

W&M ScholarWorks

Dissertations, Theses, and Masters Projects

Theses, Dissertations, & Master Projects

1996

# Exchanges of Dissolved Inorganic Nitrogen and Dissolved Organic Carbon between Salt Marsh Sediments and Overlying Tidal Water

Betty Berry Neikirk College of William and Mary - Virginia Institute of Marine Science

Follow this and additional works at: https://scholarworks.wm.edu/etd

Part of the Oceanography Commons

#### **Recommended Citation**

Neikirk, Betty Berry, "Exchanges of Dissolved Inorganic Nitrogen and Dissolved Organic Carbon between Salt Marsh Sediments and Overlying Tidal Water" (1996). *Dissertations, Theses, and Masters Projects.* Paper 1539617714.

https://dx.doi.org/doi:10.25773/v5-mf13-v998

This Thesis is brought to you for free and open access by the Theses, Dissertations, & Master Projects at W&M ScholarWorks. It has been accepted for inclusion in Dissertations, Theses, and Masters Projects by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.

#### EXCHANGES OF

# DISSOLVED INORGANIC NITROGEN AND DISSOLVED ORGANIC CARBON BETWEEN SALT MARSH SEDIMENTS AND OVERLYING TIDAL WATER

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 Betty Berry Neikirk 1996

#### APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

Master of Arts

Approved, April 1996

Richard L. Wetzel, Ph.D. Committee Co-chairman/Advisor

Iris Cofman Anderson Ph.D. Committee Co-chairman/Advisor

4

Carlton H. Hershner, Ph.D.

Howard I. Kator, Ph.D.

ler

Robert R. Christian, Ph.D East Carolina University

## TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	. v
LIST OF TABLES	viii
LIST OF FIGURES	ix
ABSTRACT	xi
INTRODUCTION	. 2
BACKGROUND INFORMATION	. 4
HYPOTHESES AND OBJECTIVES	14
METHODS AND MATERIALS	
Study site	16 19
Field Sampling Protocol	22 23 26 26
Sediment Chlorophyll a         Field Sampling Protocol         Laboratory Analyses         Sparting alterniflorg Biomass	27 27
Field Sampling Protocol	28 28
Field Sampling Protocol	29 29
STATISTICAL ANALYSIS	30
RESULTS Seasonal Differences Exchange Rates Sediment Chambers	30
Water Column Chambers	37 40
Additional Measurements (water temperature, above-ground S. alterniflora biomass, water column chlorophyll a, and sediment chlorophyll a)	40
Sediment Chambers	46 52
Sediment Chambers	52

Water Column Chambers    50      Diurnal Tidal Creek Studies    50
DISCUSSION
Material Exchanges
Dissolved Inorganic Nitrogen (DIN) Exchanges
Dissolved Oxygen (DO) Exchanges
Dissolved Organic Carbon (DOC) Exchanges
Other Considerations
Diurnal Tidal Creek Studies
Assessment of In Situ Chamber Design
LITERATURE CITED 82
VITA

#### ACKNOWLEDGMENTS

The support and guidance provided by my major professors, Dr. Iris Cofman Anderson and Dr. Richard L. Wetzel, throughout the course of my thesis research are gratefully acknowledged. I also thank Dr. Carl Hershner, Dr. Howard Kator, and Dr. Robert Christian for agreeing to serve on my examining committee and for their review of this thesis.

I must express a very heart felt thanks to Dr. Ken Moore who also was very supportive during my studies and provided me with pertinent statistical advice. I am most appreciative to my supervisors, Dick, Iris, and Ken for giving me the opportunity to pursue a masters degree while remaining a full-time employee of the Virginia Institute of Marine Science. Many times they were without my assistance so that I could tend my own research endeavors. Thanks also goes to Dr. Robert Orth, department chairman of biological sciences, for approving and supporting my desire to pursue my degree. Had it not been for the encouragement and understanding of the above mentioned, it is very unlikely that I could have successfully completed this thesis.

I am indebted to many present and former VIMS students and employees for their assistance with numerous tasks throughout this study. Amy Harris was, without a doubt, the one person who made my life a lot easier while trying to juggle work and school. Not only did she take on many tasks at hand, but her smile and companionship were a great source of inspiration. Even after leaving VIMS in order to pursue her own masters degree, she returned as a volunteer to help me with my final two experiments! Many other people also assisted me with field work and deserve special thanks. Without their help, this thesis would not have been possible. David Fugate, whose philosophical outlook on life was always a source of inspiration and a good laugh, was present for most of my experiments. Craig Tobias, who was able to assist in the last few of my experiments, not only provided humor, but also his interest in ground water sparked our curiosity enough to pursue the

v

issue further. Dr. Mark Meyers, who because he was by far the "cleanest" person around, was able to solve our contamination problems with DON/DOC filtration in the field. Bill Seufzer was present for all of my many-failed field attempts early on and a couple of my successful experiments. He was also the inventor of our "scientific equipment vehicle" which allowed us to deploy instrumentation without "getting wet". Chris Buzzelli, who assisted during a summer experiment, sacrificed himself for the rest of us as an "all natural/no preservatives added insect repellant" against green head flies. Thank goodness he was there! Chris also deserves a special thanks as an invaluable computer consultant. Last, but certainly not least, Dick and Iris also assisted in field endeavors. It's rather strange, the tides always seemed to be perfect and things always went rather smoothly during those experiments when Dick was in the field! Although, they were not yet at VIMS to participate in any of my field work, thanks go to Scott Neubauer, David Miller, and Eva Machelor who made my life a lot easier during the past few months by helping out tremendously in the lab.

I am also grateful to a number of people who were not involved with field work but were invaluable in other ways. Thanks to Dana Booth who must have autoclaved about 3,000 serum bottles for me! Dr. Joe Boyer, who at the time was with the Institute of Ecosystem Studies, pulled me out of a real predicament and volunteered to analyze ALL of my DOC samples for FREE. He also provided the lead to have my DON samples analyzed for really CHEAP. The staff of the VIMS Wachapreague laboratory, including Dr. Mark Lukenbach, Reade Bonniwell, and Nancy Lewis, deserve a huge thanks for their assistance. Not only did the Wachapreague personnel provide overnight accommodations, laboratory space, and field supplies, but they also volunteered their time and assistance most unselfishly. Thanks go to Wanda Cohen and Ruth Hershner from the VIMS publications center for their assistance. Harold Burrell from publications also deserves a very special thank you, not only for his talent and assistance in the preparation of slides for

vi

various presentations, but also for being so patient! I am grateful to George Hayes for coming into the lab at 11:00 one night, so that I could get another truck to pick up my stranded assistants in Virginia Beach, and to Roland Billips for keeping the VIMS trucks rolling! Dr. Bob Diaz deserves thanks for statistical advice and assistance. Thank you, Dr. John Ruzecki, who told me numerous times that I should go back to school!

I am grateful to Dr. Hilary Neckles for assistance with my numerous statistical questions, but most of all for the companionship, strength and encouragement she has provided me over the years. Durand Ward deserves recognition for his technical skills in helping to prepare some of my field equipment, but I am most grateful to him and his wife, Jenny, and children, Cameron and Rachel, for being there for me as a family. Very special thanks also go to Sharon Dewing, Anna Kenne, and Marcia Berman for their support and friendship. What a great thing it is to have such good friends!

I am eternally grateful to my parents, Barbara and Bill Berry, for their love and support over the years. They always kept their confidence in me. Without their encouragement, I would never have made it this far. Above all, I thank my husband, Chip Neikirk, for his patience and emotional support. His love and encouragement made this thesis a reality.

Financial support for this study was provided by the National Science Foundation and the Virginia Institute of Marine Science.

vii

## LIST OF TABLES

	Page	<u>e</u>
Table 1	Summary of annual exchanges reported in literature	
Table 2.	Sample dates of salt marsh and tidal creek exchange studies	
Table 3.	Parameters sampled for each chamber for each time period	
Table 4	Air temperature, water temperature, and precipitation at Phillips Creek	
Table 5.	Average NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , total DIN, DOC, and DO exchange rates for sediment chambers	
Table 6.	Average $NH_4^+$ , $NO_3^-$ , total DIN, DOC, and DO exchange rates for water column chambers	
Table 7.	Average $NH_4^+$ , $NO_3^-$ , total DIN, and DOC concentrations at T-0 in sediment chambers	
Table 8.	Average $NH_4^+$ , $NO_3^-$ , total DIN, and DOC concentrations at T-0 in water column chambers	
Table 9.	Average water temperatures, above-ground <i>S. alterniflora</i> biomass, water column chlorophyll <i>a</i> , and sediment chlorophyll <i>a</i> for sediment chambers	
Table 10.	Average water temperatures and water column chlorophyll <i>a</i> for water column chambers	
Table 11.	Correlation matrix of sediment chamber exchange rates with environmental parameters	
Table 12.	Multiple regression models of environmental parameters on sediment chamber exchange rates	
Table 13.	Correlation matrix of water column exchange rates with environmental parameters	
Table 14.	Multiple regression models of environmental parameters on water column chamber exchange rates	
Table 15.	Ranges of salinity, $NH_4^+$ , and $NO_3^-$ concentrations for diurnal tidal creek exchange studies	

# LIST OF FIGURES

Page

Figure	1.	Virginia Coast Reserve LTER 17
Figure	2.	Location of Phillips Creek study site
Figure	3.	Experimental chamber design 21
Figure (a-b)	4.	Seasonal $NH_4^+$ and $NO_3^-$ exchange rates for sediment and water column chambers
Figure	5.	Seasonal total dissolved inorganic nitrogen (DIN) exchange rates for sediment and water column chambers
Figure	6.	Seasonal dissolved organic carbon (DOC) exchange rates for sediment and water column chambers
Figure	7.	Seasonal dissolved oxygen (DO) exchange rates for sediment and water column chambers
Figure (a-b)	8.	Seasonal $NH_4^+$ and $NO_3^-$ concentrations in the overlying tidal water for sediment and water column chambers
Figure	9.	Seasonal total dissolved inorganic nitrogen (DIN) concentrations in the overlying tidal water for sediment and water column chambers
Figure	10.	Seasonal dissolved organic carbon (DOC) in the overlying tidal water for sediment and water column chambers
Figure	11.	Seasonal water temperatures in sediment and water column chambers
Figure	12.	Estimated above-ground Spartina alterniflora biomass
Figure	13.	Seasonal water column chlorophyll <i>a</i> concentrations in sediment and water column chambers
Figure	14.	Seasonal sediment chlorophyll <i>a</i> concentrations
Figure (a-c)	15.	Linear regression models of environmental parameters correlated to $NH_4^+$ exchange rates within sediment chambers
Figure (a-b)	16.	Linear regression models of environmental parameters correlated to NO <sub>3</sub> <sup>-</sup> exchange rates within sediment chambers
Figure (a-g)	17.	Salinity, $NH_4^+$ concentrations, and $NO_3^-$ concentrations in Phillips Creek over diurnal tidal cycles

Figure 18 (a-e)	<ul> <li>Linear regression models of creek water NO<sub>3</sub>-</li> <li>concentrations vs. salinity over diurnal tidal cycles</li> </ul>	15
Figure 19	Average monthly precipitation at Phillips Creek	7'

#### ABSTRACT

Salt marshes vary greatly in their abilities to serve as sources or sinks of dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), and dissolved organic carbon (DOC) to overlying tidal water. To gain a better understanding of the processes and conditions which regulate these exchanges, seasonal daytime measurements of DIN and DOC exchanges between vegetated salt marsh sediments and tidal water were performed in a short-form *Spartina alterniflora* Loisel salt marsh located at Phillips Creek on the Eastern Shore of Virginia.

Phillips Creek, a Long-Term Ecological Research (LTER) site, is located in close proximity to regularly farmed agricultural fields and pine forests. Exchanges of DIN and DOC between the salt marsh and tidal water were measured by isolating small areas of the vegetated sediments using in situ benthic chambers. DIN (NH<sub>4</sub>+, NO<sub>2</sub>-, and NO<sub>3</sub>-) concentrations, dissolved oxygen, water temperature, and water column chlorophyll *a* within the chambers were measured. In addition, above-ground *S. alterniflora* biomass and sediment chlorophyll *a* were measured at the study site. DIN concentrations in the adjacent creek water were measured over diurnal tidal cycles to better understand the tidal creek nutrient dynamics.

Although data were highly variable, sediments in the short-form *S. alterniflora* salt marsh at Phillips Creek appeared to be an annual sink for DOC. No significant differences in DOC exchange rates were measured between the fall, winter, and spring. DOC data were unavailable for the summer months. This area of the salt marsh also imported DIN from the flooding tidal water during all seasons except late winter when little net exchange was measured. It is believed that the observed uptake of DIN is a result of assimilation by marsh macrophytes and sediment microalgae, as well as immobilization by microbial communities on and within the salt marsh sediments. Greatest uptake of NH<sub>4</sub>+ occurred in the summer and fall when NH<sub>4</sub>+ concentrations in the tidal water and above-ground *S. alterniflora* biomass were at their highest. Greatest NO<sub>3</sub>- uptake occurred in the early spring when NO<sub>3</sub>- concentration in the tidal water and sediment microalgal biomass were at their highest.

While the vegetated salt marsh appeared to be an annual sink for DIN, at least during daylight conditions, the tidal creek appeared to be a source of DIN to surrounding salt marshes and adjacent waters. Although not addressed in this study, advected porewater from the creek bank and bottom are likely sources of the NH<sub>4</sub>+ to the ebbing creek water. NO<sub>3</sub>- concentrations in the creek water were found to be inversely related to salinity which suggests that dilution from a fresh water source occurred. Since Phillips Creek has no other permanent fresh water connections with the uplands other than runoff from storm events, and since no samplings occurred after storm events, it is suggested that ground water, enriched with fertilizer-derived NO<sub>3</sub>-, was the primary source of NO<sub>3</sub>- to the ebbing creek water. Although some NO<sub>3</sub>- was released into Phillips Creek, the short-form *S. alterniflora* salt marsh appeared to be a substantial "filter" and a crucial sink for NO<sub>3</sub>-. As a result of these exchange studies, the sink or source nature of this salt marsh may not only be controlled by biological processes, but also by the physical nature of the upland fluxes.

#### **INTRODUCTION**

Salt marshes have long been considered among the most productive ecosystems in the world. In addition, salt marshes appear to support secondary production by providing nutrients and physical habitat to a highly diversified biological community (Turner 1977, Lewis and Peters 1984, Turner 1988, Turner and Boesch 1988, Sismour 1994). Teal (1962) and Odum and de la Cruz (1967) first suggested that organic matter and nutrients exported by salt marsh ecosystems sustain, in part, the productivity in adjacent coastal and estuarine water. This idea, known as the "outwelling hypothesis", inspired great interest and curiosity among the ecological community (Nixon 1980). While the outwelling hypothesis supported the conservationists movement to preserve our wetlands, it was not until the 1970's that the hypothesis was put to a rigorous test (Axelrad 1974, Moore 1974, Axelrad et al. 1976, Valiela et al. 1978, Haines 1979, Lee 1979, Valiela and Teal 1979, Nixon 1980).

More recent exchange studies (Wolaver et al. 1983, Jordan et al. 1983, Chalmers et al. 1985, Whiting et al. 1985, Childers and Day 1988, Wolaver and Spurrier 1988, Wolaver et al. 1988, Boto and Wellington 1988, Spurrier and Kjerfve 1988, Keizer et al. 1989, Roman and Daiber 1989, Scudlark and Church 1989, Whiting et al. 1989, Childers and Day 1990, Chambers et al. 1992, Chambers 1992, Childers et al. 1993a) indicate that when salt marshes export nutrients and organic matter, those exports are of small magnitude. It remains highly uncertain to what degree estuarine and coastal systems are influenced by adjacent tidal marshes.

2

It is clear that salt marshes often behave as dissolved nutrient and particulate filters. Because salt marshes are nitrogen limited during some seasons (Day et al. 1989), they have the capability to process excess anthropogenic inputs of organic and inorganic matter (e.g. atmospheric deposition, fertilizers, sewage) and act as sinks for these inputs. In addition, recent evidence suggests that the most significant source of ammonium ( $NH_4$ +) to the tidal marsh ecosystem is that which is provided by the recycling of material within the marsh (Bowden 1986, Anderson et al. in preparation).

An estimated 50% of the United States population lives within the coastal zone. As a result, coastal wetlands are particularly susceptible to human impact. Filling of wetlands for development, construction, ditching, and disposal of toxins have been common practices over the centuries . In retrospect, these practices have proved detrimental, both ecologically and economically, to a highly integrated set of ecosystems (Marinucci 1982).

It has been a long standing paradigm that salt marshes import dissolved, oxidized forms of inorganic nitrogen, and export particulate nitrogen and dissolved, reduced forms of inorganic and organic nitrogen, as well as particulate and dissolved organic carbon (Gallagher et al. 1976, Valiela et al. 1978, Nixon 1980). Numerous studies that have been conducted to examine the exchanges that occur between salt marshes and tidal waters do not clearly support this paradigm. Most exchange studies have utilized techniques (e.g. mass balance studies, flume techniques, hydrodynamic studies) which consider the ecosystem as a whole, by integrating different marsh components (e.g. vegetated salt marshes, mud flats, creek banks, creek bottoms, oyster reefs). Such large-scale studies provide information on the net exports and imports of salt marsh systems and their relative importance to surrounding ecosystems; however, they fail to address the underlying mechanisms controlling exchange processes. The objective of this thesis was to measure exchanges at smaller temporal and spatial scales using benthic chambers. By measuring fluxes in this manner, a more precise understanding of sediment-water column exchanges of dissolved nitrogen and carbon pools could be obtained prior to utilization and transformation by the water column microbial community or before physical mechanisms (e.g. tidal mixing, dilution) altered the flux signal. At the present time, few data exist where the dissolved organic fluxes in a salt marsh have been examined in such a manner. Another unique aspect of this study is that exchange measurements were performed in conjunction with determinations of various microbial, macrophyte, and microalgal process rates (Anderson et al. in preparation) so that exchange rates could better be explained.

#### **BACKGROUND INFORMATION**

Salt marshes are intertidal ecosystems found in coastal and estuarine areas throughout the world. Although regularly influenced by tidal water, complete inundation may not occur on a daily basis due to differences in marsh elevation and irregular tidal amplitude. Few species of vascular plants are able to withstand the stress induced by regular flooding of highly saline water. *Spartina alterniflora* Loisel is the dominant plant found within salt marshes along the Atlantic and Gulf coasts and often exhibits specific zonation patterns (Chalmers 1982). A tall form of *S. alterniflora* is usually located along the more frequently inundated and better drained creek bank, while a shorter form is found situated inshore at higher elevations (Day et al. 1989).

Estimates of salt marsh primary productivity vary greatly among different marshes, as well as within the same marsh (Day et al. 1989). Net primary productivity for the dominant grasses found in salt marsh communities range from 160-1500 g C m<sup>-2</sup> yr<sup>-1</sup>. Below-ground production of grasses can be considerably higher than above-ground production with below ground estimates ranging from 220-2000 g C m<sup>-2</sup> yr<sup>-1</sup> (Schubauer and Hopkinson 1984, Dame and Kenny 1986, Blum 1993, Howarth 1993 ). Benthic microalgae found on the surface of the marsh may produce another 80-235 g C m<sup>-2</sup> yr<sup>-1</sup>

(Pomeroy et al. 1981, Howarth 1993, Pinckney and Zingmark 1993), which for some areas accounts for approximately 25% of the salt marsh's total net primary productivity (Teal 1962). Chemoautotrophic sulphur-oxidizing bacteria can also be an important primary producer in some marshes, contributing as much as 275-500 g C  $m^{-2}$  yr<sup>-1</sup> (Howarth 1993).

Salt marshes appear to act as nitrogen transformers (Nixon 1980). Possible anthropogenic sources of nitrogen to salt marshes include atmospheric deposition, fertilizers, and sewage. Nitrogen-fixation, sediment deposition, and tidal waters are natural sources of nitrogen to the salt marsh. While there are a number of possible sources of nitrogen to the salt marsh, losses of nitrogen from the system occur primarily through denitrification and tidal exchange (Valiela and Teal 1979). It has been suggested that in general, salt marshes import dissolved, oxidized forms of inorganic nitrogen, and export dissolved, reduced forms of inorganic nitrogen, as well as dissolved organic carbon and nitrogen (Gallagher et al. 1976, Valiela et al. 1978, Nixon 1980, Howes and Goehringer 1994). Transformation of materials within salt marshes, however, may vary due to biological, chemical, and physical parameters, as well as due to seasonal differences, geomorphology, hydrology, tidal amplitude, storm events, and anthropogenic inputs (Valiela et al. 1978, Odum et al. 1979, Wolaver et al. 1983, Chalmers et al. 1985, Wolaver et al. 1988, Childers and Day 1990)

In some instances *S. alterniflora* has been found to be a major factor regulating the dissolved nitrogen and carbon pools found within the salt marsh. *S. alterniflora* has been demonstrated to release dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) when submerged, suggesting tidal amplitude and inundation are important elements in the export of DON, DOC, and dissolved inorganic nitrogen (DIN)(Gallagher et al. 1976, Rice and Tenore 1981, Turner 1993). Seasonal trends of leachate loss have been observed in a Louisiana salt marsh with peak loss rates occurring in the summer and at higher

salinities (Turner 1993). Hines (1989) found that in a New England salt marsh, sulfate reduction within sediments was stimulated during the active growing season of S. alterniflora, and suggested that DOC released from roots fueled this process. Decomposition of S. alterniflora has been shown to contribute to the DOC pool in a Georgia salt marsh system both directly and indirectly (Moran and Hodson 1990). Lignocellulose-derived DOC was estimated to be responsible for approximately 44% of the existing DOC pool. Lignocellulose contains both labile and refractory DOC constituents, where labile DOC is an important and rapidly utilized carbon source for microorganisms. Fungi associated with S. alterniflora have also been shown to contribute to the degradation of DOC, but minimally when compared to bacteria (Benner et al. 1984, Benner et al. 1986). Research conducted in the Duplin River (Sapelo Island, Georgia) suggests that the labile DOC pool is regulated and controlled by planktonic microbial populations (Pomeroy et al. 1981). Upon assimilation by microorganisms, DOC and particulate organic carbon (POC) is made available as biomass to higher trophic levels (Gallagher et al. 1976, Moran and Hodson 1989, Moran and Hodson 1994). Perhaps as important, microbial populations play important roles in nutrient regeneration and the biogeochemical cycling of sulfur, manganese, iron, and nitrogen (Ducklow et al. 1986). Moran and Hodson (1994) demonstrated that some microorganisms can utilize refractory DOC elements as well, although more slowly and less efficiently than labile DOC. It is suggested that because of the longer turnover times, refractory DOC components are more likely to be available for export to the ocean than are labile components.

Numerous approaches have been utilized to examine exchanges and transformations which occur between salt marshes and their surrounding ecosystems. The approaches have included mass balance studies, flume techniques, hydrodynamic studies, and benthic chamber experiments. A wide variety of marshes differing in salinity, geographical location, geological age, tidal regime, and elevation have been studied and shown to exhibit diverse behavior relative to both the magnitude and net direction (import/export) of exchange. Table 1 is a summary of many of the exchange studies referred to in the following discussions.

The mass balance approach integrates the exchanges of all systems and components. This strategy often involves multiple experimental methods, including flume and hydrodynamic studies, and measures such processes as atmospheric deposition, groundwater, freshwater stream input, nitrogen fixation, denitrification, and exchanges that occur between sediments, vegetation, mud flats, oyster reefs, and tidal creek waters (Valiela et al. 1978, Valiela and Teal 1979, Wolaver et al. 1988, Dame et al. 1991). Material inputs to the system are compared to outputs from the system and a balance or imbalance of material exchanged is determined. Mass balance models, however, are usually based on standing stocks of nutrients within a system and do not focus on their rates of turnover times. Process rates, many of which are extremely difficult to measure, are rarely considered but can be an important factor in the exchange dynamics of a salt marsh system.

The marsh flume technique has been used in many studies of marsh-tidal creek exchanges over the last fifteen years and include the work of Lee 1979, Wolaver et al. 1983, Jordan et al. 1983, Chalmers et al. 1985, Spurrier and Kjerfve 1988, Childers and Day 1988, Wolaver and Spurrier 1988, Whiting et al. 1989, Childers and Day 1990, Dame et al. 1991, Childers 1993b. The marsh flume consists of two parallel fiberglass walls which are inserted into the marsh surface. The walls extend from the tidal creek, through the different zones of the marsh, and often into the uplands (Childers 1993a). The flume acts to channelize tidal water and prevent its lateral movement. Water is sampled periodically, usually from one end of the flume, over the course of the tidal cycle. It is assumed that any water leaving the flume on an ebbing tide is the same water that entered the flume. Material Table 1: Summary of annual NH4<sup>+</sup>, NO2<sup>-</sup>, NO3<sup>-</sup>, total DIN, DON, and DOC exchanges for studies cited in thesis. "E" indicates export of constituent from salt marsh, "I" indicates import of constituent by the salt marsh, and "O" indicates no exchange.
<sup>a</sup>Great Sippewissett, MA from Valiela et al. (1978) and Valiela and Teal (1979);
<sup>b</sup>Ware Creek and <sup>c</sup>Carter Creek, VA from Axelrad et al. (1976); <sup>d</sup>Carter Creek, VA from Wolaver (1983); <sup>e</sup>North Inlet, SC from Whiting et al. (1985) and Whiting et al. (1987); <sup>f</sup>North Inlet, SC from Wolaver and Spurrier (1988), Spurrier and Kjerfve (1988), and Whiting et al. (1989); <sup>g</sup>North Inlet, SC from Wolaver et al. (1988); <sup>h</sup>Sapelo Island, GA from Haines (1979); <sup>i</sup>Sapelo Island from Chalmers et al. (1985); <sup>j</sup>Cumberland Island, GA from Childers et al. (1993); <sup>k</sup>Barataria Basin and <sup>i</sup>Fourleague Bay, LA from Childers and Day (1990); <sup>m</sup>Great Marsh, DE from Scudlark and Church (1989); <sup>n</sup>Bay of Fundy, Canada from Keizer et al. (1989); <sup>o</sup>Phillips Creek, VA from Chambers et al. (1992); <sup>p</sup>Chickahominy River, VA from Chambers (1992).

Marsh	Exchange Technique Used	Total DIN	NH4+	NO <sub>2</sub> .	NO <sub>3</sub> -	DON	DOC
<sup>a</sup> Great Sippewissett <sup>a</sup> MA	Mass Balance		E	E	E	Е	
<sup>b</sup> Ware Creek VA	Hydrodynamic		Е	I	Ι	Е	Е
<sup>c</sup> Carter Creek VA	Hydrodynamic		Ι	I	I	Е	Е
<sup>d</sup> Carter Creek VA	Flume		Ι	E	I	Ι	
<sup>e</sup> North Inlet SC	Hydrodynamic		E		Е		
<sup>f</sup> North Inlet SC	Flume		Ι		Ι	E	0
<sup>g</sup> North Inlet SC	Mass Balance		0		0	E	
<sup>h</sup> Sapelo Island GA	Offshore Sampling	0				E	
<sup>i</sup> Sapelo Island GA	Flume						0
<sup>j</sup> Cumberland Island GA	Flume		Ι		I		0
<sup>k</sup> Barataria Basin LA	Flume		Е	Е	E	Е	Е
<sup>l</sup> Fourleague Bay LA	Flume		Ι		E		I
<sup>m</sup> Great Marsh DE	Benthic Chambers/ Diffusive Flux	0					
<sup>n</sup> Bay of Fundy Canada	Benthic Chambers				I		
°Phillips Creek VA	Benthic Chambers		Е				
<sup>p</sup> Chickahominy River VA	Benthic Chambers		I				

exchanges are calculated based on the integrated volumetric exchanges of tidal water and material concentrations through the flume. Flume studies are extremely useful when measuring exchanges for the salt marsh ecosystem as a whole; however, they fail to isolate any one component (e.g. vegetated salt marsh, mud flat).

Hydrodynamic studies involve intensive sampling of water from transects that are established across a creek or inlet (Whiting et al. 1985, Wolaver et al. 1988, Boto and Wellington 1988, Roman and Daiber 1989). In brief, throughout diurnal tidal cycles, current velocity, water depths, and nutrient concentrations are measured at numerous points along the transect. An instantaneous profile of nutrient flux at each point is calculated by multiplying concentration by velocity. Profiles are then integrated over the cross-sectional area of the creek and added together to estimate the instantaneous exchange of water and nutrients across the transect (Axelrad et al. 1976, Whiting et al. 1985). Estimations of exchanges using the hydrodynamic approach can be problematic in that often the volume of water measured entering the tidal creek does not equal that leaving the creek.

Valiela et al. (1979) used a mass balance approach to measure the nitrogen budget of the Great Sippewissett Marsh, Massachusetts, USA. The Great Sippewissett Marsh is unusual in that ground water is a major source of nitrogen to the salt marsh. In addition to ground water, rainwater and nitrogen-fixation were found to be sources of DIN and DON to the salt marsh, and appeared to provide more than enough to support the demands of marsh primary producers. During the summer, utilization by marsh primary producers resulted in an import of nutrients to the marsh. On an annual basis, however, tidal exchange was shown to export DIN and DON. Nutrient concentrations in the overlying marsh water were correlated with concentrations in the adjacent coastal water, suggesting that the salt marsh was a possible source of nutrients to the coastal water. In addition to the net export of nutrients from the salt marsh tidal water, another major loss of nitrogen from the system occurred due to high rates of denitrification. High concentrations of NO<sub>3</sub>- provided by ground water were probably responsible for the high rates of denitrification measured at this system. Valiela and Teal suggested that the Great Sippewissett Marsh was in steady state, and the outputs of nitrogen balanced the gains.

To address salt marsh exchange characteristics in the Chesapeake Bay, USA, Axelrad and Moore (Axelrad 1974, Moore 1974, Axelrad et al. 1976) utilized a hydrodynamic approach to compare nitrogen and carbon fluxes in two subestuaries of the York River. On an annual basis Ware Creek (7 ppt) and Carter Creek (12 ppt) both imported nitrite  $(NO_2)$  and nitrate  $(NO_3)$ . Annually, exports of ammonium  $(NH_4)$ , DON, and DOC were measured. Although Carter Creek showed a net export of NH<sub>4</sub>+, the salt marsh did import this constituent in the spring. Carter Creek imported particulate nitrogen (PN) while Ware Creek exported PN. When considering all nitrogen constituents together, there was a significant annual export of nitrogen from the two salt marsh ecosystems. Wolaver et al. (1983) conducted a flume experiment in the Carter Creek vegetated salt marsh which showed an uptake of DIN, DON and PN during tidal inundation with definite seasonal trends for each constituent. During late spring and early fall, tidal water was enriched with NH<sub>4</sub>+ as a result of increased agricultural activity and runoff from adjacent fields. Greater uptake of NH<sub>4</sub>+ by the marsh also coincided with water column NH<sub>4</sub>+ enrichment. Release of NH<sub>4</sub>+ to tidal water occurred in late summer at which time water column concentrations of this constituent were low. This marsh was able to remove large amounts of DIN from the tidal water, especially when concentrations of DIN were high. This demonstrated the marsh's ability to act as a sink for surplus inorganic nitrogen. In this particular case, during inundation, this marsh did not appear to be a source of organic matter and nutrients to the adjacent estuary.

In contrast, flume studies conducted by Jordan et al. (1983) in two brackish marshes (0-22 ppt) in the Rhode River of the Chesapeake Bay exhibited export of DON and NO<sub>3</sub>- and import of organic particulates and NH<sub>4</sub>+. They hypothesized that the

primary role of the salt marsh was to transform particulates into dissolved nutrients which could readily be utilized by the adjacent mudflat. Welsh (1980) also suggested that a northeastern salt marsh located in Long Island Sound, USA, was the source of nutrients for adjacent mudflats which were shown to remove nutrients from the tidal water.

The salt marsh ecosystem at North Inlet, South Carolina, USA has been studied extensively. In a hydrodynamic study of nitrogen exchange between the euhaline salt marsh and the coastal ocean, a series of tidal creeks showed consistent export of DIN (Whiting et al. 1987, Whiting et al. 1989). Concentrations of DIN increased during the ebb flow. Peak NH<sub>4</sub>+ export occurred in the summer, whereas peak NO<sub>2</sub>- + NO<sub>3</sub>- export occurred in the fall and winter. Dame et al. (1991) found that oyster reefs were a significant source of the DIN that was observed to leave the creek on the ebbing tide.

Flume studies examining nitrogen and carbon exchanges between a vegetated salt marsh and the adjacent tidal creek were also performed at North Inlet (Spurrier and Kjerfve 1988, Wolaver and Spurrier 1988, Whiting et al. 1989). During tidal inundation the salt marsh imported DIN and PN and exported DON. Import of DOC was noted, although insignificant. There was, however, a net export of nitrogen from the system which was attributed to DON. Seasonal patterns of uptake and release of DIN were exhibited and appeared dependent on nutrient concentrations in the flooding tidal water. Rain events during marsh surface exposure caused an increase in the export of PN to the tidal creek. Although seasonal variations were observed, this system appeared to act as a sink for POC and by means of runoff and seepage during low tide exposure, a source for DOC. Annually, however, carbon exchange between the vegetated marsh and the tidal creek appeared to be insignificant. A mass balance study, where exchanges between water column, vegetated salt marsh, oyster reefs, freshwater streams, ground water and rain were integrated, displayed insignificant DIN exchange and an annual export of DON (Wolaver et al. 1988).

The salt marshes of Sapelo Island, Georgia, USA have been the focus of many studies since the mid 1950's (Wiegert et al. 1981). Among the studies, nutrient dynamics and material exchanges have been examined using flumes, mass balance, and hydrodynamic approaches. Haines (1979) compared nutrient concentrations between tidal water within salt marshes and offshore waters and suggested that there was no net movement of DIN between the systems. She suggested a net import of PN and a net export of DON. Based on flume studies in the Duplin River salt marshes, Chalmers et al. (1985) reported no significant exchange of DOC. They hypothesized that although DOC and POC were exported down the river, the bulk of this material was resuspended during flood tide and deposited back onto the marsh. During low tide drainage and rainstorms, however, they reported that salt marshes appeared to be significant sources of DOC. Childers et al. (1993b) chose three sites differing in geologic age, sediment characteristics, topography, and elevation to conduct a series of flume experiments in the Cumberland Island estuary of Georgia. The geologically youngest salt marsh, which also corresponded to the lowest in elevation, displayed greater DIN and DOC uptake than the older salt marshes, although DOC import was not statistically significant. These younger marshes exported material when inundated for unusually long periods of time.

Few studies exist for marsh-water column nutrient exchanges in the microtidal environments of Gulf Coast salt marshes. Childers and Day (1990) used a modified flume technique to measure tidal exchanges between brackish and saline, deteriorating/erosional salt marshes and water. The deteriorating, subsiding Louisiana salt marshes were shown to export DON, DIN, and DOC. They suggested that DIN export may be attributed to erosion, whereby nitrogen that had accumulated during the marsh's developmental stages was being released. In an accreting, younger, coastal, brackish marsh system seasonal differences in DIN import and export were observed. The marsh acted as a sink for DIN in the spring when DIN concentrations in tidal water were highest and exported DIN in the summer and fall when tidal water concentrations were low and decomposition rates were high. Unlike the deteriorating salt marsh, this marsh imported DOC.

Nutrient exchange studies employing benthic chambers have been used more typically in subtidal environments (Nowicki and Nixon 1985, Teague et al. 1988, Rizzo 1990). Few chamber studies have been conducted in the intertidal areas of salt marshes (Keizer et al. 1989, Scudlark and Church 1989, Chambers 1992, Chambers et al. 1992). Areas of sediment and tidal creek water are isolated by placing chambers into the marsh surface. By sampling nutrient concentrations of water (or other constituents of interest) over a given period of time, a direct measure of the exchange of material between sediments and overlying water can be determined.

In Great Marsh bordering on Delaware Bay, USA, Scudlark and Church (1989) used direct exchange measurements obtained from chambers and compared them to the potential diffusive flux of nutrients out of the sediments. They found no significant exchange of DIN and hypothesized that nutrients were rapidly processed in surface sediments which enabled the salt marsh to maintain high levels of productivity. In contrast, in the macrotidal environment of the Cumberland Basin in the Bay of Fundy, Keizer et al. (1989) used benthic chambers and measured uptake of NO<sub>3</sub>- by the salt marsh during all seasons except late fall. Chambers (1992) used a fluctuating water level chamber in a tidal freshwater marsh located on the Chickahominy River, Virginia, USA and determined that NH<sub>4</sub>+ uptake was greater in the vegetated marsh than in the unvegetated marsh and noted a high degree of heterogeneity in exchange processes. Chambers et al. (1992) utilized the same fluctuating water level chambers in salt marshes on the Eastern Shore of Virginia, USA and concluded that the salt marsh was a source of NH<sub>4</sub>+ to tidal waters when overlying water concentrations were low.

Both small temporal changes (e.g tidal inundation, diel light effects) and large temporal changes (e.g. seasons) influence the transformation of organic material and

nutrients within the salt marsh. Tidal creek water is the major pathway by which materials are exchanged between the marsh and surrounding ecosystems. Most of the exchange studies considered above treated the ecosystem as a whole by integrating different marsh components. Benthic chamber experiments, as those cited above, may assist in interpreting the processes responsible for dissolved nitrogen and carbon fluxes that may not be apparent in large-scale experiments.

This thesis will describe a study of DIN and DOC exchanges between a short-form *S. alterniflora* salt marsh and tidal water. Bimonthly studies were performed using benthic chambers deployed on the surface of the vegetated salt marsh. The exchanges between salt marsh and tidal water will be described and related to processes which occur both in the salt marsh sediments and the adjacent tidal creek.

### HYPOTHESES AND OBJECTIVES

A seasonal study of DIN and DOC exchanges between a short-form *S. alterniflora* salt marsh and tidal creek water was conducted on the Eastern Shore of Virginia (Phillips Creek), using in situ benthic chambers which isolated small areas of the salt marsh. The hypotheses tested were:

(1) On an annual basis, the Phillips Creek vegetated salt marsh will import DIN from the creek water and will exhibit seasonal and constituent  $(NO_2^-, NO_3^-, and NH_4^+)$  variations in magnitude.

Because nitrogen is limiting in most salt marsh ecosystems (Day et al. 1989) an annual import of DIN is expected. DIN will be imported by the vegetated salt marsh during times of high DIN concentration within the tidal water and low concentrations in salt marsh sediments (late winter and early spring) which will, in part, correspond to agricultural activity, runoff, and ground water inputs. Import will also occur during the summer growing season when primary producers (e.g. *S. alterniflora*, benthic microalgae, and microbial populations) utilize DIN directly as a nutrient source.  $NH_4$ + release is expected in the late summer and fall due to senescence and degradation of vegetation, as well as lower concentrations of  $NH_4$ + in the water column. Benthic microalgal populations have been found to be more extensive on the vegetated marsh in the winter than in the summer (Pomeroy et al. 1981), suggesting their presence on the marsh surface will most likely utilize available DIN throughout the winter and little, if any export of DIN will be observed.

(2) On an annual basis, the Phillips Creek vegetated salt marsh will export DOC to the creek water and will exhibit seasonal variations in magnitude.

Greatest export of DOC will be during the growing season (spring and summer) when *S. alterniflora* suffers leachate loss and also again during the fall as a result of macrophyte decomposition. Although the more labile DOC components are likely to be rapidly consumed by microorganisms, especially during the warmer months (Pomeroy and Imberger 1981), recalcitrant organics will be available for export. By measuring exchanges at smaller temporal and spatial scales through the use of the benthic chamber technique, it is anticipated that DOC flux signals will be measured prior to utilization and/or transformation.

The primary objectives of this investigation were to:

#### (1) Measure the seasonal variability of dissolved nutrient exchanges

(DIN and DOC) between the vegetated salt marsh and tidal waters.

(2) Determine seasonal DIN concentrations in the tidal creek adjacent to the salt marsh over diurnal tidal cycles.

While the emphasis of this study was on the exchanges that occur exclusively between the vegetated salt marsh and the tidal creek, other systems including mud flats, creek bottoms, and oyster reefs, come in contact with the tidal creek water and can have major impacts on material exchange as well.

#### **METHODS AND MATERIALS**

#### Study Site

Phillips Creek, on the Eastern Shore of Virginia (Figures 1 and 2), was chosen for study because of its location at the Virginia Coast Reserve/Long-Term Ecological Research (LTER) site. As an LTER site, the Phillips Creek marsh afforded the opportunity to take advantage of ongoing studies and monitoring efforts that were being conducted by numerous research programs (e.g. Virginia Institute of Marine Science, University of Virginia, East Carolina University, Old Dominion University).

Phillips Creek (37° 26' 38.49" N, 75° 52' 04.99" W) is a mainland marsh which is part of an extensive lagoonal ecosystem consisting of oyster reefs, mud flats, vegetated marsh, and complex creek systems. It is considered to be a geomorphologically young marsh, consisting of a relict sand ridge that was flooded by rising sea level within the last 200 years (Oertel personal communication). The marsh is located in close proximity to regularly farmed agricultural fields and pine forests. Sediments are loamy in texture with Figure 1: The Virginia Coast Reserve LTER



Figure 2: Location of Phillips Creek study site



organic matter concentrations varying from 5 to 19% to a depth of 30 cm (Barr 1989, Blum, 1993). The dominant plant species at the study site is *S. alterniflora* Loisel. The tall-form of *S. alterniflora* occurs within 1-2 m of the creek bank with a short-form located inshore.

Exchange studies were conducted along a 30 m transect in the interior of the salt marsh which consisted of short-form *S. alterniflora*. (mean length of 44.9 cm at the end of the growing season). There appeared to be little variation in elevation along this expanse of salt marsh which allowed for a uniform movement of tidal water across the marsh surface. To minimize disturbance of the salt marsh surface during set-up and sampling, permanent boardwalks were constructed and placed within the marsh.

#### Materials and Experimental Design - Exchange Studies

Seven in situ chamber exchange experiments were conducted (Table 2): March 1994, May 1994, July 1994, September 1994, December 1994, February 1995, and April 1995. Experiments occurred bimonthly except for the month of November 1994 when severe weather conditions caused delays in sampling. The November experiment was postponed until December, and the bimonthly sampling regime continued thereafter.

Chamber Description. Benthic chambers 0.61 m in height were constructed from 30.48 cm diameter (I.D.), 6.35 mm (wall), clear acrylic tubing (Figure 3). Chambers were bevelled at the bottom to ease installation and minimize disturbance of the sediment surface. Two, 2.54 cm diameter holes were drilled into each chamber on opposite sides, 10.16 cm from the bottom, so that after deployment, tidal water could rise and fall within the chambers. Although the study transect flooded regularly, complete inundation did not occur during tides of extremely low amplitude (neap tides, wind induced ebbing, etc.). In order to conduct all studies under similar tidal conditions, experiments were performed

Sample Date	Season
March 14 - 15, 1994	Winter/Spring
May 25 - 26, 1994	Spring
July 13 - 14, 1994	Summer
September 18-19, 1994	Summer/Fall
December 6 - 7, 1994	Fall
February 1 - 2, 1995	Winter
April 17 - 18, 1995	Spring

Table 2:Sample dates and seasons for salt marsh and<br/>tidal creek exchange studies

# **CHAMBER DESIGN**



Figure 3: Experimental chamber design used at the Phillips Creek salt marsh ecosystem

during tides of highest amplitude (i.e. at or near spring tides) and were conducted during the latter part of the daylight flooding tide (generally between 1000 and 1400 hours).

**Field Sampling Protocol.** One week prior to the sampling date, five benthic chambers were installed approximately 1.5 m apart along a transect of a short-form *S. alterniflora* to allow for acclimation. Similar numbers of shoots were included within each chamber. Placement of chambers was marked so that they could be deployed in the exact location for each of the seven experiments. Chambers were pushed into the salt marsh sediment until the drilled holes were flush with the sediment surface. The five replicate chamber designations were C1 - C5 and hereinafter referred to as "sediment chambers".

One day prior to the start of each experiment, the inside of each sediment chamber was cleaned using a sponge and deionized water to remove any surface films. Sediment chambers were allowed to flood one last time with creek water before the experiment was initiated.

On the rising tide of the following day, four chambers with fixed bottoms, but otherwise identical to the sediment chambers, were placed on the marsh surface along the same transect as the others. These four chambers represented the water column and their purpose was to monitor the contribution of water column processes to the nutrient dynamics on the flooded salt marsh. Replicate chamber designations were B1- B4 and hereinafter are referred to as "water column chambers".

All chambers were allowed to fill with creek water to  $\geq 12$  cm in depth (height of water above sediment surface or bottom of water column chambers). After filling with tidal water, the holes were plugged with neoprene-rubber stoppers; battery operated stirrers (Edmund Scientific) were started and allowed to run for the duration of the experiment (2 hours). Sampling started immediately.

Both sediment and water column chambers were sampled at 20 minute intervals over a two hour period (T-0 through T-6). Water from the creek itself was also sampled
using the identical sampling regime. All water samples were taken in triplicate. Each chamber and the creek water were sampled as follows (Table 3): (1) the height of the water inside each chamber was measured every sampling period in order to calculate the water volume within the chamber; (2) dissolved oxygen (DO) and temperature were measured using an Orbisphere 2607 polarographic oxygen sensor; (3) water samples from each chamber were collected in 15 ml opaque bottles (deionized water-rinsed) for analysis of chlorophyll a and immediately placed on ice; (4) approximately 15 ml of water for DIN measurements (NO<sub>2</sub>-, NO<sub>3</sub>-, and NH<sub>4</sub>-) were sampled using 30 ml acid washed syringes; (5) water samples were immediately filter sterilized. The first 2 ml of water were filtered through 0.20 µm syringe filters (Gelman supor acrodiscs) and discarded. The remaining water was filtered into autoclaved serum bottles and stored on ice; (6) approximately 12 ml of water for DON and DOC measurements were sampled using sterilized 10 ml polypropylene/polyethylene syringes (Aldrich). The first 2 ml of water were filtered through 0.45 µm syringe filters (Gelman nylon acrodiscs) and discarded. The remaining water was filtered as two separate 5 ml aliquots into acid washed and previously combusted (500 °C for 5 hours) glass scintillation vials. Vials were capped with acid washed teflon caps. All DOC and DON samples were acidified with 12 N HCl to a pH < 2.0 and stored on ice.

After the last sampling period (T-6) benthic chambers were removed from the marsh, and samples were brought back to the laboratory (Virginia Institute of Marine Science, Gloucester Point, Virginia) for further analyses.

**Laboratory Analyses.** Immediately upon return to the laboratory, water samples were analyzed for  $NH_4$ + and water column chlorophyll *a* (within 5-7 hours after sampling).  $NH_4$ + analyses were performed on the filter sterilized water samples using a spectrophotometric methodology (Solorzano 1969). Chlorophyll *a* samples were analyzed as follows (Hayward and Webb personal communication): 5 ml of each water sample Table 3:Parameters sampled for each chamber for each time period. Numbers<br/>indicate the number of replicate readings or samples taken per chamber<br/>per time period.

Parameters	<b>T-0</b>	T-1	T-2	T-3	T-4	T-5	<b>T-6</b>
H <sub>2</sub> O ht.	1	1	1	1	1	1	1
DO	1	1	1	1	1	1	1
H <sub>2</sub> O temp.	1	1	1	1	1	1	1
DIN	3	3	3	3	3	3	3
DON	3			3			3
DOC	3			3			3
$H_2O$ chla a	3						3

were filtered through 25 mm Whatman glass fiber filters (GFF). Filters was placed in blackened test tubes containing 8 ml of an acetone/dimethyl sulfoxide (DMSO) extractant (45% acetone, 45% DMSO, 10% deionized water, and 1% diethylamine (DEA)) and allowed to extract for at least 24 hours at room temperature. Extracts were then poured into cuvettes and read on a Turner Designs 10-AU fluorometer and a dilution factor (8 ml extractant/5 ml sample = 1.6) was applied to readings to give concentration values in  $\mu$ g chl *a* 1-1. Chlorophyll *a* concentrations were not corrected for degradation products.

The morning following the exchange study, filter sterilized samples were analyzed for NO<sub>2</sub>- and NO<sub>3</sub>- using an Alpkem Flow Solution Autoanalyzer (Perstorp 1992). Since in all cases NO<sub>2</sub>- concentrations were negligible, results are reported as combined NO<sub>2</sub>- + NO<sub>3</sub>- for data comparisons and statistical analyses. From here throughout the remainder of this discussion, NO<sub>2</sub>- + NO<sub>3</sub>- will be referred to as NO<sub>3</sub>-.

For analyses of DOC, samples were sent to the Institute of Ecosystem Studies in Milbrook, New York and analyzed using a Shimadzu 5050 Total Organic Carbon Analyzer which incorporates a high-temperature catalytic oxidation (680 °C) step. Calibrations were performed using potassium hydrogen phthalate made with low carbon water from a Milli-Q system. Dissolved inorganic carbon was measured by quantifying the  $CO_2$  generated following phosphoric acid addition and was subtracted from total carbon to give DOC (mg-DOC 1-1).

DON samples were sent to Florida International University in Miami, Florida for analysis using methodologies described by Jones and Frankovich (in review) on an Antek 7000N nitrogen analyzer. Equipment malfunction, however, resulted in a lengthy delay in analyses of the samples. As a result of this delay, DON results and discussion could not be included in this thesis material.

Exchange Rate Calculations for DIN, DOC, and DO (Salt Marsh). Exchanges of NO<sub>3</sub>-, NH<sub>4</sub>-, DOC, and DO between the salt marsh and overlying water were calculated as follows: (1) for both sediment and water column chambers and for each sample period, mean concentrations for all parameters were obtained from triplicate samples (with the exception of DO where a single reading was obtained); (2) mean concentrations were regressed against time; (3) the mean water column slope for the four water column chambers was calculated; (4) to correct for water column processes, the mean slope value of the water column chambers was subsequently subtracted from the individual slopes of each of the sediment chambers; (5) the corrected slopes were then multiplied by the average water volume (mean volumes over the course of the experiment) for the appropriate sediment chamber; (6) these values were converted to areal (per square meter) estimates by dividing them by the sediment surface area of the chambers (0.0729 m-2); (7) exchange rates of each nitrogen constituent were reported as  $\mu$ mol-N m-2 h-1, for DOC as mg-DOC m<sup>-2</sup> h<sup>-1</sup>, and for dissolved oxygen as mg-O<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>; (8) exchange rates of the five sediment chambers were averaged to give the exchange rates of NO<sub>3</sub>-, NH<sub>4</sub>-, DOC, DO between the vegetated salt marsh and overlying tidal water for each sample date.

Exchange Rate Calculations for DIN, DOC, and DO (Water Column). To determine exchanges of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>-</sup>, DOC, and DO in the water column alone, calculations were as follows: (1) for each water column chamber and for each sample period, mean concentrations for all parameter were obtained from triplicate samples (with the exception of DO where a single reading was obtained); (2) mean concentrations were regressed against time; (3) slopes were then multiplied by the average water volume (mean volumes over the course of the experiment) for the appropriate water column correction chamber; (4) these values were converted to areal (per square meter) estimates by dividing them by the surface area of the chambers (0.0729 m<sup>-2</sup>); (5) exchange rates for each of the nitrogen species were reported as  $\mu$ mol-N m<sup>-2</sup> h<sup>-1</sup>, for DOC as mg-DOC m<sup>-2</sup> h<sup>-1</sup>, and for

DO as mg-O<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>; (6) exchange rates of the four water column chambers were averaged to give the exchange rates of the overlying water for each sample date.

## Materials and Experimental Design - Sediment Chlorophyll a

Sediment chlorophyll *a* concentrations were measured for each experiment in order to determine whether relationships existed between nutrient exchange rates and the benthic microalgal community.

Field Sampling Protocol. Twelve, 2.54 cm diameter sediment cores were taken on the day of each exchange experiment. Sediments were sampled along the same transect and in close proximity to the sediment chambers. Sediments were not sampled within chambers. Since chambers were to be placed in the same location for each of the seven experiments, preservation of an undisturbed sediment surface within each chamber was deemed necessary. Sediment cores were placed on ice and brought back to the laboratory for processing.

Laboratory Analyses. Upon return to the laboratory, the top 5 mm section of each sediment core was placed in individual glass scintillation vials, and stored in the freezer (-20 °C) until analyses could be performed. Sediment samples were analyzed according to the protocols of Lorenzen (1967) and Pinckney and Zingmark (1994). Chlorophyll *a* concentrations were not corrected for degradation products. A mean concentration of all twelve samples was calculated and normalized per square meter to give a final sediment chlorophyll *a* concentration in mg chl *a* m<sup>-2</sup>.

# Materials and Experimental Design - Spartina alterniflora Biomass

Estimates of above-ground S. alterniflora biomass were obtained in order to

determine whether relationships existed between nutrient exchange rates and above-ground *S. alterniflora* productivity. Biomass was sampled for every exchange experiment except March 1994 and February 1995. No living shoots were available for harvest from the salt marsh during these periods.

Field Sampling. A non-destructive technique similar to that of Morris and Haskin (1990) was used to obtain estimates of S. *alterniflora* above-ground biomass in each sediment chamber. The total number of shoots within each chamber was counted. Heights of ten randomly chosen shoots were measured from the sediment surface to the tip of the tallest leaf. In addition, 25-50 shoots were harvested along the same transect and in close proximity to the sediment chambers, placed on ice, and brought back to the laboratory for processing. Shoots were stored in the refrigerator until processed.

Laboratory Analyses. S. alterniflora shoots were lightly wiped with a paper towel, heights measured from the base to the tip of the longest leaf, and then individually placed in pre-weighed aluminum envelopes. Shoots were dried at 50 °C to a constant weight and weighed to obtain dry weights.

Above-ground *S. alterniflora* biomass per sediment chamber was estimated as follows: (1) a fourth order polynomial regression of individual shoot dry weight as a function of stem height was derived using all harvested shoots from the May 1994, July 1994, September 1994, December 1994, and April 1995 experiments; (2) using the derived polynomial regression, stem heights of the ten measured shoots within each chamber were transformed to estimate their dry weights; (3) the ten estimated shoot dry weights were summed; (4) the number of shoots per sediment chamber was divided by the number of measured shoots (ten) and then multiplied by the summed dry weights to obtain grams dry weight (g DW) of above-ground *S. alterniflora* per sediment chamber; (5) values were normalized per square meter to give biomass estimates per sediment chamber in g DW m<sup>-2</sup>.

### Materials and Experimental Design - Diurnal Tidal Creek Studies

In conjunction with bimonthly exchange experiments, creek water was sampled hourly during an entire tidal cycle. These data provided DIN concentrations entering and leaving the creek at the time of the exchange experiment.

Field Sampling Protocol. Approximately 24 hours before each exchange experiment was initiated, an automated sampler (Isco) was deployed in Phillips Creek adjacent to the study site. The sampler was programmed to sample creek water every hour for a 27 hour period. The intake for the water sampler was located just off of the creek bottom. Because water samples had to sit for up to 27 hours without filtration or cooling, upon initiation of the experiment, 0.250  $\mu$ l of 12 N HCl (to obtain a pH < 2.0) was added to each of the 27 sample bottles for sample preservation. A Datasonde III (Hydrolab Inc.) was also deployed in the tidal creek in order to monitor water depth, temperature, salinity, conductivity, dissolved oxygen, and pH at 15 minute intervals. When the exchange study ended, sampling of the creek water was terminated. Samples were brought back to the laboratory for DIN analyses.

**Laboratory Analyses.** Upon return to the laboratory, creek water samples were placed in the refrigerator until analyses could be performed (1-2 days). Just prior to DIN analyses, all samples were neutralized to a pH of 4.0 - 9.0 using 6 N NaOH. Following neutralization, water was filtered through 0.20  $\mu$ m filters (Gelman Supor Acrodiscs). NH<sub>4</sub>+ samples were analyzed using the spectrophotometric methodology of Solorzano (1969). NO<sub>3</sub>- samples were analyzed on an Alpkem Flow Solution Autoanalyzer (Perstorp 1992).

#### STATISTICAL ANALYSIS

All data were stored using Microsoft Excel (version 5.0) for the Macintosh. STATISTICA for Macintosh (StatSoft 1991) was used to perform all statistical analyses. Seasonal differences in exchange rates, nutrient concentrations, water column chlorophyll *a* concentrations, above-ground *S. alterniflora* biomass, and water temperature were analyzed using one-way analysis of variance (ANOVA) with repeated measures (StatSoft 1991, Zar 1996). When the ANOVA was significant ( $p \le 0.05$ ), a Tukey's multiple comparison test was used to determine seasonal differences. Sediment chlorophyll *a* data were analyzed using one-way ANOVA. When the ANOVA was significant ( $p \le 0.05$ ), Tukey's test was performed to determine seasonal differences.

Relationships between exchange rates, nutrient concentrations, water column chlorophyll *a* concentrations, above-ground *S. alterniflora* biomass, and water temperature were investigated using a Pearson correlation matrix with associated probabilities. Where significant correlations existed ( $p \le 0.10$ ) multiple regression analyses and coefficients of determination (R<sup>2</sup>) were performed (StatSoft 1991, Zar 1996).

## RESULTS

Table 4 displays the monthly means for air temperature, water temperature, and precipitation. These data were obtained from the Phillips Creek LTER meteorological station data base (Krovitz et al. 1994-95).

## Seasonal Differences - Exchange Rates

Sediment Chambers. Table 5 and Figures 4a, 5, 6, and 7 present the  $NH_{4^+}$ ,

- Table 4:Monthly averages for air temperature, water temperature, and<br/>precipitation at the Phillips Creek salt marsh ecosystem. Data were<br/>obtained from the LTER meteorological station (Krovitz et al.<br/>1994, 1995) at Phillips Creek unless otherwise indicated.
  - \* = dates on which exchange experiments were conducted
  - \*\* = due to malfunction of Phillips Creek equipment, data are from the Hogg Island meteorological station

Year	Month	Air Temperature °C	H <sub>2</sub> O Temperature °C	Precipitation mm
1994	Jan	0.7		94.8
	Feb	3.5		134.3
	Mar*	8.2	14.6***	252.3
	Apr	15.7		12.9
	May*	16.4	24.4***	71.0
	Jun	24.2		66.6
	Jul*	26.4	32.3***	157.3
	Aug	23.6		105.7
	Sept*	20.5	21.3***	78.5
	Oct	14.7		49.9
	Nov	12.5		70.1**
	Dec*	7.9	16.6***	25.1**
1995	Jan	5.1		40.0**
	Feb*	2.1	7.0***	41.4**
	Mar	8.0**		42.9**
	Apr*	13.6	17.0***	75.8**

\*\*\* = data are from exchange experiment measurements

Average (mean  $\pm$  s.d.) exchange rates for sediment chambers (n = 5). Averages reflect correction for water column processes. Superscripts a, b, c, d, and e denote statistical similarity (one-way ANOVA repeated measures; Tukey's test; p $\leq$ .05). Negative (-) values indicate an uptake of a constituent by the salt marsh. Positive values indicate a release of a constituent by the salt marsh. Table 5:

\* = no data available

	NH4+	NO <sub>3</sub> .	Total DIN	DOC	DO
Date	µmol-N m-2 hr-1	μmol-N m-2 hr-1	μmol-N m-2 hr-1	mg-DOC m-2 hr-1	mg-O <sub>2</sub> m- <sup>2</sup> hr- <sup>1</sup>
March 1994	38.88 ± 35.20ac	-209.00 ± 30.80	-170.80 ± 57.20abc	*	*
May 1994	-41.71 ± 9.92bde	$-63.26 \pm 14.15^{ab}$	-104.97 ± 20.23abcde	*	$16.61 \pm 26.76^{abcde}$
July 1994	$-142.43 \pm 32.50^{cd}$	-32.12 ± 9.41abc	-174.54 ± 40.11abc	*	-41.46 ± 14.25 <sup>abc</sup>
September 1994	-310.92 ± 65.49	-25.33 ± 12.12 <sup>bc</sup>	-336.25 ± 72.87	$-27.05 \pm 33.18^{a}$	7.21 ± 44.05abce
December 1994	-71.31 ± 21.52 <sup>bcde</sup>	$-58.48 \pm 16.06^{ab}$	-129.80 ± 21.89abce	-34.73 ± 13.38ª	$71.83 \pm 37.36^{ade}$
February 1995	-10.52 ± 3.19abde	$-6.24 \pm 5.69^{bc}$	-16.76 ± 5.80 <sup>bde</sup>	$7.20 \pm 33.77^{a}$	28.87 ± 15.74acde
April 1995	-65.63 ± 27.68 <sup>bde</sup>	$-15.25 \pm 7.43^{bc}$	-80.88 ± 29.28 <sup>bcde</sup>	-29.02 ± 6.55 <sup>a</sup>	$-41.08 \pm 29.75^{abc}$



Figure 4: Seasonal NH<sub>4</sub>+ and NO<sub>3</sub>- exchange rates at Phillips Creek (a) for experimental chambers (N=5) and (b) for water column chambers (N=4). Negative (-) values indicate an uptake of NH<sub>4</sub>+ and NO<sub>3</sub>- and positive values indicate a release of NH<sub>4</sub>+ and NO<sub>3</sub>-. Errors bars represent standard deviations.



Figure 5: Seasonal total DIN (NH<sub>4</sub>+ + NO<sub>3</sub>-) exchange rates at Phillips Creek for sediment chambers (N=5) and water column chambers (N=4). Negative (-) values indicate an uptake of total DIN and positive values indicate a release of total DIN. Error bars represent standard deviations



Figure 6: Seasonal DOC exchange rates at Phillips Creek for sediment chambers (N=5) and water column chambers (N=4). Negative (-) values indicate an uptake of DOC and positive values indicate a release of DOC. Error bars represent standard deviations. No data were available for Mar-94, May-94, and Jul-94.



Figure 7: Seasonal DO exchange rates at Phillips Creek for sediment chambers (N=5) and water column chambers (N=4). Negative (-) values indicate an uptake of DO and positive values indicate a release of DO. Errors bars represent standard deviations. No data were available for Mar-94

 $NO_3^-$ , total DIN ( $NH_4^+ + NO_3^-$ ), DOC, and DO exchange rates between the salt marsh and the overlying tidal water during the course of the study. Exchange rate values have been corrected for water column processes. Negative (-) numbers indicate uptake by the salt marsh, while positive numbers reflect a release by the salt marsh. All exchanges were significantly different (p<.01) between sample daters except for DOC (p>.06).

For NH<sub>4</sub>+ exchange, all months displayed an uptake of NH<sub>4</sub>+ by the marsh except March 1994, when the marsh exported this constituent (38.88  $\mu$ mol-NH<sub>4</sub>+ m<sup>-2</sup> h<sup>-1</sup>). Greatest NH<sub>4</sub>+ uptake occurred during September 1994 (-310.92  $\mu$ mol-NH<sub>4</sub>+ m<sup>-2</sup> h<sup>-1</sup>), when NH<sub>4</sub>+ exchange differed significantly from all other months (p<.01).

The salt marsh exhibited an uptake of NO<sub>3</sub>- for all experiments. Highest NO<sub>3</sub>uptake occurred in March 1994 (-209.00  $\mu$ mol-NO<sub>3</sub>- m<sup>-2</sup> h<sup>-1</sup>) when NO<sub>3</sub>- exchange differed significantly from all other months (p<.01).

When  $NH_4$ + and  $NO_3$ - were added together to obtain total DIN exchange, the salt marsh imported DIN during all experiments. September 1994 had the highest uptake rate (-336.25  $\mu$ mol-N m<sup>-2</sup> h<sup>-1</sup>) and was significantly different than all other months (p<.01).

As a result of contamination problems, samples collected in March, May and July 1994 for DOC analyses could not be used. There were no significant differences (p>.05) between DOC exchanges for the four months in which measurements were obtained. Uptake of DOC by the salt marsh occurred in September, December 1994, and April 1995, with a possible release of DOC in February 1995.

In March 1994 the Orbisphere oxygen meter failed to operate correctly; therefore, DO could not be measured on this date. The salt marsh appeared to be net autotrophic for all months except July 1994 and April 1995.

Water Column Chambers. Table 6 and Figures 4b, 5, 6, and 7 summarize the NH<sub>4</sub>+, NO<sub>3</sub>-, total DIN, DOC, and DO exchange rates of the water column chambers.

Average (mean  $\pm$  s.d.) exchange rates for water column chambers (n = 4). Superscripts a, b, c, d and denote statistical similarity (one-way ANOVA repeated measures; Tukey's test; p≤.05). Negative (-) values indicate an uptake of a constituent by the water column. Positive values indicate a release of a constituent by the water column. Table 6:

\* = no data available

	+ <sup>+</sup> HN	.00 <sup>3-</sup>	Total DIN	DOC	DO
Date	µmol-N m <sup>-2</sup> hr <sup>-1</sup>	µmol-N m <sup>-2</sup> hr <sup>-1</sup>	µmol-N m <sup>-2</sup> hr <sup>-1</sup>	mg-DOC m <sup>-2</sup> hr <sup>-1</sup>	mg-O <sub>2</sub> m <sup>-2</sup> hr <sup>-1</sup>
March 1994	-50.28 ± 27.86abde	-35.18 ± 25.54 <sup>a</sup>	-85.46 ± 8.01 <sup>ab</sup>	*	*
May 1994	-61.48 ± 71.42 <sup>abde</sup>	8.81 ± 8.95 <sup>a</sup>	-52.68 ± 72.91abd	*	148.02 ± 10.06
July 1994	-132.91 ± 22.93 <sup>ab</sup>	62.53 ± 9.78	-70.39 ± 23.68 <sup>abd</sup>	*	72.48 ± 3.66
September 1994	76.56 ± 59.13 <sup>cd</sup>	-1.93 ± 37.92ª	74.64 ± 45.48 <sup>cd</sup>	$-28.28 \pm 6.07^{a}$	193.73 ± 21.56
December 1994	13.79 ± 18.62acde	6.87 ± 16.89 <sup>a</sup>	20.66 ± 28.67 <sup>bcd</sup>	$18.17 \pm 21.71^{b}$	-31.66 ± 11.54
February 1995	-26.71 ± 21.28 <sup>ade</sup>	-2.40 ± 10.28ª	-29.11 ± 31.18 <sup>abd</sup>	$-31.05 \pm 8.46^{a}$	-3.26 ± 3.98
April 1995	-27.18 ± 37.73 <sup>ade</sup>	$1.27 \pm 2.39^{a}$	-25.91 ± 38.19 <sup>abd</sup>	$2.34 \pm 1.21^{b}$	36.35 ± 5.66

Negative (-) numbers indicate uptake by the water column, while positive numbers reflect a production in the water column. Significant differences between seasons were found for all exchanges (p<.04).

Uptake of NH<sub>4</sub>+ by the water column occurred for all experiments except September and December 1994. Highest uptake occurred in July (-132.91  $\mu$ mol-NH<sub>4</sub>+ m<sup>-2</sup> h<sup>-1</sup>).

The water column was a sink for NO<sub>3</sub>- in March, September 1994, and February 1995, with greatest uptake in March (-35.18  $\mu$ mol-NO<sub>3</sub>- m<sup>-2</sup> h<sup>-1</sup>). NO<sub>3</sub>- was released from the water column in May, July, December 1994, and April 1995. Highest release was in July (62.54  $\mu$ mol-NO<sub>3</sub>- m<sup>-2</sup> h<sup>-1</sup>).

Uptake of total DIN by the water column occurred for all months except September and December 1994. Highest release of total DIN was in September 1994 (74.64  $\mu$ mol-N m<sup>-2</sup> h<sup>-1</sup>). Highest uptake of total DIN was in March 1994 (-85.46  $\mu$ mol-N m<sup>-2</sup> h<sup>-1</sup>).

Of the four months sampled, the water column was a sink for DOC in September 1994 and February 1995 and a source of DOC in December 1994 and April 1995. Highest uptake of DOC was in February 1995 (-31.05 mg-DOC m<sup>-2</sup> h<sup>-1</sup>) and highest release was in December 1994 (18.17 mg-DOC m<sup>-2</sup> h<sup>-1</sup>).

DO exchange in the water column was significantly different between all months (p<.02). The water column was a source of oxygen during May, July, September 1994, and April 1995, with greatest release in September 1994 (193.73 mg-O<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>). The water column was a sink for oxygen in December 1994 and February 1995, with greatest uptake in December 1994 (-31.66 mg-O<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>).

#### Seasonal Differences - Nutrient Concentrations

Sediment Chambers. Table 7 and Figures 8a, 9 and 10 summarize the  $NH_4$ +,  $NO_3$ -, total DIN, and DOC concentrations present in the sediment chambers at the beginning of each experiment (T-0). Each nutrient exhibited significant differences between experiments (p<.01).

NH<sub>4</sub>+ concentrations in the overlying water were highest in July 1994 and September 1994 (3.91 and 3.78  $\mu$ M-NH<sub>4</sub>+) and were statistically different than all other months (p< .01). Lowest NH<sub>4</sub>+ concentrations were measured in December 1994 and February 1995 (1.45 and 1.44  $\mu$ M-NH<sub>4</sub>+). Concentrations of NO<sub>3</sub>- in the overlying water were highest in March 1994 (6.08  $\mu$ M-NO<sub>3</sub>-) and this month was significantly different than all other months (p<.01). Lowest NO<sub>3</sub>- concentrations occurred in February and April 1995 (0.63 and 0.57  $\mu$ M NO<sub>3</sub>-). The highest concentration of total DIN in the tidal water was measured in March 1994 (8.14  $\mu$ M-N) and this month was significantly different than all other months (p<.01). Lowest total DIN was measured in February 1995 (2.07  $\mu$ M-N).

Of the four months sampled for DOC concentration in the tidal water, only September 1994 was significantly different from all other months (p<.01). This month also exhibited the highest concentration of DOC (3.92 mg-DOC).

Water Column Chambers. Table 8 and Figures 8b, 9 and 10 summarize the  $NH_4^+$ ,  $NO_3^-$ , total DIN, and DOC concentrations in the water column chambers at the beginning of each experiment (T-0). Each nutrient exhibited significant seasonal differences (p<.04).

DIN concentrations in the water column chambers followed the same trends as did the sediment chambers.  $NH_4^+$  concentration was highest in July 1994 (5.03  $\mu$ M  $NH_4^+$ )

ā	
n = 5). Superscripts a,	Jukey's test; p<.05).
Ŀ	Γ.
verage (mean $\pm$ s.d.) T-0 nutrient concentrations for sediment chambers (	and d denote statistical similarity (one-way ANOVA repeated measures; 7
K	ပ်
Table 7:	

ັ
بىد
3
18
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
- 60
đ
تت
ಿ
-
0
Ē
_
11
*

	4. HN	NO.	Total DIN	DOC
Date	μM	ми	μM	mg ŀ1
March 1994	2.06 ± 0.54 <sup>abd</sup>	6.08 ± 1.41	8.14 ± 1.26	*
May 1994	$2.49 \pm 0.51^{ab}$	1.81 ± 0.13 <sup>ab</sup>	$4.30 \pm 0.62^{a}$	*
July 1994	3.91 ± 0.55 <sup>c</sup>	$1.49 \pm 0.03$ abc	$5.41 \pm 0.52^{a}$	*
September 1994	3.78 ± 0.60°	$1.33 \pm 0.21^{abc}$	$5.12 \pm 0.77^{a}$	<b>3.92 ± 0.12</b>
December 1994	1.45 ± 0.12 <sup>ad</sup>	$1.27 \pm 0.21^{abc}$	$2.72 \pm 0.15^{b}$	$3.22 \pm 0.17^{a}$
February 1995	1.44 ± 0.15 <sup>ad</sup>	0.63 ± 0.09 <sup>bc</sup>	$2.07 \pm 0.10^{b}$	3.46 ± 0.27ª
April 1995	2.19 ± 0.65 <sup>abd</sup>	$0.57 \pm 0.11^{bc}$	$2.76 \pm 0.70^{b}$	$3.31 \pm 0.24^{a}$



Date

Figure 8: Seasonal concentrations of NH<sub>4</sub>+ and NO<sub>3</sub>- in the overlying water at Phillips Creek for (a) sediment chambers (N=5) and (b) water column chambers (N=4). Values indicate concentrations at the initiation of each experiment (T-0). Error bars represent standard deviations.



Figure 9: Seasonal total DIN concentrations in the overlying water at Phillips Creek for sediment chambers (N=5) and water column chambers (N=4). Values indicate concentrations at the initiation of each experiment (T-0). Error bars represent standard deviations.



Figure 10: Seasonal DOC concentrations in the overlying water at Phillips Creek for sediment chambers (N=5) and water column chambers (N=4). Values indicate concentrations at the initiation of each experiment (T-0). Error bars represent standard deviations. No data were available for Mar-94, May-94, and Jul-94.

Average (mean $\pm$ s.d.) T-0 nutrient concentrations for water column chambers (n = 4). Superscripts	a, b, c, d, e, and f denote statistical similarity (one-way ANOVA repeated measures; Tukey's test; p≤.05)
Table 8:	

e O
Ē
3
/ai
a
Ita
ç
ou
11
*

$\begin{array}{c c} Date & DH_4 \\ Date & \mu M \\ March 1994 & 3.25 \pm 1 \end{array}$	4+ +		Total DIN	
Date $\mu M$ March 1994 $3.25 \pm 1$			T ULAL INTIV	
March 1994 3.25 ± 1		μM	hМ	mg l-1
	1.12abdf	8.48 ± 0.44	11.73 ± 1.54	*
May 1994 2.92 ± 0.	0.15abdef	$1.94 \pm 0.18^{ab}$	4.85 ± 0.23 <sup>abc</sup>	*
<b>July 1994</b> 5.03 ± 0	0.67cd	$1.55 \pm 0.14^{abc}$	6.58 ± 0.79 <sup>ab</sup>	*
<b>September 1994</b> 4.18 ± 1	1.09abcd	1.24 ± 0.19bce	5.42 ± 1.11 <sup>ab</sup>	$3.25 \pm 0.07^{a}$
<b>December 1994</b> 1.43 ± 0	0.44 <sup>bef</sup>	2.07 ± 0.56 <sup>ab</sup>	$3.50 \pm 0.26^{bcd}$	$3.00 \pm 0.12^{a}$
<b>February 1995</b> 1.45 ± 0	0.29 <sup>bef</sup>	0.47 ± 0.07 <sup>de</sup>	$1.92 \pm 0.27^{cd}$	$3.31 \pm 0.17^{a}$
<b>April 1995</b> $  1.71 \pm 0$	0.24 <sup>abef</sup>	$0.57 \pm 0.05$ cde	2.28 ± 0.26 <sup>cd</sup>	$3.06 \pm 0.17^{a}$

and lowest in December 1994 and February 1995 (1.43 and 1.45  $\mu$ M-NH<sub>4</sub>+). Overlying water NO<sub>3</sub>- concentration was highest in March 1994 (8.48  $\mu$ M NO<sub>3</sub>-) and lowest in February and April 1995 (0.47 and 0.57  $\mu$ M-NO<sub>3</sub>-). Total DIN concentration was highest in March 1994 (11.73  $\mu$ M-N) and lowest in February and April 1995 (1.92 and 2.28  $\mu$ M-N).

DOC concentrations in the water column ranged between 3.00 to 3.31 mg-DOC l<sup>-1</sup>. There were no significant differences between DOC concentrations for the four dates sampled. It should be noted that these concentration values are in agreement with those of (MacMillin et al. 1992) who measured tidal water DOC concentrations in Phillips Creek. Measurements taken by MacMillin et al. during the summer months were also similar in concentration (3.5 mg-DOC l<sup>-1</sup>) to those measured in the present study.

## Seasonal Differences - Additional Measurements

Sediment Chambers. Water temperature, *S. alterniflora* biomass, water column chlorophyll *a*, and sediment chlorophyll *a* concentrations all demonstrated significant seasonal variations (p<.01). Table 9 and Figures 11, 12, 13, and 14 summarize these data.

Water temperature was significantly different for each of the sample dates (p<.01). Highest temperature was in July 1994 (32.3 °C) while the lowest temperature was in February 1995 (7.0 °C).

Above-ground *S. alterniflora* biomass was sampled on all dates except March 1994 and February 1995. No living shoots were available for harvest during these periods. *S. alterniflora* biomass was highest in September 1994 (266.36 g DW m<sup>-2</sup>) and was significantly different than all other months (p<.02). The least amount of measurable biomass was in April 1995 (50.22 g DW m<sup>-2</sup>).

As a result of equipment failure, samples taken for water column chlorophyll a were

Average (mean  $\pm$  s.d.) water temperatures, *S. alterniflora* biomass, water column chla *a* for sediment chambers (n = 5) and sediment chla *a* (n = 10). Superscripts a, b, and c denote statistical similarity (one-way ANOVA repeated measures; Tukey's test; for sediment chla *a*; one-way ANOVA; Tukey's test; p≤.05) Table 9:

\* = no data available
\*\* = S. alterniflora biomass not sampled due to lack of living shoots

	C 11	S. alterniflora		1;F-0
Date	п20 Temperature °С	Above-ground Biomass g DW m-2	$\mu_2 O$ column chla <i>a</i> $\mu g$ l-1	Sedment chla <i>a</i> mg m-2
March 1994	14.6 ± .1	*	$69.21 \pm 13.10$	$16.34 \pm 6.66^{ac}$
May 1994	24.4 ± .1	129.54 ± 59.62 <sup>abc</sup>	12.28 ± 1.58 <sup>abc</sup>	7.39 ± 5.93 <sup>bd</sup>
July 1994	32.3 ± .2	163.44 ± 34.12 <sup>ab</sup>	$19.60 \pm 0.91^{ab}$	$14.41 \pm 4.51$ acd
September 1994	21.3 ± .3	266.36 ± 109.76	$10.78 \pm 1.07^{abc}$	6.92 ± 3.24 <sup>bd</sup>
December 1994	16.6 ± .3	68.81 ± 24.59ac	7.14 ± 1.05 <sup>ac</sup>	$10.50 \pm 2.74^{bcd}$
February 1995	7.0 ± .1	*	15.42 ± 0.83 <sup>abc</sup>	6.65 ± 3.40 <sup>bd</sup>
April 1995	17.0 ± .2	50.22 ± 30.42 <sup>ac</sup>	*	8.66 ± 3.66 <sup>bcd</sup>



Figure 11: Seasonal water temperatures at Phillips Creek in sediment chambers (N=5) and water column chambers (N=4). Error bars represent standard deviations.



Figure 12: Estimated seasonal above-ground *Spartina alterniflora* biomass at the Phillips Creek salt marsh ecosystem. Means were calculated based on 25-50 shoots. No live shoots were available for harvest in Mar-94 and Feb-94. Error bars represent standard deviations.



Figure 13: Seasonal water column chlorophyll *a* concentrations at Phillips Creek in sediment chambers (N=5) and water column chambers (N=4). No data were available for Apr-95. Error bars represent standard deviations.



Figure 14: Seasonal sediment chlorophyll *a* concentrations at Phillips Creek (N=10). Error bars represent standard deviations.

unable to be processed for the April 1995 experiment. Water column chlorophyll *a* concentration in the sediment chambers was highest in March 1994 (16.34  $\mu$ g chl *a* l<sup>-1</sup>) and was significantly different than all other months (p<.01). December 1994 exhibited the least amount of chlorophyll *a* (7.14  $\mu$ g chl *a* l<sup>-1</sup>).

Sediment chlorophyll *a* concentration was highest in March 1994 (16.34 mg chl *a* m<sup>-2</sup>) and was significantly different (p<.05) than all other months except July (p>.90). Lowest concentrations of sediment chlorophyll *a* were in September 1994 and February 1995 (6.92 and 6.65 mg chl *a* m<sup>-2</sup>).

Water Column Chambers. Table 10 and Figures 11 and 13 summarize the monthly means of water temperature and water column chlorophyll a for the water column chambers. Both displayed significant (p<.01) differences between sampling dates.

Water temperature was significantly different (p<.01) between all months except December 1994 and April 1995 (p>.90). Highest water temperature was in July 1994 (33.1 °C), while lowest was in February 1995 (7.5 °C).

March 1994 had the highest water column chlorophyll *a* concentration (32.51  $\mu$ g chl *a* l<sup>-1</sup>) and was significantly different (p<.01) than all other months. Lowest concentration was in December 1994 (3.33  $\mu$ g chl *a* l<sup>-1</sup>).

## **Exchange Rates - Correlation and Multiple Regression Analyses**

Sediment Chambers. All seven experiments were combined to develop a correlation matrix (Table 11) for exchange rates and environmental parameters. Table 12 summarizes the results of multiple regression analyses. Because sediment chlorophyll a samples could not be taken within the chambers themselves, multiple regression analyses as above could not be performed; however, simple linear regressions were performed between the various exchange rates and sediment chlorophyll a.

Table 10: Average (mean  $\pm$  s.d.) water temperatures and water column chla *a* for water column chambers (n = 4). Superscripts a, b, and c denote statistical similarity (one-way ANOVA repeated measures; Tukey's test; p $\leq$ .05).

\* = no data available

Date	H <sub>2</sub> O Temperature °C	H <sub>2</sub> O column chla a μg l·1
March 1994	16.3 ± 0.5	32.51 ± 2.84
May 1994	$25.1 \pm 0.1$	7.47 ± 0.40acd
July 1994	<b>33.1 ± 0.3</b>	12.99 ± 0.47bd
September 1994	22.3 ± 0.1	4.33 ± 0.13ac
December 1994	$17.3 \pm 0.2^{a}$	3.33 ± 0.56°
February 1995	7.5 ± 0.1	9.65 ± 0.90 <sup>abd</sup>
April 1995	17.4 ± 0.2 <sup>a</sup>	*



Table 11: Correlation matrix of sediment chamber exchange rates with environmental parameters \*=R<sup>2</sup> value; p=probability level; n=number of samples.

	H <sub>2</sub> O Temperature (°C)	NH4 <sup>+</sup> Concentration (μM)	NO <sub>3</sub> + Concentration (µM)	DOC Concentration (mg I-1)	H <sub>2</sub> O Chla <i>α</i> (μg 1-1)	S. alterniflora Above-ground Biomass (g DW m·2)
NH4 <sup>+</sup>	45266*	70864	.37731	41675	.49608	70659
Exchange	p<.006	p<.000	p<.025	p<.068	p<.005	p<.000
(μmol-N m-2 h-1)	n = 35	n = 35	n = 35	n = 20	n = 30	n = 25
NO <sub>3</sub> -	.10563	.17996	96281	.25755	84269	.15008
Exchange	p<.546	p<.301	p<.000	p<.273	p<.000	p<.474
(μmol-N m-2 h-1)	n = 35	n = 35	n = 35	n = 20	n = 30	n = 25
DOC	52050	29850	43037	13598	.35291	.26119
Exchange	p<.022	p<.214	p<.066	p<.579	p<.197	p<.367
(mg-DOC m-2 h-1)	n = 19	n = 19	n = 19	n = 19	n = 15	n = 14
DO	41379	51478	.06938	29431	73510	10626
Exchange	p<.023	p<.004	p<.716	p<.000	p<.000	p<.613
(mg-O <sub>2</sub> m- <sup>2</sup> h-1)	n = 30	n = 30	n = 30	n = 20	n = 25	n = 25

Multiple regression models of environmental parameters on sediment	chamber exchange rates. Forward stepwise regressions performed.	(NH <sub>4</sub> <sup>+</sup> conc=NH <sub>4</sub> <sup>+</sup> concentration, NO <sub>3</sub> <sup>-</sup> conc=NO <sub>3</sub> <sup>-</sup> concentration,	DOC conc=DOC concentration, $H_2O$ chla <i>a</i> =water column chla <i>a</i>	concentration, Biomass=above-groundS. alterniflora biomass, H <sub>2</sub> O	temp=water temperature).
Table 12:					

Exchange	u	Correlated Variables	Multiple R2	R2 Change	p-level
NH4+	20	NH <sub>4</sub> + conc H <sub>2</sub> O chla <i>a</i> Biomass H <sub>2</sub> O temp	.5022 .6814 .9680 .9746	.5022 .1792 .2867 .0066	.0007 .0074 .0000 .0674
NO <sub>3</sub> -	30	NO <sub>3</sub> - conc H <sub>2</sub> O chla <i>a</i>	.9270 .9277	.9270 .0007	.0000 .6171
DOC	19	H <sub>2</sub> O temp	.2709	.2709	.0223
DO	15	H <sub>2</sub> O chla <i>a</i> NH <sub>4</sub> + conc DOC conc	.5404 .8957 .9939	.5404 .3553 .0982	.0024 .0001 .0000

NH<sub>4</sub>+ uptake was positively correlated with water temperature, concentration of NH<sub>4</sub>+ in the water column, and above-ground *S. alterniflora* biomass (multiple R<sup>2</sup>=.9746, .5022, and .9680 respectively; p<.07; Figures 15 a-c). NO<sub>3</sub>- uptake was positively correlated with concentration of NO<sub>3</sub>- in the water column (multiple R<sup>2</sup>=.9270; p<.001; Figure 16a) and sediment chlorophyll *a* (R<sup>2</sup>=.5201; Figure 16b). NH<sub>4</sub>+ and DOC concentrations in the overlying water were significantly related to DO exchange (Multiple R<sup>2</sup> =.8957, and .9939 respectively; p<.001). No strong correlations were observed between DOC exchange and any of the environmental parameters measured.

Water Column Chambers. Table 13 is a correlation matrix of all measurements performed on the water column chambers. Table 14 summarizes multiple regression analyses performed on the exchange rates.

Correlation and multiple regression analyses suggested a relationship between  $NH_4$ + uptake and water temperature, and also for  $NH_4$ + release and water chlorophyll a; however, these relationships were rather weak (multiple R<sup>2</sup>=.1385; p<.08 and R<sup>2</sup>=.2951; p<.05 respectively). NO<sub>3</sub>- release was positively correlated with water temperature and NO<sub>3</sub>- uptake was positively correlated with NO<sub>3</sub>- concentration (multiple R<sup>2</sup>=.3693; p<.01 and R<sup>2</sup>=.5299; p<.02 respectively). DOC uptake was related only to DOC concentration in the water column (R<sup>2</sup>=.6156; p<.01). NH<sub>4</sub>+ concentration was the only variable significantly related to DO release (R<sup>2</sup>=.3898; p<.01).

#### **Diurnal Tidal Creek Studies**

Table 15 is a summary of the ranges in salinity,  $NH_4$ + and  $NO_3$ - concentrations over diurnal tidal cycles for the seven tidal creek samplings at Phillips Creek. No salinity



Figure 15: Linear regression models of environmental variables which were correlated to NH<sub>4</sub>+ exchange rates within sediment chambers (N=5) at Phillips Creek. Negative (-) values indicate uptake of NH<sub>4</sub>+ by the salt marsh and positive values indicate a release of NH<sub>4</sub>+ from the salt marsh. a) NH<sub>4</sub>+ exchange rate vs. water temperature. b) NH<sub>4</sub>+ exchange rate vs. NH<sub>4</sub>+ concentration in the overlying water. c) NH<sub>4</sub>+ exchange rate vs. *S. alterniflora* above-ground biomass. Error bars represent standard deviations.



Figure 16: Linear regression models of environmental parameters related to NO<sub>3</sub>-exchange rates for sediment chambers (N=5) at Phillips Creek. Negative (-) values indicate uptake of NO<sub>3</sub>- by the salt marsh. a) NO<sub>3</sub>- exchange rate vs. NO<sub>3</sub>- concentration in the overlying water; b) NO<sub>3</sub>- exchange rate vs. sediment chlorophyll *a* concentration. Error bars represent standard deviations.
	$H_2O$	NH4+	NO3+	DOC	02H
	Temperature	Concentration	Concentration	Concentration	Chia a
	(°C)	(µM)	(µM)	(mg l-1)	(µg l-1)
NH4+	*37217	28463	14138	.19535	.35317
Exchange	p<.051	p<.142	p<.473	p<.468	p<.090
(μmol-N m-2 h-1)	n = 28	n = 28	n = 28	n = 16	n = 24
NO <sub>3</sub> -	.60769	.47223	44120	17911	38023
Exchange	p<.001	p<.011	p<.019	p<.507	p<.067
(μmol-N m-2 h-1)	n = 28	n = 28	n = 28	n = 16	n = 24
DOC	.23506	41894	.54438	78458	59879
Excnange	p<.381	p<.100	p<.029	p<.000	p<.040
(mg-DOC m-2 h-1)	n = 16	n = 16	n = 16	n = 16	n = 12
DO	.52514	.62437	.14085	.35998	07436
Exchange	p<.008	p<.001	p<.512	p<.171	p<.755
(mg-O <sub>2</sub> m <sup>-2</sup> h <sup>-1</sup> )	n = 24	n = 24	n = 24	n = 16	n = 20

Multiple regression models of environmental parameters on water column	chamber exchange rates. Forward stepwise regressions performed.	(NH <sub>4</sub> + conc=NH <sub>4</sub> + concentration, NO <sub>3</sub> - conc=NO <sub>3</sub> - concentration, DOC	conc=DOC concentration, $H_2O$ chla a=water column chla a concentration,	H <sub>2</sub> O temp=water temperature).
Table 14:				

Exchange	u	Correlated Variables	Multiple R <sup>2</sup>	R2 Change	p-level
NH4 <sup>+</sup>	24	H <sub>2</sub> O temp H <sub>2</sub> O chla <i>a</i>	.138 <b>5</b> .2951	.1385 .1566	.0739 .0425
NO <sub>3</sub> -	24	H <sub>2</sub> O temp NO <sub>3</sub> - conc NH <sub>4</sub> + conc	.3693 .5299 .5634	.3693 .1606 .0335	.0018 .0144 .2300
DOC	12	DOC conc NO <sub>3</sub> - conc	.6156 .6572	.6156 .0416	.0031 .3232
DO	24	NH <sub>4</sub> + conc	.3898	.3898	.0012

and NO <sub>3</sub> - concentrations for tidal creek	
Ranges of salinity, NH <sub>4</sub> +,	exchange studies
Table 15:	

- \* = no data available
  \*\* = incomplete data set

Date	Salinity psu	NH4+ µМ	NO <sub>3</sub> - µМ
March 1994	8.6 - 24.0	0.00 - 2.48	0.72 - 57.64
May 1994	24.2 - 31.6	1.46 - 6.81	1.59 - 11.48
July 1994	21.8 - 33.7 **	0.46 - 27.87	1.01 - 4.84
September 1994	*	4.12 - 11.89	1.14 - 2.58
December 1994	23.0 - 32.0	2.41 - 6.49	1.15 - 6.78
February 1995	26.0 - 33.0	0.91 - 5.23	0.25 - 6.00
April 1995	27.0 - 33.0	2.94 - 15.72	0.86 - 6.03

data were available for September 1994. Salinity (8.6 - 24.0 psu) and NO<sub>3</sub>- (0.72 - 57.64  $\mu$ M-NO<sub>3</sub>-) concentration displayed the greatest variations during the March 1994 tidal cycle, which was also during a time when the greatest amount of precipitation was recorded (Table 3). Salinity varied the least in April 1995 (27.0 - 33.0 psu), while the least variation in NO<sub>3</sub>- concentration occurred in September 1994 (1.14 - 2.58  $\mu$ M-NO<sub>3</sub>-). Largest difference in NH<sub>4</sub>+ concentration over a tidal cycle was in July 1994 (0.46 - 27.87  $\mu$ M-NH<sub>4</sub>+) while the least difference was in March 1994 (0.00 - 2.48  $\mu$ M-NH<sub>4</sub>+).

Figures 17a-g illustrate the changes in salinity,  $NH_4$ + and  $NO_3$ - concentrations over tidal cycles. On all occasions measured, salinity decreased with the ebbing tide.  $NH_4$ + and  $NO_3$ - concentrations, on the other hand, generally increased on the ebbing tide.

#### DISCUSSION

## Material Exchanges

**DIN Exchanges.** As hypothesized, the Phillips Creek vegetated salt marsh appeared to be a sink for DIN throughout the year.  $NH_4$ + was taken up by the marsh in the spring, summer, and fall, while little if any net exchange occurred in the winter. The salt marsh was also a sink for NO<sub>3</sub>- during all seasons.

Phillips Creek salt marsh is a geologically young, accreting marsh. Over the past 50 years the Phillips Creek salt marsh area is estimated to have increased by 8.2% with a sediment accretion rate of 0.64 cm<sup>-2</sup> y<sup>-1</sup> (Kastler 1983). Sea level rise at the site is estimated to range from 2.8-4.2 mm y<sup>-1</sup> (Oertel et al. 1989). Anderson et al. (in preparation) calculated that in order to keep up with this rate of sea level rise, more nitrogen was required to support the Phillips Creek salt marsh ecosystem than what is newly

Figure 17: Salinity, NH<sub>4</sub>+ concentrations, and NO<sub>3</sub>- concentrations in Phillips Creek over diurnal tidal cycles (Time=time of sampling; High Tide=time of high tide).
a) March 1994; b) May 1994; c) July 1994 (incomplete salinity data set);
d) September 1994 (no salinity data available); e) December 1994; f) February 1995; g) April 1995.





63















deposited by fresh sediments (N% = .1743).

Phillips Creek salt marsh appears to fit the model of Vitousek and Reiners (1975) which predicted that geologically younger, immature ecosystems sequester nutrients. Geologically younger marshes examined by Childers et al. (1993b) in Georgia, Childers and Day (1988) in Louisiana, and Whiting et al. (1989) in South Carolina support the model as well, by consistently showing higher rates of DIN import in comparison to older marshes in comparison.

Previous exchange studies in salt marshes throughout the East and Gulf Coasts have also shown that most vegetated salt marshes are sinks for DIN on an annual basis. Unlike observations at Phillips Creek, seasonal shifts in both uptake and release were often observed within the same marsh (Childers 1993b, Spurrier and Kjerfve 1988, Whiting et al. 1989, Wolaver and Spurrier 1988, Wolaver et al. 1983). The fact that no net releases of DIN were observed at Phillips Creek could result either from differences in rates of biological processes or from experimental design. The studies cited above were all conducted with flumes. In general, flumes were constructed in such a manner that they extended from the tidal creek to the uplands. Sources of DIN contributing to the measured releases, may have included the uplands, mud flats, or porewater advected from creek banks. At the Phillips Creek salt marsh, in situ chamber measurements reflected only exchanges between the vegetated salt marsh and the overlying water column.

A unique aspect of this study was that exchange measurements were performed in conjunction with determinations of process rates by Anderson et al. (in preparation). This afforded the opportunity to make direct comparisons between DIN exchanges and the following process rates: nitrification, denitrification, mineralization, nitrogen-fixation, atmospheric deposition, sediment import, above-ground macrophyte uptake, sediment microalgal uptake, sediment burial, and microbial immobilization. Anderson et al. found that the autotrophic uptake by sediment microalgae and by *S. alterniflora* (7.15 and 27.8 g

N m<sup>-2</sup> h<sup>-1</sup> respectively) accounted for most of the NH<sub>4</sub>+ assimilation. Microbial immobilization was also a significant sink for NH<sub>4</sub>+ (10.29 g N m<sup>-2</sup> h<sup>-1</sup>), whereas coupled nitrification /denitrification and sediment burial accounted for small amounts of NH<sub>4</sub>+ uptake (4.07 and 3.63 g N m<sup>-2</sup> h<sup>-1</sup>).

Experiments conducted by White and Howes (1994) at the Great Sippewissett Marsh, MA, labeled the sediment NH<sub>4</sub>+ pool with <sup>15</sup>N early in the growing season. They suggested that salt marsh plants and nitrifying/denitrifying bacteria compete for DIN which was supplied by the flooding creek water, and also suggested that significant loss of nitrogen to the overlying tidal water was unlikely. They observed a rapid loss of NH<sub>4</sub>+ from salt marsh sediments (20% of that applied) which they attributed to coupled nitrification/denitrification, while the remaining was incorporated into plant tissue. Rate of loss by this pathway rapidly declined and after seven years, more than 40% of the added <sup>15</sup>N remained within the dead organic nitrogen pool. Of the total sinks for NH<sub>4</sub>+ calculated and/or measured at Phillips Creek salt marsh, nitrification accounted for only 7.5% (Anderson et al. in preparation).

Valiela and Teal (1979) found the Great Sippewissett Marsh, a system greatly enriched with NO<sub>3</sub>- from a ground water source, exhibited losses of nitrogen from the salt marsh system primarily through denitrification; however, loss through tidal exchange was similar in magnitude (6,940 and 5,350 kg N yr<sup>-1</sup> respectively;). Overall, it was concluded that the losses of nitrogen by denitrification and tidal export balanced the gains to the system. To the contrary, rates of denitrification at Phillips Creek were extremely low (Anderson et al. in preparation) and tidal water was a source of DIN to vegetated salt marsh sediments (Table 5; Figure 4a).

Results of this study indicate that at Phillips Creek, DIN uptake by the vegetated salt marsh sediments was strongly and positively related to DIN concentration in the

overlying water column (Table 12; Figures 15b and 16a). It is suggested that microbial processes and assimilation by sediment microalgal and macrophytic communities created the observed flux of DIN into the salt marsh sediments. Although it was hypothesized that release of NH<sub>4</sub>+ would be observed in the summer and fall due to senescence and degradation of vegetation, greatest uptake of NH<sub>4</sub>+ occurred in July and September 1994. Greatest  $NH_4$ + uptake rates corresponded to times when  $NH_4$ + concentrations in the overlying water and above-ground S. alterniflora biomass were at their highest (Tables 5,7, and 9; Figures 4a, 8a, 12, and 15b-c). Greatest NO<sub>3</sub>- uptake occurred in the early spring (March 1994) when NO<sub>3</sub><sup>-</sup> concentration in the overlying water and sediment microalgal biomass were at their highest (Tables 5, 7 and 9; Figures 4a, 8a, 14, and 16a-b). Observations that creek water NO<sub>3</sub>- concentrations were inversely correlated with salinity strongly suggest that ground water was the major source responsible for high NO<sub>3</sub>concentrations in March 1994. The presence of ground water at Phillips Creek will be addressed more thoroughly later in the discussion. Generally, seasonal exchanges of DIN were at their lowest when concentrations of DIN in the overlying water were at their seasonal lowest (Table 5 and 7; Figures 5 and 9), when no living S. alterniflora was present (Figure 12), and when sediment microalgal biomass was at its lowest (Figure 14). The relationship between DIN exchange and DIN concentration in the overlying tidal water at Phillips Creek was also in agreement with numerous other salt marsh exchange studies (Childers and Day 1988, Childers and Day 1990, Spurrier and Kjerfve 1988, Whiting et al. 1989, Wolaver et al. 1988, Wolaver et al. 1983). While seasonal patterns and directions of exchange did vary among other sites along the East and Gulf Coasts, exchanges were most often related to concentrations of DIN in the overlying tidal water.

In contrast to results obtained from this study, in situ chamber experiments conducted at Phillips Creek by Chambers et al. (1992) found the salt marsh to be a source

of  $NH_4$ + to the overlying water during the growing season.  $NO_3$ - exchanges were not measured. Differences in exchange direction may be explained by two differences in experimental design:

1) Chambers et al. used either low nutrient seawater (1.0  $\mu$ M-NH<sub>4</sub>+) obtained offshore or a low nutrient synthetic seawater (2.5  $\mu$ M-NH<sub>4</sub>+) as the overlying water source within in situ chambers. The mineralization of organic matter can cause NH<sub>4</sub>+ to accumulate within the salt marsh sediments. As a result, a concentration gradient along which NH<sub>4</sub>+ moves to the surface and eventually into the overlying water column can occur if concentrations in the overlying water are less than those in the sediments. By the presence of a low nutrient flood water, as in the Chambers et al. experiments, a release of NH<sub>4</sub>+ into the overlying water could have occurred by the means just described. In the present study ambient marsh water, with significant concentrations of NH<sub>4</sub>+ (1.43 to 5.03  $\mu$ M-NH<sub>4</sub>+), was allowed to flood the marsh sediments which may have reversed the concentration gradient of NH<sub>4</sub>+ back into the sediments.

2) The accumulation of nutrients in surface films can occur during times in which the marsh surface is not flooded (Gallagher 1975, Keizer et al. 1989). Under normal flooding conditions, the initial stages of tidal inundation have been reported to "pick up" these concentrated reservoirs of nutrients. Chambers et al. suggested that at Phillips Creek, the most  $NH_4$ + release occurred during the initial stages of the flooding tidal cycle. By use of a fluctuating water level chamber, which was designed to simulate true tidal action, Chambers et al. were able to sample nutrients in this initial flooding period and therefore were able to "catch" the concentrated pool of  $NH_4$ +. In the present study, exchange measurements did not start until the marsh was well flooded (at least 12 cm.), often as much as a half an hour after the marsh surface was inundated. Any reservoir of concentrated  $NH_4$ + would have been diluted by the time samples were taken. **DO Exchange.** Since standing dead *S. alterniflora* and intertidal sediments have been observed to have substantial oxygen demands, an uptake of oxygen by the vegetated salt marsh is generally expected (Christian et al. 1981). DO exchanges between the Phillips Creek salt marsh sediments and the overlying tidal water were highly variable within and between sampling dates and both releases and uptakes were observed (Tables 5; Figure 7).

The observed production of DO in the water column chambers suggests that an autotrophic community dominates the water column of the Phillips Creek salt marsh ecosystem during all seasons except winter (Table 6; Figure 7). Despite the variability of the salt marsh DO exchange data, the salt marsh was a source of oxygen to the tidal water during the winter months (December 1994 and February 1995). It is suggested that the Phillips Creek salt marsh community became net autotrophic during seasons when there was little or no living above-ground *S. alterniflora* (Figures 7 and 12), thereby demonstrating the importance of sediment microalgal photosynthesis to the system .

**DOC Exchange**. It had been hypothesized that the Phillips Creek vegetated salt marsh would be a source of DOC to the tidal water. Although highly variable, data suggest that the salt marsh was, to the contrary, a sink for DOC (Table 5; Figure 6). No significant differences were measured between the fall, winter, and spring. Unfortunately, no conclusions can be drawn for the summer season, since data collected for analyses were not usable. Several flume experiments have shown similar variability with respect to DOC exchange. Childers et al. (1993a) measured significant import of DOC in geologically younger and accreting marshes in Cumberland, Georgia as did Childers and Day (1990) in Louisiana. Wolaver and Spurrier (1988) also found annual import of DOC in the geologically young Bly Creek, South Carolina salt marsh, although the import was not significant. Chalmers et al. (1985) measured no significant exchanges of DOC in Sapelo Island, Georgia although it was suggested that during rainstorms and periods of low tide drainage, marshes were significant sources of DOC to tidal creeks.

In the present study it was anticipated that by measuring exchanges at small temporal (2 hour) and spatial scales (0.0792 m<sup>-2</sup>), a release of DOC from the vegetated marsh sediments would be measurable before its utilization by the microbial community. This was not the case. Bacterial utilization of DOC derived from *S. alterniflora* leachates has been observed to occur rapidly upon introduction of DOC to bacteria (Gallagher et al. 1976, Turner 1978, Moran and Hodson 1989). If a source of labile DOC were provided by the Phillips Creek vegetated salt marsh, it was likely to have been rapidly utilized before export out of the system. Christian et al. (1981) reported similar results in the Duplin River, Georgia. They measured rapid consumption of labile DOC by the bacterial community and found that little if any DOC produced by the marsh left the river as DOC.

**Other Considerations.** Logistics did not allow night time sampling at Phillips Creek salt marsh. The effect of dark conditions on DIN exchange rates was beyond the scope of this study. However, the relationship that may occur between diel variation and material exchanges can have important ramifications which need to be considered.

It is expected that the benthic autotrophic community present on the salt marsh sediment surface has the ability to intercept and assimilate a portion of DIN that could potentially be released from the sediments. Autotrophic assimilation of DIN by microalgae is more likely to occur during the day when photosynthetically active. Nowicki and Nixon (1985) estimated that approximately 25% of the NH<sub>4</sub>+ released from subtidal coastal lagoon sediments to the overlying water column was intercepted by a benthic microfloral population. Rizzo (1990) reported reduced NH<sub>4</sub>+ release from autotrophic subtidal sediments during lighted conditions as opposed to darkened conditions. Andersen (1986) investigated salt marsh sediment DIN exchanges and found that under laboratory conditions, short term changes in temperature had significant effects on exchange rates on exchange rates suggesting that diel variation may be important. Anderson et al. (in preparation) calculated that the uptake of  $NH_4$ + by sediment microalgae in the Phillips Creek marsh was approximately 40% of that which was taken up by the macrophyte community. Implications for this study are that although an annual uptake of DIN was observed to occur during daylight conditions, uptake of DIN may be greatly reduced or switch to a release during the night when sediment mircroalgae are not actively assimilating DIN for photosynthetic processes.

The effects of burrowing crab populations and their behaviors on material exchanges were also not considered in this study. From field observations, fiddler crabs were plentiful within vegetated sediments throughout the course of this study. Crab activity was much greater in the warmer months, but was not lacking in the colder months. Crab bioturbation has been reported to promote extensive aeration, water percolation and erosion in the upper 10-20 cm. of salt marsh sediments (Pomeroy and Imberger 1981) and is, therefore, likely to increase losses of DIN by coupled nitrification/denitrification within salt marsh sediments.

### **Diurnal Tidal Creek Studies**

It was not the intention of this investigation to perform an intensive hydrodynamic study of the tidal creek exchange characteristics at the Phillips Creek site. DIN exchanges between the salt marsh and adjacent coastal waters, based on water volumes moving in and out of the creek, therefore, were not calculated. Tidal creek sampling occurred in conjunction with the salt marsh exchange studies in order to gain a better idea of the DIN concentrations and variations in concentrations that occurred throughout diurnal tidal cycles. For most experiments, the continuous increase in DIN concentrations as water left the creek implies that Phillips Creek exported DIN on the ebbing tide (Figures 17a-g). These findings are in agreement with numerous other mass balance and hydrodynamic studies which have taken place in salt marsh tidal creeks (Axelrad et al. 1976, Valiela and Teal 1979, Whiting et al. 1985, Whiting et al. 1987, Wolaver et al. 1988, Dame et al. 1991). Export of  $NO_3$ - in creek water during ebb tide was much more clearcut in this study than was the export of  $NH_4$ +.

Since the vegetated salt marsh appeared to be a significant sink for DIN, intuitively an export of DIN by the tidal creek would not seem likely. To explain the observed export of DIN out of the creek, sources of DIN must be identified. Nitrification within the creek water or within creek sediments could, in part, explain the high NO<sub>3</sub><sup>-</sup> concentrations observed at low tide, especially since more atmospheric oxygen is available to nitrifying bacteria in a low tide situation. However, it is unlikely that nitrification was the source of NO<sub>3</sub>- observed leaving the tidal creek, since NH<sub>4</sub>+ concentrations within sediments were lowest during March 1994 (Anderson et al. in preparation). It is hypothesized that ground water was the source of NO<sub>3</sub>- observed at low tide in Phillips Creek. Several other studies have also suggested ground water as a significant source of DIN to the salt marsh (Valiela and Teal 1979, Wolaver et al. 1988, Dame et al. 1991). Of the five dates when data were available, salinities of the creek water were always inversely proportional to concentrations (Figures 18a-e). The concentration of  $NO_3$ - that would exist at 0.0 psu was determined from the intercept of the regression of NO<sub>3</sub>- vs. salinity. The values thus calculated here  $(16.0 - 86.0 \,\mu\text{M}-\text{NO}_3)$  are in the same range as creek bank well water samples that were measured by Tapper (1995) close to the present study site. These data imply there was a source of fresh water to the creek. It is suggested that since Phillips Creek salt marsh has no other permanent fresh water connections with the uplands, other than runoff from storm events (no samplings for the present study occurred after storm events), the fresh water source must have come from ground water. There is strong evidence in support of this

Figure 18: Linear regression models of creek water NO<sub>3</sub>- concentrations vs. salinity at Phillips Creek over diurnal tidal cycles. Little or no salinity data were available for the July 1994 and September 1994 experiments. a) March 1994; b) May 1994; c) December 1994; d) February 1995; e) April 1995.





suggestion.

Extensive research conducted at the Phillips Creek site by Tapper (1995) suggested that fertilizers applied to the adjacent agricultural fields were a significant source of DIN to ground water in the Phillips Creek ecosystem. These studies determined a substantial ground water flow from the agricultural fields in the direction of the adjacent marsh and creek. Isotopic composition of NO<sub>3</sub>- in well water samples along the creek bank showed evidence of fertilizer-derived NO<sub>3</sub>-. Ground water wells placed along a transect starting in the agricultural field, through the salt marsh, and to the creek bank displayed a considerable decrease in NO<sub>3</sub>- concentration from the field to the creek bank (836  $\mu$ M to 65  $\mu$ M). Tapper proposed that as ground water moved from field to creek, dilution, denitrification, and utilization by marsh vegetation could be responsible for the decrease in NO<sub>3</sub>- concentration.

It is also important to note that ground water discharge rates can exhibit seasonal variations and can be influenced by precipitation events (Tapper 1995). At the Phillips Creek site, ground water discharge rates may be directly related to ground water contributions of NO<sub>3</sub>- into the tidal creek. The present study observed highest NO<sub>3</sub>- concentration and highest NO<sub>3</sub>- uptake by the marsh for the March 1994 experiment, during a time of above average rainfall (Figure 19) This implies that an increased discharge of ground water into the creek may have occurred as a result of rainfall. Lowest concentrations of NO<sub>3</sub>- and lowest NO<sub>3</sub>- uptake by the marsh were measured the following year in February and April 1995, during a time of less than average rainfall.

Although not as well-defined as the  $NO_3$  export,  $NH_4$ + export by the creek water was observed on most occasions. No evidence exists, however, that ground water was the source of this  $NH_4$ +. In fact,  $NH_4$ + concentrations in well water samples along the creek bank, as well as those in the salt marsh and agricultural field were negligible (Tapper



Figure 19: Average monthly precipitation at Phillips Creek

1995). It is hypothesized that advection of porewater from the creek bank, and subtidal advective water flux from the creek bottom were responsible for the export of  $NH_4$ + out of Phillips Creek. Although no data exists for this site, studies conducted in other East Coast salt marsh systems have suggested that upon low tide exposure, advection of porewater rich in  $NH_4$ + can occur from the creek bank sediments into the tidal creeks (Wolaver et al. 1983, Wolaver et al. 1984, Jordan and Correll 1985, Howes and Goehringer 1994). Whiting and Childers (1989) estimated that subtidal advective flux in a North Inlet, South Carolina marsh creek supplied more than three times as much  $NH_4$ + as low tide runoff from the vegetated marsh. While porewater advection from creek banks and creek bottoms appeared to be a source of  $NH_4$ + to the tidal creek, it was not found to be a significant means of transfer of DIN from salt marsh sediments to the adjacent creek water (Howes and Goehringer 1994) and may be the case at Phillips Creek as well.

Another interesting observation made from the Phillips Creek diurnal tidal creek sampling data was that on most occasions, night time  $NH_4$ + concentrations were higher than daytime concentrations. This diel variation reflects the uptake/release dynamics of the marsh and suggests that uptake of  $NH_4$ + by the creek water and the salt marsh may be greatly reduced and /or release of  $NH_4$ + may occur by the marsh at night. Diel variation was not observed for  $NO_3$ - concentration.

#### Assessment of in situ Chamber Design

The use of in situ chambers which isolate small areas of the marsh appeared to be an effective means of measuring material exchanges between the vegetated salt marsh sediments and the overlying water column. Although rather tedious and very weather dependent, experiments using in situ chambers offered near ambient conditions. Unlike a naturally flooding marsh, the same water impounded within the chambers, stayed on top of the marsh sediment surface for two hours, although stirring did take place. Since DIN uptake rates were found to be significantly related to DIN concentrations in the overlying water, and as there was a continuous depletion of the DIN pool within a chamber over the course of the experiment, uptake rates measured in the present study could be a slight underestimate of actual uptake rates at Phillips Creek.

Using in situ chambers to measure DOC exchanges did not prove to be as consistent and reliable as the DIN exchange measurements. No other studies of this nature have been conducted on DOC exchange dynamics, therefore no other data exists to compare Phillips Creek DOC exchanges with. More studies should be conducted to determine whether in situ measurements at smaller temporal and spatial scales are a feasible means of measuring DOC exchange dynamics.

To determine the effects of temporal and spatial heterogeneity on exchange rates, in situ chamber experiments, as those performed in this investigation, could easily be conducted in unvegetated areas of the salt marsh and under night conditions as well, given sufficient manpower and resources. Although results would have been greatly enhanced, it was not physically possible nor within the scope of this thesis research to perform both vegetated/unvegetated and day/night experiments, .

## CONCLUSIONS

This study suggests that during tidal inundation, the Phillips Creek short-form *S*. alterniflora salt marsh is an annual sink for DIN during daytime flooding tides. The salt marsh exhibited uptake of both  $NH_4$ + and  $NO_3$ - during all seasons except for the latter part of the winter when little net exchange occurred. Further studies must be conducted in order to determine the night time exchange dynamics of this salt marsh system. It is believed that the observed uptake of DIN is a result of assimilation by marsh macrophytes and sediment microalgae, as well as immobilization by microbial communities on and within the salt marsh sediments.

Contrary to what was hypothesized, this area of the vegetated salt marsh did not appear to be a source of DOC to the overlying tidal water. Although measurements were highly variable and low in magnitude, uptake of DOC was measured during the fall, winter and spring. It is likely that the microbial community rapidly utilized most of the DOC that was produced by the salt marsh before export to the overlying water was able to take place.

Tidal creek nutrient dynamics suggest that Phillips Creek exports DIN during all seasons and therefore, may be a source of DIN to surrounding salt marshes and adjacent coastal waters. It is suggested that while the short-form S. alterniflora salt marsh appeared to be a sink for NH<sub>4</sub>+ during most seasons, porewater advection out of the creek bank and subtidal advection were the possible sources of NH<sub>4</sub>+ observed leaving the marsh creek through the ebbing creek water. Since NO<sub>3</sub>- concentrations in the creek water were inversely related to salinity and the vegetated salt marsh sediments were a sink for NO3during most seasons, it is suggested that ground water was the primary source of NO<sub>3</sub>- to the ebbing tidal water. Some of the  $NO_3$ - that entered the ground water as a result of fertilization of the adjacent agricultural fields is likely to have been intercepted and utilized by the salt marsh, while it is likely that some was assimilated by the ground water microbial community. Although some NO<sub>3</sub>- was still released into Phillips Creek, the area of salt marsh under investigation appeared be a substantial "filter" and a crucial sink for surplus nitrogen. Further studies on the nature of advection and ground water discharge into the tidal creek would greatly enhance the understanding of the contribution of these processes to the exchange dynamics at the Phillips Creek salt marsh ecosystem.

As a result of these exchange studies at Phillips Creek, the sink or source nature of

this salt marsh seems to not only be controlled by biological processes, but also by the physical nature of the upland fluxes.

#### LITERATURE CITED

- Andersen, F.O. 1986. Influence of Spartina detritus enrichment on exchange of nutrients between sediment and water in an intertidal area of Bay of Fundy. Marine Ecology Progress Series. 29: 7-14.
- Axelrad, D.M. 1974. Nutrient flux through the salt marsh ecosystem. Ph. D. College of William and Mary.
- Axelrad, D.M., K.A. Moore, and M.E. Bender. Nitrogen, phosphorus and carbon flux in Chesapeake Bay marshes. Virginia Polytechnic Institute.
- Barr, L.H. 1989. Sedimentation and fallout cesium-137 cycling in a Virginia salt marsh M. S. thesis. University of Virginia.
- Benner, R., S.Y. Newell, A.E. Maccubbin, R.E. Hodson. 1984. Relative contributions of bacteria and fungi to rates of degradation of lignocellulosic detritus in salt-marsh sediments. Applied and Environmental Microbiology. 48: 36-40.
- Benner, R., M.A. Moran, and R.E. Hodson. 1986. Biogeochemical cycling of lignocellulosic carbon in marine and freshwater ecosystems: Relative contributions of procaryotes and eucaryotes. Limnology and Oceanography. 31: 89-100.
- Blum, L.K. 1993. Spartina alterniflora root dynamics in a Virginia marsh. Marine Ecology Progress Series. 102: 169-178.
- Boto, K.G. and J.T. Wellington. 1988. Seasonal variations in concentrations and fluxes of dissolved organic and inorganic materials in a tropical, tidally-dominated, mangrove waterway. Marine Ecology Progress Series. 50: 151-160.
- Bowden, W.B. 1986. Nitrification, nitrate reduction, and nitrogen immobilization in a tidal freshwater marsh sediment. Ecology. 67: 88-99.
- Chalmers, A.G. 1982. Soil dynamics and the productivity of *Spartina alterniflora*, In: V.S. Kennedy (ed.), Estuarine Comparisons, 231-242. Academic Press, New York.
- Chalmers, A.G., R.G. Wiegert, and P.L. Wolf. 1985. Carbon balance in a salt marsh: Interactions of diffusive export tidal deposition and rainfall-caused erosion. Estuarine, Coastal and Shelf Science. 21: 757-771.
- Chambers, R.M. 1992. A fluctuating water-level chamber for biogeochemical experiments in tidal marshes. Estuaries. 15: 53-58.
- Chambers, R.M., J.W. Harvey, and W.E. Odum. 1992. Ammonium and phosphate dynamics in a Virginia salt marsh. Estuaries. 15: 349-359.
- Childers, D.L. and J. W. Day. 1988. A flow-through flume technique for quantifying nutrient and material fluxes in microtidal estuaries. Estuarine, Coastal and Shelf Science. 27: 483-494.

- Childers, D.L. and J. W. Day. 1990. Marsh-water column interactions in two Louisiana estuaries. II. Nutrient dynamics. Estuaries. 13: 404-417.
- Childers, D.L. 1993a. Fifteen years of marsh flume--a review of marsh-water column interactions in southeastern USA estuaries, INTECOL Fourth International Wetlands Conference., Elsevier Press.
- Childers, D.L., S. Cofer-Shabica, and L. Nakashima. 1993b. Spatial and temporal variability in marsh-water column interactions in a southeastern USA salt marsh estuary. Marine Ecology Progress Series. 95: 25-38.
- Christian, R.R., R.B. Hanson, J.R. Hall, and W.J. Wiebe. 1981. Aerobic microbes and meiofauna, In: L.R. Pomeroy and R.G. Wiegert (ed.), The Ecology of a Salt Marsh, 113-135. Springer Verlag, New York.
- Dame, R.F. and P.D. Kenny. 1986. Variability of Spartina alterniflora primary production in the euhaline North Inlet estuary. Marine Ecology Progress Series. 32: 71-80.
- Dame, R.F., J.D. Spurrier, T.M. Williams, B. Kjerfve, R.G. Zingmark, R.G. Wolaver, T.H. Chzaowski, H.N. McKellar, and F.J. Vernberg. 1991. Annual material processing by a salt marsh-estuarine basin in South Carolina, USA. Marine Ecology Progress Series. 72: 153-166.
- Day, J.W., C.A.S. Hall, W.M. Kemp, and A. Yanez-Arancibia., ed. *Estuarine Ecology*. 1989, John Wiley & Sons: New York.
- Ducklow, H.W., D.A. Purdie, P.J.L. Williams, and J.M. Davies. 1986. Bacterioplankton: A sink for carbon in a coastal marine plankton community. Science. 232: 865-867.
- Gallagher, J.L. 1975. The significance of the surface film in salt marsh plankton metabolism. Limnology and Oceanography. 20: 120-123.
- Gallagher, J.L., W.J. Pfeiffer, and L.R. Pomeroy. 1976. Leaching and microbial utilization of dissolved organic carbon from leaves of *Spartina alterniflora*. Estuarine and Coastal Marine Science. 4: 467-471.
- Haines, E.B. 1979. Nitrogen pools in Georgia coastal waters. Estuaries. 2: 34-39.
- Hines, M.E., S.L. Knollmeyer, and J.B. Tugel. 1989. Sulfate reduction and other sedimentary biogeochemistry in a northern New England salt marsh. Limnology and Oceanography. 34: 578-590.
- Howarth, R.W. 1993. Microbial processes in salt-marsh sediments., In: T.E. Ford (ed.), Aquatic Microbiology An Ecological Approach, 239-259. Blackwell Scientific Publications, Cambridge, Massachusetts.
- Howes, B.L. and D.D. Goehringer. 1994. Porewater drainage and dissolved organic carbon and nutrient losses through the intertidal creek banks of a New England salt marsh. Marine Ecology Progress Series. 114: 289-301.

- Jordan, T.E., D.L. Correll, and D.F. Whigham. 1983. Nutrient flux in the Rhode River: Tidal exchange of nutrients by brackish marshes. Estuarine, Coastal and Shelf Science. 17: 651-667.
- Jordan, T.E. and D.L. Correll. 1985. Nutrient chemistry and hydrology of interstitial water in brackish tidal marshes of Chesapeake Bay. Estuarine, Coastal and Shelf Science. 21: 45-55.
- Kastler, J.A. 1983. Sedimentation and landscape evolution of Virginia salt marshes. M. S. thesis. University of Virginia.
- Keizer, P.D., B.T. Hargrave, and D.C. Gordan, Jr. 1989. Sediment-water exchange of dissolved nutrients at an intertidal site in the upper reaches of the Bay of Fundy. Estuaries. 12: 1-12.
- Krovitz, D.K., J.H. Porter, and D.L. Richardson. 1994-95. Meteorological measurements of the Virginia Coast Reserve LTER. Data of the Virginia Coast Reserve Long-term Ecological Research Project.
- Lee, V. 1979. Net nitrogen flux between the emergent marsh and tidal waters. M. S. thesis. University of Rhode Island.
- Lewis, V.P. and D.S. Peters. 1984. Menhaden a single step from vascular plant to fishery harvest. Journal of Experimental Biology and Ecology. 84: 95-100.
- Lorenzen, C. 1967. Determination of chlorophyll and phaeopigments: spectrophotometric equations. Limnology and Oceanography. 12: 343-346.
- MacMillin, K.M., L.K. Blum, and A.L. Mills. 1992. Comparison of bacterial dynamics in tidal creeks of the lower Delmarva Peninsula, Virginia, USA. Marine Ecology Progress Series. 86: 111-121.
- Marinucci, A.C. 1982. Trophic importance of *Spartina alterniflora* production and decomposition to the marsh-estuarine ecosystem. Biological Conservation. 22: 35-58.
- Moore, K.A. 1974. Carbon transport in two York River, Virginia marshes. M. S. thesis University of Virginia.
- Moran, M.A. and R.E. Hodson. 1989. Formation and bacterial utilization of dissolved organic carbon derived from detrital lignocellulose. Limnology and Oceanography. 34: 1034-1047.
- Moran, M.A. and R.E. Hodson. 1990. Contributions of degrading *Spartina alterniflora* lignocellulose to the dissolved organic carbon pool of a salt marsh. Marine Ecology Progress Review. 62: 161-168.
- Moran, M.A. and R.E. Hodson. 1994. Dissolved humic substances of vascular plant origin in a coastal marine environment. Limnology and Oceanography. 39: 762-771.

- Morris, J.T. and B. Haskin. 1990. A 5-yr record of aerial primary production and stand characteristics of *Spartina Alterniflora*. Ecology. 71: 2209-2217.
- Nixon, S.W. 1980. Between coastal marshes and coastal waters A review of twenty years of speculation and research on the role of salt marshes in estuarine productivity and water chemistry, In: P. Hamilton and K.B. MacDonald (ed.), Estuarine and Wetland Processes, 437-525. Plenum Press, New York.
- Nowicki, B.L. and S.W. Nixon. 1985. Benthic nutrient remineralization in a coastal lagoon ecosystem. Estuaries. 8: 182-190.
- Odum, E.P. and A.A. de la Cruz. 1967. Particulate organic detritus in a Georgia salt marsh-estuarine ecosystem, In: G.H. Lauff (ed.), Estuaries, 383-388. American Association for the Advancement of Science,
- Odum, W.E., J.S. Fisher, and J.C. Pickral. 1979. Factors controlling the flux of particulate organic carbon from estuarine wetlands, In: R.J. Livingston (ed.), Estuarine Perspectives, 69-89. Plenum Press, New York.
- Oertel, G.F., F.T.F. Wong and J.D. Conway. 1989. Sediment accumulation at a fringe marsh during transgression, Oyster, Virginia. Estuaries. 12: 18-26.
- Perstorp. 1992. Nitrate + Nitrite in Seawater. Perstorp Analytical Corporation.
- Pinckney, J.L. and R.G. Zingmark. 1993. Modeling the annual production of intertidal benthic microalgae in estuarine ecosystems. Journal of Phycology. 29: 396-407.
- Pinckney, J.L. and R. Zingmark. 1994. Comparison of high-performance liquid chromatographic, spectrophotometric, and fluorometric methods for determining chlorophyll *a* concentrations in estuarine sediments. Journal of Microbiological Methods. 19: 59-66.
- Pomeroy, L.R., W.M. Darley, E.L. Dunn, J.L. Gallagher, E.B. Haines, and D.M. Whitney. 1981. Primary production, In: L.R. Pomeroy and R.G. Wiegert (ed.), The Ecology of a Salt Marsh, 21-36. Springer-Verlag, New York.
- Pomeroy, L.R. and J. Imberger. 1981. The physical and chemical environment, In: L.R. Pomeroy and R.G. Wiegert (ed.), The Ecology of a Salt Marsh, 21-36. Springer-Verlag, New York.
- Rice, D.L. and K.R. Tenore. 1981. Dynamics of carbon and nitrogen during the decomposition of detritus derived from estuarine macrophytes. Estuarine, Coastal and Shelf Science. 13: 681-690.
- Rizzo, W.M. 1990. Nutrient exchanges between the water column and a subtidal benthic microalgal community. Estuaries. 13: 219-226.
- Roman, C.T. and F.C. Daiber. 1989. Organic carbon flux through a Delaware Bay salt marsh: tidal exchange, particle size distribution, and storms. Marine Ecology Progress Series. 54: 149-156.

- Scudlark, J.R. and T.M. Church. 1989. The sedimentary flux of nutrients at a Delaware salt marsh site: A geochemical perspective. Biogeochemistry. 7: 55-75.
- Schubauer, J.P. and C.S. Hopkinson. 1984. Above-and belowground emergent macrophyte production and turnover in a coastal marsh ecosystem. Georgia. Limnology and Oceanography. 29: 1052-1065.
- Sismour, E.N. 1994. Contributions to the early life histories of alewife and blueback herring: rearing, identification, ageing, and ecology. Ph. D. dissertation. College of William and Mary.
- Solorzano, L. 1969. Determination of ammonia in natural waters by the phenol hypochlorite method. Limnology and Oceanography. 14: 799-801.
- Spurrier, J.D. and B. Kjerfve. 1988. Estimating the net flux of nutrients between a salt marsh and a tidal creek. Estuaries. 11: 10-14.
- StatSoft. 1991. Statistica/Mac. Tulsa, Oklahoma.
- Tapper, R.J. 1995. A stable isotopic assessment of the inorganic nitrogen input to the ground water near an agricultural area of eastern Virginia. M. S. thesis. University of Virginia.
- Teague, K.G., C.J. Madden, and J.W. Day, Jr. 1988. Sediment-water oxygen and nutrient fluxes in a river-dominated estuary. Estuaries. 11: 1-9.
- Teal, J.M. 1962. Energy flow in the salt marsh ecosystem of Georgia. Ecology. 43: 614-624.
- Turner, R.E. 1977. Intertidal vegetation and commercial yields of penaeid shrimp. Transactions of the American Fisheries Society. 106: 411-416.
- Turner, R.E. 1978. Community plankton respiration in a salt marsh estuary and the importance of macrophytic leachates. Limnology and Oceanography. 23: 442-451.
- Turner, R.E. and D.F. Boesch. 1988. Aquatic animal production and wetland relationships: Insights gleamed following wetland loss or gain., In: D. Hooks (ed.), Ecology and management of wetlands, 25-39. Timber Press, Portland.
- Turner, R.E. 1993. Carbon, nitrogen, and phosphorus leaching rates from *Spartina* alterniflora salt marshes. Marine Ecology Progress Series. 92: 135-140.
- Valiela, I., J.M. Teal, S. Volkmann, D. Shafer, and E.J. Carpenter. 1978. Nutrient and particulate fluxes in a salt marsh ecosystem: Tidal exchanges and inputs by precipitation and groundwater. Limnology and Oceanography. 23: 798-812.
- Valiela, I. and J.M. Teal. 1979. The nitrogen budget of a salt marsh ecosystem. Nature. 280: 652-656.
- Vitousek, P.M. and W.A. Reiners. 1975. Ecosystem succession and nutrient retention: a hypothesis. BioScience. 25: 376-381.

- Welsh, B.L. 1980. Comparative nutrient dynamics of a marsh-mudflat ecosystem. Estuarine and Coastal Marine Sciences. 10: 143-164.
- White, D.S. and B.L. Howes. 1994. Long-term <sup>15</sup>N-nitrogen retention in the vegetated sediments of a New England salt marsh. Limnology and Oceanography. 39: 1878-1892.
- Whiting, G.J., H.N. McKellar, Jr., B. Kjerfve, and J.D. Spurrier. 1985. Sampling and computational design of nutrient flux from a Southeastern U.S saltmarsh. Estuarine, Coastal and Shelf Science. 21: 273-286.
- Whiting, G.J., H.N. B. Kjerfve, and J.B. Spurrier. 1987. Nitrogen exchange between a southeastern USA salt marsh ecosystem and the coastal ocean. Marine Biology. 95: 173-182.
- Whiting, G.J., H.N. McKellar, J.B. Spurrier, and T.G. Wolaver. 1989. Nitrogen exchange between a portion of vegetated salt marsh and the adjoining creek. Limnology and Oceanography. 34: 463-473.
- Whiting, G.J. and D.L. Childers. 1989. Subtidal advective water flux as a potentially important nutrient input to southeastern U.S.A. saltmarsh estuaries. Estuarine, Coastal and Shelf Science. 28: 417-431.
- Wiegert, R.G., L.R. Pomeroy, and W.J. Wiebe. 1981. Ecology of Salt Marshes: An Introduction, In: L. R. Pomeroy and R.G. Wiegert (ed.), The Ecology of a Salt Marsh, 3-18. Springer-Verlag, New York.
- Wolaver, T.G., J.D. Zieman, R.L. Wetzel, and K.L. Webb. 1983. Tidal exchange of nitrogen and phosphorus between a mesohaline vegetated marsh and the surrounding estuary of lower Chesapeake Bay. Estuarine, Coastal and Shelf Science. 16: 321-332.
- Wolaver, T.G., S. Johnson, and M. Marozas. 1984. Nitrogen and phosphorus concentrations within North Inlet, South Carolina-speculation as to sources and sinks. Estuarine, Coastal and Shelf Science. 19: 243-255.
- Wolaver, T.G. and J.D. Spurrier. 1988. Carbon transport between a euhaline vegetated marsh in South Carolina and the adjacent tidal creek: contributions via tidal inundation, runoff and seepage. Marine Ecology Progress Series. 42: 53-62.
- Wolaver, T.G., G.J. Whiting, R.F. Dave, T.M. Williams, and J.D. Spurrier. 1988. Bly Creek ecosystem study - nitrogen exchange within a euhaline salt marsh basin of North Inlet, South Carolina. Marine Ecology Progress Series. 49: 107-116.
- Zar, J. 1996. Biostatistical Analysis. Prentice-Hall, Inc., Upper Saddle River, New Jersey.

# VITA

# Betty Ellen Berry Neikirk

Born in Roanoke, Virginia, 1 May 1961. Graduated from Fort Defiance High School, Fort Defiance, Virginia in 1979. Received B. S. in Biology from Randolph-Macon College in 1983. Started working at the College of William and Mary, Virginia Institute of Marine Science, School of Marine Science in September, 1983. Entered the College of William and Mary, School of Marine Science in September 1991.