

# AND WOODS HOLE OCEANOGRAPHIC INSTITUTION

FINAL REPORT

OXYGEN UPTAKE AND NUTRIENT REGENERATION IN THE PECONIC ESTUARY

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# OXYGEN UPTAKE AND NUTRIENT REGENERATION IN THE PECONIC ESTUARY

**Final Report** 

**April 1998** 

**Prepared For:** 

# SUFFOLK COUNTY DEPARTMENT OF HEALTH SERVICES

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### PREFACE

Exchanges of oxygen and nutrients between water column and sediments were measured on six cruises from August 1994 -- December 1995. Associated measurements of sediment carbon and nitrogen content, porosity and grain size and water column respiration, particulate carbon, particulate nitrogen and chlorophyll a were conducted to aid in evaluating the role of the sediments in the oxygen dynamics of the Peconic Estuary. In addition, a mooring was placed in Great Peconic Bay to assess the frequency and duration of potential low oxygen events in the near bottom waters. The goal of the Benthic Flux Study was to help parameterize the numerical model of the Peconic Estuary that is being developed by Tetra Tech. What follows is a Summary Report from the Study. This report is not meant to present a full biogeochemical or ecosystem interpretation of the Peconic Estuary.

### April 1997

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### **EXECUTIVE SUMMARY**

# Oxygen Uptake and Nutrient Regeneration in the Peconic Estuary

Rates of oxygen consumption and nutrient regeneration were measured annually throughout the Peconic Estuarine System. Sediment and water column oxygen uptake were measured in order to determine the potential for development of bottom water hypoxia and the magnitude of organic matter cycling throughout the system. Sediment oxygen demand was found to dominate oxygen uptake within the upper estuary with water column processes becoming increasingly important in the better flushed deeper waters of the outer estuary. Water column respiration appeared to be dominated by phytoplankton production based upon similarity in the observed relationship between particulate organic matter concentration and oxygen uptake throughout all of the embayments. The potential for periodic depletions of bottom water dissolved oxygen focussed on the warmer summer periods when oxygen pools are lowest and the rates of consumption highest. Within the poorly flushed upper estuary, observations of periodic water column stratification and rates of oxygen consumption indicated the potential for the depletion of dissolved oxygen to ecologically stressful levels (<4-3 mg/l). Continuous records of bottom water oxygen concentrations during July and August 1995 were consistent with the rate measures, indicating large high-frequency variations in the oxygen field.

Regeneration of inorganic nitrogen and phosphorus was related to the distribution of

phytoplankton and organic matter deposition to the sediments. Organic matter degradation and flux to overlying waters appears to play an important role in the nutrient economy of Peconic Estuary waters. Regeneration of nitrogen within the upper estuary significantly magnified inputs from terrestrial sources and helped to support generally higher chlorophyll a levels. It appears that organic matter cycling within sediments of the Peconic Estuary is enhancing oxygen depletion of bottom waters both directly through oxygen uptake and indirectly by the recycling of phytoplankton nutrients to support further organic matter production and water column oxygen consumption.

### MANAGEMENT UTILITY

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Bottom water oxygen levels are a major habitat-structuring feature of shallow eutrophic systems like the Peconic Estuary. Water column and sediment respiration and water column stratification are the proximate controls on bottom water oxygen levels and relate directly to organic matter inputs, primarily through phytoplankton production. In addition, sediments provide temporal storage of nutrients helping to increase the delivery of phytoplankton nutrients during the higher regeneration periods in summer/fall.

Quantitative measures of oxygen uptake and nutrient regeneration can also be used to support predictions of the potential for bottom water hypoxia. Restoration of benthic communities within the Peconic Estuary first requires the establishment of adequate oxygen conditions. At present, within portions of the estuary, oxygen demand periodically exceeds oxygen supply resulting in ecologically stressful conditions. The "over production" within inner Peconic Bay results directly from nutrient stimulation of phytoplankton production within bay waters and the degradation of this organic production within the Bay System. One approach to reducing eutrophying levels of nutrients within an estuary is to reduce terrestrial inputs. Assessment of a nutrient reduction approach must include the contribution of sediment recycling to the nutrient economy of the system. Since organic matter degradation and nutrient regeneration within water column and sediments appear to play key roles in both the habitat quality and nutrient economy of the Peconic system, it is essential that these parameters be coupled with hydrodynamics in future water quality modeling.

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### INTRODUCTION

Sediment nutrient and oxygen fluxes play major roles in the nutrient and oxygen economy of coastal ecosystems. Marine sediments can represent major sources of nutrients and oxygen demand. In shallow nearshore systems, sediment-water column exchange processes can impact the entire ecosystem. Much of the reason for the high productivity of phytoplankton, fish and shellfish in coastal versus offshore environments is due to the smaller volume of water overlying the sediments which enhances the cycling between water column and sediments. However, this lower dilution of sediment effects can lead to ecosystem degradation if nutrient loading exceeds the assimilative capacity of the system. In fact, much of the assimilative capacity for new nutrient inputs is ultimately due to sediment recycling processes. When nutrient loading becomes excessive, the anoxic zone of the sediment begins to move upward and penetrate the aerated surface layer. The impact to the water column is buffered by the aerobic zone within the sediments and the major result is increased rates of nutrient regeneration and oxygen demand. Under elevated nutrient loading an accumulation of nutrients and oxygen demand develops within the sediments which continues to impact the water column even after inputs are reduced. At higher levels of loading, the aerated zone of the sediments continues to diminish until the sediments become anoxic at the surface, leading ultimately to a rapid depletion of oxygen in the overlying bottom waters and the decline of infaunal communities and fish populations which use them as a food source. Anoxic or hypoxic events need only to occur periodically in order to maintain a depauparate benthic community.

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Sediment oxygen demand (SOD) and nutrient regeneration are, therefore, cornerstone processes impacting and structuring nearshore systems. They are major variables affecting all levels

of ecosystem functioning, and are part of major feedback processes which can enhance or destroy the utility of aquatic coastal ecosystems. The relative importance of these key biogeochemical processes is generally directly related to the depth of the overlying water and the frequency and duration of water column stratification. The impact of sediments on nutrient related water quality is inversely related to water depth (deeper waters having more of the nutrient and oxygen cycling occurring in the water column, therefore less in the sediment). The impact of stratification is more complex with sediment oxygen demand being more important in stratified systems (since oxygen inputs from the atmosphere are diminished), but sediment nutrient regeneration more important in vertically mixed systems where released nutrients are transported to the euphotic zone. In the latter case, the rapid transfer of regenerated nutrients to the euphotic zone and subsequent stimulation of primary production may potentially add to eutrophication. Sediment nutrient and oxygen fluxes also vary in response to a variety of environmental factors but are driven primarily by temperature, organic matter loading and to a lesser extent bioturbation and physical mixing. The complexity of these interactions, therefore, requires a number of samples be collected throughout the year and at a variety of sites along the nutrient/organic matter loading gradients within a given estuary.

As a result of the growing concern over the eutrophication of coastal waters and recognition of the important role of the sediments in nutrient and oxygen balances, these measures have been included in the developing model for the Peconic Estuary. Consisting of over 100 embayments and tributaries, the Peconic Estuary system is now potentially threatened by nutrient and pollutant loading from both point and non-point source discharges. Although the areal extent of the Bays System is extensive at ca. 160 square miles (about half of which fall in the Gardiners Bay province), the threat of nutrient related water quality decline is currently significant in the system's smaller embayments and tributaries. The Peconic Estuary's corresponding watershed encompasses roughly 110,000 acres and supports both extensive wetlands as well as 15 rare ecosystems designated as "priority communities" by the New York Natural Heritage Program (Opaluch et al. 1995). Both the number of embayments and the surface area of the waterbody make the Peconic System one of the major estuaries along the Northeastern coast of the U.S. (eg. Buzzards Bay, MA has 27 embayments and is ca. 200 sq. mi.), and therefore of significance in its ecological and economic contribution to the coastal Mid-Atlantic region.

The high aesthetic, recreational and economic value of this estuary is primarily the result of its historically high levels of water quality. Increased nutrient loading to the system, however, is of serious concern as it represents a potential and considerable long-term threat to the estuary's ecological health. The development of appropriate management plans to protect the Peconic Estuary from environmental decline requires determination of the significance of natural processes in ultimately determining water quality in the estuary. The importance of natural processes to evaluating management objectives and/or potential remediation measures is reflected in the significant impact of a brown tide bloom on scallop and oyster harvests in the mid-1980's. The interaction between anthropogenic impacts and natural processes is extremely complex and often difficult to identify, however it is that very aspect which will ultimately determine the environmental health of our coastal environments in the future. Sediment nutrient and oxygen fluxes can represent

a significant component in the overall ecological health of a coastal water body, influencing both water column and benthic habitat quality necessary to supporting healthy animal and plant communities. As well, these processes can reflect/integrate both natural and human impacts such as alterations to circulation, deposition, nutrient/organic matter loading, etc. Understanding the relative contribution of benthic fluxes is important to long-term prediction of environmental quality, especially as increased attention is being given to maintaining the high levels of water quality generally characteristic of the Peconic Estuary.

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To address these issues in the Peconic Estuary, we made measurements of benthic nutrient and oxygen fluxes across a gradient of nutrient and organic matter loading. Following an initial reconnaissance cruise, sampling commenced with six cruises spanning late August 1994 through December 1995. Ten stations, ranging from the Peconic River/Meetinghouse Creek to Gardiners Bay, were measured on each cruise. To provide better spatial coverage to the measurements, six additional stations were measured during July 1996. Annual flux estimates for these six additional sites was estimated from an empirical relationship based upon the seasonal measurements throughout the estuary. Also, to determine the temporal variability in bottom water oxygen concentrations, a mooring was placed in mid-summer of 1995 to continuously record bottom water dissolved oxygen. These combined measurements, in concert with other system structuring parameters like circulation, provide the base for evaluating the importance of sediment/water column interactions to the ecological health of the Peconic Estuary System.

# METHODOLOGY

Sampling Sites: Measurements of sediment-water column exchanges of nutrients and oxygen and associated water column parameters were conducted throughout the Peconic Estuary. Ten sites were selected for seasonal measurements in order to achieve spatial coverage and measurements in key areas (Figure 1). An additional, six sites were assayed in July 1995 in order to further improve spatial coverage and to assess the potential importance of smaller constituent basins (Table 1). Sites ranged from soft mud to sand and from 1.6-11.5 meters depth. Station location for sampling was determined using a Northstar 931X differential global positioning system (DGPS) with horizontal accuracies of three to five meters.

<u>Sediment Flux Incubations</u>: Based upon experience in a variety of systems from shallow embayments to deeper harbors (Nantucket to Buzzards Bay) representing a range of nutrient and organic matter loadings, we used a sediment core incubation technique to determine rates of benthic oxygen and nutrient exchange (Cibik and Howes 1995, Howes 1997). Large diameter cores (15 cm i.d.) were collected by SCUBA diver at each location. Ten sites were measured seasonally (6 samplings from August 1994-December 1995) with an additional six sites assayed on July 7, 1995 (Table 1). The three to four cores collected per location were held at *in situ* temperatures during transport through the completion of the incubation period. Cores were held within their temperature controlled baths on a gimballed table to reduce disturbance during transport. Oxygen levels within the core headspaces was maintained by continuous aeration. The cores were transferred directly from the ship to the field laboratory at the Suffolk County Marine Education Center on the shore of the estuary.

In the field laboratory the cores were maintained in the dark at *in situ* temperatures. Water overlying the sediment was replaced with 0.2 um filtered water collected at the coring location and the cores were stoppered to prevent gas exchange with the atmosphere. At appropriate intervals (determined by the rate of oxygen uptake), usually 1-6 hrs, nutrient concentrations were measured. Oxygen tensions were not allowed to drop below 50% of *in situ* oxygen levels. Nutrient flux measurements were made on six occasions over at least 24 hours. Headspace waters were filtered (0.22um Millipore) and held as in Table 2 and analyzed by procedures given in Table 3. When incubations were completed, samples of the surface (0-2cm) sediments were collected for sand/silt/clay analysis and for determination of total organic carbon and nitrogen (Perkin Elmer 2400 Elemental Analyzer). These later data were used to determine the area over which the flux data was to be integrated (based upon sediment maps), and the relation of organic matter content to flux.

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The rate of sediment-water column exchange for each core was determined by linear regression of the change in concentration of each analyte through time. Only the linear portions of time-course measurements were used in the determinations.

<u>Water column Parameters</u>: Water samples were collected by Niskin Sampler at each station. Triplicate samples of bottom water dissolved oxygen (Winkler titration) and respiration were collected at each coring site. Water column respiration samples were incubated at *in situ* temperatures and assayed by Winkler titration using a high precision Radiometer Titrator. Water column particulate organic carbon and nitrogen (POC, PON) were assayed by filtering water samples through pre-combusted glass fiber filters, with analysis by high temperature combustion (Perkin Elmer 2400 Elemental Analyzer). In addition, water column stratification was checked by CTD profiling (Seabird) coupled to a fluorometer to determine chlorophyll a levels. These profiles, along with bottom water oxygen levels, were used to establish the general environmental conditions at each station (salinity, temperature, D.O. and stratification).

# TABLE 2

# **Monitoring Parameters**

PARAMETER	VOLUME	CONTAINER	PROCESSING & STORAGE
Nitrate & TDN	60 ml	polyethylene (acid washed)	0.22 um membrane stored on ice (dark) or frozen to -20°C
Ammonium	60 ml	polyethylene (acid washed)	0.22 um membrane stored on ice (dark); run within 24 hrs
Ortho-Phosphate	60 ml	polyethylene (acid washed)	0.22 um membrane stored on ice (dark); run within 24 hrs
Total Organic Carbon/Nitrogen	Solids	polyethylene	combusted GFF, dried or glass (acid washed)
Flux (oxygen uptake)	15 cm core	Probe	

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PARAMETER	MATRIX	UNITS	METHOD	REFERENCE
Nitrate + Nitrite	water	μM	Autoanalyzer	a
TDN	water	μΜ	Digestion/Nitrate	b
Ammonium	water	μΜ	Indophenol	с
Orthophosphate	water	μΜ	Molybdenum blue	d
Total Organic Carbon/Nitrogen	sediment	µg/cm³	Acid treatment, drying Elemental Analysis	e
Oxygen uptake	sediment	mmol/m²/h	time-course O2 uptake	f
Nutrient flux	sediment	µmol/m²/d	time-course [conc]	g

TABLE 3 Laboratory Analyses

a Lachat Autoanalysis procedures based upon the following techniques:

--Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Ass. U.K. 47:23-31.

--Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in sea water. J. Mar. Res. 11: 87-96.

b D'Elia, C.F., P.A. Stuedler, P.A. and N. Corwin. 1977. Determination of total nitrogen in aqueous solutions. Limnol. Oceanogr. 22:760-774.

c Scheiner, D. 1976. Determination of ammonia and Kjeldahl nitrogen by indophenol method. Water Resources 10:31-36.

d Murphy, J. and J.P. Reilly. 1962. A modified single solution for the determination of phosphate in natural waters. Anal. Chim. Acta 27: 31-36.

e Perkin-Elmer Model 2400 CHN Elemental Analyzer Technical Manual.

f Jorgensen, B. 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnol. Oceanogr. 22:814-832.; Albro, C., J. Kelley, J. Hennessy, P. Doering, J. Turner. 1993. Combined Work/Quality Assurance Project Plan (CW/QAPP) for Baseline Water Quality Monitoring: 1993-1994. MWRA, Boston MA.

g Klump, J. & C. Martens. 1983. Benthic nitrogen regeneration In: Nitrogen in the Marine Environment, (Carpenter & Capone, eds.). Academic Press.

<u>Oxygen Mooring</u>: The mooring supported an array of **two** pulsed oxygen sensors (Endeco T1184) held vertically at 25 cm and 45cm above the sediment surface. Each sensor also recorded temperature and salinity necessary for calculation of degree of oxygen saturation. Two moorings were deployed July 7, 1995 through August 22, 1995. However, data was only recovered from the Great Peconic Bay mooring as the Little Peconic Bay mooring was rendered inoperable by a state environmental trawler soon after its placement.

# **Conversion Table for Figures and Tables**

Reference	Change	Conversion
Dissolved Oxygen (Fig. 14,15,16)	uM to mg/l	multiply value by 0.0320
Water Column Carbon (Fig. 20)	mmol /m <sup>3</sup> to mg/l	multiply value by 0.0120
Sediment Oxygen Uptake (Fig. 23)	mol C/m <sup>2</sup> /yr to g $O_2/m^2/day$	multiply value by 0.0877
Sediment Oxygen Uptake (summary tables)	mmol/m <sup>2</sup> /day to g/m <sup>2</sup> /day	multiply value by 0.0320
Sediment DIN Flux (Fig. 24)	mol/m <sup>2</sup> /yr to mg/m <sup>2</sup> /day	multiply value by 38.4
Sediment NH4-N Flux (summary tables)	umol/m²/yr to mg/m²/day	multiply value by 0.0000384
Sediment NO3-N Flux (summary tables)	umol/m²/yr to mg/m²/day	multiply value by 0.0000384
Sediment PO4-P Flux (summary tables)	umol/m²/yr to mg/m²/day	multiply value by 0.0000877
Water Column Respiration (summary table)	uM/day to mg/l/day	multiply value by 0.0320

# DATA SYNOPSIS

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<u>Station Sediments</u>: Sediments within the Peconic Estuary were not of uniform composition. Sediments within the low velocity regions of the estuary tended to have higher concentrations of organic carbon and nitrogen and be dominated by fine sands, silt and clays than the "sandy" stations which were composed of coarser sands (Tables 4 & 5). All of the sandy stations that were routinely sampled were within the upper estuary, Flanders Bay and shallower regions of Great Peconic Bay. The apparent coarse sand nature of the Peconic River/Meetinghouse Creek confluence resulted from a prevalence of broken shells (Table 5). The measured porosities were typical of sand and mud sediments with values of ca. 40 mL/100 cm<sup>3</sup> and >70 mL/100 cm<sup>3</sup>, respectively.

The highest levels of organic matter were associated with the tributaries and smaller depositional basins. Meetinghouse Creek (7% carbon) was extra-ordinarily organic rich due to nutrient loadings from a variety of sources: 1) historic loadings from agricultural sources such as the duck farms located in the watershed; 2) development activities within the watershed; and 3)

direct input of organic material from the bordering marsh habitats. The high organic carbon levels within the freshwater/saltwater zone within the Upper Peconic River are likely due to deposition of riverine transported material. West Neck Bay and Reeves Bay sediments show high organic matter levels most likely as a result of their restricted basins, low water exchanges and high productivities (i.e. high organic deposition). The more open regions of the Estuary showed sediment characteristics typical of coastal sediments throughout the region.

<u>Annual Cycle</u>: Sampling appears to have captured the full seasonal cycle of water temperatures (Figure 2). While all sites showed similar seasonal temperature excursions, there were consistent differences due to location and water depth. The deeper waters of Gardiners Bay (11.5m) were consistently cooler during summer and cooled more slowly in the fall than the shallower waters of the Inner Peconic Estuary (Figure 2). Similarly stations within the Estuary with depths greater than five meters were cooler in summer than shallower stations (<5m). Although the differences are relatively small (<2°C), the pronounced effect of temperature on respiration rates ( $Q_{10}$ =2-3) suggests a mechanism for enhanced respiration in the shallower water of the Estuary (other factors being equal).

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Sediment oxygen uptake and nutrient regeneration rates are primarily determined by temperature and the amount of deposited labile organic matter and secondarily mediated by the composition of infaunal communities. Water column respiration is also dependant upon temperature and labile organic matter. However, in a system like the Peconic Estuary where much of the particulate organic matter within the water column is produced *in situ* by photosynthesis, rates of respiration are likely more variable than the sediment where rates are "smoothed" due to their storage of deposited organic matter. Combining water column and sediment respiration rates can be used as a measure of total system organic matter

remineralization and to estimate the rate of re-aeration required at night to maintain bottom water oxygen levels.

We can construct a composite annual cycle of sediment oxygen uptake and water column respiration from the four seasonal measurements and the summer values from July 1995 and August/September 1994 (Figure 3). At all **ten** monitoring sites the maximum rates of oxygen uptake were found at the highest temperatures in either July or August. However, at some sites the pattern of oxygen uptake departed significantly from temperature variations. Maximum rates were observed in the July 1995 sampling for the shallow, relatively warmer Upper or Western portion of the estuary, the muddy and sandy sites from the mouth of the Peconic River/Meetinghouse Creek, through Reeves Bay, Flanders Bay and Great Peconic Bay (Figure 3a,b,c). In contrast, the deeper, cooler and better flushed Eastern Estuary (Noyack Bay, West Neck Bay and Gardiners Bay) all showed cycles of oxygen uptake which more closely followed the temperature cycle (Figure 2).

The difference in total system metabolism between the Upper (western) and Lower (eastern) estuary may be associated with the Brown Tide bloom which occurred in 1995 but not 1994 (SCDHS Cell Counts, 1995). The effect of the dense bloom would be to increase oxygen uptake within the Upper shallower regions of the estuary and have less of an effect in the deeper more well flushed portions of the estuary where cell counts were generally lower. Given the similarity in temperatures between July and August, differences in oxygen uptake can be viewed as differences in organic matter mass. Within the regions of muddy sediments of Peconic River/Meetinghouse Creek, Reeves Bay, Great Peconic Bay and the sandy sediments of Flanders and Great Peconic Bays (Figure 3), both water column and sediment respiration rates appeared to be enhanced in the bloom year. The higher total respiration within Gardiners Bay, West Neck

Bay and Noyack Bay in August 1994 in the non-brown tide year was primarily the result of higher rates of water column respiration, possibly due to a bloom of a different phytoplankton. Overall, the only stations to show dramatically lower August than July rates of sediment respiration were the very innermost stations of Peconic/Meetinghouse Creek, Reeves Bay and Great Peconic/Flanders Bay. The composite annual yearly rates of sediment oxygen uptake represents an averaging of the observed interannual differences. However, even for the innermost three stations the difference in integrated annual rates between 1994 and 1995 should be relatively small, since the major portion of the bloom was for only about one month.

Sediment respiration was relatively similar throughout the estuary. However, sandy stations showed consistently lower (ca. 50%) rates than nearby muddy stations and there was a trend for the deeper portions of the estuary (eastern) to have lower rates than the shallower inner regions (western). These trends were especially clear in the July survey of 16 stations (Figure 4).

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Sediment nutrient regeneration rates paralleled rates of sediment oxygen uptake (Figure 5a,b,c). Rates of dissolved inorganic nitrogen (DIN) release were dominated by ammonium at all muddy sites. In contrast, at sandy sites (Great Peconic/Flanders Bay & Flanders Bay) both ammonium and nitrate fluxes were near the detection limit for most of the year and showed a slight net uptake. DIN uptake at these stations is likely the result of a combination of algal uptake and denitrification, as algae were observed at these sites and their sandy nature may facilitate nitrification/denitrification reactions. However, it should be cautioned that the uptake rates are near the detection limit. As with oxygen uptake, DIN fluxes tended to follow the trend of Western Estuary>Eastern Estuary>Sandy Sites, and is best seen in the July survey of 16 sites (Figure 6). It appears that factors other than remineralization rates may be mediating nitrogen fluxes (see below).

Total dissolved nitrogen fluxes were measured as the combination of dissolved inorganic and organic nitrogen. The methods for assaying of dissolved organic nitrogen (DON) are much less sensitive than for DIN and the exchanges must be interpreted accordingly. There was no consistent pattern of DON flux between the sediment stations with location or sediment type. Overall, the rates tended to be smaller than DIN fluxes with almost all sites showing periodic uptake and release (Figure 5). Annually integrated rates of oxygen uptake, DIN and DON flux are presented in Appendix I.

<u>July Survey and Annual Oxygen Uptake</u>: Seven of the ten annual flux stations had fine or muddy sediments. At these seven stations there was an excellent correlation between the July oxygen uptake rate and the annually integrated rate ( $R^2=0.85$ ; Figure 11). From this empircal relationship, it is possible to estimate annual oxygen uptake rates for the **six** additional sites measured only in the July survey. These sites can then be used to increase the spatial coverage for a system-wide organic matter balance (Appendix I).

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Sediment oxygen and nitrogen flux relationships: At all stations, ammonium dominated DIN flux in spring and summer, while during winter ammonium and nitrate fluxes were about equal in the stations showing positive nitrate fluxes (a positive flux indicates release from the sediments). In winter and spring about half of the measurements showed sediment nitrate uptake and the innermost stations occasionally showed sediment ammonium uptake and nitrate release (Figure 7). This seasonality in the partitioning of DIN flux follows the cycle of more oxidizing sediments in winter and more reducing sediments in summer. The result of this oxidationreduction cycle is that more of the DIN is oxidized to nitrate before release in spring/winter, while ammonium release greatly exceeds nitrate flux in summer. However, there was no unifying pattern of ammonium to nitrate fluxes at any period within the study. This was

expected due to the number of mediating factors which determine the partitioning of the DIN flux (e.g. bioturbation, oxidation-reduction potential, rate of remineralization etc.).

Similarly there was no clear pattern between the rate of DIN and DON fluxes (Figure 8). However, it appears that DIN generally represents a relatively constant fraction of the total dissolved nitrogen flux during the summer season (Figure 9). When DIN and TDN are compared throughout the estuary, the TDN is only 1.1 times the DIN flux alone (R<sup>2</sup>=0.78). The lack of relation in direct comparisons between DIN and DON fluxes most likely stems from a combination of greater variability in the DON assay coupled to the "real" natural variability in DON flux (bioturbation, infaunal direct release, phytoplankton leaching, heterotrophic release etc.). In addition, DON and DIN fluxes are only weakly associated, since for DIN flux to occur organic matter must be remineralized, but DON flux only needs cells to lose soluble organic matter. Similarly, DIN fluxes can be reduced by uptake by benthic algae, whose presence which may lead to increased DON fluxes through leaching. In summary, the dynamics controlling DIN and DON fluxes are not tightly coupled and therefore the lack of similar patterns in rates are not unexpected.

In contrast, there was a much clearer relationship between oxygen consumption to remineralize organic matter and the flux of remineralized nitrogen (DIN). Assuming that one carbon atom is remineralized for each two atoms of oxygen consumed in the process (RQ=1), the measured DIN and SOD fluxes can be used to suggest the C/N ratio of the organic matter being remineralized. Rates of carbon to nitrogen remineralization for July and August when decomposition and remineralization are most active yield an average flux ratio of ca. 17. This flux ratio is roughly twice the C/N ratio (ca. 8) of water column particulate matter within the estuary's waters (Valiela 1994) and indicates that during decomposition, relatively more carbon

is remineralized than DIN is released. This C/N patter likely results from coupled nitrificationdenitrification of nitrogen regenerated within the sediments (with a small additional amount of N buried and possibly some sediment DIN uptake). Rates of denitrification accounting for about 50% of the nitrogen remineralized within coastal sediments is common (Seitzinger 1988, Nowicki et al. in press, Howes 1997). While these data are not sufficient to quantify denitrification for an estuarine mass balance, they provide a clear indication of the potential importance of sediment denitrification to the nitrogen balance of the Peconic Estuary.

Organic Matter and Respiration: Sediment oxygen uptake was directly related to the amount of organic carbon within the upper two cm of the sediments at each of the 16 sites within the Peconic Estuary. The relationship was fairly robust except for the very highly organic sediment within the Upper Peconic River (PRU) and Meetinghouse Creek (MC). All of the stations are exposed to a similar temperature regime. Therefore, the similarity in respiration per unit organic matter suggests a relatively constant fraction of the carbon pool is labile (Figure 12).

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Similarly, water column respiration was also directly related to the particulate organic carbon pool within the water column (R<sup>2</sup>=0.93, Figure 13). As in the sediment comparison, the similarity in temperature between the sites west of Shelter Island indicates a relatively constant fraction of the POC pool is labile. Note that water column respiration includes both the respiration of heterotrophs and phytoplankton dark respiration. Relationships of both sediment and water column respiration to organic carbon levels allow modeling of oxygen uptake from more easily assayed parameters (e.g. POC). However, it is likely that the goodness of fit of the sediment relationship results from the relatively depauperate infaunal populations. The lack of healthy infaunal populations removes a major variable in sediment carbon pool-oxygen uptake dynamics.

Bottom Water Oxygen Fluctuations: The mooring placed within the basin of Great Peconic Bay (Figure 1), yielded data on oxygen, salinity and temperature of bottom waters from July 6 through August 22, 1995. Duplicate meters were deployed at 25 cm and 45 cm above the sediment surface. Bottom water oxygen levels were relatively low throughout the deployment. However, the major depletion occurred shortly after the major bloom of Brown Tide. Based upon the SCDHS cell counts, there is an agreement between the timing of the bloom and the timing and duration of the larger hypoxic period in Great Peconic Bay (Figure 14).

There was a clear tidal cycle super-imposed upon the longer diurnal and bloom cycles (Figure 15). Lower oxygen was typically found during ebb versus flood tides. This is consistent with more organic rich waters from the Upper Estuary being transported seaward in the ebbing tidal waters. In addition, the transported Upper Estuary waters may be lower in D.O. as a result of the higher respiration rates due to the import of organic matter into those sub-systems.

The sediments were clearly involved in the low oxygen levels at the Great Peconic Bay site. Oxygen levels recorded by the bottom sensor were typically lower than those recorded by the sensor placed only 20 cm higher in the water column supporting the concept of an important oxygen sink within the sediments (Figure 16). When lower oxygen was found at the deeper sensor it was generally matched by slightly higher salinities and lower temperatures. The salinity and temperature data suggests that the bottom waters may have been stratified, thus reducing reaeration and increasing the potential for oxygen decline. During the interval (July 20-25) when salinity and temperature were similar at the two sensors, oxygen levels were also similar (Figure 16). Distribution of Organic Matter Remineralization: The respiration results suggest a consistent gradient in labile organic matter running from the Peconic River and Meetinghouse Creek to Gardiners Bay. The gradient is most clearly seen in water column respiration (Figure 17) which decreases linearly with the log of the distance from the head of the estuary (Peconic River). While sediment respiration follows a similar relationship with distance from the headwaters, there appears to be more variability in the data. The variability is due to the presence of sandy (non-depositional) sediments within portions of the estuary (shown by "\*\*" in Figure 17). However, when only the depositional sediments are considered the relationship of decreasing respiration within increasing distance along the estuary is very clear.

Based upon the sediment oxygen and nutrient flux and water column respiration data it is possible to determine the potential of various regions of the Peconic Estuary to develop low oxygen conditions. From the July rates of oxygen uptake at all 16 stations, we can calculate the time required to consume all of the oxygen within a 1 m<sup>3</sup> parcel of water in contact with 1 m<sup>2</sup> of the sediment surface (Figure 18). We calculated the total amount of oxygen in one cubic meter of bottom water and divided the result by the rate of uptake to determine the time required to remove all of the oxygen from the cubic meter of water. From this simple analysis it is clear that within the upper regions (headwaters to Reeves Bay) even brief periods of stratification (<1 day) can result in hypoxic conditions. Although rates of oxygen uptake continue to decline throughout the remainder of the estuary from Flanders Bay to Gardiners Bay, hypoxic conditions are generally possible with periodic water column stratification events of <1 day.

As expected from the relationships between DIN flux, distance from the estuary headwaters and sediment oxygen uptake (Figure 10 & 18), the DIN flux also decreases with increasing distance from the headwaters (as do nutrient concentrations). Based upon the sediment DIN

fluxes and water column pools of DIN and particulate organic nitrogen (PON), it is possible to gauge the role of the sediments in the nitrogen economy of the water column. We can calculate how long it takes for sediment DIN regeneration to replace the water column DIN+PON pool (=turnover). Although the N concentrations decline moving seaward, the water depth, hence dilution, also increases. The result is that sediment nitrogen regeneration from muddy sediment areas takes weeks to months to replace the entire water column pool (Figure 19). However, within the muddy stations of the upper estuary (PRU, PMS, MC, RB) the slow rates of water exchange and the high rates of regeneration suggest that these sediments may play an important role in magnifying the impacts of nitrogen loading within this region.

Spatial distribution: Based upon the sediment surveys and the bathymetry it is possible to gain an understanding of the likely areal coverage of benthic metabolic activity and controlling substrate pools. There appear to be four provinces of water column organic matter levels following the gradient from the head of the Estuary to Gardiners Bay. Particulate organic carbon levels varied more than an order of magnitude from the very high levels in Reeves Bay and Flanders Bay to the low levels in the near-oceanic waters of Gardiners Bay (Figure 20). West Neck Bay appears to be a net phytoplankton producer as it had three times the POC levels as the incoming waters. However, the POC distribution was only roughly correlated with water column chlorophyll a fluorescence (Figure 21). Chlorophyll a showed a more patchy distribution than POC, but with clear bloom conditions within the inner regions of the estuary and West Neck Bay.

Sediment oxygen uptake is determined both by the production (or import) of organic matter within the water column and its deposition to the sediments. The lower rates of oxygen uptake (and associated DIN fluxes) within Flanders Bay and Reeves Bay compared to Little Peconic Bay parallels the pattern of depositional and non-depositional sediments. It appears that the higher organic matter loadings to the Upper Estuary, which result in the highest water column respiration rates in the inner bays and tributaries, are not deposited wholly within the local sediments (Figure 22). Instead, the particulate organic matter produced within the inner estuary is partially transported seaward to enhance loadings to the depositional basins (Figure 23). In addition, the sediments of Flanders Bay and at the Flanders/Great Peconic junction are generally sandy and exhibit very low or negative DIN release (uptake, see Figure 24). These low rates are likely due both to uptake by benthic photoautotrophs within the shallower waters where algae were observed and to microbial denitrification. The very high rates of organic matter mineralization and DIN flux within Meetinghouse Creek may result from a continuing depuration of the sediments, but on-going nitrogen and organic matter inputs may be playing an even more important role. Based upon the available information, it is not possible to determine the relative importance of historic versus on-going inputs to current fluxes. In contrast, it is most likely that mineralization rates within the Bays are supported by current inputs and production as influenced by hydrodynamics. Spatial patterns of water column respiration appear primarily influenced by the Estuary's gradient in production and water exchange, while sediment mineralization, although similarly influenced, is affected by additional structuring factors. The additional complexity in the spatial pattern of sediment fluxes stems from the need for organic matter to be deposited and the mediating influence of sediment oxidation status on coupled nitrification-denitrification and therefore DIN fluxes. In addition, infaunal communities can alter the patterns of DIN fluxes. As water quality improves within the Peconic Estuary, it is likely that significant changes may occur in the rates and distribution of oxygen uptake and DIN release. The recolonization of the estuary's benthos will likely result in a short-term increase in nutrient loading due to "mining" of the sediments through infaunal bioirrigation. The magnitude of this infaunal effect cannot be gauged at the present time.

### CONCLUSIONS

1) Sediment and water column respiration represent significant sinks for oxygen within the Peconic Estuary. Oxygen uptake and water column oxygen depletion is most pronounced in the summer and generally decreases from the Peconic River to Gardiner's Bay. However, the gradient in respiration is most pronounced in the water column as there were pronounced "hot spots" in measured sediment oxygen uptake.

2) Benthic nitrogen fluxes also generally declined from the Peconic River to Gardiner's Bay. During summer when phytoplankton nutrient levels are reduced, benthic nitrogen fluxes throughout the estuary are sufficient to replace the most active nitrogen pools (PON+DIN) about once. However, within the Upper Estuary benthic regeneration may replace this nitrogen pool every 2-3 weeks.

3) Sediment fluxes were correlated with organic matter deposition, while water column respiration was coupled to particulate concentrations.

4) Sediments within the upper estuary (MHC, PRU and RB) and its tributaries exhibit highly eutrophic nitrogen/oxygen fluxes. This effect is more noticeable in the muddy sediments.

5) Water column respiration accounts for two-thirds of the carbon turnover within the Peconic Estuary.

6) Sediment Oxygen Demand and bottom water respiration are high throughout the Upper Estuary, with rates sufficient to produce bottom water hypoxia if vertical mixing is restricted for periods of 0.5-1.5 days.

7) Bottom waters of the Upper Estuary (Great Peconic Bay) are currently exhibiting a high degree of temporal variablility with periodic short-term hypoxic events in the summer months.

8) Sediment denitrification is a major gap in our understanding of the nitrogen cycle of the Peconic Estuary. The sediment flux data suggest that denitrification rates will have a very patchy distribution and therefore require a survey approach.

9) There appears to be a relationship of Brown Tide to inter-annual variations in sediment oxygen and nutrient fluxes in the western portion of the estuary. However, the mechanism cannot be discerned from the existing data.

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Figure 2. Seasonal cycle of bottom water temperature within Gardiners Bay (GB), shallow (<5m) and deep (>5m) flux stations within the Peconic Estuary. Measurements are from the six surveys, 1994-1995.





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Figure 5. Annual nitrogen flux from sediments within the Peconic Estuary. (A) Muddy stations in Western Estuary, (B) Muddy stations in Eastern Estuary and (C) Sandy stations. I.D.'s refer to stations in Table 1.



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Figure 6. Survey of 16 stations throughout the Peconic Estuary, July 5-7, 1995. Rates of nitrogen flux tend to be highest within the muddy stations of the western estuary (inner) and lowest in at the sandy eiter (shown by \*\*). The trend is most pronounced in dissolved inorganic nitrogen fluxes



Figure 7. Relationship of nitrate and ammonium fluxes within the Peconic Estuary in (A) winter, (B) spring and (C) summer.

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# Peconic Summer Nitrogen Flux

All stations for June, July, and August



Figure 8. Relationship of dissolved inorganic nitrogen (DIN) to dissolved organic nitrogen (DON) within the Peconic Estuary in during summer. Peconic Summer Nitrogen Flux All stations for June, July, and August

23×



Figure 9. Relationship of dissolved inorganic nitrogen (DIN) to total dissolved nitrogen (DON+DIN) within the Peconic Estuary in during summer. All summer stations measured in June, July and August.



Annual rates for stations sampled only in July are based on regression of July rates and annual rates for the other stations. MC and PRU not included in regression. Sandy stations are starred

Figure 10. Relationship of sediment oxygen uptake to dissolved inorganic nitrogen (DIN) flux at all study sites withing the Peconic Estuary, (A) annual rates and (B) summer rates (June-August).



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Figure 13. Relationship of watercolumn respiration to particulate organic carbon levels throughout the Peconic Estuary.



Figure 14. Average bottom water oxygen levels in Great Peconic Bay from two moored sensors 25 cm and 45 cm above the sediment surface.

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Bottom sensor: 0.25 m above sediment Top sensor: 0.45 m above sediment



Figure 16. Bottom water oxygen, salinity and temperature at sensors 25 cm and 45 cm above the sediment surface in Great Peconic Bay during the interval of lowest oxygen.







Absolute mass of carbon degraded requires adjustment for watercolumn depths. Letters represent ID's of 16 Stations sampled in July 1995.

Figure 17. Decline in watercolumn and sediment oxygen uptake with increasing distance from the head of the Peconic Estuary. The relationship between distance and sediment oxygen uptake is most clear when depositional sediments are considered separately (sandy sediments denoted by \*\*).



Time required to consume all oxygen in 1 m3 of water overlying sediments in July. Oxygen Depletion by Sediment and Watercolumn Uptake.

Figure 18. Time to consume all of the bottom water oxygen within a  $1 \text{ m}^3$  parcel of water in contact with  $1 \text{ m}^2$  of the sediment surface. Data are from the July survey of the 16 flux stations.



Figure 19. Time to regenerate an amount of dissolved inorganic nitrogen (DIN) equivalent to the pool of DIN + PON within the watercolumn overlying each sediment flux site in July.





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![](_page_60_Figure_0.jpeg)

![](_page_61_Figure_0.jpeg)

![](_page_62_Figure_0.jpeg)

Appendix 1. Sediment Oxygen and Nutrient Exchange: Summary Tables

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DIN/PO4 Ratio	26	62	18		26	312	-38	80	19	34								
Annual WC-Resp Flux (mol/m3/y)	1.96	4.60	3.61	1.89	2.30	3.21	3.35	4.39	6.33	4.57								
Annual SOD Flux (mol/m2/y)	9.61	11.70	11.10	14.74	9.08	8.14	10.01	9.26	17.98	17.64	*7.59	<b>00</b> .6*	*7.71	*8.61	* 42 EA	+0.0+	<b>*</b> 26.91	
Annual PO4 Flux (mmol/m2/y)		7	51	169	19		လု	ი	38	19								
Annual TDN Flux (mmol/m2/y)	762	524	339	2579	BDL	-25	-460	200	382	691								
Annual DIN Flux (mmol/m2/y)	598	449	896	1867	512	241	122	-96-	715	650	*464	*767	*173	+300	1000	SSUL-	*1255	
Annual NO3 Flux (mmol/m2/y)	204	68	135	73	60	13	-61	-17	217	45								
Annual NH4 Flux (mmol/m2/v)	705	465	761	1794	452	229	183	49	499	605								
Station Type		Soft Mind	Soft Mud	Soft Mud	Soft Mud	Sand	Sand	Sand	Mud	Mud/Shell	Soft Mud	Mud	Sandy Mud	Sandy Mud	Calluy Wide	Soft Mud	Soft Mud	
Depth (meters)			7 1	6.8	012 7 2	i 0	0.4	<b>P</b> C	- i C	1 0 0 0	9 9 9 9	64			t t	1.6	2.6	
Station			an	2	יי	ט מ ט מ			2 - 0	SWa						PRU	MC	

\* Calculated from regression of July rate and annual rate, for sandy and muddy stations separately.

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	Sediment PO4 Flux (S.E.)	7.9 7.9 119.9 17.1 29.3 136.3 27.1 27.1 32.1 32.1	Sediment PO4 Flux (S.E.)	15.3 4.5 5.1 8.1 2.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0	Sediment PO4 Flux (S.E.)	19.7 6.9 15.6 9.2 7.0 9.4 1.7 9.4
	Sediment PO4 Flux (uMol/m <sup>2</sup> /d)	19.1 6.9.4 7.64.5 7.64.5 1.765.5 1.764.5 1.765	Sediment PO4 Flux (uMol/m^2/d)	38.5 -10.7 33.5 28.6 0.0 -6.8 -12.0	Sediment PO4 Flux (uMol/m^2/d)	122.5 -19.3 67.9 67.9 33.1 -9.8 38.8 -28.8
	Sediment TDN Flux (S.E.)	1180 1504 1505 14305 14305 1611 1011 1655 1011 1655	Sediment TDN Flux (S.E.)	2018 835 835 759 759 1230 1230 1076 548 548 548 548	Sediment TDN Flux (S.E.)	243 316 556 607 193 89 89 89
	Sediment TDN Flux (uMol/m^2/d)	6272 7757 5899 5899 21973 6096 -789 -789 -789 1311 1311	Sediment TDN Ftux (uMol/m^2/d)	6325 3035 4443 3234 3234 868 1737 1956 1956 201	Sediment TDN Ftux (uMol/m^2/d)	-221 2300 1158 1158 -501 -532 -125 -125 -125
<u>.</u>	Sediment NO3 Flux (S.E.)	555555555555 26555555555555555555555555	Sediment NO3 Flux (S.E.)	1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Sediment NO3 Flux (S.E.)	44 92 44 92 44 92 44 92 45 92 92 92 92 92 92 92 92 92 92 92 92 92
	Sediment NO3 Flux (uMol/m^2/d)	7357 1357 1357 1357 1357 1357 1358 1358 1358 1358 1358 1358 1358 1358	Sediment NO3 Flux (uMol/m^2/d)	168 123 161 161 161 184 293 293	Sediment NO3 Flux (uMol/m^2/d)	197 -278 -102 170 -170 -170 -170 -151 -151 -151 246 246 244
	Sediment NH4 Flux (S.E.)	67 67 677 677 677 623 623 623 623 623 623 623 7228 777	Sediment NH4 Flux (S.E.)	120 7 75 655 655 76 76 76 17 13 8 8	Sediment NH4 Flux (S.E.)	200 18 97 10 20 20 20 20 20 20 20 20 20 20 20 20 20
	Sediment NH4 Flux (uMol/m^2/d)	2005 124 124 1750 2570 2570 2531 2660 3805	Sediment NH4 Flux (uMol/m^2/d)	77 80429884088	Sediment NH4 Flux (uMol/m^2/d)	472 163 401 405 1122 1152 1152 1152 1152 1152 1152 11
	Sediment Oxygen Uptake (S.E.)	2.6 2.7 2.7 2.7 2.7 2.7 2.7 2.7 2.7 2.7 2.7	Sediment Oxygen Uptake (S.E.)	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	Sediment Oxygen Uptake (S.E.)	5.0 7.1.3 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.1.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7
An an	Sediment Oxygen Uptake (mMot/m*2/d)	. 37.1 55.1 107.8 39.5 39.5 39.5 39.5 28.7 28.7 28.7 28.7 50.1 49.7	Sediment Oxygen Uptake (mMol/m^2/d)	2230 2230 2230 2230 2230 2230 2230 2230	Sediment Oxygen Uptake (mMol/m^2/d)	35.3 35.3 37.3 37.3 37.3 37.3 37.3 37.3
	Water Column (S.E.)	0.10 0.28 0.28 0.13 0.13 0.13 0.13 0.13 0.13 0.13 0.13	Water Column Respiration (S.E.)	0.04 0.25 0.25 0.242 0.242 0.21 0.21 0.21 0.21 0.21	Water Column Respiration (S.E.)	0.0 0.1 0.0 0.0 0.0 0 0 0 0 0
	Water Column Respiration { (uM/d)	281 74.8 28.4 20.6 20.4 20.5 20.5 20.5 20.5 20.5 20.5 20.5 20.5	Water Column Respiration   (uM/d)	0.255 7.2557 7.2557 7.2557 7.2557 7.2557 7.2557 7.2557 7.2557 7.2557 7.2557 7.	Water Column Respiration (uM/d)	7.9 7.9 7.9 7.9 7.1 7.1 7.1 7.1 7.1 7.1 7.1 7 7.1 7 7 7 7
	owes 55 Cores (n=)	" """""""""""""""""""""""""""""""""""""	996 Cores (n=)		Cores (n=)	
	tuary H August 31, 195 Temp. (C)	20.6 20.6 21.1 21.1 22.2 22.2 22.2 22.2 22.2 22	February 28, 1: Temp. (C)	222222222	April 27, 1996 Temp. (C)	9 4 7 7 7 7 7 7 9 8 9 4 7 9 9 7 9 9 7 9 9 7 9 9 9 9 9 9 9 9
	Peconic Est Cruise 1 Station	GB WNB WNB CPD GPS GPS GPS GP/FB FB FB FB FB	Cruise 2 Station	GB WNB NB CPD CPD CPS CPS CPS FB FB FB	Cruise 3 Station	GB CB CP CP CP CP CP CP CP CP CP CP CP CP CP

Howes Peconic Es Cruise 4	ituary Junei 14, 1996	-	Water	Water	Sediment	Sediment	Sediment NH4	Sediment NH4	Sediment NO3	Sediment NO3	Sediment TDN	Sediment TDN	Sediment PO4	Sediment PO4
Station	Temp. (C)	Cores (n≕)	Respiration (uM/d)	Respiration (S.E.)	Uptake (mMol/m^2/d)	Uptake (S.E.)	Flux (uMol/m^2/d)	Flux (S.E.)	Flux (uMol/m^2/d)	Flux (S.E.)	Flux (uMol/m^2/d)	Flux (S.E.)	Flux (uMol/m^2/d) ====================================	Flux (S.E.)
					35.3	2.9	1430	488	496	164	1132	382	31.4	9.7
95	0.41	., •			9.0E	60	2193	132	-312	128	1072	318	96.7	12.7
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515	0.01	, <	130	40	49.2	2.6	-342	104	-104	8	-2198	421	-87.8	25.7
01/19 01	0.01		171	0.2	38.6	3.3	-165	4	-72	ក្ត	-5140	686	-48.0	17.8
	0.01	, e.	25.8	0.7	64.3	6.1	2015	109	1549	186	2237	208	334.1	40.8
PMS	20.0		3 12.6	0.0	64.2	1.4	2344	161	94	8	1113	12	113.8	52.9
Cruise 5	July 7, 1996				:		the second second	Codimont	Codiment	Sadimant	Sediment	Sediment	Sediment	Sediment
			Column	Column	Sediment Oxygen	Oxvaen	Segiment NH4	NH4	NO3	NO3	TDN	TDN	PO4	PO4
Ctation	Temn	Cores	Respiration	Respiration	Uptake	Uptake	Flux	Flux	Flux	Flux	Flux	Flux		ХП Ц
Claticity	(O)	(=u)	(p/l/loWn)	(S.E.)	(mMol/m^2/d)	(S.E.)	(uMol/m^2/d)	(S.E.)	(uMol/m^2/d)	(S.E.)	(uMol/m^2/d)	(S.E.)	(uMol/m^2/d)	(S.E.)
					65.0	1.9	3292	295	1060	78	2437	800	203.4	18.8
25	0.01			- <del>-</del>	67.3	3.3	2301	203	227	31	-1316	1014	361.6	27.6
	0.42		146	40	78.1	2.8	4665	226	190	36	5233	666	172.3	3.2
9 9 2	2 C 7 C 7 C	₩ <b>\$</b> *1	3 151	0.4	84.0	1.8	6066	255	-451	69	3595	924	398.2	41.6
ייי	203		3 21.2	0.9	72.7	6.5	2415	1134	-305	158	3335	217	133.3	33.6
S S S	22.5		3 31.5	1.7	32.9	2.5	1377	151	137	32	-213	55	-14.2	0.05
GP/FB	22.5		3 35.7	0.7	61.2	3.2	141	24	89 9	5 F	1001-	1001	40.0 4	0.2
FB	23.0		3 56.9	4.7	45.1	9.5 4.1	259	165	42	4/4	1061		307 7	9.9 20
RB	23.0		3 79.6	0.5	107.5	5.7	6609	128	0471		4000	010	2000	1128
PMS	24.0		4 68.7	3.7	90.3	9.2	5279	1389	004 004	5 5	4071 5715	7107	284.7	044
LPS	24.5	-	3 22.4	4.	96.0	- n 1 - 0	6107	27 F F		15	0213 6711	046	725.6	2195
LP/GP	23.0		3 22.9	0.5	62.6	 	0410 202	114/	203	53	-2096	107	103.4	6.4
SB	24.0		3 17.8	9.0	C.42 2.85	0.0	0081 P081	814	-20	3 E	2479	10	-19.9	78.9
HMN	0.02 72 70		01 10./	- C	2019	5.3	4309	2	4078	209	4995	2222	303.7	11.2
NA MC	21.0	-	2 85.0	0.0	145.2	2.6	9299	1162	481	106	9190	1390	343.6	12.7

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 $S^{(2)}_{i}$