	TDOC	COC	HA	PC	TOC	%DDC(1)	%HDOC(2)	%SMWDOC(3)
26MAY82 11JUN82 14JUL82 17AUG82 26NOV82 09MAR83 03JUN83 15JUL83 31AUG83 110CT83 06APR84	6.8 12.7 11.7 11.0 8.7 4.9 8.0 7.0 5.6 11.0	4.4	1.2	4.8 2.9 3.5 1.7	8.09 4.0 1.007 4.30 1.007 4.30	14.8 17.6 15.7 9.9 7.2 10.8 9.7 8.9 11.8	46 72 7∛ 88 68 74 72 63 93	55 37 50 30	

Percentage of total organic carbon that is in the dissolved organic form.
 Percentage of dissolved organic carbon in humic form.
 Percentage of dissolved organic carbon that is of a size less than 30,000 molecular weight.

Table 4. Monthly average of nitrogen and orthophosphate concentration at stations 10 and 11. All values are in units of micro-moles per liter (um/l).

DATE	NH4+	NOx-	DIN	DON	PN	TN	(1)	(5)	(3)	(4)	P04-
26MAY82 11JUN82 14JUL82 17AUG82 26NOV82 09MAR83 03JUN83 15JUL83 31AUG83 11DCT83 06APR84	3.2 20.0 2.3 1.4 1.1 1.5 4.9 1.4 6.1 0.8	27.1 10.4 11.5 16.0 23.5 5.8 23.7 16.5 13.0 10.3 8.1	30.3 26.3 18.3 24.8 25.2 21.2 14.4 16.5 9.0	25.5 46.6 24.9 21.7 23.4 11.7 17.7 46.8 15.6 42.3	35.6 17.0 17.1 5.7 16.0 16.8 16.5 23.1 6.3	91.4 68.3 36.1 52.9 55.0 77.7 59.2 57.0	90 44 88 95 84 94 78 90 63 91	33 38 19 48 39 18 30 16	42 73 59 80 42 52 74 40 88	28 36 65 22 32 60 28 74	.85 .80 1.10 1.30 1.13 .52 1.20 .67 .90 .83

Percentage of dissolved inorganic nitrogen that is nitrite plus nitrate.
 Percentage of total nitrogen in dissolved inorganic form.
 Percentage of total organic nitrogen in dissolved organic form.
 Percentage of total nitrogen in dissolved organic form.

TABLE 5 Nutrient concentrations in large rivers of the world. All units are um utless otherwise noted.

RIVER	T	:0 <b>_</b> 3-	ND,	- +N03		NH "+	1	ÎN .	DCCC	g/L)	TOC	eg/L)
ALTAKAHA	0.3 0.8 9.9	(8) (12,3) (12)	6.3 10.5 15.1	(2,8) (12,3) (12) (12)	1.1 2.3 4.3	(8) (12,3) (12)	49 ( 60	12,3) (12)	9.2 8.3	(12,3) (12)	110.9	(12,3) (12)
AMAZON	9.4	(5)	3.05	(5)	1		20	5)	1.2-3	(11	4.5	(5)
ZAIRE	0.7	(5)	6.7	(5)	0.5	(5)			† I		18.9	(5)
MISSIEE1691	2.3	(5)	160	(2)	<i>(</i> ,6	(5)	320	ıç,	12.4	ę	17.2 12.4 124.0	(9) (4) (5)
ST. LAWRENCE	1.5	(5)	14	(2)	1		1					
JANGES	2-4	(5)	10-20	(2)	10	(5)	40	(5)			1	
COLUMBIA	0.5	(5)	12	(2)	1	(5)	Í		1.6-2.4	(11)	2.2-3.3	2 (11)
RHINE	12	(5)	294	(5)	90	(5)	<129	(5)			14.4	(5)
DNIEPER	2.0	(5)	14.1	(5)	25	(5)	155	(5)			1:1.2	(5)
PC	1.4	(5)	71.5	(5)	15	(5)		   				
VISTULA	1.7	(5)	70	(5)	25	(5)					!	
NORTH SWEDEN	0.2	(5)	5	(5)	1		55	(5)			5.0	(5)
SOUTH SWEDEN	0.6	(5)	33	(5)	   		61	(5)			18.4	(5)
SOUTH AFRICA	0.6	(5)	18.4	(5)								
SOVIET UNION	0.5	(5)	29	(5)							:3.2	(5)
ST. JOHN											10.9	(4,6)
CONNECTICUT	1										6.9	(4,6)
SUSQUEHANNA											3.2	(4,6)
POTOMAC							126	(7)			7.1	(4)
SANTEE	0.3	(8)	4.8	(8)	2.3	(8)					7.6	(4)
SAVANNAH	0.8	(8)	17.7	(8,2)	4.1	(8)					4.8	(6)
APALACHICOLA	0.6	(6)					54	(1)	6.6	(1)	7.9 7.5	(4) (1)
WINISKI											8.0	(4)
TRINITY											7.6	(6)
NUECES									7.1	(9)	6.9 9.9	(4,6) (9)
ALABAMA		I									7.4	(4,6)
PEE DEE	0.6	(8)	8.1	(8)	1.3	(8)						

#### Table 5. Continued.

RIVER	P0.3-	NO e +NOs -	NH .+	TN	DOC(ag	g/1)	TOCing	/L)
BRAZDS				1	3.3	(9)	6.9	(9)
MISSOURI					4.6	(9)	24.6	(9)
OHIC					3.1	(0)	4.9	(9)
SOPCHOPPY		1			27	(9)	28.6	(9)
ATCHAFALYA					4.8-8.3	(10)	7.9-12.1	(10)

- Total dissolved phosphorous
   Nitrate only
   Flow weighted avg.
   Mulholland and Watts (1982)
   Van Bennekom and Salomons (1975)
   Elder and Mattraw (1982)
   Bennett (1983)
   Windos, Dunstan and Gardner (1975)
   Halcolm and Durum (1976)
   Lambou and Hern (1983)
   Dahm et al. (1981)
   This study

Table 6. Pearson correlation of input concentration with riverflow. Riverflow was log10 transformed for all correlations. A Log10 transformation was used to normalize other variables that were found to be non-normally distributed. A negative r indicates a trend of decreasing concentration with increasing riverflow. A positive r indicates a trend of increased concentrations with increasing riverflow.

VARIABLE	r	ALPHA	N
SECCHI(1) TEMP(1) ND x <sup>-</sup> NH 4 + (1) PD 4 <sup>3-</sup> DON DDC DHC SS(1) SOM PC DIN TON TOC TN %SOM(2) %DIN(3) %PN(4) %DON(5) %DOC(6) %PC(7)	2142 6214 .4506 4705 5070 .6359 .4469 .8056 4338 .1104 5903 29500 29500 29500 5498 0582 .1022 4053 .7931 7378 7378 8700 .8989 .6359 6191	53 04 14 17 13 09 19 19 28 99 40 01 00 10 10	11 10 10 10 10 10 10 10 10 10 10 10 10 1

Variable was log<sub>10</sub> tranformed.
 Percentage of total suspended solids that is organic.
 Percentage of total nitrogen in the dissolved inorganic form.
 Percentage of total nitrogen in the particulate organic form.
 Percentage of total nitrogen in the dissolved organic form.
 Percentage of total nitrogen in the dissolved organic form.
 Percentage of total organic carbon in the particulate organic form.
 Percentage of total organic carbon in the particulate organic form.

Table 7. Pearson correlation of input concentration with water temperature. water temperature was log<sub>10</sub> transformed for all correlations. A Log<sub>10</sub> transformation was used to normalize other variables that were found to be non-normally distributed. A negative r indicates a trend of decreasing concentrations during increasing temperature. A positive r<sup>=</sup> indicates a trend of increased concentrations with increasing temperature.

VARIABLE	r	ALPHA	N
SECCHI <sup>®</sup> FLOW <sup>®</sup> ND × <sup>®</sup> PO × PO × DON DOC HA <sup>®</sup> SOM PC DIN TON TON TON TOC TN %DON <sup>1</sup> %DON <sup>2</sup> %DON <sup>3</sup> %DOC <sup>3</sup> %PC <sup>4</sup>	2056 6214 .1828 .3953 .2909 1734 0768 9377 .7811 .4086 .34086 .3462 .3265 .1347 .5989 8318 .6344 .5830 6365 4578 .4506	.57 .06 .61 .29 .41 .71 .85 .22 .04 .36 .38 .363 .71 .22 .17 .22 .17 .22 .17 .30 .31	10 10 9 17 8 37 7 8 8 9 6 7 6 7 6 6 6 6 7 7

Variable was log<sub>10</sub> tranformed
percentage of total suspended solids that is organic
percentage of total nitrogen in the dissolved inorganic form
percentage of total nitrogen in the particulate organic form
percentage of total nitrogen in the dissolved organic form
percentage of total nitrogen in the dissolved organic form
percentage of total organic carbon in the dissolved organic form
percentage of total organic carbon in the particulate organic form

These authors did not examine dissolved orthophosphate data and it is probably not a constant proportion of the total phosphorus pool, therefore no direct relationship can be assumed.

# Quantitative Changes in Nutrient Concentrations During Passage Through Tidal Freshwater Portions of the Altamaha River

Carbon:

Some studies have shown that tidal marshes and wetlands export organic carbon because of their high productivity and the flushing effect of tidal action (Axelrad et al., 1976; Armstrong and Hinson, 1978).

Other studies (Heinle and Flemer, 1976) have found no net export of organic carbon. These results have been achieved by measuring the fluxes of carbon at the inflow and outflow of individual isolated marshes. Few studies have attempted to determine if there is an observable effect in the in-stream concentration of the rivers which receive the outflow from these marshes. One study which did examine longitudinal gradients was done by Dahm et al. (1981) in the Columbia River. They found no longitudinal gradient in carbon concentrations in the lower 200 km of river. In a large tidal river with extensive bordering wetlands such as the Altamaha, we may expect to see an increase in organic carbon as water passes through the tidal portion of the river.

-40-

As expected, organic carbon concentration showed a down river increase on four of the eleven sampling dates and a downriver decrease was never observed (Table 8).

During the month of highest riverflow (March 1983) total organic carbon increased by more than 50% from 9.7 mg/l to 15.1 mg/l between the farthest upstream station and station 1 (Figure 5). This change was due to increases in the dissolved organic form of carbon which increased from 8.4 mg/l to 10.4 mg/l (Figure 6).

Total organic carbon concentrations also showed a downriver increase during the lowest flow month of this study (October 1983). On this occasion, total organic carbon increased from 8.8 to 10.4 mg/l (Figure 7). This increase was due to dissolved organic carbon which increased from 5.5 to 6.7 mg/l (Figure 8). Unlike the high flow sampling on March 9, 1983, neither particulate carbon or suspended organic matter increased. This may be related to decreased flooding of the wetlands that occurs during times of low riverflow. All of the increase in dissolved organic carbon on this date was due to the increase in small molecular weight compounds which increased from 4.5 mg/l to 5.9 mg/l (Figure 9). Although total dissolved organic carbon increased on this date, there was a downriver decrease in large molecular weight compounds from 1.2 to 0.8 mg/l (though there was not a significant correlation with distance). Small molecular weight carbon may have originated from metabolic products of decomposition in the tidal wetlands or as leachate from wetland macrophytes (Pakulski, 1986).

-41-

Table 8.

Regression analysis of nutrient concentration and river kilometer. Only data from stations in the main river were used for this analysis. Data from estuarine stations (i.e. salinity present) were excluded from this analysis in order to remove effects of dilution. A positive correlation coefficient (r) indicates that concentration decreases with distance downriver from station 11. Non-linear changes were tested after Logic transforming the concentration data.

DATE	VARIABLE	r	ALPHA	N
26MAY82 26MAY82 14JUL82 17AUG82 17AUG82 26NDV82 312MAR83 12MAR83 03JUN83 03JUN83 03JUN83 03JUN83 31AUG83 31AUG83 31AUG83 11DCT83 11DCT83 11DCT83 11DCT83 06APR84 06APR84 06APR84	NO X DIN PO 4CHI DDC SECN DC X 4 7 SECN DC X 4 7 SECN SEC	.9736 .9993 .8277 .7975 8167 9099 .6554 .8497 .7099 8363 .7188 .5977 .7289 6799 689146 75260 75260 73666 73520 73666	.03 .02 .02 .02 .04 .07 .01 .05 .04 .07 .02 .05 .01 .05 .01 .05 .01 .05 .01 .05 .01 .05 .01 .05 .01 .05 .01 .05 .02 .02 .02 .02 .02 .02 .02 .02 .02 .02	437677888877700000056666665665555599999

\* Variable is non-normally distributed

Figure 5. Longitudinal distribution of total organic carbon on March 12, 1983



Figure 6. Longitudinal distribution of dissolved organic carbon on March 12, 1983



Figure 7. Longitudinal distribution of total organic carbon on October 11, 1983.



Figure 8. Longitudinal distribution of dissolved organic carbon on October 11, 1983.



-50-

Figure 9. Longitudinal distribution of SMW dissolved organic carbon on October 11, 1983.



-52-

This would be suggested by the higher concentrations of dissolved organic carbon (7.1 mg/l) found in Lewis creek than in the main river (5 - 6 mg/l) (figure 9).

Dissolved organic carbon also increased downriver in August 1982 from a concentration of 11.1 mg/1 10 12.8 mg/l (Figure 10). Dissolved organic carbon concentration in Lewis Creek on this day was as high as 13.1, again indicating that much of this increase was probably due to exports from tidal wetlands. Particulate carbon data is not available for this month.

The final month that downriver changes in carbon were observed was August 1983 when dissolved humic carbon values more than doubled from 3.1 mg/l to 6.7 mg/l (Figure 11). Much of this humic material probably was exported from the wetlands as suggested by elevated levels (8.2 mg/l) in the discharge from the Lewis Creek swamp forest catchment. Residence time of water within the tidal freshwater system was approximately 3.5 days during this period (Table 2). This was the longest residence time observed during the study and probably enhanced the accumulation of dissolved humic carbon in the water. Nitrogen:

While particulate and total nitrogen never showed any significant overall changes in concentration downriver, there were changes in both dissolved organic and dissolved inorganic species on several dates (Table 8).

-53-

Figure 10. Longitudinal distribution of dissolved organic carbon on August 17, 1982.



Figure 11. Longitudinal distribution of dissolved humic carbon on August 17, 1983.



Klopatek (1978) suggested that organic nitrogen is the primary form exported from tidal freshwater wetlands and dissolved organic nitrogen export was observed in tidal brackish marshes by Axelrad et al. (1976) and Heinle and Flemer (1976). In this study, as with organic carbon, the organic form of nitrogen showed downriver increases on several dates and there was never a downriver decrease. In August, 1982, dissolved organic nitrogen increased from 16.1 mg/l to 28.6 mg/l (Figure 12). In October, 1983, there was an increase in dissolved organic nitrogen from 16.2 mg/l to 19.8 mg/l (Figure 13). Also on this date, dissolved organic nitrogen values in Lewis Creek reached as high as 32.9 mg/l. As would be expected, these increases of organic nitrogen were associated with similar increases in organic carbon on the same date. These increases were observed during warmer months and probably resulted from exports of organic production within the wetlands along the river.

Studies have indicated that tidal marshes can export inorganic nitrogen during certain times of the year (Haines 1977, Stevenson et al. 1977, Wolaver et al. 1980, Armstrong and Hinson 1978). Other researchers have found that marshes import dissolved inorganic nitrogen (Heinle and Flemer 1976, Axelrad 1974, Grant and Patrick 1970, Aurand and Daiber 1973). In this study, downriver increases of nitrate plus nitrite which would indicate export from the wetlands were never observed. On the other hand, nitrate plus nitrite showed a downriver decrease on three dates.

-58-

Figure 12. Longitudinal distribution of dissolved organic nitrogen on August 17, 1982.



Figure 13. Longitudinal distribution of dissolved organic nitrogen on October 11, 1983.



-62-
On March 9, 1983, concentrations were quite low throughout the river and decreased from 5.9 mg/l to 4.4 mg/l (Figure 14). Lower concentrations of nitrate plus nitrite found in Lewis creek on this date suggest that the tidal wetlands were the site of this loss. Riverflow was greatest during this month and there was extensive flooding of the wetlands. Uptake by litter and soils of the wetlands may be a retention mechanism for the tidal system that helps support of the new spring growing season. Denitrification is another possible process that would result in loss of nitrite plus nitrate. Flooded soils can lead to reduced conditions and low oxygen levels. Under such conditions heterotrophic, dinitrifying bacteria utilize nitrate and nitrite as an electron acceptor, reducing it to  $NO_2^-$  and  $N_2^-$ (Engler and Patrick 1974, Fenchel and Blackburn 1979). Tidal freshwater wetlands have been observed to exhibit this phenomenon (Lee et al. 1975, Patrick and Tusneem 1972).

There also was a downriver decrease in nitrate plus nitrite during low flow months as well as high flow months. In May 1982, concentrations decreased from 27.2 to 25.2 mg/l (Figure 15). In November, 1982 levels decreased from 23.5 mg/l to 15.8 mg/l (Figure 16) and likewise in June 1983, it decreased from 23.3 mg/l to 13.0 mg/l (Figure 17).

Ammonium concentration showed a downriver decrease on three days and an increase on one day. In November 1982, values decreased from 1.4 to 1.0 mg/l (Figure 18). Nitrate plus nitrite also decreased downriver on this date.

-63-

Figure 14. Longitudinal distribution of nitrate plus nitrite on March 9, 1983



-65-

Figure 15. Longitudinal distribution of nitrate plus nitrite on May 26, 1982



Figure 16. Longitudinal distribution of nitrate plus nitrite on November 26, 1982.



Figure 17. Longitudinal distribution of nitrate plus nitrite on June 3, 1983.



Figure 18. Longitudinal distribution of ammonium on November 26, 1982.



-73-

This, and the observation that both of these nitrogen forms were low in Lewis Creek indicate loss processes occurring in the tidal wetlands rather than in the main river channel. Plant uptake, microbial uptake or coupled nitrification/denitrification are all processes which could explain these losses. In June 1983, annonium concentrations decreased from 1.4 mg/l to 0.08 mg/l (Figure 19). In April 1984 concentration decreased from 0.83 to 0.73 mg/l (Figure 20). The one month when a downriver increase in ammonium concentration was observed was July 1983, when concentrations increased from 4.9 mg/l to 6.2 mg/l (Figure 21). High rates of ammonification during this warmer months could explain this increase.

## Orthophosphate:

Orthophosphate import by tidal marshes has been recorded by Hobbie et al. (1975), Simpson and Wingham (1978), and Grant and Patrick (1970). Conversely, orthophosphate export from a tidal marsh was found by Heinle and Flemer (1976). In this study, as with nitrate plus nitrite, orthophosphate was observed to decrease downriver on several dates and a increase was never observed (Table 8). Orthophosphate concentrations decreased downriver on three separate dates. In November 1982, it decreased from 1.20 mg/l to 0.65 mg/l (Figure 22). In July of 1982, it decreased from 1.10 mg/l to 0.65 mg/l (Figure 23) and in June 1983, orthophosphate decreased from 1.20 mg/ to 0.83 mg/l (Figure 24). All three of these dates are during the peak plant growing seasons and concentrations were also quite low in Lewis Creek during these dates.

-74-

Figure 19. Longitudinal distribution of ammonium on June 3, 1983.



-76-

Figure 20. Longitudinal distribution of ammonium on April 6, 1984.



Figure 21. Longitudinal distribution of ammonium on July 15, 1983.



-80-

Figure 22. Longitudinal distribution of orthophosphate on Nov. 26, 1982.



-82-

Figure 23. Longitudinal distribution of orthophosphate on July 14, 1982.



Figure 24. Longitudinal distribution of orthophosphate on June 3, 1983.



This indicates that as with inorganic nitrogen, the tidal freshwater wetlands and bottomland hardwood forests act as sinks for orthophosphate. Klopatek (1978) suggests that tidal freshwater marshes can retain more than 50% of the orthophosphate entering and that some macrophytes are able to absorb orthophosphate directly from the water.

## Quantitative Importance of Nutrient Exports From the Altamaha Carbon:

Total river input of carbon is equal to 10% of the total carbon available in the coastal interface system of the Georgia Bight (Table 9). Macrophyte plant material from the salt marshes supplies the greatest amount of carbon with 54% of the total. The salt marshes in this area are one of the most productive types of ecosystems and it is not surprising that they provide the largest fraction of carbon. As a result of the high productivity and large area of the nearshore zone, nearshore phytoplankton growth supplies roughly a quarter of the total. This high plankton production in the nearshore area results from a combination of increased water clarity and relatively high nutrient concentrations (Haines 1974, Thomas 1966). Algal production (benthic and planktonic combined) supplies about the same amount of carbon (appx. 10% of the total) as riverine input.

There are few coastal aquatic systems where all the carbon sources have been studied.

-87-

Table 9. Comparison of sources of organic carbon input to the coastal interface zone (CIZ). The total input from each source is prorated over the width of the entire CIZ. Details of calculations are described below.

Carbon source	Emperical Data	Input(1)	% Total
Macrophytes(2)	1520 g/m²/yr	500 g/m²/yr	54
Benthic Algae(3)	150 g/m≡/yr	62 g/m²/yr	7
Nearshore phytoplankton(4)	400 g/m≊/yr	235 g/≞≋/yr	26
Estuarine phytoplankton(5)	79 g/m=/yr	32 g/m²/yr	·3
River Input(6)	10.9 mg/L	93 g/m²/yr	10

Physical Dimensions used:

Area of estuarine zone: 4.0 \*10<sup>2</sup>km coast of Georgia bight (Windom et al, 1975) \* 7.0 km wide estuary between mainland and barrier islands (Pomeroy and Wiegert, 1981) = 2.8\*10<sup>9</sup> m<sup>2</sup>.

- Area of intertidal marsh: Area of estuarine zone \* .8 (80% of estuary is marsh (Pomeroy and Wiegert, 1981)) = 2.24\*107 m<sup>2</sup>.
- Area of estuarine water bodies: Area of estuarine zone \* .2 (20% of estuary is open water (Pomeroy and Wiegert, 1981)) = 5.6\*10° m<sup>2</sup>.
- Area of nearshore zone: 400 km coast of Georgia bight \* 10 km wide nearshore zone of low salinity water (Blanton and Atkinson, 1978) = 4.0\*10° m<sup>2</sup>.
- Area of coastal interface zone (CIZ): Combined area of estuarine zone and nearshore zone = 6.8\*107 m<sup>2</sup>.
- Riverine discharge to CIZ: Nine major rivers (Pee Dee, Black, Santee, Cooper, Ogeechee, Altamaha, Satilla, St. John) discharge 95% of total riverine input to the Georgia bight (Windom et al, 1975). Average total annual discharge from these rivers is 5.8\*10<sup>13</sup> liters (USGS; 1982, 1983, 1984).
- Volume of water in nearshore zone: Volume of water in Georgia bight out to the 20m isobath (appx 10 km) = 11.2\*10<sup>13</sup> l (Haines, 1974)

Footnotes:

- 1) Prorated over entire coastal interface zone.
- 2) A. Rate of Primary production of intertidal marsh macrophytes: 1520 gC/m<sup>=</sup>/yr (Pomeroy and Wiegert, 1981)
  - B. Primary production of intertidal marsh macrophytes : Rate of primary production # Area of intertidal marsh 1520 gC/m<sup>2</sup>/yr # 22.4\*10<sup>a</sup> m<sup>2</sup> = 3.40\*10<sup>1</sup> gC/yr

Table 9. continued.

- C. Primary production of intertidal marsh macrophytes prorated over CIZ: Primary production / Area of CIZ (3.4\*10<sup>12</sup> gC/yr) / (6.8\*10<sup>7</sup> m<sup>2</sup>) = 5.0\*10<sup>2</sup> gC/m<sup>2</sup>/yr
- 3) A. Rate of Primary production of benthic algae: 150 gC/m<sup>#</sup>/yr (Pomeroy and Wiegert, 1981)
  - B. Primary production of benthic algae: Rate of primary production \* Area of estuarine zone (150 gC/m²/yr) \* (2.8\*10<sup>9</sup> m²) = 4.2\*10<sup>11</sup> gC/yr
  - C. Primary production of benthic algae prorated over CIZ: Primary production / Area of CIZ (4.2\*10<sup>11</sup> gC/yr) / (6.8\*10<sup>9</sup> m<sup>2</sup>) = 62 gC/m<sup>2</sup>/yr
- 4) A. Rate of Primary production of nearshore phytoplankton: 400 gC/m<sup>₽</sup>/yr. Estimate based on literature values of 250 gC/m<sup>₽</sup>/yr (Haines, 1974) and 500 gC/m<sup>₽</sup>/yr (Thomas, 1966)
  - B. Primary production of nearshore phytoplankton: Rate of primary production \* Area of nearshore zone 400 gC/m<sup>2</sup>/yr \* 4.0\*10<sup>7</sup> m<sup>2</sup> = 1.6\*10<sup>12</sup>gC/yr
  - C. Primary production of nearshore phytoplankton prorated over CIZ: Primary production / Area of CIZ (1.6\*10<sup>1</sup> gC/yr) / (6.8\*10<sup>7</sup>m<sup>2</sup>) = 235 gC/m<sup>2</sup>/yr
- 5) A. Rate of Primary production of estuarine phytoplankton: 79 gC/m<sup>=</sup>/yr (Pomeroy and Wiegert, 1981).
  - B. Primary production of estuarine phytoplankton: Rate of primary production \* Area of estuarine zone (79 gC/m<sup>2</sup>/yr) \* (2.8\*10<sup>7</sup> m<sup>2</sup>) = 2.2\*10<sup>11</sup>gC/yr
  - C. Primary production of estuarine phytoplankton prorated over CIZ: Primary production / Area of CIZ (2.2\*10<sup>11</sup> gC/yr) / (6.8\*10<sup>7</sup> m<sup>e</sup>) = 32 gC/m<sup>e</sup>/yr
- 6) A. Total organic carbon concentration of rivering input: Average total organic carbon concentration of riverine discharge is assumed to be equal to the flow weighted average total organic carbon concentration of the Altamaha. Flow weighted average concentration of total organic carbon from the Altamaha is 10.9 mg/l (Table 5)
  - B. Total riverine input of total organic carbon (TOC): Total annual riverine discharge \* TOC concentration (5.8\*10<sup>13</sup> l/yr) \* (10.9 mg/l) = 6.3\*10<sup>14</sup> mgC/yr
  - C. Total riverine input of total organic carbon prorated over CIZ: Total riverine input of total organic carbon / Area of CIZ (6.3\*10<sup>13</sup> gC/yr) / (6.8\*10<sup>7</sup> m<sup>2</sup>) = 93 gC/m<sup>2</sup>

In the Nanaimo estuary of British Columbia it was found that the river supplied as much carbon to the mudflats at the mouth of the river as all other autochthonous and allochthonous sources combined (Naiman and Siebert, 1978).

Haines (1977) studied the origins of detritus in Georgia estuaries near the Altamaha River using stable carbon isotopes and suggested that carbon from salt marshes was not the dominant carbon input for the estuarine food webs. She suggested that river input may account for a significant input and calculated a rough estimate of  $300 \text{ g/m}^2/\text{yr}$  of carbon input from rivers to the open waters of the estuary. This estimate is fairly close to the value of  $138 \text{ g/m}^2/\text{yr}$  that results from this study if only the open waters of the estuary and nearshore zone are considered as the receiving system.

Quantitative budgets such as this are only a first approximation of the true importance of riverborne carbon for the coastal interface zone. The dynamics of each of the carbon sources listed in Table 9 are probably different dependent on the chemical composition and physical dynamics of each type. Many studies have suggested that much of the riverborne carbon is refractory material though more recent studies have indicated that this carbon may be more available to microbial decomposition than previously believed (Berner et al., 1988). In this study it was found that 30 - 55% of the dissolved organic carbon in Altamaha river was humic carbon as defined by the method used (Table 3).

-90-

Nitrogen:

One measure of the quantitative importance of riverine nitrogen is to compare it with the total input from all external sources. When this is done, riverine input accounts for a majority (52%) of the total nitrogen input (Table 11). The majority of this riverine input (74%) is in organic form. Nitrogen fixation in the salt marsh and nearshore waters accounts for the majority of the remaining nitrogen inputs with 46% of the total.

A second estimate of the importance of riverine input of nitrogen is to compare it against the total needs of all the primary producers in the coastal interface zone. The nitrogen budget in Table 10 indicates that riverine input of nitrogen can supply 12% of the needs of autotrophic organisms. Of this input, only 26% is in an inorganic form that is readily available to primary producers and the remainder is organically bound (Table 9). At present, it is unclear how much of the organic nitrogen is made available to autotrophic organisms. A fraction is probably available though some evidence has suggested that much of the terrestrially derived nitrogen is refractory and remains relatively stable within the coastal waters of Georgia (Haines and Dunstan, 1975).

Comparing the total input of new nitrogen (Table 11) to the total demand by autotrophic organisms (Table 10) indicates that new input can support 23% of the total annual needs of primary producers.

-91-

Table 10. Nitrogen demand by primary producers within the coastal interface zone (CIZ). Biological rates were taken from the literature and prorated over the entire CIZ.

Source	Demand (gN/mª/yr)		
Spartina Spp.(1) Estuarine Phytoplankton(2) Nearshore Phytoplankton(3) Benthic Algae(4)	5.1 4.2 30.5 8.0		
Total Demand	47.8		
Riverine Input(5)	5.9		

Physical Dimensions used: see table 9.

Footnotes:

- A. Rate of external nitrogen needed to support production of marsh macrophytes: 15.4 gN/m<sup>e</sup>/yr (Hopkinson, 1984)
  - B. Total external nitrogen needed to support production of marsh macrophytes: Rate of external nitrogen need \* Area of intertidal marsh 15.4 gN/m<sup>P</sup>/yr \* 22.4\*10<sup>o</sup> m<sup>P</sup> = 3.45\*10<sup>1</sup>° gN/yr
  - C. Total external nitrogen needed to support production of marsh
    macrophytes prorated over CI2:
     Total external nitrogen needed / Area of CI2
     (3.45\*10<sup>10</sup> gN/yr) / (6.8\*10<sup>7</sup> m<sup>2</sup>) = 5.1 gN/m<sup>2</sup>/yr
- 2) A. Primary production of estuarine phytoplankton prorated over CIZ: 32 gC/m<sup>m</sup>/yr (Table 9)
  - B. C:N ratio of Phytoplankton biomass: 7.696 gC/gN (Redfield ratio)
  - C. Total nitrogen needed to support this production: Primary production/ C:N ratio of Plankton biomass (32 gC/m<sup>=</sup>/yr) / (7.696 gC/gN) = 4.2 gN/m<sup>=</sup>/yr
- 3) A. Primary production of nearshore phytoplankton prorated over CI2: 235 gC/m<sup>2</sup>/yr (Table 9)
  - B. C:N ratio of Phytoplankton biomass: 7.696 gC/gN (Redfield ratio)
  - C. Total nitrogen needed to support this production: Primary production/ C:N ratio of Plankton biomass (235 gC/m=/yr) / (7.696 gC/gN) = 30.5 gN/m=/yr
- 4) A. Primary production of benthic algae prorated over CIZ:
   62 gC/m<sup>2</sup>/yr (Table 9)
  - B. C:N ratio of Phytoplankton biomass: 7.696 gC/gN (Redfield ratio)

Table 10. continued.

- C. Total nitrogen needed to support this production: Primary production/ C:N ratio of Plankton biomass (62 gC/m<sup>2</sup>/yr) / (7.696 gC/gN) = 8.0 gN/m<sup>2</sup>/yr
- 5) A. Total nitrogen concentration of riverine input: Average total nitrogen concentration of riverine discharge is assumed to be equal to the flow weighted average concentration of total nitrogen from the Altamaha. Flow weighted average concentration of total nitrogen in the Altamaha is .69 mg/l (Table 5)
  - B. Total riverine input of total nitrogen: Total annual riverine discharge \* total nitrogen concentration (5.8\*10<sup>13</sup> 1/yr) \* (.69 mg/1) = 4.0\*10<sup>10</sup> gN/yr
  - C. Total riverine input of total nitrogen prorated over CI2: Total riverine input of total nitrogen / Area of CI2 (4.0\*10<sup>1</sup>° mgC/yr) / (6.8\*10<sup>7</sup> m<sup>2</sup>) = 5.9 gN/m<sup>2</sup>

Table 11. Nitrogen inputs to coastal interface zone (CIZ). Values have been taken from the literature and prorated over the entire CIZ.

Source I	nput (gN/m≞/yr)	% Total
Rivers Dissolved inorganic(1) Organic(2) Total(3)	1.5 4.4 5.9	12 39 52
Marsh N Fixation(4) Nearshore N Fixation(5) Rainfall(6) Advection(7)	5.0 .3 .2 0	43 3 2 0
Total Input	11.3	100

Physical Dimensions used: see Table 9.

## Footnotes:

- A. Total dissolved inorganic nitrogen concentration of riverine input: Average dissolved inorganic nitrogen concentration of riverine discharge is assumed to be equal to the flow weighted average concentration of dissolved inorganic nitrogen from the Altamaha. Flow weighted average concentration of dissolved inorganic nitrogen in the Altamaha is .18 mg/l (Table 5)
  - B. Total riverine input of dissolved inorganic nitrogen: Total annual riverine discharge \* dissolved inorganic nitrogen concentration (5.8\*10<sup>13</sup> l/yr) \* (.18 mg/l) = 1.0\*10<sup>10</sup> gN/yr
  - C. Total riverine input of dissolved inorganic nitrogen prorated
     over CI2:
     Total riverine input of dissolved inorganic nitrogen / Area of
     CI2
     (1.0\*10<sup>10</sup> gN/yr) / (6.8\*10<sup>9</sup> m<sup>2</sup>) = 1.5 gN/m<sup>2</sup>/yr
- 2) A. Total organic nitrogen concentration of riverine input: Average total organic nitrogen concentration of riverine discharge is assumed to be equal to the flow weighted average concentration of total organic nitrogen from the Altamaha. Flow weighted average concentration of total organic nitrogen in the Altamaha is .52 mg/l (this study)
  - B. Total riverine input of total organic nitrogen: Total annual riverine discharge \* total organic nitrogen concentration (5.8\*10<sup>13</sup> l/yr) \* (.52 mgN/l) = 3.0\*10<sup>10</sup> gN/yr
  - C. Total riverine input of total organic nitrogen prorated over CIZ: Total riverine input of total organic nitrogen / Area of CIZ (3.0\*10<sup>1</sup>° gN/yr) / (6.8\*10<sup>7</sup> m<sup>2</sup>) = 4.4 gN/m<sup>2</sup>/yr

Table 11. continued.

- 3) A. Total nitrogen concentration of riverine input: Average total nitrogen concentration of riverine discharge is assumed to be equal to the flow weighted average concentration of total nitrogen from the Altamaha. Flow weighted average concentration of total nitrogen in the Altamaha is .69 mg/l (this study)
  - B. Total riverine input of total nitrogen: Total annual riverine discharge \* total nitrogen concentration (5.8\*10<sup>13</sup> 1/yr) \* (.69 mg/l) = 4.0\*10<sup>19</sup> gN/yr
  - C. Total riverine input of total nitrogen prorated over CIZ: Total riverine input of total nitrogen / Area of CIZ (4.0\*10<sup>10</sup> mgN/yr) / (6.8\*10<sup>9</sup> m<sup>2</sup>) = 5.9 gN/m<sup>2</sup>/yr
- 4) A. Rate of nitrogen fixation in intertidal marsh soils: 15 gN/m<sup>e</sup>/yr (Hanson, 1977).
  - B. Total nitrogen fixation in intertidal marsh soil: Rate of fixation \* Area of intertidal marsh (15 gN/m²/yr) \* (2.24\*10<sup>9</sup> m²) = 3.4\*10<sup>10</sup> gN/yr
  - C. Total nitrogen fixation in intertidal marsh soil prorated over CIZ: Total nitrogen fixation / Area of CIZ (3.4\*10<sup>10</sup> gN/yr) / (6.8\*10<sup>7</sup> m<sup>2</sup>) = 5.0 gN/m<sup>2</sup>/yr
- 5) A. Rate of nitrogen fixation in nearshore zone: .016 mgN/l/yr (Dunstan and Atkinson, 1976)
  - B. Total nitrogen fixation in nearshore zone: Rate of nitrogen fixation \* volume of water in nearshore zone (.016 mgN/l/yr) \* (11.2\*10<sup>13</sup> l) =  $1.8*10^{9}$  gN/yr
  - C. Total nitrogen fixation in nearshore zone prorated over CIZ: Total nitrogen fixation in nearshore zone / Area of CIZ (1.8\*10<sup>7</sup> gN/yr) / (6.8\*10<sup>7</sup> m<sup>2</sup>) = .3 gN/m<sup>2</sup>/yr
- 6) A. Total amount of direct rainfall to the CIZ is assumed to be equal to the amount of rainfall along the Georgia coast. The total average yearly rainfall on the Georgia coast is 1.3 m<sup>3</sup>/m<sup>2</sup>/yr (Climatic atlas of the U.S., 1968).
  - B. The average Total nitrogen concentration of this rainfall is assumed to be .18 mgN/1 (Haines, 1974)
  - C. Total direct rainfall to CIZ: Average yearly rainfall \* Area of CIZ (1.3 m<sup>3</sup>/m<sup>2</sup>/yr) \* (6.8\*10<sup>7</sup> m<sup>2</sup>) \* (1000 1/m<sup>3</sup>) = B.8\*10<sup>12</sup> 1/yr<sup>3</sup>
  - D. Total nitrogen input to CIZ from rainfall: Total direct rainfall \* average total nitrogen concentration (8.8\*10<sup>12</sup> l/yr) \* .18 mg/l = 1.6\*10° gN/yr
  - E. Total rainfall input of nitrogen prorated over CIZ: Total rainfall input of nitrogen / Area of CIZ (1.6\*10<sup>o</sup> gN/yr) / (6.8\*10<sup>o</sup> m<sup>2</sup>) = 0.23 gN/m<sup>2</sup>/yr
- 7) A. Assumes offshore water has lower nitrogen concentration, therefore any advective exchange can only cause net loss of nitrogen.

This relatively large quantitative input of new nitrogen suggests that 23% of the total annual primary productivity of this system could be exported with no net loss in the annual productivity. This may be why these systems are so productive as nursery areas for juvenile fishes and can sustain large commercial fisheries for adult populations. Other coastal marine systems show a smaller importance of external input of nitrogen when compared to the annual needs of primary productivity. In St. Margaret Bay, it was found that freshwater input supplies 11% of the annual needs for primary production (Sutcliff, 1972). In both Long Island Sound (Harris, 1959) and the Pamlico Estuary (Keunzler et al 1979), riverine inputs of inorganic nitrogen supplies only 5% of the total demand of primary producers. In Naragansett Bay, total nitrogen input by rivers supplies 25% of the annual needs for primary production (Nixon, 1981). Nixon (1981) has summarized studies from many coastal marine systems and found that, as suggested here for the coastal interface zone of the Georgia Bight, most primary productivity in these systems is probably supported by recycling of nutrients.

-96-

## SUMMARY

The first objective of this study was to examine riverflow related temporal patterns as well as qualitative aspects of carbon, nitrogen and phosphorous inputs to the tidal portion of the Altamaha. Throughout the study, the largest fraction of carbon and nitrogen was nearly always in the dissolved organic form. This is what would be expected in a relatively non-eutrophic river. For carbon, much of the dissolved organic form was humic acid, particularly during high flow periods. Though total nitrogen and total carbon concentrations were not related to riverflow, there were changes in the form of these nutrients with increased riverflow. It was found that as riverflow increased, the dissolved organic fractions increased in quantitative importance. This trend of increased dissolved organic fraction during high riverflow means that the vast majority of the total annual carbon and nitrogen input from the rivers watershed is in these forms. Orthophosphate was the only form of phosphorous examined, and its concentration showed no relationship to riverflow. It was found that none of the nutrient concentrations were significantly correlated with water temperature, indicating that riverflow patterns are more closely related to nutrient concentrations than seasonal temperature patterns.

-97-

The second objective was to determine if there was any modification of nutrient concentrations as the water passed downriver through the tidal freshwater portion of the Altamaha. It was found that all dissolved nutrient forms showed some net loss or input during this study but particulate forms did not. Concentration changes were observed on all dates except the date when residence time in the tidal freshwater system was lowest (appx 0.5 days). Dissolved organic forms (dissolved organic carbon, dissolved organic nitrogen) showed downriver increases on several dates and never a downriver loss. The opposite was observed for inorganic nutrients (nitrite plus nitrate, orthophosphate and ammonium) which showed only a net loss during downriver transport except on one date when annonium increased. These observations indicate that the tidal freshwater ecosystem of the Altamaha transforms nutrients from inorganic to organic (particularly dissolved organic) forms with relatively little effect on total nitrogen and carbon concentrations. These transformations were observed during all seasonal and flow conditions with no obvious pattern as to the conditions most favorable to nutrient modifications (Table 12).

The final objective was to approximate the quantitative importance of riverine nutrient export. Riverine carbon supplies about 10% of the total organic carbon available for secondary producers within the coastal interface zone. Riverine input of nitrogen can supply 12% of the total external nitrogen needs of primary producers.

-98-
These river inputs as well as fixation of atmospheric carbon and nitrogen provide nutrient subsidies to the coastal waters of Georgia which support high productivity as well as allow export to adjacent ecosystems and harvests by commercial fisheries. Table 12. Summery of physical and nutrient chranics in the tidal freehuater system of the Altanuaha. Dates are ordered horizontally in order of increasing residence times (2). Each box presents the following information:

-Concentration observed at the uppermost station (generally W or 11). Whether there was a downriver increase (+) or decrease (-) observed. 25.2

- Whether Lewis Creek appeared have a higher (L), (ower (L) or indistinguishable ( ) concentration than the main river.

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............ 1) Longitudinal distance (km) downriver slong which concentration gradient in the tidal freehwater river was veriad between months because of the differing andent of aslinity intrusion.
2) Residence time in area of river measured. This value is equal to: (Residence time (rable 2)) / (50 km)) \* (Dist.)
3) Small Moleculer Weight DOC anly.
4) Average flow (m /sec) during the 10 days preceeding sampling (USGS). :

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