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Exchanges of carbon and nitrogen between tidal freshwater wetlands and adjacent tributaries : a final report

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A Final Report Prepared for the

Virginia Coastal Resources Management Program Virginia Department of Environmental Quality

for a project entitled

EXCHANGES OF CARBON AND NITROGEN BETWEEN TIDAL FRESHWATER WETLANDS AND ADJACENT TRIBUTARIES

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by

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[February 1998]



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Abstract

Tidal freshwater marshes are hypothesized to export materials and energy that support primary and secondary production in estuaries, yet there are few data available to test this hypothesis. A major objective of our study was to measure net exchange of carbon between marsh and atmosphere to determine whether biogenic carbon inputs are in excess of those required to produce observed biomass, satisfy the measured accretion rate, and keep pace with the historical rate of sea level rise. To determine whether the marsh exports materials and energy we measured exchanges of nutrients between marsh sediments and overlying water and of nutrients, total suspended solids, and chlorophyll a between the adjacent tidal creek and river. Studies were performed in Sweet Hall Marsh, a National Estuarine Research Reserve, located on the Pamunkey River in Virginia. A gaseous carbon flux model was developed to calculate annual net CO₂ and CH₄ fluxes between the atmosphere and marsh. In addition, we performed seasonal measurements of macrophyte diversity and biomass, sediment microalgal biomass, standing stocks of porewater nutrients, %C and %N in sediments and macrophytes, and sediment gross mineralization and nitrification. Based upon two years of measurements of net ecosystem metabolism, the marsh is net heterotrophic. Estimates of sediment respiration based on net sediment metabolism greatly underestimated the true respiration rate. When gross N-mineralization, expressed in units of carbon, was used as a surrogate for sediment respiration, net autotrophic fixation accounted for estimated biomass production. A process-based carbon mass balance model for Sweet Hall Marsh was constructed to determine whether calculations of carbon exchange using the gaseous carbon flux model and results of exchange studies were reasonable and to guide future research at Sweet Hall Marsh. Results of mass balance analysis showed that inputs and exports of carbon to or from the marsh are reasonably in balance. While additional information on sediment and chlorophyll exchanges would strengthen our model, it appears that on an annual basis Sweet Hall Marsh imports sediments and exports chlorophyll. In addition, the marsh is a sink for NO₃- throughout the year. NH₄+ produced by organic matter mineralization appears to be removed by coupled nitrification denitrification so that there is little, if any, export of dissolved inorganic nitrogen from the marsh. These conclusions indicate that tidal freshwater marshes may export materials (chlorophyll) to adjacent waters, but the ultimate fate of these materials and their effects on estuarine primary and secondary production are still unknown.

Introduction

In Virginia tributaries, tidal freshwater marshes make up a significant portion of wetland habitats and are located near 'head-of-estuary' where watershed influences are focused. Extensive brackish (5 to 0.5 ppt salinity) and freshwater (<0.5 ppt salinity) marshes occupy the upper regions of the tributaries and are among the first tidal wetland systems to interact with watershed inputs of nutrients and suspended solids (sediments). In Virginia tributaries (James, York and Rappahannock rivers), these emergent marshes make up greater than 66,000 acres of wetlands (Hershner and Wetzel 1987). As opposed to salt marshes, which are dominated by a few species of salt-tolerant plants, brackish and freshwater wetlands are co-dominated by many plant species which increases their biodiversity and general habitat value. However, in comparison to salt marshes, brackish and freshwater wetlands are poorly understood ecologically, and ecosystem process models lack the necessary data for realistic model development and analysis.

It has long been hypothesized that tidal freshwater marshes serve as nursery grounds for many important species of fish that inhabit Chesapeake Bay and its tributaries. Fisheries yields in estuaries have been shown to be statistically related to the areal extent of intertidal wetlands (Turner 1977; Turner and Boesch 1988). Tidal freshwater marshes and their associated tidal creeks represent high quality habitats likely to support high rates of secondary production. These wetlands characteristically undergo distinct seasonal changes in dominant vegetation which is not consumed directly and produce high quality detritus as suggested by their high 2 - 4% nitrogen and low crude fiber content (Odum 1988). Sismour (1994), working in tidal freshwater areas of the Pamunkey River (Virginia), characterized the wetland and tidal creek environments as "high quality nursery habitats" for river herring (alewife and blueback herring). He demonstrated significantly higher growth rates of river herring larvae in freshwater wetland - tidal creek habitats than in riverine areas, and attributed this to higher secondary plankton production and greater larval prey availability. He further suggested that these habitat characteristics are related to freshwater marsh - tidal creek organic matter and nutrient cycling processes.

Marshes are also believed to serve as traps and natural biological filters of nutrients and sediments from both tidal waters and uplands. Attempts to determine the magnitude and direction of fluxes of materials, both inorganic and organic, dissolved and particulate, between marshes and adjacent waters have produced contradictory results. Most such studies have been performed in salt or brackish systems (Axelrad et al. 1976; Jordan et al. 1983; Wolaver et al. 1983; Wolaver and Zieman 1983; Whiting et al. 1989; Childers 1993; Neikirk 1996; Anderson et al., 1997). Only a few have been performed in tidal freshwater marshes (Ledwin 1988; Bowden et al. 1991; Chambers 1992).

In order to understand how tidal freshwater marshes impact living resources and water quality in adjacent tributaries and estuaries, it is necessary to assess the magnitude of exchanges of nutrients and suspended solids between marshes and adjacent tributaries and to identify mechanisms responsible for those exchanges. Such data can then be used for development of an ecosystem process model for tidal freshwater marshes typical of lower Chesapeake Bay tributaries. Model development to this point in time is restricted to salt marsh communities characteristic of the mesohaline (5 to 18 ppt salinity) and polyhaline (>18 to 30 ppt salinity) regions of the tributaries (Buzzelli, 1996).

As a first step in model development and to assess the impact of tidal freshwater marshes on adjacent tributaries, a gaseous carbon flux model was developed for Sweet Hall Marsh, taking into account exchanges of carbon dioxide (CO_2) and methane (CH_4) between the atmosphere and marsh communities. Concurrently, exchanges of dissolved nutrients and materials were measured between the marsh and adjacent Sturgeon Creek as well as between Sturgeon Creek and the Pamunkey River.

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Exchanges derived from the gaseous carbon flux model along with observed net exchanges of materials and nutrients between marsh, overlying water, creek, and river were be used to build a process-based model for Sweet Hall Marsh.

The primary objective of the study described here was to provide basic ecological information on marsh productivity and nutrient dynamics to support implementation of an ecosystem model for tidal freshwater marshes.

Study Objectives

The principal objectives of this project were to:

(1) Collect field data necessary for parameterization and calibration of a process-based mass balance model for a tidal freshwater marsh. Field measurements collected seasonally (Table 1) included:

(a) macrophyte and sediment community metabolism

(b) macrophyte above ground biomass, carbon to nitrogen ratios (C/N) and diversity (c) sediment microal calculated above rational calculated above <math>rational calculated above carbon to nitrogen ratios (C/N) and diversity

(c) sediment microalgal chlorophyll a

(d) bulk density, C/N, and percent organic matter through the sediment depth profile

(e) standing stocks of sediment porewater nutrients

(f) sediment nitrogen cycling processes (nitrification, mineralization)

(g) nutrient exchanges between marsh sediments and overlying tidal water

(h) exchanges of inorganic nutrients, total suspended solids, and chlorophyll a between tidal creek and Pamunkey River

(2) Develop a gaseous carbon flux mass balance model for Sweet Hall Marsh.

(3) Develop a process-based carbon mass balance model for Sweet Hall Marsh.

Methods

1. Study Site

Sweet Hall Marsh is a NOAA-National Estuarine Research Reserve (NERR) site located 69 km from the mouth of the York River on the Pamunkey River (Figure 1). It has been the site of numerous studies conducted by VIMS scientists (Ledwin 1988; Booth 1989; Reay 1989; Perry 1991). The site consists of an extensive tidal, freshwater marsh with adjacent nontidal bottomland forests on the mainland side and shallow mudflats on the river side. The adjacent uplands consist of an agricultural site, mixed hardwood and pine forests, and a pine plantation managed by St. Laurent Pulp and Paper, Inc. The loblolly pine plantation was clearcut in 1982, replanted, and is due for harvest again in 2004. The Pamunkey and the Mattaponi rivers are considered to be among the most pristine on the east coast of the U.S. Although this site presently shows little impact by human activity, a proposal to withdraw water from the Pamunkey and Mattaponi rivers for urban use may cause significant changes in wetland habitat.

The site (Figure 1) chosen for this study is isolated from mainland influences by a thoroughfare. Sturgeon Creek, completely surrounded by marsh, drains the site and flows into the Pamunkey River. Tidal range is approximately 80 cm, and much of the marsh is flooded on high tides. Our study site (and on average, the entire marsh) is dominated by the broadleaf macrophytes *Peltandra virginica* and *Pontederia cordata* through most of the growing season while the grass *Zizania aquatica* becomes abundant late in the growing season. At the start of the study (1996), boardwalks were built along three transects extending 30 m into the marsh and perpendicular to the creek bank (Figure 2).

Measurement	May 96	June 96	July 96	Aug 96	Sept 96	Oct 96	Nov 96	Dec 96	Jan 97	Feb 97	Mar 97	Apr 97	May 97	June 97	July 97	Aug 97	Sept 97
Photosynthesis/ Respiration		х			х		х				х	x	х		x		x
Vegetation biomass		Х			Х		Х					Х	Х		Х		
Sediment Chlorophyll a		x			x		X					x	x		x		•
C:N (vegetation)		Х			Х		Х										•.
C:N (sediment)				Х			Х					Х					
Porewater DIN					Х								Х		Х		
Porewater DIC							Х						Х		Х		
Sediment Bulk Density		x		X			x					x					
Sediment % Organic Content		X		X			x					x					
Mineralization		Х			Х		Х					Х					
Nitrification		Х			Х		Х					Х					
Sediment/Water Exchange		x		x			x						x				
Tidal Creek Exchange		x		X			x						x				

Table 1. Measurements Performed from May 1996 through September 1997

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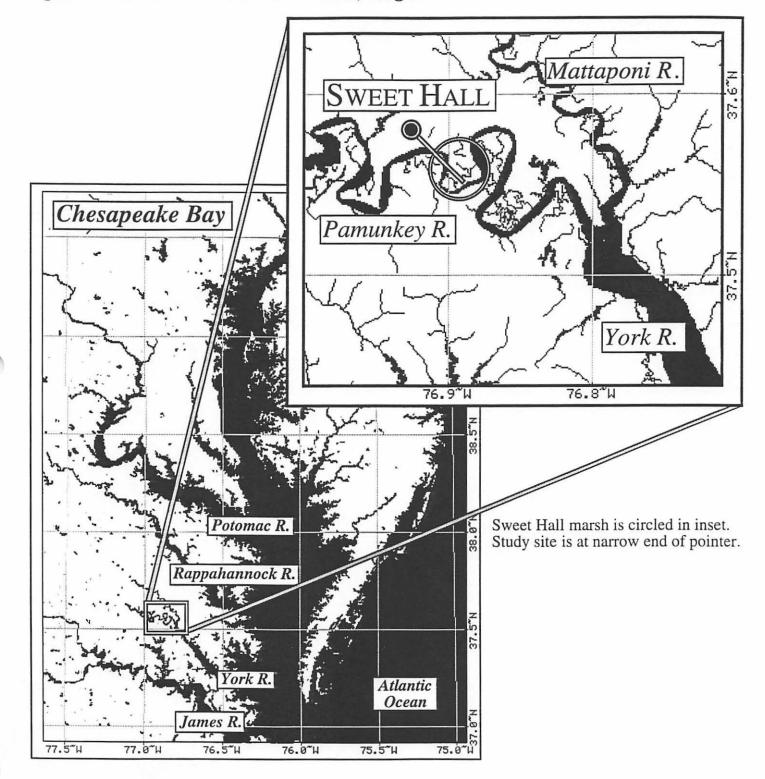
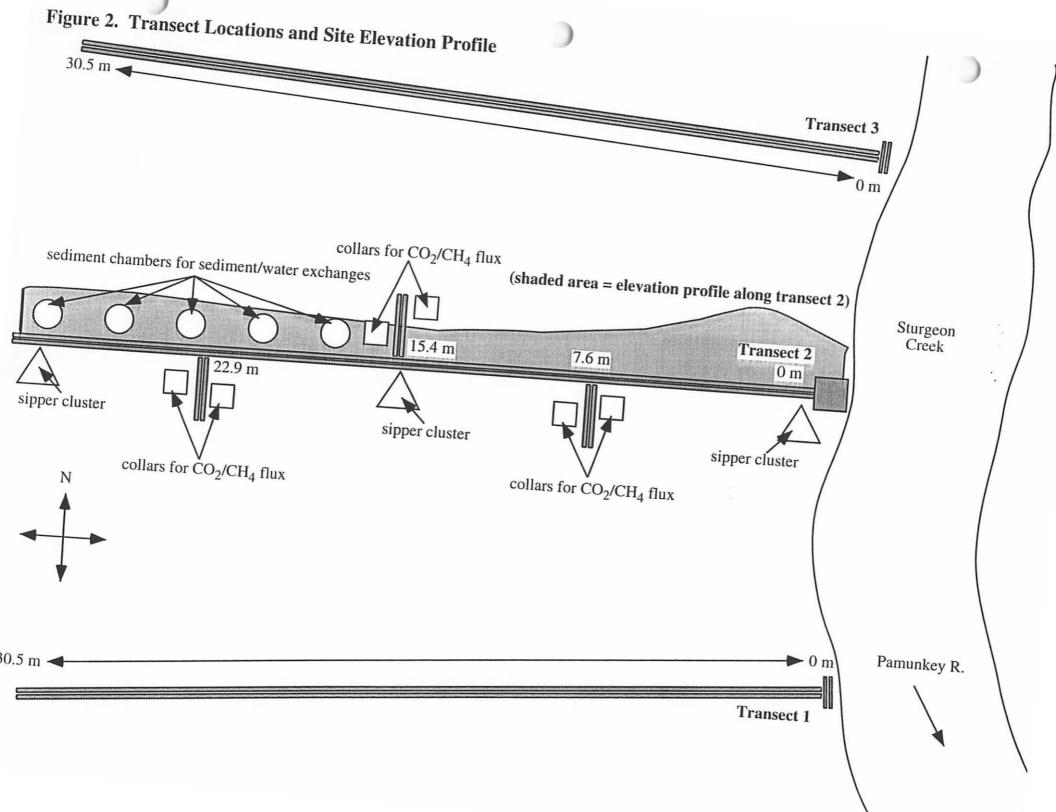


Figure 1. Location of Sweet Hall Marsh, Virginia

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2. Flux Measurements

Marsh community CO_2 and CH_4 flux studies were performed using a large temperature-controlled chamber (695 L, Figure 3), as described by Whiting et al. (1992), and sediment metabolism measured using a small chamber (0.6 L). During spring 1996 six collars for the community flux chambers were installed along one transect and left for the duration of the study in order to minimize disturbance to the site. Fluxes were measured during June, September, November of 1996 and March, April, May, July, and September of 1997 (Table 1). Measurements were made during daytime low tides. In order to maximize light intensities for flux measurements, sampling dates were chosen so that slack low water occurred between 11 am and 1pm. Sampling did not take place on cloudy or rainy days. Flux measurements in the community metabolism chamber were made in the light and dark and at intermediate light levels using shade cloths in order to construct photosynthesis : irradiance (P : I) and respiration : temperature (R : T) curves for each season. Sediment metabolism was measured only in the light and dark.

Prior to making flux measurements community metabolism chambers were clamped to their collars and allowed to equilibrate for 10 - 15 minutes. In order to maintain chamber temperature to $\pm 2^{\circ}$ of ambient, ice water was pumped through a heat exchanger within the chamber and head space air stirred by three fans. The sediment chamber, which was generally shaded by macrophytes, did not have a cooling system.

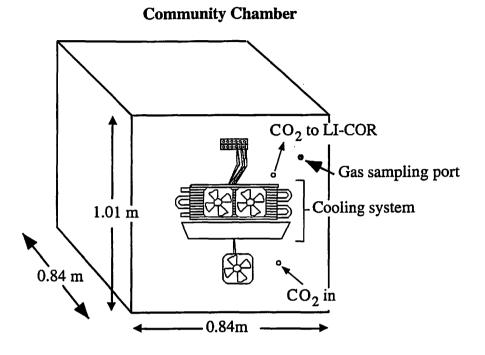
 CO_2 concentrations in each chamber were measured in the field using a LiCor, model 6252 infrared gas analyzer (IRGA). Headspace air was circulated (500 ml min⁻¹) from the chamber through the IRGA and back to the chamber; CO_2 concentrations were measured and recorded at 1 minute intervals using a LiCor model 1000 data logger. Between 5 and 10 measurements were made at each light level. Slopes were generally linear with r² values greater than 0.95. Calibrations were performed daily just before making field measurements after zeroing the IRGA for 15 - 30 min with N₂ passed sequentially through soda lime (to remove CO_2), Nafion tubing packed in silica gel (to remove water) and magnesium perchlorate (MgClO₄, to remove water). Gas standards used for calibration contained 350, 408, or 1000 ppmv CO_2 in N₂ (Scott Specialty Gases, Inc).

Samples for determination of CH₄ fluxes were taken by withdrawing 60 ml of gas from the chamber at 10 minute intervals. Thirty-five ml of the sample was used to flush, and the remainder to pressurize a gas-tight Hungate tube (12.8 ml). Tubes were stored inverted, in brine until analyzed. CH₄ analyses were performed by injecting 50 μ l samples into a Hewlett Packard, model 5890 gas chromatograph, equipped with flame ionization detector and molecular sieve 13x column. Oven temperature was 80°C, and detector temperature was 220°C. A single point calibration of the instrument was performed routinely before and during analyses using a 9.02 ppmv CH₄ in N₂ standard (Scott Specialty Gases, Inc.). Rates of CH₄ flux were linear and showed no response to short term changes in light.

Concurrent with gas flux measurements, incident irradiance was measured using a LiCor 2π light sensor placed on top of the chamber and a 4π sensor at 15cm above the sediment surface within the plant canopy. Temperatures were measured using thermistors similarly positioned outside and inside the chamber as well as in the sediment at a depth of 10-15 cm. Light and temperature data were logged at one-minute intervals on a LiCor, model 1000 data logger.

Tidal effects on CO₂ and CH₄ fluxes were determined during September 1997. Sampling was conducted both during daytime and nighttime high and low tides. CO₂ and CH₄ fluxes in the chamber head space were measured at high tide as were fluxes of dissolved inorganic carbon (DIC) and dissolved CH₄ in water overlying the marsh. Samples for DIC analysis were filtered (0.45 μ m, Gelman Supor) into 12.8 ml gas-tight Hungate tubes, which were stored in brine until analyzed by

Figure 3. Community and Sediment Metabolism Chambers



Community chamber

- encloses surface area of 0.699 m^2 and a volume of 695.8 L
- clear teflon and plexiglass panels
- cooling system to maintain interior temperature at \pm 1°C of ambient
- battery-powered fans to provide air circulation
- LI-COR 2π and 4π light sensors
- thermocouples to measure interior and exterior temperatures
- injection port for injection/removal of gas samples from sealed chamber
- collars to provide air-tight seal with marsh surface

Sediment Chamber (not shown)

- encloses surface area of .008 m^2 and a volume of 0.80 L
- clear polycarbonate cylinder permanently deployed in marsh
- LI-COR 2π light sensors
- thermocouples to measure interior and exterior temperatures
- stopcock for injection/removal of gas samples from sealed chamber

injection (200 µl) into a vessel filled with 0.05 M H_2SO_4 and continuously sparged with CO_2 -free N_2 (300 ml min⁻¹) into an IRGA. Calibrations were performed routinely before and during analyses by injections of 1, 5, and 10 mM NaHCO₃. For dissolved CH₄ water samples (30 ml, unfiltered) were shaken for 30 sec with an equal volume of CH₄-free argon in a 60 ml syringe. The gas was transferred to a 30 ml syringe with stopcock and analyzed within 1-day of collection. CH₄ concentrations in water were calculated using the Ostwald solubility coefficient.

3. Sediment Physical - Chemical Analyses

(1) Sediment Chlorophyll a:

For analysis of microalgal chlorophyll a, sediment was collected using 2 cm diameter core tubes to a depth of at least 1 cm. Triplicate cores were taken at five points along each of two transects from the same areas as sampled for macrophyte biomass. Cores were plugged and kept in the dark until processed. The 0-5 mm section of each core was removed and stored frozen until analyzed. Analysis was performed according to the protocol of Lorenzen (1967), as modified by Pinckney and Zingmark (1994) to include extraction of the sediment (unground) with a mixture of solvents (45% methanol, 45% acetone, 10% DI water) at -15°C for > 1 week.

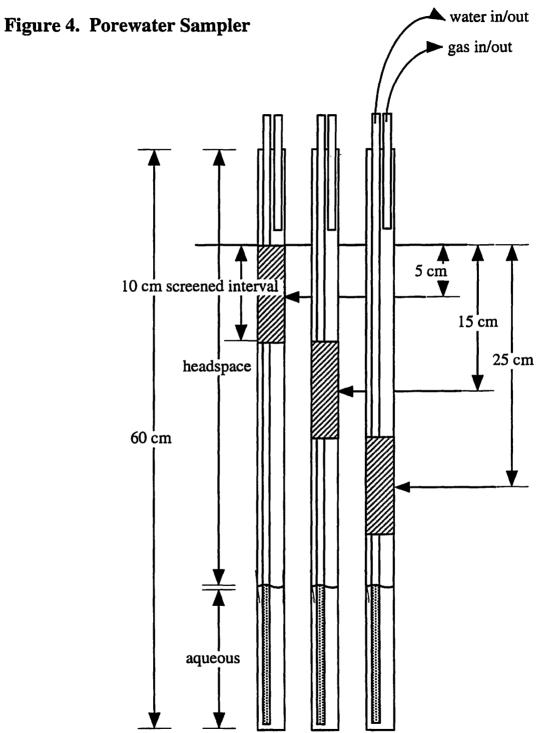
(2) Porewater Sampling

Porewater samplers (sippers) (Figure 4) were installed along transect 2 in August 1996. Clusters of three sippers (with sampling depths of 5, 15, and 25 cm) were placed at 1, 15, and 30 m along the boardwalk. Sampling was conducted on low tide only. All sippers were purged of water using a Nalgene hand vacuum pump. They were then evacuated to 50 to 60 mm Hg and allowed to refill for one to two hours before sampling. Water was collected from the sipper using the hand pump. When water volume was sufficient, the first 30 ml were discarded. The next 30 ml were filter-sterilized with 0.45 μ m syringe filters (Gelman supor acrodiscs) and frozen in whirlpak bags until analyzed. Porewater was analyzed for dissolved inorganic nitrogen (DIN) including ammonium (NH₄+), nitrate (NO₃-) and nitrite (NO₂-) as described below and during some months for DIC, as described above.

(3) Sediment Bulk Density, Percent Organic Matter, and C/N Ratios

Sediment cores (55 cm²) were taken in triplicate to a depth of 30 cm at five points along each of three transects. Minimal compaction was noted for the majority of the cores, although some compaction did occur as the core depth approached 30 cm. Cores were immediately sectioned at the following depth intervals: 0-2, 2-5, 10-13, 18-21, and 27-30 cm and sections stored in preweighed aluminum foil envelopes. Sections were weighed upon return to the lab, and dried at 50°C for three to four weeks. Samples were reweighed and (dry) bulk density was calculated.

Dried samples were split in half. Half was reweighed, combusted at 500°C for 5 hours, and reweighed to determine organic matter content. Loss on ignition was assumed to represent all organic matter within the sediment section. The remaining sediment fraction was ground in a Wiley mill (#40 screen) for determination of percent carbon and nitrogen (%C and %N). A portion of each dried, ground sample was weighed into ashed silver cups and acidified (HCl, 1-2 drops, 10%) to remove carbonates. Samples were placed on a hot plate to evaporate excess acid. The acidification step was then repeated, and samples were allowed to dry fully in a 80°C drying oven overnight. Percent N, % C, and C/N ratios were measured using a Fison model EA 1108 elemental analyzer.



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(4) Aboveground macrophyte biomass:

Seasonally, aboveground macrophyte biomass was clipped at five points along each of two transects in the marsh. Sampling locations were determined by selecting a random point from within each of five strata per transect (determined by overall vegetation characteristics). A 0.11 m² ring was blindly dropped at each sampling point; all vegetation rooted within the ring was clipped and returned to the lab for sorting. Samples were sorted by species into living (50 - 100% green), dying (0-50% green), and dead fractions, dried at 50°C for three to four weeks and weighed.

A portion of each sample was ground in a Wiley mill (#40 screen) and weighed into ashed silver or tin cups. Percent N, % C, and C/N ratios were measured using a Fison model EA 1108 elemental analyzer.

4. Sediment Microbial Processes

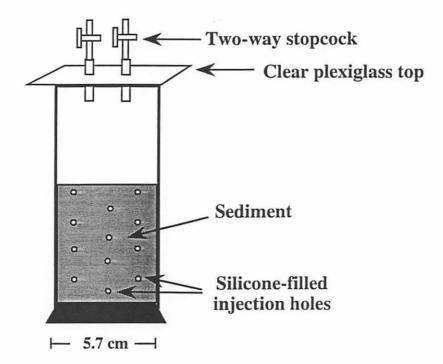
(1) Gross Nitrogen Mineralization

Gross mineralization was determined by ¹⁵NH₄+ isotope pool dilution as described in Anderson et al. (1997). Sediment cores (10 cm deep) were collected seasonally in triplicate at 5 randomly selected points along each transect using polycarbonate core tubes (20 cm tall by 25.5 cm², Figure 5). Each core was injected with 4.0 ml (0.1 ml per hole) of argon-sparged ¹⁵N-labelled ammonium sulfate ((15NH₄)₂SO₄, 10 mM, 99.7 atom percent) to a final concentration of 1 mM and 30 atom % 15N enrichment in porewater. Cores were incubated at ambient temperature in the dark for either 0, 24, 48 h (November 96) or 0, 6, 24 h (September 96 and April 97). After each incubation period one of each set of three cores was sacrificed by addition of KCl (255 ml, 2M). Sediment slurries were shaken in whirlpak bags for 1 hour on a rotary shaker at room temperature and centrifuged. Supernatants were filter sterilized using 0.45 µm syringe filters (Gelman supor acrodiscs) and stored frozen in whirlpak bags until analyzed for NH₄+, NO₃-, and NO₂- as described below. Remaining supernatants were then transferred to sterile, disposable specimen cups. After addition of magnesium oxide (MgO, 0.2g) NH₃ was trapped on acidified (KHSO₄, 10 µl, 2.5M) paper filters (Whatman #3, 7 mm) for 6 days, as described by Brooks (1989). Disks were dried overnight in a desiccator over concentrated H_2SO_4 , wrapped in tin capsules, and analyzed for %C, %N, and ¹⁵N enrichment using an elemental analyzer coupled to an isotope ratio mass spectrometer at the University of California at Davis. Rates of mineralization were determined using a model described by Wessel and Tietema (1992) which takes into account both the change in atom % enrichment of the ¹⁵N-labelled pool as well as the change in total concentration of that pool (15N + 14N).

(2) Gross Nitrification

Nitrification was determined by ¹⁵NO₃- isotope pool dilution as described in Anderson et al. (1997). Measurements were performed as described for mineralization with the following modifications. Core tubes (9 cm tall by 25.5 cm², 15 per transect) were used to collect 3 cores at each of five randomly selected positions along each transect. Cores were injected with 1.4 ml argon-sparged K¹⁵NO₃ (10 mM, 30 atom %) to a final concentration of 1 mM and 30 atom % ¹⁵N enrichment. Incubations times were 0, 3, 6 hours at ambient temperature in the dark. Following extraction with KCl (2M, 75 ml), centrifugation, and filter-sterilization (as above), MgO (0.2 g) was added to the supernatant and the specimen cups left uncovered for 2 days. Devarda's alloy (0.4 g) was then added to the supernatant, to reduce NO₃- to NH₄+. NH₃ was collected by diffusion onto acidified filter paper disks for 6 days, and filters were treated as described above.





5. Sediment - Water Column Exchanges

Seasonal in situ chamber exchange experiments were conducted (Table 1) during May/June 1996, August 1996, November 1996, and April/May 1997, as described in Neikirk (1996). For each season, experiments were performed under both light and dark conditions. Dark conditions were simulated by placing a double layer of black plastic over each chamber.

(1) 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 6). Chambers were bevelled at the bottom to ease installation and minimize disturbance of the sediment surface. Holes (2.54 cm) 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 in daylight between 1000 - 1400 hours during tides of highest amplitude (i.e. at or near spring tides) and were started approximately 2 h before slack high tide.

(2) Field Sampling Protocol

In order to minimize disturbance effects to the marsh, the benthic chambers were installed one week prior to each sampling date, at equal intervals between the 15 and 30 m marks of the middle transect. Similar vegetation was included within each chamber. Positions were marked so that chambers could be deployed in the exact location for each of the four sampling periods. Chambers were pushed into the marsh sediment until the drilled holes were flush with the sediment surface.

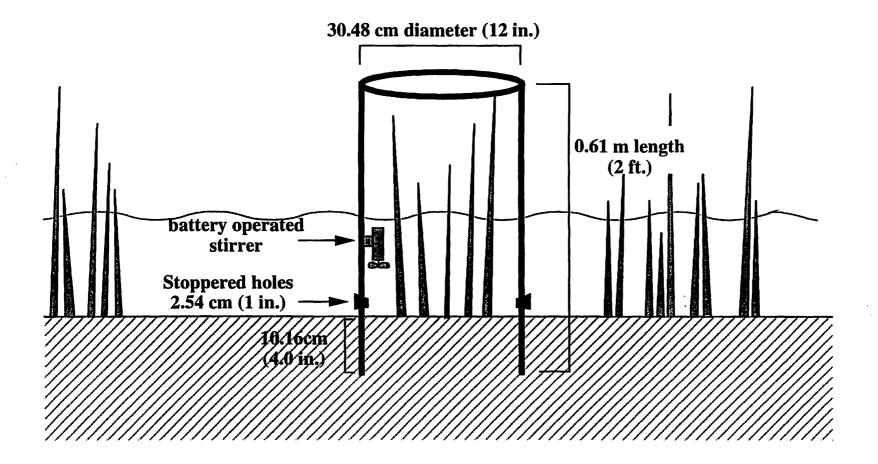
One day prior to the start of each experiment, the inside of each sediment chamber was cleaned using a sponge and deionized water to remove any surface film. Sediment chambers were allowed to flood one last time with creek water before the experiment was initiated. On the rising tide of the following 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 water column chambers were used to monitor contributions of water column processes to nutrient dynamics on the flooded marsh.

All chambers were allowed to fill with creek water to ≥ 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 sampling initiated. Both sediment and water column chambers were sampled in triplicate at 30-45 minute intervals over a two to three hour period. Each chamber was sampled as follows: (1) water temperature was measured in each chamber at the beginning and end of each experiment; (2) the height of the water inside each chamber was measured every sampling period in order to calculate water volume within the chamber; (3) approximately 15 ml of water for DIN and dissolved inorganic phosphate (DIP) analyses were sampled using 30 ml acid washed syringes; (4) water samples were immediately filter sterilized. The first 2 ml of water were filtered through 0.45 μ m syringe filters (Gelman supor acrodiscs) and discarded. The remaining water was filtered into whirlpak bags and stored on ice. Samples were returned to VIMS and stored frozen until analyzed as described below.

6. Tidal Creek Exchanges

In order to provide information on physico-chemical changes occurring in Sturgeon Creek concurrent with marsh sediment - water column exchange studies, an automated sampler was used to sample creek





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water at hourly intervals over one or two 24 h periods, as described in Neikirk (1996). Samples were analyzed for DIN, DIP, total suspended solids (TSS), organic content, and chlorophyll *a*.

(1) <u>Chemical Properties</u>

Approximately 24 hours before each sediment - water column exchange experiment was initiated, an automated sampler (ISCO, model 6700) was deployed in Sturgeon Creek adjacent to the study site. The sampler was programmed to sample 500 ml of creek water every hour for a 24 hour period. The intake for the water sampler was attached to a float and sampled just above the creek bottom. Each sample bottle contained sodium azide (50 μ l, 1M) as a preservative.

(2) Physical Properties

A Datasonde III (Hydrolab Inc.) equipped with datalogger was deployed in the tidal creek in order to monitor water depth, temperature, salinity, conductivity, dissolved oxygen (DO), and pH at 15 minute intervals.

7. Nutrient, Suspended Solid, and Pigment Analyses

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(1) Dissolved Inorganic Nitrogen

Filter sterilized water samples were analyzed for NH_4 + immediately upon return to the laboratory. Samples for NO_3^- , NO_2^- , and PO_4^{3-} analyses were frozen until analyzed. Sediment porewater samples and KCl extracts from the nitrification - mineralization experiments were frozen until analyzed. NH_4 + was determined by the technique of Solorzano (1969). NO_3^- was reduced to NO_2^- using a cadmium reduction column and determined by diazotization using an Alpkem "Flow Solution" autoanalyzer (Perstorp 1992).

(2) Dissolved Inorganic Phosphate

Filter-sterilized water samples were analyzed for orthophosphate using the method of Parsons et. al. (1984).

(3) Water Column Chlorophyll a

Chlorophyll a in 5 ml water samples was analyzed on filters (25 mm Whatman GFF), extracted for 24 h at room temperature in the dark in a mixture of DMSO and acetone (8 ml; 45% acetone:45% DMSO:10% deionized water containing 0.1% diethylamine), using a method developed by Hayward and Webb (personal communication). Samples were analyzed using a Turner Designs Fluorometer, Model 10-AU. Chlorophyll a concentrations were not corrected for degradation products.

(4) Total Suspended Solids

Total suspended solids were determined following filtration of known volumes of water through pre-combusted (500°C for 5 hrs) and pre-weighed Gelman (47 mm) GFF filters. Filters and sediments were dried to constant weight at 50°C and re-weighed for dry weight. Organic matter content was determined as the mass difference before and after combustion of the dried filters at 500°C for 5 h.

1. Sediment Properties

(1) Sediment Bulk Density and Percent Organic Matter

Sediment bulk densities and percent organic matter through the sediment profile to 30 cm depth are shown for April 1997 (Figure 7), June 1996 (Figure 8), August 1996 (Figure 9), and November 1996 (Figure 10). With progression from creek bank toward marsh interior, percent organic matter increased and bulk density decreased. The mean bulk density for all sections and seasons ranged from 0.35 - 0.46 gdw cm⁻³ and was highest in June. Mean percent organic matter for all sections and seasons ranged from 17 - 21% and was highest in the 0-2 cm section in June (mean = 28%).

(2) Sediment Chlorophyll a

Standing stocks of microalgal biomass in sediments, as represented by chlorophyll a concentrations, are shown in Table 2. Conversions to carbon units assumed a carbon to chlorophyll ratio of 50 : 1. Chlorophyll concentrations were highest in May and decreased from summer through fall.

(3) Sediment %C and %N

Results of analyses of total %C and %N in sediments sampled during August 1996, November 1996, and April 1997 are shown in Table 3. Surface sediment (0-2 cm) contained higher %C and %N in August than in November or April. In November %C and %N increased with depth of sediment whereas in April there was little variation with depth. Percent C averaged for each season ranged from 5.66 - 7.05 and %N from 0.49 - 0.58. The ratio of C/N ranged from 11.4 - 12.0.

(4) Porewater Properties

Porewater properties, shown in Table 4, are for samples taken at depths of 5, 15, and 25 cm in sediment and at positions of 1, 15, and 30 m from the creek bank. In general, concentrations of all species of DIN, but especially NO_3 - were low. The highest concentrations of porewater NH_4 + were found in samples taken during May from surface sediments. DIC concentrations increased with depth. The range in porewater pH was 5.53 - 6.60.

2. Marsh Macrophytes

(1) <u>Macrophyte Diversity</u>

The number of macrophyte species observed in Sweet Hall Marsh increased during progression of the growing season from spring to fall. The lowest number of species was observed during June 1996 (4) and the highest during September 1996 (10) (Table 5).

(2) Aboveground Macrophyte Biomass

Aboveground macrophyte biomass (AGB) was at a maximum during May - June and declined throughout the remainder of the growing season (Table 6). Not only was biomass highest during spring and early summer, but the %C was also higher (47%) than in succeeding months (November, 29.6%). Throughout the growing season the macrophyte community demonstrated successional changes. During the early part of the growing season (April - June) *Peltandra virginica* was the

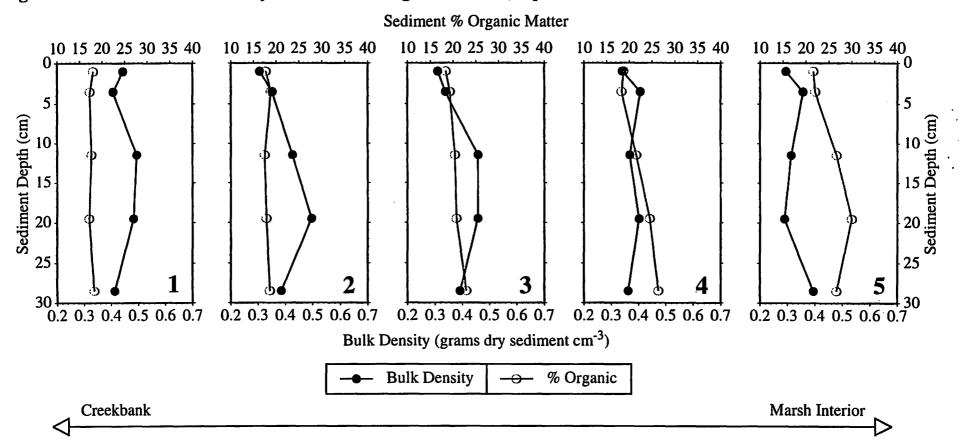
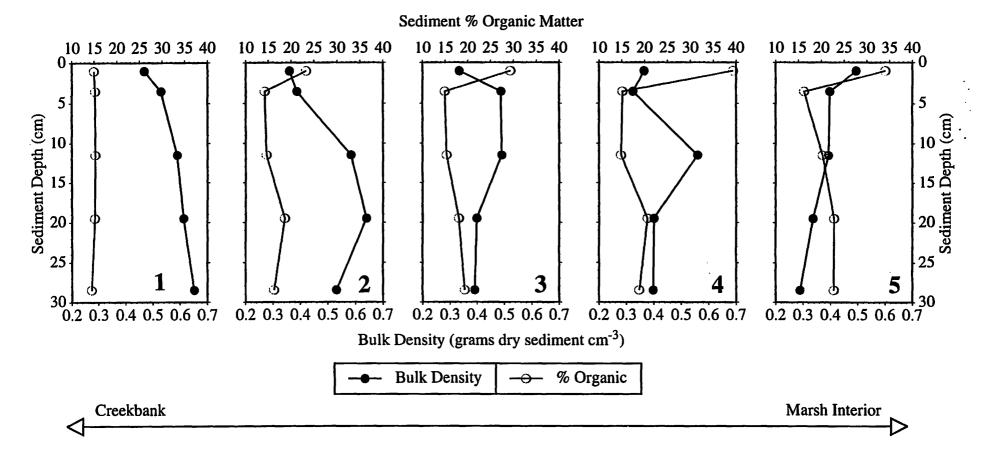
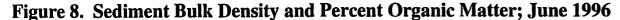


Figure 7. Sediment Bulk Density and Percent Organic Matter; April 1997





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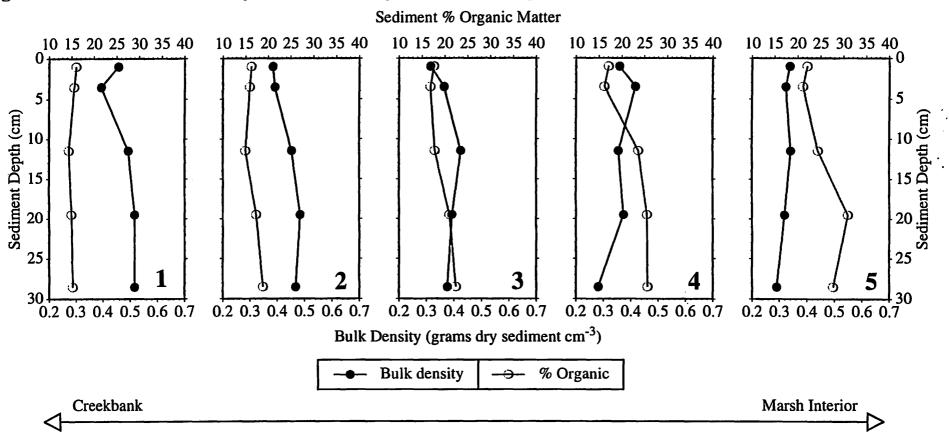


Figure 9. Sediment Bulk Density and Percent Organic Matter; August 1996

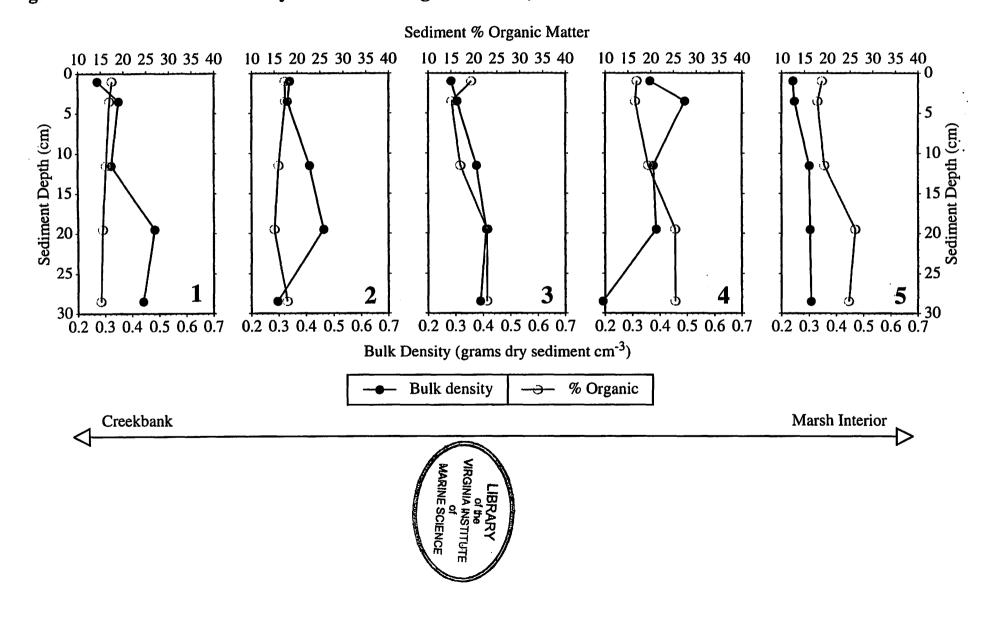


Figure 10. Sediment Bulk Density and Percent Organic Matter; November 1996

Month	# Samples	$(\mu g chl a cm^{-2})$	(g C m ⁻²)
June 1996	29	1.55 (± 0.12) ^a	0.77 (± 0.06)
Sept 1996	30	1.04 (± 0.08)	0.52 (± 0.04)
Nov 1996	29	0.87 (± 0.07)	0.44 (± 0.04)
Apr 1997	30	1.10 (± 0.11)	0.55 (± 0.06)
May 1997	30	2.31 (± 0.20)	1.15 (± 0.10)
July 1997	30	1.65 (± 0.07)	0.82 (± 0.04)

Table 2. Sediment Chlorophyll a

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^a Standard errors are given in parentheses.

Month	Depth (cm)	# Samples	%C	%N	C/N
Aug 1996	0-2	4	7.48 (±1.19) ^a	0.61 (±0.08)	12.20 (±0.38)
	2-5	5	6.70 (±0.84)	0.56 (±0.05)	11.92 (±0.30)
Nov 1996	0-2	10	5.20 (±0.17)	0.47 (±0.01)	11.14 (±0.21)
	2-5	10	5.01 (±0.17)	0.47 (±0.01)	10.69 (±0.16)
	10-13	3	6.11 (±1.21)	0.52 (±0.09)	11.69 (±0.25)
	18-21	3	7.93 (±2.24)	0.60 (±0.13)	12.88 (±0.69)
	27-30	3	7.89 (±2.20)	0.58 (±0.12)	13.14 (±0.96)
Apr 1997	0-2	5	5.69 (±0.34)	0.52 (±0.03)	11.05 (±0.22)
	2-5	5	5.57 (±0.14)	0.48 (±0.01)	11.50 (±0.08)
	10-13	1	5.56 (nd)	0.47 (nd)	11.78 (nd)
	18-21	1	5.96 (nd)	0.48 (nd)	12.31 (nd)
	27-30	1	5.78 (nd)	0.45 (nd)	12.77 (nd)

Table 3. Sediment %C, %N, and C/N Ratios

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^a Standard errors are given in parentheses.

Date	Position ^a (m)	Depth (cm)	[NO ₂ ·] μΜ	DIN [NO ₃ ·] μΜ	[NH ₄ +] μM	DIC mM	pH
Sept 96	0	5 15 25	0.11 0.13 0.19	0.47 0.29 1.29	3.66 5.48 13.47		
	15.2	5 15 25	0.10 0.07 0.23	0.40 0.19 0.27	3.77 2.81 1.09		
	30.5	5 15 25	0.06 0.15 0.14	0.36 0.37 0.84	1.00 0.99 9.73		
Nov 96	0	5 15 25		······································		1.08 1.89 2.73	
	15.2	5 15 25				3.28 3.11 6.49	
	30.5	5 15 25				1.76 3.65 4.81	
May 97 (early)	0	5 15 25	0.13 0.00 0.15	1.51 0.10 0.15	33.37 5.86 2.40		
	15.2	5 15 25	0.12 0.11 0.20	0.00 0.00 0.00	12.64 1.22 3.15		
	30.5	5 15 25	0.07 0.14 0.19	0.23 0.00 0.11	2.38 2.53 3.55		
May 97 (late)	0	5 15 25	0.02 0.04 0.11	0.74 0.42 0.35	1.11 0.24 0.40	5.27 4.77 na	6.60 6.31 na
	15.2	5 15 25	0.04 0.11 0.15	0.30 0.17 0.49	0.40 0.45 2.46	4.63 5.02 5.79	5.74 6.03 6.22
	30.5	5 15 25	0.09 0.04 0.31	1.01 0.34 0.21	0.25 0.31 0.93	2.92 3.71 4.37	5.53 5.81 5.94
July 97	0	5 15 25	0.11 1.64 1.25	0.57 0.30 0.99	3.62 4.34 3.54		
	15.2	5 15 25	2.30 1.61 0.00	0.00 0.35 1.12	2.46 4.93 2.16		
	30.5	5 15 25	1.83 1.01 0.33	0.25 0.85 1.37	3.50 2.75 8.25		

Table 4. Porewater Properties

a Position along transect is measured (m) as distance from Sturgeon Creek

Species	June 1996	Sept 1996	Nov 1996	Apr 1997	May 1997	July 1997
Echinochloa walteri		X	X			
Hibiscus moscheutos	X			X	X	
Leersia oryzoides		X	X		Х	Х
Peltandra virginica	X	X	Х	Х	Х	Х
Polygonum arifolium		X			Х	
Polygonum densiflorum		X				
Polygonum punctatum		X				
Pontederia cordata	X	X	Х	Х	Х	Х
Sagittaria latifolia		X			Х	Х
Spartina cynosuroides		X				
Zizania aquatica	X	Х	Х	Х	Х	Х
unknown #1			Х			
unknown #2 (grass)				Х		
unknown #3						X
total # of species	4	10	6	5	7	6

 Table 5. Macrophyte Community Composition

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Table 6.	Aboveground	Macrophyte	Bio	ma	ass	

		Aboveground	Macrop	hyte Biomass	Per	cent of Live Ab	oveground Bion	nass
Month	# Samples	(gdw m ⁻²)	% C	(g C m ⁻²) ^a	Peltandra virginica	Pontederia cordata	Zizania aquatica	other
June 1996	10	632.05 (±54.37) ^b	46.81	295.86 (±25.45)	73.42 (±8.56)	22.22 (±7.75)	3.19 (±1.82)	1.17 (±1.17)
Sept 1996	10	258.24 (±67.85)	35.79	92.42 (±24.28)	33.42 (±10.91)	41.18 (±10.42)	1.76 (±1.76)	23.64 (±10.23)
Nov 1996	10	58.54 (±16.95)	29.64	17.35 (±5.02)	47.39 (±12.43)	c	36.76 (±12.45)	15.85 (±9.12)
Apr 1997	10	76.44 (±16.97)	nd	35.78 (±7.94) ^d	74.23 (±4.65)	17.73 (±4.22)	0.17 (±0.17)	7.87 (±2.91)
May 1997	10	593.24 (±105.40)	nd	277.70 (±49.34) ^d	82.74 (±3.82)	10.24 (±3.90)	6.01 (±2.39)	1.01 (±0.49)
July 1997	10	454.05 (±56.95)	nd	212.54 (±26.66) ^d	41.16 (±8.84)	12.07 (±4.07)	37.92 (±8.00)	8.85 (±5.88)

^a Dry live biomass (gdw m⁻²) was converted to g C m⁻² by multiplying by average monthly % C numbers (from Table 7).

^b Standard errors are given in parentheses.

• All P. virginica and P. cordata leaves had senesced and it was impossible to differentiate between the species on the basis of petiole morphology both of these species are grouped under *P. virginica*. ^d Carbon biomass based on June 1996 % C determinations.

dominant macrophyte, accounting for 70 - 80% of AGB. During July Zizania aquatica increased in abundance, making up 38% of biomass whereas *P. virginica* made up 41% and *Pontederia cordata* and other species accounted for the remainder. By November *P. virginica* and *P. cordata* had undergone senescence and *Z. aquatica* and a variety of other plants were dominant.

(3) Percent C and N of Marsh Macrophytes

Percent C and N in living AGB for the most common macrophytes observed at our study sites in Sweet Hall Marsh are shown in Table 7 for June 1996, September 1996, and November 1996. The lowest ratios of C/N were observed during June for *P. virginica* and *P. cordata*. As these plants underwent senescence the C/N of their AGB increased. The C/N ratio in *Z. aquatica* leaves and stems was higher than in *P. virginica* or *P. cordata* for all seasons.

3. Macrophyte Community Metabolism

(1) Gross Community Photosynthesis (GCP) vs. Irradiance (I) Curves

In order to calculate annual rates of carbon fixation using short-term measurements of CO_2 exchange, it was necessary to determine how photosynthesis (P) varies with I. CO_2 exchanges were measured as a function of I, which was changed by covering the community metabolism chamber with various layers of shade cloth. Curves showing relationships between GCP, measured as mgC m⁻² min⁻¹, and I are shown for the months of March, April, May, June, July, September, and November (Figures 11 and 12). Data from six chambers, placed at intervals along the marsh transect extending from creek bank toward the interior of the marsh, were used to generate each of the curves. Curves fit to the data were in the form of a hyperbola, and hyperbolic parameters for equations describing the data are given on Figure 12 along with r² values for each of the curves. For several months variations in I explained as little as 30% of changes observed in GCP (e.g. April 1997). When P vs. I curves were generated using data from individual chambers, as shown in Figure 13, the r² values improved dramatically; however, for mass balance calculations made later in this report, P vs. I relationships represented data aggregated from all chambers during a month.

(2) Community Respiration (CR) vs. Temperature--Q₁₀ Values

Calculation of GCP requires that CO_2 released by community respiration (CR) during the day be accounted for; however CR varies as a function of T. To correct for temperature effects we calculated Q_{10} values for spring (3.24), summer (1.94), and fall (2.13) (Figure 14).

4. Sediment Community Metabolism

(1) Gross Sediment Microalgal Photosynthesis (GMiP)

Because of shading by macrophytes, sediment microalgae were exposed to a narrow range of ambient irradiances compared to macrophytes. In addition, the P_{max} for microalgae is lower than that for macrophytes. Thus, we did not develop P vs I curves for GMiP.

(2) <u>Sediment Respiration (SR) vs. Air Temperature</u>

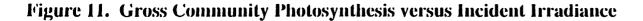
Because sediment temperatures vary little within months, we were unable to calculate seasonal Q_{10} values. Figure 15 shows the annual variation in sediment respiration, expressed as mgC m⁻² min⁻¹, with air temperature. There was a more significant relationship with air temperature than with sediment temperature. The Q_{10} calculated for this relationship is 5.07.

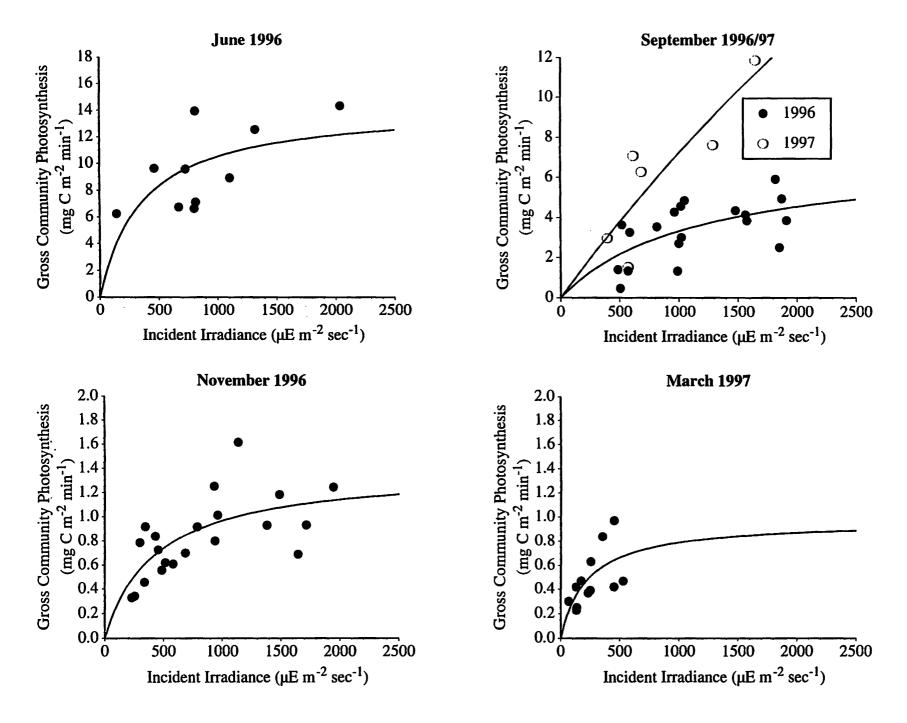
Month	Species	# Samples	C/N	%C	%N	gdw m-2	g C m ⁻² b	g N m-2 b
June 1996	Peltandra virginica	10	12.38 (±0.30) ^a	48.59 (±0.29)	3.95 (±0.09)	485.82 (±79.53)	236.06 (±38.65)	19.19 (±3.14)
	Pontederia cordata	9	11.48 (±0.37)	47.53 (±0.29)	4.17 (±0.13)	118.99 (±35.94)	56.56 (±17.08)	4.96 (±1.49)
	Zizania aquatica	3	19.24 (±0.85)	40.26 (±1.00)	2.10 (±0.11)	21.87 (±12.57)	8.80 (±5.06)	0.46 (±0.26)
	other c	1	11.42	42.10	3.69	5.38 (±5.38)	2.26 (±2.26)	0.20 (±0.20)
Sept 1996	Peltandra virginica	2	14.44 (±0.10)	38.78 (±1.09)	2.69 (±0.09)	52.95 (±23.24)	20.55 (±9.01)	1.43 (±0.63)
	Pontederia cordata	9	15.48 (±0.85)	35.81 (±1.77)	2.40 (±0.23)	28.52 (±8.15)	10.21 (±2.92)	0.68 (±0.20)
	Pelt./Pont. stems	7	23.48 (±3.27)	35.23 (±5.81)	1.60 (±0.27)	100.51 (±55.86)	28.33 (±16.23)	1.29 (±0.74)
	Zizania aquatica	1	24.29	39.88	1.64	11.22 (±11.22)	4.47 (±4.47)	0.18 (±0.18)
	other c	2	23.61 (±1.35)	34.97 (±0.80)	1.56 (±0.34)	73.85 (±44.65)	25.83 (±15.61)	1.15 (±0.70)
Nov 1996	Pelt./Pont. stems	9	18.65 (±2.03)	29.55 (±2.48)	1.62 (±0.10)	16.56 (±7.20)	4.89 (±2.13)	0.27 (±0.12)
	Zizania aquatica	8	26.04 (±3.01)	32.76 (±3.02)	1.39 (±0.23)	11.80 (±5.26)	3.86 (±1.72)	0.16 (±0.07)
	other c	1	12.11	13.39	1.11	4.91 (±2.62)	0.66 (±0.35)	0.05 (±0.03)

Table 7. Aboveground Biomass %C, %N, and C/N Ratios

^a Standard errors are given in parentheses.

^b Dry live biomass (gdw m⁻²) was converted to g C m⁻² and g N m⁻² by multiplying by %C and %N, respectively.
^c In June 1996, *Hibiscus moscheutos* was the "other" sample analyzed for %C and %N, and accounted for all the "other" June biomass. In September and November 1996, *Echinochloa walteri* samples were analyzed for %C and %N. In both months this species comprised over 50% of the "other" biomass.

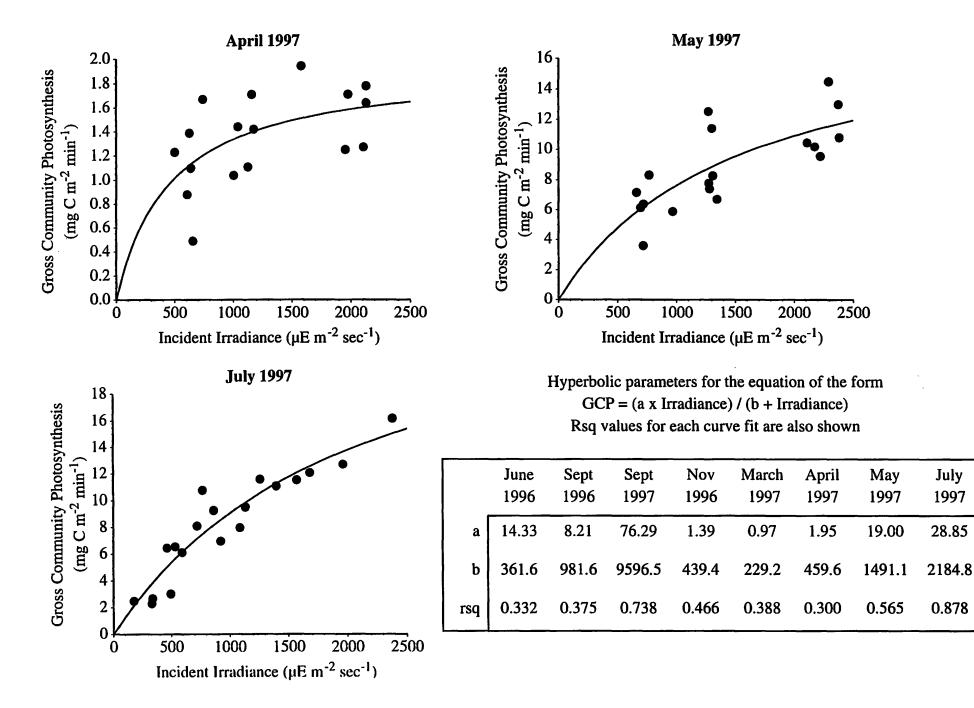




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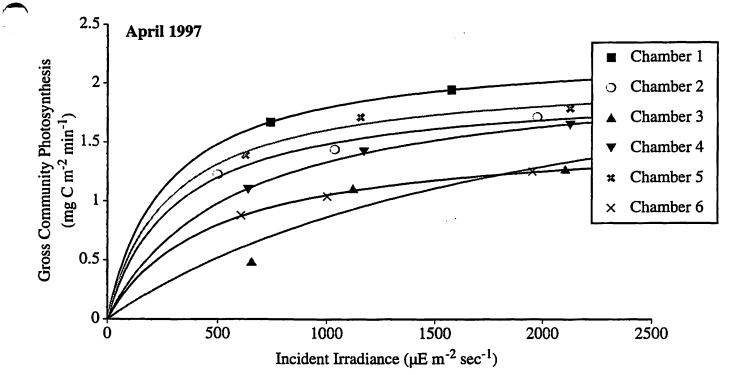


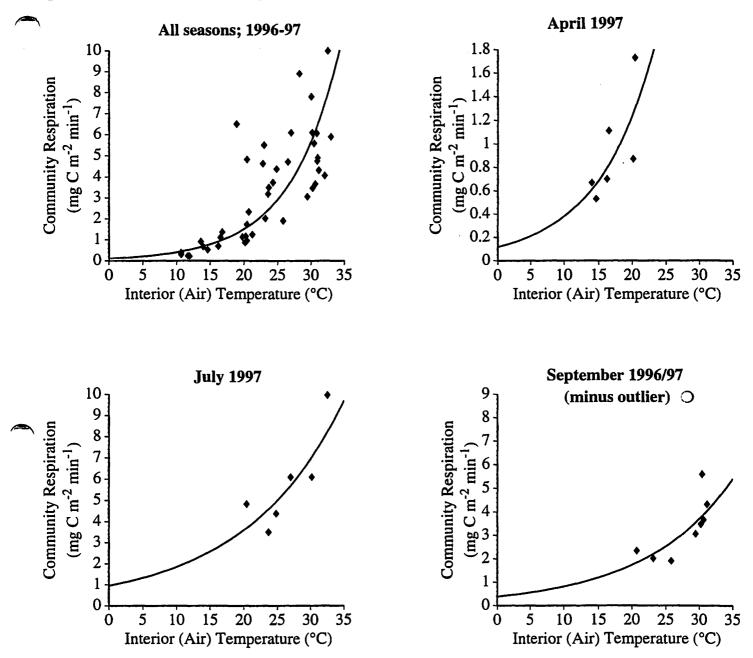
Figure 13. Gross Community Photosynthesis versus Irradiance, Individual Chambers

Hyperbolic parameters for the equation of the form GCP = (a x Irradiance) / (b + Irradiance). Rsq values for each curve fit are also shown.

C1 to C6 represent individual chambers.

	a	b	rsq
C1	2.26	262.11	1.0000
C2	1.94	305.47	0.9572
C3	2.55	1952.67	0.8379
C4	2.08	559.58	0.9983
C5	2.05	278.03	0.9398
C6	1.54	463.97	0.9962
all	1.95	459.57	0.3004





 Q_{10} values were calculated from exponential curve fits of CR vs T.

Q10 vs Air Temp	Q10	rsq
All seasons	3.763	0.743
April only	3.240	0.577
July only	1.941	0.658
Sept only (minus outlier)	2.131	0.636

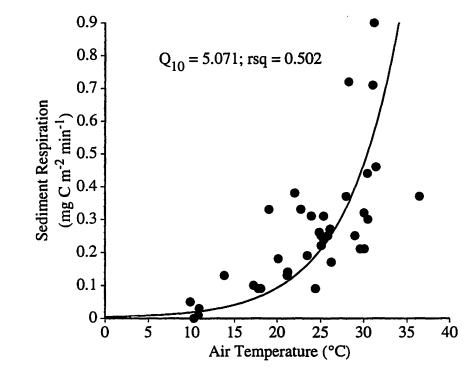


Figure 15. Sediment Respiration versus Air Temperature

(3) Methane Production

Products of sediment respiration include both CO_2 and CH_4 ; thus, for calculation of net carbon exchange it was necessary to take into account CH_4 emissions from soils. Since solubility of CH_4 in water is low, transport through sediment takes place primarily through plants. Gas fluxes from the macrophyte community, measured using the large community flux chamber, are shown in Figure 16. Fluxes are shown as negative since they represent loss from the marsh. During September, 1997 methane fluxes were measured during both day and night; fluxes at night were approximately half those measured during the day (Figure 16). Sediment CH_4 fluxes were measured using the sediment metabolism chamber in November 1996 and September 1997. These fluxes accounted for a small percent of total community CH_4 flux (data not shown).

5. Tidal Effects on Macrophyte and Sediment Community Metabolism

(1) Tidal Effects on Community Respiration

Community respiration was determined using the large metabolism chambers at times near slack high and slack low tides during both day and night. Results shown in Figure 17 suggest that marsh flooding reduced both CH_4 and CO_2 emissions during day and night. In addition, fluxes of CH_4 were 50% lower during night than day, suggesting that a light-driven process was responsible for transport of CH_4 through macrophytes.

(2) Tidal Effects on Gross Community Production

For modeling efforts it was necessary to determine how tidal inundation affected GCP. During September 1997, community metabolism was measured at times close to slack high and slack low during daylight. P vs. I curves for high and low tides were dramatically different (Figure 18); however, when these curves were used to calculate GCP for the entire month of September there was only a 4% difference in total C fixation.

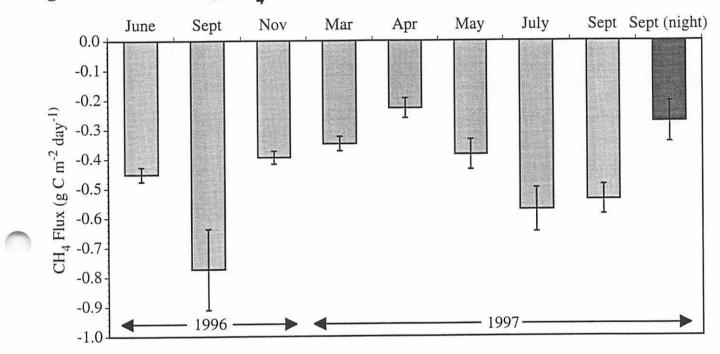
6. Microbial Nitrogen Cycling Processes

(1) Gross Nitrogen Mineralization

Gross mineralization rates were highly variable. Rates in mid-transect were highest during September whereas in April mineralization was highest close to the creek bank (Figure 19).

(2) Gross Nitrification

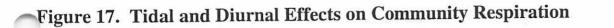
Measurement of gross nitrification was limited by the high rates of denitrification in cores amended with ¹⁵N-NO₃⁻. Gross nitrification was measured during the periods of May - June 1996, August - September 1996, November 1996, and April - May 1997 at the same times that nutrient exchanges between marsh and overlying water were determined (see below). We were unable to use the data collected during May - June and report here only results from the other three seasons. Gross nitrification rates were highest during September (Figure 19) and were higher in the mid portion compared to either the creek bank or interior marsh ends of each transect. Nitrification rates were of the same magnitude as mineralization rates.

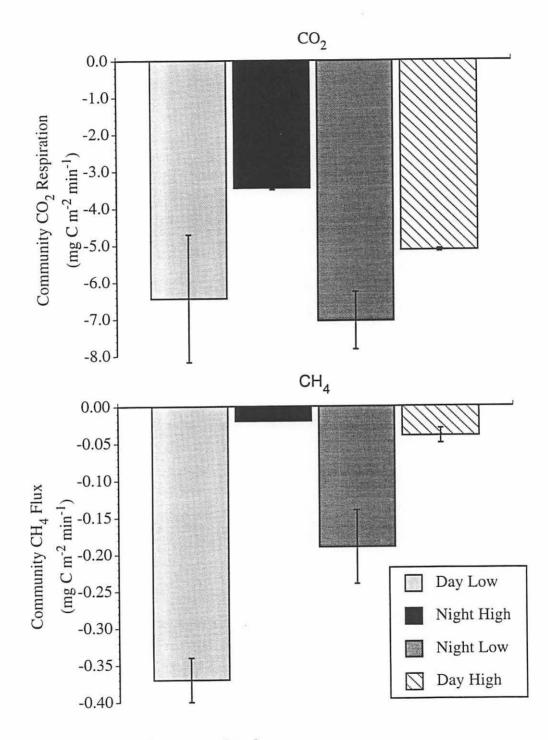


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Figure 16. Community CH₄ Fluxes

Error bars represent one standard error; n = 4 to 7





Error bars represent one standard error; n = 2 to 3 CO₂ fluxes were adjusted to constant temperature (30°C) using Q₁₀ of 1.94.



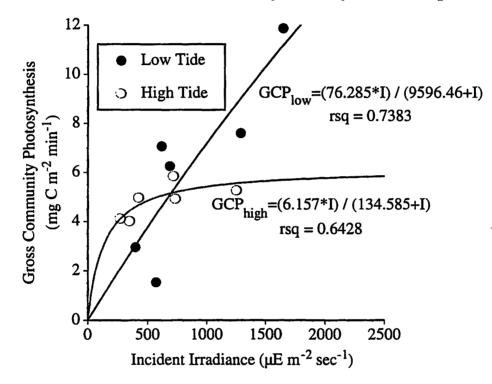
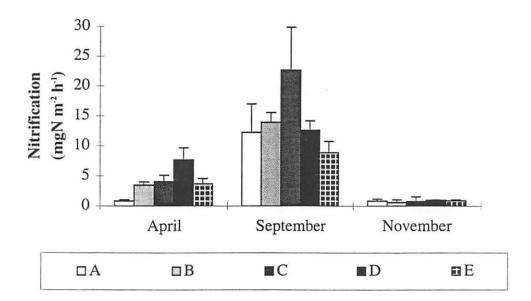
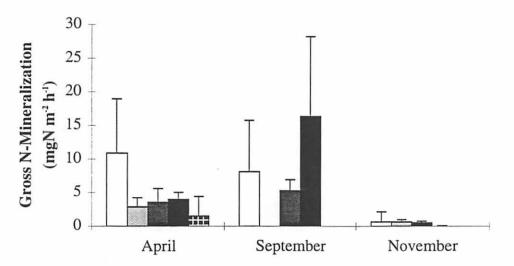
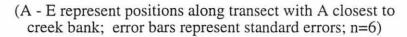


Figure 19. Gross Nitrification



Gross N-Mineralization





7. Exchanges of Nutrients between Marsh Sediments and Overlying Tidal Water

(1) <u>Ammonium Exchanges</u>

Significant NH_4^+ release from sediments to overlying water was observed only during May - June 1996 and uptake was significant during November 1996. Uptake was higher in the light than in the dark (Figure 20). The high sediment - water uptake rates observed in November corresponded to low rates of microbial nitrification and mineralization (Figure 19) measured during this same period.

(2) Nitrate Exchanges

There was significant NO₃- uptake in the dark during all seasons (Figure 20). In the light NO₃- uptake was either not significant (May - June) or there was slight release (August). Creek sources of NO₃- were highest during seasons when uptake was highest (Figure 21).

(3) Ortho Phosphate Exchanges

Phosphate exchanges were not significantly different from zero at our marsh sites (Figure 20).

8. Creek Exchanges over Diurnal Tidal Cycles

(1) Nutrient Exchanges

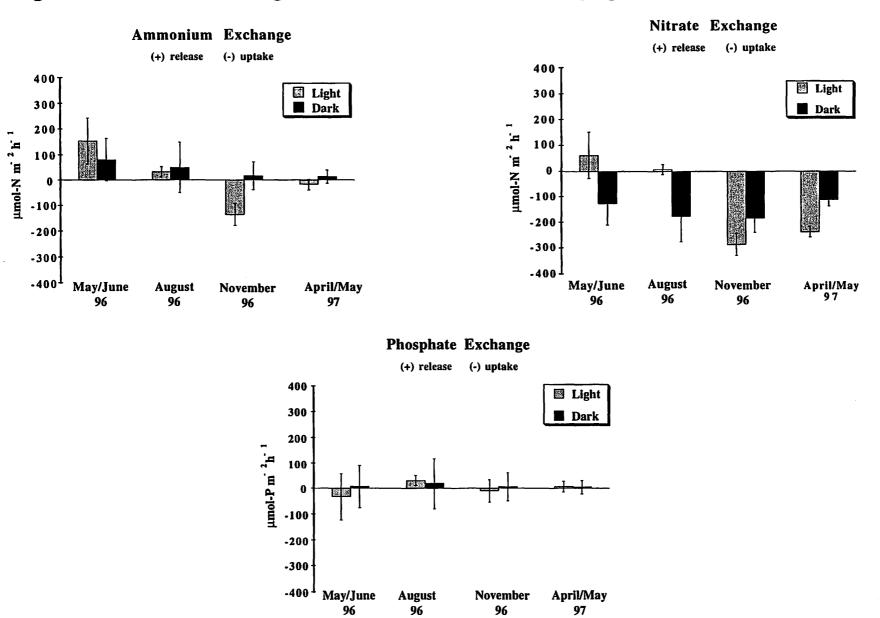
During all seasons NO₃- concentrations in Sturgeon Creek water were at a maximum during slack flood tides and a minimum during slack low tides, suggesting that NO₃- was supplied by the river and removed by marsh and perhaps creek bottom sediments (Figure 21). Sediment - water exchange studies similarly showed NO₃- uptake by marsh sediments during all seasons (see above, Figure 20). NH₄+ concentrations in creek water showed the opposite trend during April and November when concentrations were at a maximum at slack low tide and a minimum at slack flood tide. These results suggest that either marsh or creek sediments were the source of NH₄+. The highest concentrations of porewater NH₄+ were observed during April - May and unfortunately no porewater data are available for November (Table 4). April was also a period when gross mineralization rates in sediments close to the creek bank were high relative to nitrification rates (Figure 19).

(2) Total Suspended Solids (TSS) and Organic Content

Changes in TSS in Sturgeon Creek over diurnal cycles are shown in Figure 22. Suspended solids concentrations peaked during ebbing or flooding tides when tidal energy was highest. When TSS were highest, % organic content of the material was lowest. These data suggest that much of the TSS resulted from resuspension of creek bank or bottom sediments.

(3) <u>Chlorophyll a</u>

Chlorophyll *a* in the tidal creek was highest during May and August, and concentrations peaked at slack ebb tide suggesting that the marsh was the source of the chlorophyll (Figure 23). During August there were additional peaks of chlorophyll which appeared during flooding and ebbing tides when energy was highest. These peaks are likely due to resuspension of creek bottom chlorophyll. During November and April resuspension appeared to be responsible for the small peaks of chlorophyll observed during flooding and ebbing tides.

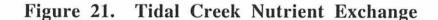


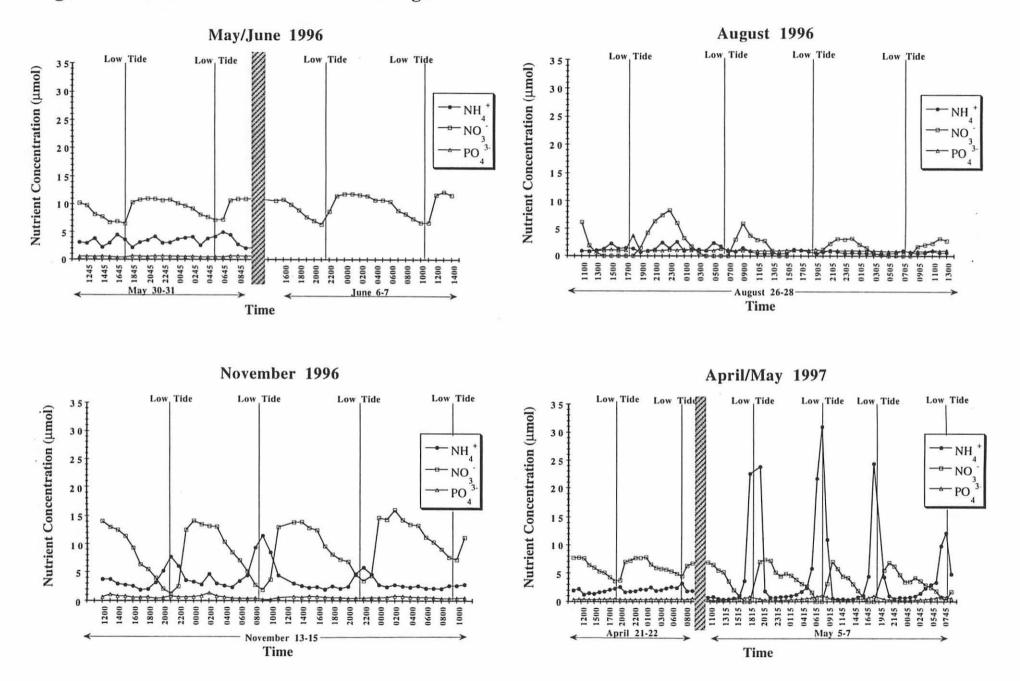
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Figure 20. Nutrient Exchanges Between Sediments and Overlying Water

Error bars represent standard errors for n=5.

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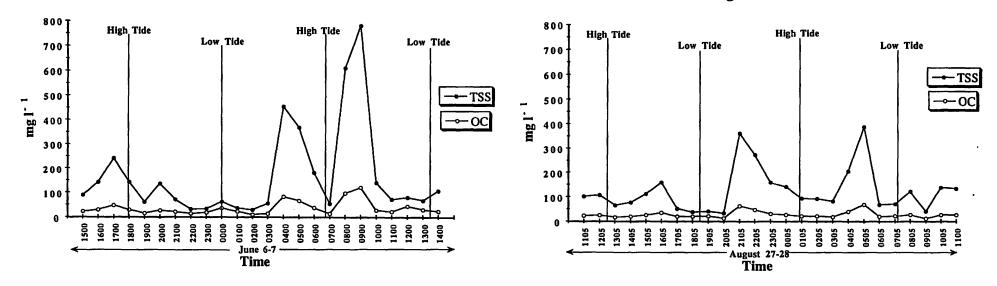


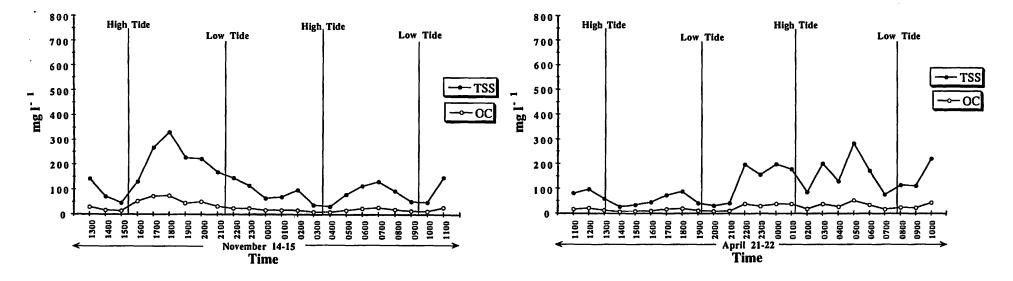
Figure 22. Tidal Creek Exchanges of Total Suspended Solids (TSS) and Organic Content (OC)





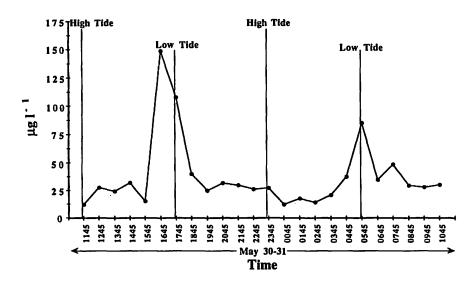


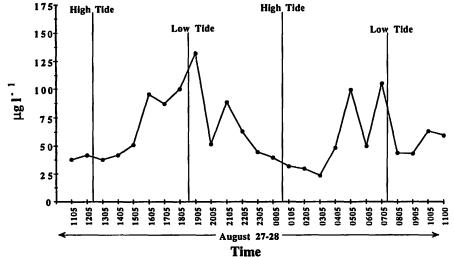
April/May 1997



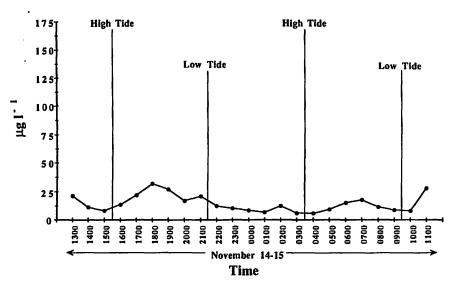


May/June 1996

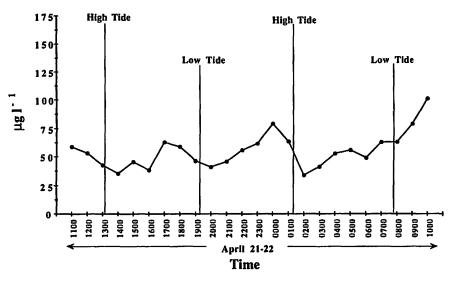




November 1996



April/May 1997



August 1996

(4) Water Column Physical Properties

Changes in water column properties over diurnal and tidal cycles during various seasons are shown in Table 8. Salinity in Sturgeon Creek never exceeded 0.3 ppt; thus, Sweet Hall Marsh satisfies the definition of a freshwater marsh (<0.5 ppt salinity). Dissolved oxygen (DO) in creek water varied over wide ranges, from nearly anaerobic to supersaturated, over day - night cycles especially during spring and summer.

A Gaseous Carbon Flux Model for Sweet Hall Marsh

1. Model Construction

In order to estimate over an annual cycle whether there is net import or export of carbon between Sweet Hall Marsh and its adjacent tidal creek, a gaseous carbon flux model was developed to allow us to scale short term carbon flux measurements to annual rates. Steps followed for development of the model are described below and shown in Figure 24. Calculation of the net annual gaseous carbon flux for Sweet Hall Marsh requires consideration of both carbon input terms (macrophyte and microalgal photosynthesis) and loss terms (macrophyte and sediment CO_2 and CH_4 production). Field measurements of light and dark community and sediment CO_2 and CH_4 fluxes formed the basis for this model. The model is driven by seasonal changes in these rates, which, in turn, are controlled by hourly and daily changes in irradiance and temperature measured at the Virginia Institute of Marine Science (VIMS, 1997) and predicted tidal inundation of the marsh.

(1) Tidal Effects on Carbon Balance

Field observations of marsh tidal inundation showed that Sweet Hall Marsh is flooded for approximately three hours on either side of slack high water; thus, the marsh is flooded for half of any given day, and dry for the other half. This was incorporated into the carbon flux model by modeling the tides as a cosine wave:

tide stage =
$$-\cos\left[\pi * \frac{(t-x)}{6.25}\right]$$

where t is the elapsed number of hours in a particular month;

x is a constant for each month that varies to allow modeled and predicted tides to match; 6.25 creates a wave with a 25 hour period

When the tidal stage was greater than zero, high tide effects (as discussed above) were modeled. Likewise, when tidal stage was less than zero, the marsh was exposed to air and flux calculations were adjusted appropriately. It was assumed that the depth of water overlying the marsh did not affect carbon flux rates; the important factor was if the marsh was "wet" or "dry."

(2) Calculation of Hourly, Monthly and Annual Gross Community Photosynthesis

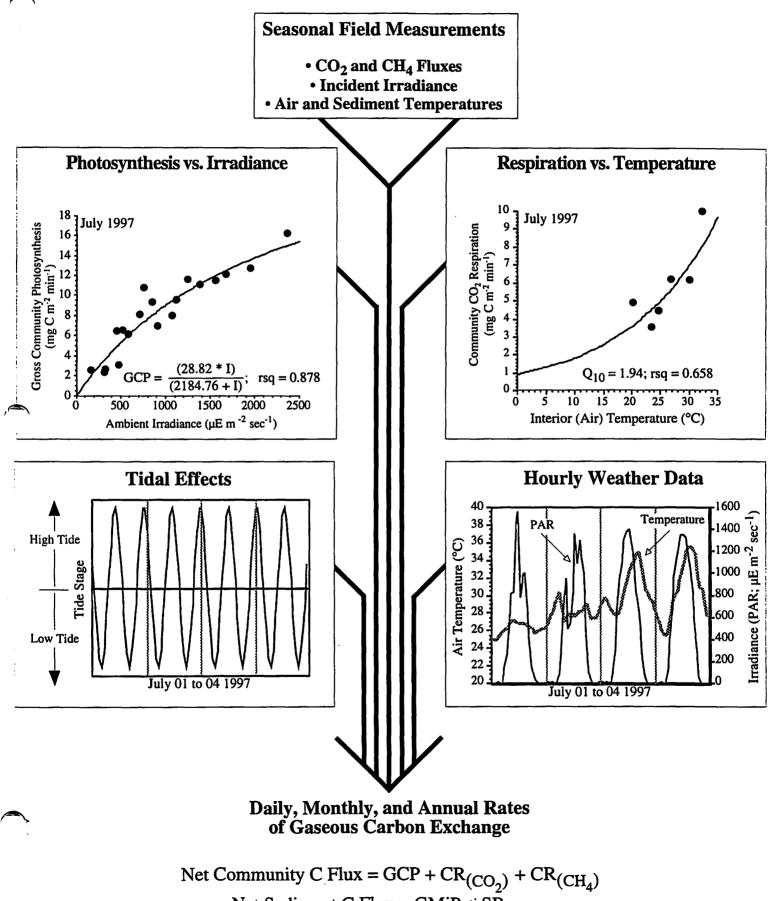
Carbon fluxes were modeled for the two-year period from January 1996 through the end of December 1997. In most cases, data were collected in a particular month during one year, but not the other (i.e. June 1996 but not June 1997). In order to model fluxes over the entire two year period, we assumed that hyperbolic P vs. I and R vs. T relationships did not change from year to year. Thus, interannual

Date	(m)	(°C)	(ppt)	(mg l ⁻¹)
	Water Depth	Water Temp	Salinity	Dissolved O ₂
30-31 May 1996	0.61-1.47	16.6–22.0	0.0-0.1	6.45–10.30
	(1.04 ± 0.26) ^a	(19.9 ± 1.5)	(0.09 ± 0.03)	(8.72 ± 0.93)
06–07 June 1996	0.0-1.1	21.0–26.6	0.0-0.2	1.24–11.09
	(1.0 ± 0.3)	(22.7 ± 1.1)	(0.12 ± 0.04)	(7.25 ± 2.60)
26–28 Aug 1996	0.3-1.2	24.3–30.5	0.1-0.3	2.35-8.54
	(0.78 ± 0.23)	(27.4 ± 1.5)	(0.16 ± 0.06)	(5.22 ± 1.26)
14–15 Nov 1996	0.21–1.06	3.4–11.6	0.0-0.1	5.00–8.57
	(0.72 ± 0.27)	(7.9 ± 2.6)	(0.03 ± 0.05)	(7.34 ± 1.00)
05–06 May 1997	0.12-1.22	13.8–25.9	0.0-0.3	1.42-10.72
	(0.72 ± 0.37)	(18.7 ± 3.8)	(0.05 ± 0.08)	(7.10 ± 2.56)

 Table 8.
 Sturgeon Creek Physical Properties

^a Ranges of each parameter, with mean and standard deviations in parentheses; n=89 to 205.





Net Sediment C Flux = $GMiP + SR_{(CO_2)}$

variations in modeled carbon fluxes were primarily due to variability in incident irradiance and temperature rather than differences in community responses to these variables.

Hourly GCP rates were calculated for a particular month by using a P vs. I curve for that month (Figures 11 and 12) and weather data from the Virginia Institute of Marine Science (VIMS, 1997). Hourly GCP fluxes were calculated using the following equation:

$$\text{GCP}_{t} = 60 \ * \left[\frac{(a * I_{t})}{(b + I_{t})} \right]$$

where GCP₁ is gross community photosynthesis at time t (mg C $m^{-2} hr^{-1}$)

60 converts mg C m⁻² min⁻¹ to mg C m⁻² hr⁻¹

a is an empirically derived constant (mg C m^{-2} min⁻¹)

b is an empirically derived constant ($\mu E m^{-2} sec^{-1}$)

It is the average hourly irradiance for time t ($\mu E m^{-2} sec^{-1}$)

Monthly fluxes were the sum of hourly fluxes for that month, and annual fluxes were the sum of monthly fluxes. For months where field data were not collected, flux rates were estimated by linear interpolation. In Figures 25 and 26 positive fluxes represent a flux of CO_2 from the atmosphere into the marsh plant - sediment community (i.e. photosynthesis) whereas negative fluxes indicate a flux of carbon out of the marsh community (i.e. respiration).

(3) <u>Calculation of Hourly, Monthly, and Annual Gross Microalgal Production</u>

GMiP was also modeled but in a different manner. Because of a lack of low light intensity measurements (less than 200 μ E m⁻² sec⁻¹) during field studies, suitable GMiP vs I curves could not be developed. Similarly, a lack of data prohibited us from modeling microalgal photosynthetic responses to flooding. In order to scale short-term rates to monthly and annual fluxes, we assumed that microalgae operated at full photosynthetic efficiency at irradiances greater than 50 μ E m⁻² sec⁻¹. Below this level, there was no photosynthesis. Holmes and Mahall (1982) showed that net CO₂ exchange for saturated intertidal sediments from California plateaued between 50 and 75 nE cm⁻² sec⁻¹ (equivalent to μ E m⁻² sec⁻¹); thus our assumption of a constant microalgal photosynthetic rate above 50 μ E m⁻² sec⁻¹ appears reasonable. Average short-term rates of GMiP (mg C m⁻² sec⁻¹) were multiplied by 60 to obtain hourly rates. Hourly rates were summed to obtain daily, monthly, and annual rates.

(4) Calculation of Hourly, Monthly, and Annual Community Respiration Rates

CR vs. T coefficients (Q_{10} values; Figure 24) were determined for each season. Monthly Q_{10} values were combined with hourly weather data and average respiration rates measured for each month to calculate hourly rates of community CO₂ respiration using the following equation:

$$CR_{t} = 60 * (0.54) * CR_{0} * Q_{10} \begin{bmatrix} (T_{t} - T_{0}) \\ 10 \end{bmatrix}$$

where CR_t is community respiration at time t (mg C m-2 hr⁻¹)

60 converts mg C m⁻² min⁻¹ to mg C m⁻² hr⁻¹

0.54 is added during nighttime high tides

 CR_0 is the average CR rate measured in the field (mg C m⁻² min⁻¹)

 Q_{10} is a seasonal Q_{10} value

 T_t is the air temperature at time t (°C)

 T_0 is the air temperature at the time field measurements were made (°C)

Respiration was calculated for twenty-four hours per day. Because of differences in measured day and nighttime respiration rates, night was defined as any period when the average hourly irradiance was less than 50 μ E m⁻² sec⁻¹. Hourly rates were summed to obtain daily and monthly community CO₂ respiration rates:

For months where field data did not show a significant relationship between respiration and temperature (possibly due to low temperature ranges during these seasons), Q_{10} values from seasons with similar vegetation characteristics were substituted. For example, the Q_{10} value calculated from July 1997 (Q_{10} =1.94) was also used for May and June calculations since all three months were characterized by high total community biomass and a dominance by the broadleaf plants *Peltandra virginica* and *Pontederia cordata*.

(5) <u>Calculation of Hourly, Monthly, and Annual Sediment Respiration Rates</u>

Sediment CO_2 fluxes were modeled using a form of the equation used for community CO_2 respiration. Because of a lack of data, tidal effects on sediment respiration rates could not be modeled, so the following equation was used to model all sediment CO_2 fluxes.

$$SR_t = 60 * SR_0 * Q_{10} \left[\frac{(T_t - T_0)}{10} \right]$$

where SR₁ is sediment respiration at time t (mg C $m^{-2} hr^{-1}$)

60 converts mg C m⁻² min⁻¹ to mg C m⁻² hr⁻¹

 SR_0 is the average SR rate measured in the field (mg C m⁻² min⁻¹)

 Q_{10} is an annual Q_{10} value

 T_t is the air temperature at time t (°C)

 T_0 is the air temperature at the time field measurements were made (°C)

Once hourly rates were calculated, they were summed to obtain daily, monthly, and annual community CO₂ respiration rates.

(6) <u>Calculation of Hourly, Monthly, and Annual Community Respiratory CH₄ Production</u>

On monthly and annual time scales, we were unable to calculate a Q_{10} value to relate CH₄ production to temperature. Thus, the average short-term CH₄ production rate (mg C m⁻² min⁻¹) for each season was corrected for time of day (day vs. night) and used to calculate hourly rates according to the following equation:

$$CH_{4, t} = 60 * (0.50) * (0.12) * CH_{4, 0}$$

where CH_{4, t} is low tide, daytime methane respiration at time t (mg C m⁻² hr⁻¹)

60 converts mg C m⁻² min⁻¹ to mg C m⁻² hr⁻¹

0.50 is added as necessary to convert daytime to nighttime rates

0.12 converts low tide to high tide fluxes (as needed)

 $CH_{4,0}$ is the average CH_4 rate measured in the field (mg C m⁻² min⁻¹)

Hourly rates were summed to obtain monthly and annual fluxes.

(7) <u>Calculation of Hourly, Monthly, and Annual Sediment Respiratory CH₄ Production</u>

Sediment CH_4 fluxes were measured in November 1996 and September 1997. In each case, the flux was only a couple percent of the total community CH_4 flux so sediment CH_4 fluxes were not modeled.

2. Results of Model Calculations

(1) Annual Rates of GCP and CR

With the exception of June monthly rates of CR exceeded GCP (Figure 25). On an annual basis our Sweet Hall Marsh site fixed 913 gC m⁻² but respired 1150 gC m⁻². The annual net carbon balance for the total community was -238 gC m⁻².

(2) <u>Annual Rates of GMiP and SR</u>

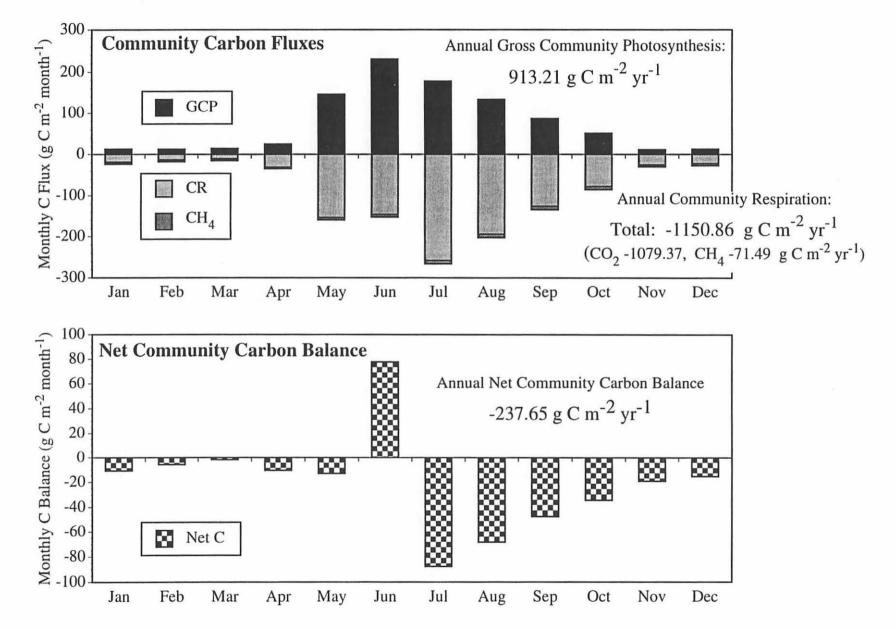
During the months of November through May microalgal production exceeded sediment respiration whereas from June through October the reverse was true (Figure 26). On an annual basis sediment GMiP was closely in balance with sediment respiration with a slight excess flow of carbon into the marsh of 6 gC m⁻². In this study sediment respiration was measured in the absence of any vegetation. Since nearly all of the CH₄ and probably much of the CO₂ produced in the sediment is transported through air spaces in macrophytes, sediment respiration is likely underestimated.

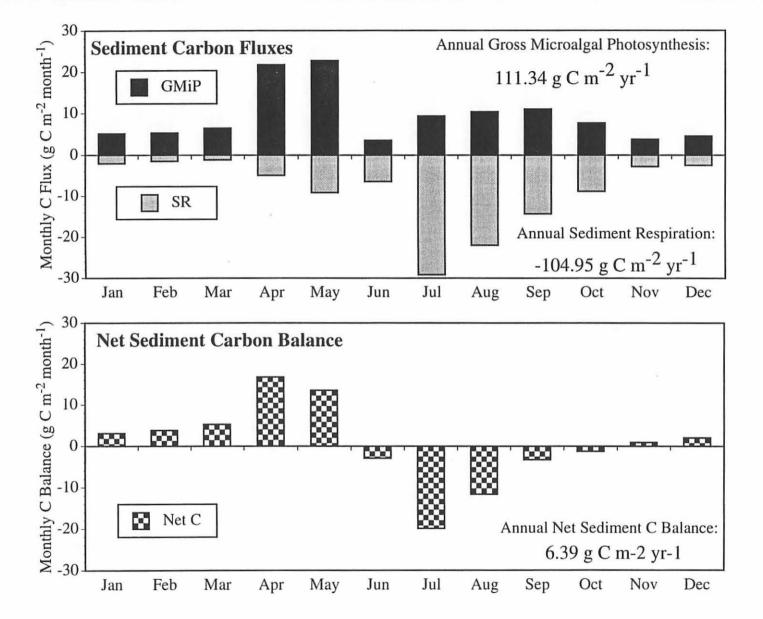
Discussion

Based upon our estimates of gaseous carbon flux Sweet Hall Marsh would appear to be net heterotrophic on an annual basis, suggesting that it could not keep up with the measured long term net accretion rate of 5.47 mm y⁻¹ (based on ¹³⁷Cs profiles; Campana, personal communication). Yet the distribution of macrophyte communities at Sweet Hall has been stable for at least 40 years, based upon aerial photographs (Doumlele, 1981; Ledwin, 1988). This suggests that an exogenous source of carbon is critical for this marsh. We have, therefore, created a process based carbon mass balance Model, shown in Table 9, in order to consider the relative importance of various inputs and exports from the marsh. We do not consider this model to be final but rather a tool to enable us to better plan our future research on tidal freshwater marshes such as Sweet Hall.

Of the input and output values for carbon shown in Table 9, by far the most uncertain are those for sediment import and chlorophyll export. Net values for sediment exchange between marshes and their adjacent tidal creeks are difficult to estimate and are extremely uncertain. Attempts to collect gross sediment deposition data using sediment traps (Ledwin, 1988) suggest that gross input is a order of magnitude or more greater than the net sediment input value listed in Table 9. Other studies (Kraeuter and Wetzel, 1986) indicate that much of the sediment collected in sediment traps is derived from resuspension of local material. We calculated net sediment exchange by averaging differences in TSS measured at slack high and slack low tides during various seasons, but not including winter. In addition, since we did not have a local tide gauge available for this study, our estimate of 25 cm of water overlying the marsh at high tide is a relatively crude approximation of mean high tide level. Similar caveats apply to estimates of chlorophyll export. In addition to the difficulty in estimating the physical exchanges of chlorophyll *a*, our conversion of chlorophyll *a* to units of carbon is highly uncertain since the 50 : 1 ratio used for this conversion is known to vary over a wide range. Due to lack of data we have not included stochastic events such as storms which have been shown important in salt marshes (Chalmers et al., 1985).









Inputs of Carbon	gC m ⁻² y ⁻¹	Outputs of Carbon	gC m ⁻² y ⁻¹
Autotrophic Fixation		Autotrophic Respiration	209°
Macrophytes	802ª	Sediment Respiration	942 ^d
Microalgae	111ª	Burial	118 ^e
Sediments	219 ^b	Export	259 ^f
Annual Sums	1132		1528

Table 9. Carbon Mass Balance, Sweet Hall Marsh

a. Calculated using gaseous carbon flux model and measured CO₂ fluxes

b. Net sediment input calculated based on measured differences in TSS during peak high and low tides in Sturgeon Creek and assuming flooding 2 times per day, with a depth of 25 cm of water overlying the marsh at maximum flood and % C in TSS same as in surface sediments.

c. Community respiration calculated using gaseous flux model. Autotrophic respiration = CR-SR.

d. Although SR was measured using sediment metabolism chambers we were unable to use those numbers since much of the gas respired in sediments is transported through macrophyes. We, therefore, substituted measured gross N-mineralization converted to units of carbon based on the measured C/N ratio of sediment.

- e. Estimated burial values are based on sediment accretion rates calculated from ¹³⁷Cs profiles of cores taken from a nearby *Phragmites communis* -dominated marsh (M. Campana, personal communication)
- f. Export was calculated for chlorophyll *a* in carbon units based on measured differences in chlorophyll *a* during peak high and low tides in Sturgeon Creek and assuming flooding 2 times per day, with a depth of 25 cm of water overlying the marsh at maximum flood and a C : chlorophyll ratio of 50.

In spite of these uncertainties, the inputs and exports balance reasonably well. We believe that we may have underestimated net sediment input, and further research is required to reduce uncertainty. Measurements of exchanges during stochastic events would be extremely useful.

Sweet Hall Marsh is an extremely dynamic environment from the point of view of nutrient cycling. Porewater measurements demonstrate low standing stocks of DIN during most seasons. Determinations of N-cycling process rates show that pools of NH_4^+ and NO_3^- turn over extremely rapidly in the marsh. Microbial mineralization in sediments accounts for release of 40 g of NH_4^+ -N m⁻² y⁻¹; however, when gross mineralization rates were highest (September), marsh sediment did not exhibit net export of NH_4^+ . On the other hand, nitrification rates equaled and often exceeded mineralization rates, especially during September. These data suggest that much of the NH_4^+ released during mineralization is rapidly nitrified, and since porewater concentrations of NO_3^- are extremely low, the NO_3^- produced by nitrification is subsequently denitrified. Thus, there is little DIN available for export. In addition, we suggest that any DIN that is released to overlying water is rapidly taken up by sediment microalgae or water column phytoplankton, which may then be exported from the marsh as particulate matter.

Conclusions

Based upon our measurements and modeling efforts over a two-year period, we conclude that:

- Sweet Hall Marsh must import sediment carbon in order to keep pace with apparent sea level rise.
- there is net export of chlorophyll from Sweet Hall Marsh.
- NO_3 is imported during all seasons, and there is little if any export of NH_4 +.
- NH₄+ produced by microbial mineralization in sediments is rapidly removed by coupled nitrification denitrification. Any excess NH₄+ may support sediment microalgal or phytoplankton production in overlying water.

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