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The community metabolism and nutrient dynamics of a shoal sediment in a temperate estuary, with emphasis on temporal scales of variability (sediment/water exchange, euphotic, chlorophyll-a, Virginia)

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THE COMMUNITY METABOLISM AND NUTRIENT DYNAMICS OF A SHOAL SEDIMENT IN A TEMPERATE ESTUARY, WITH EMPHASIS ON TEMPORAL SCALES OF VARIABILITY

A Dissertation
Presented to
The Faculty of the School of Marine Science
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of

Doctor of Philosophy

by
William M. Rizzo
1986
This dissertation is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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This dissertation is dedicated to my parents, Anthony and Beverly Rizzo
who always warned about the perils of scholarship.
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ABSTRACT

The oxygen metabolism and exchanges of nutrients between sediment and water were studied on a submerged sandy shoal in the York River, Virginia from March to December 1983. Particular emphasis was placed on the variability in metabolic estimates over different time scales. Variation in rates was examined over the photoperiod, between successive sampling days, between tidal condition (mid-day high vs. low tide), and among seasons. The coefficient of variation for 4 to 22 estimates of hourly net production (NP) and respiration (R) over the photoperiod averaged 23% and 75% respectively. Morning NP was significantly greater than afternoon NP over the study. Mean hourly NP and R were significantly different between successive days in 4 of 6 tests, and 2 of 6 tests respectively. The coefficients of variation for average NP, R and chlorophyll a over these two-day periods ranged from 4 to 43%, 1 to 34% and 0 to 80%. R was significantly higher on days with mid-day low tides (noon + 2 hours). Mean hourly NP was 49% greater on days with mid-day low tides and R was 70% greater. Hourly NP and R were significantly different among seasons. R peaked in summer and NP in fall. Coefficients of variation for mean hourly NP and R over the seasons were 57% and 59% respectively. Plots of mean hourly NP and R by month were made using all data for a given month and compared to plots made by randomly selecting a single measurement for each month. The latter plots are based on 12 data points, the former on 185 points. The two types of plots produced very similar annual rate estimates but differed radically in their depiction of seasonal changes.

Within opaque domes, hourly fluxes of ammonium and phosphate ranged from -21 (uptake) to 364 ug-at N m^-2 and -3 to 76 ug-at P m^-2. Nitrate + nitrite fluxes were generally small and erratic, comprising an average of only 15% of the total dissolved inorganic nitrogen flux. Releases of ammonium and phosphate peaked in summer, were an exponential function of temperature, and a linear function of respiration. Within the transparent domes, hourly fluxes of ammonium ranged from -162 to 244 ug-at-N m^-2. Average release in the transparent domes was only 25% of the average release in the dark domes. Phosphate fluxes were nearly identical to those in the dark domes, ranging from -6 to 80 ug-at P m^-2. Nitrate + nitrite fluxes comprised an average of 17% of the total dissolved inorganic nitrogen flux of the transparent domes. Ammonium fluxes were significantly different between dome treatments, fluxes of the other nutrients were not significantly different.

Within the dark domes, ratios of O:N and O:P were both equally and anomalously high (ca. threefold). The greatest O:N anomalies occurred in May. The O:N anomalies are attributed to nitrification/denitrification processes. The anomalous O:P ratios are attributed to trapping of phosphorus into iron–manganese complexes sorbed to sediments under the oxic conditions at the study site.

The sediment is generally capable of supplying its photosynthetic nutrient demands, and all of the occasional water column deficits in nitrogen remineralization, but only 19-63% of the phosphate deficits.
COMMUNITY METABOLISM AND NUTRIENT DYNAMICS OF A SHOAL SEDIMENT IN A TEMPERATE ESTUARY, WITH SPECIAL EMPHASIS ON SCALES OF TEMPORAL VARIABILITY
CHAPTER 1

GENERAL INTRODUCTION
The burgeoning human population within the Chesapeake Bay watershed has produced many changes in the Bay. Some impacts, such as the loss of marshland or submerged grass meadows have been obvious, others, such as the introduction of toxic compounds and excess nutrients, have had more subtle effects. Concern over the environmental degradation of the Chesapeake Bay, and the determination to effect a "clean-up" have recently become national issues. While the pressing nature of the problems is obvious, temperate estuaries such as the Chesapeake Bay and its tributaries are very complex systems. Our scientific understanding of these systems is not keeping pace with the rate at which we alter their natural functioning. The lack of understanding of the basic natural processes occurring in the Bay hampers our ability to assess change in these processes. With regard to nutrient enrichment, for example, much of the Chesapeake Bay, particularly the upper Bay, is already moderately to heavily enriched (Heinle et al. 1980). However, some lower Bay estuaries such as the York River, are still relatively unaffected, affording the opportunity to examine unimpacted estuarine processes.

Estuaries such as the York River are comprised of smaller interacting ecosystems such as salt marshes, seagrass beds, unvegetated submerged sediments, intertidal flats and an extensive water column. Relative to the area of permanently submerged bottom, there is little unvegetated intertidal area. The submerged benthos can be subdivided into shoal areas within the euphotic zone (≤ 2 m deep), and deeper, aphotic bottom. The least studied major ecosystem component of the York River, in terms of primary production and nutrient dynamics is the large subtidal benthic area unvegetated with macrophytic vegetation.
The annual production of benthic microfloral communities in subtidal habitats without macrophytic vegetation ranges from 100 to 280 g C m$^{-2}$y$^{-1}$ (Marshall et al. 1971; Nowicki and Nixon 1985; Rizzo and Wetzel 1985). This range also encompasses the annual production estimates reported for benthic microflora in sediments of salt marshes (Pomeroy 1959; Whitney and Darley 1981; van Raalte et al. 1976; Zedler 1980; Rizzo and Wetzel 1985), intertidal sandflats (Riznyk and Phinney 1972a; Riznyk et al. 1978; Rutgers van der Loeff et al. 1981; Rizzo and Wetzel 1985), intertidal mudflats (Riznyk and Phinney 1972a; Cadee and Hegeman 1974; Joint 1978; Baillie and Welsh 1980; van Es 1982; Colijn and de Jonge 1984; Rizzo and Wetzel 1985), and submerged grass meadows (Murray 1963; Rizzo and Wetzel 1985). Lower annual rates of benthic microfloral production, 65-100 mg C m$^{-2}$y$^{-1}$, are occasionally reported (Gallagher and Daiber 1974; Cadee and Hegeman 1977; Joint 1978; van Es 1982; Colijn and de Jonge 1984; Varela and Penas 1985), but rates less than 65 mg C m$^{-2}$y$^{-1}$ have been reported only from an intertidal mudflat (Leach 1970) and a sand beach (Steele and Baird 1970). Considering the wide range of methods, sediment environments and geographic locations represented by these studies, the similarity of the annual rates is striking. While finer sediments have relatively greater concentrations of motile, suspendable diatoms (Gargas 1970; Round 1971), and may have relatively greater respiration than gross production (and therefore lower gross production:respiration ratios) than coarser sediments (Riznyk and Phinney 1972a; Shaffer and Onuf 1983), recent studies have shown that stations differing in sediment grain size were not significantly different in hourly rates of gross production (Shaffer and Onuf 1983), and that five different types of habitats representing both coarse and fine sediment types
and both intertidal and subtidal elevations were not significantly different in either gross production or respiration (Rizzo and Wetzel 1985).

Many variables influence primary production by the benthic microfloral community. Light is the factor most frequently cited as limiting to microfloral production. Light limitation may result from many factors including water column turbidity, seasonal changes in irradiance, competition from phytoplankton, sediment grain size (light penetration is reduced in finer sediments), elevation and/or water depth (Famatmat 1968; Gargas 1970; Leach 1970; Fenchel and Staarup 1971; Marshall et al. 1971; Hickman and Round 1970; Riznyk and Phinney 1972a; 1972b; Admiraal 1977a; Amspoker 1977; Cadee and Hegeman 1977; Joint 1978; Admiraal and Peletier 1980; Shaffer and Onuf 1983).

Temperature may also affect photosynthesis by affecting the activity of the enzymatic reactions which fix CO$_2$ into organic matter. When there is sufficient light to saturate the photosystems of the microfloral cells, temperature can limit organic matter production. Studies of the effects of temperature on benthic microfloral productivity differ in their findings, however. Some in situ measurements have shown significant correlations between production and temperature (Leach 1970; Cadee and Hegeman 1974). Another study found temperature and light to be significant controls on gross production at one station, while only light was significant at two other stations (Famatmat 1968). In laboratory studies, the highest division rates of six species of benthic diatoms occurred at the highest temperatures, but division rates were similar among the species and over the temperature range tested (4 - 25°C) (Admiraal and Peletier 1980). At fixed light intensities, Leach (1970) found that temperature was highly correlated with $^{14}$C uptake, but Colijn and van Buurt (1975) reported only a
10% increase in photosynthesis between 4 and 20 C when light was provided at a saturating intensity.

Other factors affecting benthic microfloral production include grazing, hydrologic effects and nutrients. Although grazing is frequently postulated to account for seasonal changes in benthic microfloral abundance (Hickman and Round 1970; Cadee and Hegeman 1974; Gallagher and Daiber 1974; van Raalte et al. 1976; Admiraal 1977b; Joint 1978; Admiraal and Peletier 1980), and the importance of benthic microfloral production in the nutrition of grazers, from protozoa to fishes is widely reported (Odum 1968; Admiraal 1977b; Wetzel 1977; Pace et al. 1979; Weisberg and Lotrich 1982), few investigators have examined grazing effects on the microfloral community. On an intertidal mudflat, grazing by the mud snail *Ilvamassa obsoleta*, was sufficient to consume virtually all the daily net production of the mudflat microflora (Pace et al. 1979), and removal of mud snails typically results in immediate increases in sediment chlorophylls and/or cell numbers (Nichols and Robertson 1979; Pace et al. 1979; Ludwig 1982).

Hydrologic conditions also affect benthic metabolism through resuspension of sediments by waves and tidal currents. Cadee and Hegeman (1974) proposed that sporadic high winds caused the random fluctuations of chlorophyll a concentration in an intertidal mudflat sediment. Other authors have also noted greater benthic microfloral production in sheltered areas (Steele and Baird 1968; Gargas 1970). Quantitative evidence of storm impacts on benthic microfloral production is scarce, but a study in a southern California lagoon which experienced a severe storm showed that storm-related deposition of fine sediments over a formerly sandy area resulted in decreased community gross production, increased community
respiration and replacement of the diatom community with a blue-green cyanobacterial community (Shaffer 1984).

Since sediments are generally assumed to be nutrient-rich (Riznyk and Phinney 1972b; de Jonge 1980) relatively little attention has been given to the nutrient dynamics of benthic microfloral communities. Artificial fertilization of salt-marshes has had differing effects on benthic microfloral production. In a year-long study of a dwarf Spartina alterniflora marsh, nitrogen was limiting in summer and phosphorus in winter (Sullivan and Daiber 1975). However, in a late summer study, Estrada et al. (1974) found no changes in microfloral biomass in either short or tall S. alterniflora marshes. Short-term fertilization experiments indicated nitrogen limitation in short S. alterniflora marshes, but not in creek bank marshes (Darley et al. 1981).

Shaffer and Onuf (1981) recently measured gross production at 17 intertidal and subtidal stations, and calculated regressions of gross production on six independent variables (solar radiation, water temperature, sediment size, chlorophyll a, initial oxygen concentration and respiration rate). They showed that each independent variable was most important in explaining variation in gross production rate on at least one of the twelve study dates. Rizzo and Wetzel (1985) also found significant differences in gross production, respiration and chlorophyll a among five intertidal and subtidal habitats on individual sampling dates, though these habitats were not significantly different over the entire study. In addition, Rizzo and Wetzel (1985) found significant differences in gross production, respiration and chlorophyll a among sampling dates for each habitat and for respiration and chlorophyll a in data pooled across habitats. However, these temporal differences did not reflect any obvious seasonal relationship. The studies
of Shaffer and Onuf (1983) and Rizzo and Wetzel (1985) point out the multiplicity of factors affecting benthic microfloral production, and the rapidity with which both benthic microfloral production and the dominant factors which control production change over brief spatial and temporal scales.

Even if nutrients do not limit benthic microfloral production, uptake of nutrients by benthic microflora may still greatly affect the exchanges of nutrients with the water column. Benthic microfloral growth may have significant impacts on water column nutrients, since sediment release of nutrients has been postulated to control water column concentrations of ammonium and phosphorus and thus their availability to phytoplankton (Nixon and Filson 1983). However, the role of sediments in nutrient exchanges with the water column in euphotic environments is not well known. Few measurements of nutrient fluxes between sediments and water have been made concurrently with measurements of benthic community production. Studies carried out in subtidal euphotic environments show little sediment release of nutrients when photosynthesis is simultaneously occurring, indicating that the benthic community recycles most remineralized nutrients (Kartwig, 1976; Propp et al. 1980; Phoel et al. 1981). However, in a heavily-enriched estuary (water column ammonium concentrations of 60 to 5500 ug-at N l⁻¹) an intertidal sandflat sediment took up ammonium and nitrate regardless of the direction of oxygen flux and took up ammonium against a concentration gradient (Rutgers van der Loeff et al. 1981). The authors concluded that nutrients were not limiting to the benthic microflora in this highly enriched system, and that the observed fluxes were bacterially-mediated.

In contrast, there have been a number of measurements of nutrient fluxes between sediment and water in aphotic sediments. Sediments release

In aerobic sediments ammonium release is correlated with oxygen uptake, although usually at rates less than those predicted by oxygen uptake measurements, assuming Redfield stoichiometry (Redfield et al. 1963; Nixon et al. 1976; Boynton et al. 1980; Hopkinson and Wetzel 1982; Boynton and Kemp 1985). Temperature also influences nutrient dynamics by increasing both aerobic and anaerobic remineralization of organic matter (Hargrave 1969; Nixon et al. 1976; Boynton et al. 1980). In addition to biological metabolism, phosphorus is also subject to physical/chemical controls. Phosphorus is trapped in the sediments by incorporation into iron-manganese-phosphorus complexes which are sorbed to the sediments under oxic conditions (Martens and Goldhaber 1978; Nixon et al. 1980; Klump and Martens 1981; Callender and Hammond 1982).

The rapid turnover of benthic microfloral communities (0.13-3.2 divisions day$^{-1}$ Williams 1964; Admiraal 1977a; Admiraal and Peletier 1980) manifests itself in high spatial and temporal variability in productivity. This high variability may be one reason for the similarity in annual benthic microfloral production and the dissimilarity of the apparent seasonal patterns among studies. A second cause may be an artifact of sampling design. Most studies measure metabolism for only a brief part of the
photoperiod. If short-term variation is high, measurements only a few hours apart may give very different estimates of production when extrapolated to days and/or months. Fortuitous sampling may average out some of the effects of short-term variability yielding similar estimates of long-term, i.e., annual production, but essentially random timing of peaks and troughs in seasonal plots of hourly production rates. Rizzo and Wetzel (1985) calculated that 50% of their individual measurements of hourly production derived from short (1-3 h) incubations would produce an annual estimate of production within one standard deviation of a mean derived from 16 annual production estimates reported in the literature when multiplied by the estimated annual photoperiod. Twenty-three percent of the measurements yielded annual estimates greater than two standard deviations from this mean. Thus five samples per year would be highly likely to be in general agreement with annual production values in the literature, but also sufficient to produce an outlying value, a value which could be interpreted as a significant peak or trough in a seasonal plot of changes in hourly production rates. Therefore, the seasonal (i.e., month-to-month) changes typically reported may actually be equivalent to changes over hours, days, or tidal conditions since sampling designs seldom integrate variability in production on these scales. Accurate description of seasonal changes in production, and better estimates of annual production require consideration of the imbedded scales of temporal variability.

Changes over short time scales have received little attention, but available results indicate high variability. Over the photoperiod, changes in salt-marsh benthic microalgal productivity range from six to tenfold in a tall S. alterniflora marsh, and about twofold in a dwarf S. alterniflora marsh (Gallagher and Daiber 1973). Week-to-week tidal changes also affect
benthic microfloral production. Benthic microalgal production on permanently submerged sand shoals was greater on days with mid-day low tides than days with mid-day high tides due to improved light conditions (Marshall et al. 1971).

In contrast to many estuaries where most of the subtidal bottom is aphotic and dominated by a heterotrophic community (Nixon and Pilson 1983), estuaries such as the York River have large shoal areas supporting autotrophic communities. Because of the large areal extent of these shoals, they may greatly affect the primary production and the nutrient dynamics of this estuary. The purpose of this study was to: 1. Determine the magnitude of the community production of a shoal sediment; 2. Determine the magnitude of the exchanges of nutrients between the sediment and the water column; 3. Evaluate the environmental factors regulating community production and the exchanges of nutrients; 4. Evaluate the changes in rates of hourly oxygen metabolism over temporal scales of hours (photoperiod), days (day-to-day), tides (week-to-week) and seasons.
CHAPTER 2

TEMPORAL VARIABILITY IN OXYGEN METABOLISM OF AN ESTUARINE SHOAL SEDIMENT
Introduction

Estuaries are productive ecosystems whose functioning is heavily influenced by the metabolism of microscopic organisms. Temporal variability in the metabolism of microautotrophic and heterotrophic communities has immediate consequences for materials cycling and energy flow since these communities are tightly coupled. Knowledge of both the magnitude and the temporal variability of production and consumption by microorganisms are critical to a better understanding of the functioning of estuaries. Unfortunately, few investigations have adequately addressed temporal variability in the estimation of rate processes associated with microorganisms or the consequences of subsequent extrapolation of measurements to different spatial or temporal scales.

Continuous measurements of primary productivity or community metabolism are seldom made for periods longer than one day. More commonly the measurement intervals are a few hours. However, estimates derived from such brief measurements are often extrapolated to daily rates, the daily rates subsequently extrapolated to monthly estimates, and the monthly estimates summed to calculate annual rates. Less commonly, measurements over the photoperiod are made and extrapolations proceed from this point. In addition, changes in either hourly or daily rate estimates between sampling intervals are often interpreted as changes associated with season. If the variation in hourly estimates over a day and/or day-to-day variation over the month is high, extrapolation to longer time periods produces estimates with large and often unknown confidence limits. Similarly, interpreting changes between single monthly rate estimates as the consequence of changes
on large scales, i.e. as seasonal changes, may be invalid since the
difference may result from a change in the process over periods of hours or
days rather than weeks or months. Nevertheless, extrapolated rate
measurements are typically the estimates used to compare both habitats
within estuaries as well as different estuarine systems. The question
remains: How reliable are conclusions based on this type of comparison?

Shallow water sediments supporting photosynthesis by benthic
microflora are ideal study areas for addressing the temporal variability of
community productivity. Over the past 25 years many measurements of the
standing crop and productivity of benthic microflora have been made (Pomeroy
1959; Pamatmat 1968; Steele and Baird 1968; Gargas 1970; Leach 1970;
Marshall et al. 1971; Riznyk and Phinney 1972a; Cadee and Hegeman 1974;
1977; Gallagher and Daiber 1974; van Raalte et al. 1976; Joint 1978; Riznyk
et al. 1978; Admiraal and Peletier 1980; Baillie and Welsh 1980; Zedler
1980; van Es 1982; Murray 1983; Colijn and de Jonge 1984; Shaffer and Onuf
1983; Rizzo and Wetzel 1985). The extent of the practice of extrapolating
hourly rates to longer periods is illustrated by the fact that only three of
these twenty-one studies actually measured production over the entire
photoperiod (Steele and Baird 1968; Cadee and Hegeman 1974; 1977), while ten
report daily rates and 18 report annual rates. Since extrapolation of
short-term experimental measurements to longer periods of time is virtually
unavoidable due to various limitations, estimates of the variability of such
measurements over short time scales are needed in order to assess the
effects of extrapolations on estimates of the magnitude of processes and the
changes in those processes over longer time intervals, i.e. annual scales.

This study was initiated to investigate the variation in measurements
of hourly community metabolism of a benthic community over time scales of
hours (within the photoperiod), days (day-to-day), tidal conditions (week-to-week) and seasons. The variability in standing crop of chlorophyll a over 2 to 12 day periods was also examined.

Study Site

The study site was a permanently submerged sand shoal in the York River, located at the Virginia Institute of Marine Science at Gloucester Point, Virginia (37°14′N, 76°31′W - Fig. 2.1). The York River is a temperate estuary typical of the tributaries of the Chesapeake Bay. It is approximately 50 km long and contains about 132 km² of permanently submerged bottom, based on the mean low water datum plane. Shoal areas less than 2 m deep are within the photic zone, support photosynthesis by benthic microalgae and comprise 38% of the bottom surface area. The area has semi-diurnal tides with a range of ca. 0.7 m. The shoal sediments are comprised primarily of sand (97.2% by weight), with small amounts of both fine sediments (1.8%), and gravel (1.0%).

Materials and Methods

Studies of sediment oxygen metabolism were made each month from March through December 1983. Change in dissolved oxygen concentration was used to calculate net production (NP), and respiration (R) in two transparent and two opaque plexiglass domes, each covering 0.16 m² of sediment. Gross production (GP) was calculated as the sum of NP + R. The domes were internally partitioned to provide water column and sediment + water column chambers within the same dome in order to correct for water column
Figure 2.1. Location of the study site in the York River, Virginia, a tributary of the Chesapeake Bay. Stippled area indicates depths less than 2 meters.
metabolism. Oxygen probes (Model 2710 Oxygen Monitor, Orbisphere Corp., Geneva, SW.) were placed in the bottom chamber of each dome and stirring rods attached to the probe assemblies provided continuous stirring. Oxygen concentrations were determined before and after incubation intervals that ranged from 0.5-2.0 hours. Incubations were begun about 2.5 hours after sunrise and continued sequentially over the photoperiod, until about 1.0 hour before sunset. The sequential incubations were interrupted at 3-4 h intervals by pumping out the incubation water and replacing it with ambient river water. This was necessary to prevent supersaturation of the transparent domes and oxygen depletion in the opaque domes. Equilibrium with ambient water column oxygen concentrations was achieved in 30-45 minutes. The sediment surface was not visibly disturbed by the flushing process.

Chlorophyll a (chl.) concentrations were determined by extracting the top 1 cm of sediment in 100% acetone overnight at 5 C (Jacobsen 1978). A second extraction was necessary to achieve complete extraction of the chl. Following extraction, the volume was adjusted to 20 ml with 90% acetone. Chl. was estimated spectrophotometrically using a single wavelength (665 nm) and a pheophytin correction (Riemann 1978). Concentrations were calculated using the equation given by Lorenzen (1967). Chl. concentrations were determined on each of five core samples (2.10 cm I.D.) collected for 2-12 consecutive days each month except March, when collections were made on 5 and 15 March only.

Three core samples for organic matter analyses were collected on the chl. sampling dates using the same size cores. The surface centimeter of the sediment was dried to a constant weight at 60 C, and then ashed for 12
hours at 500°C. The carbon concentrations reported in this study were
determined following procedures described in Rizzo and Wetzel (1985).

Photosynthetically active radiation (PAR) reaching the sediment surface
was measured with a LiCor 185A quantum radiometer (LiCor, Inc. Lincoln, NE),
and was continuously recorded. Temperatures were measured with the
thermistors within the oxygen probe assemblies. Salinity was measured with
a temperature compensated salinity refractometer (Model AO 10419 American

The data were tested for normality using the Kolmogorov-Smirnov test
for goodness of fit (Hull and Nie, eds. 1981), and for homoscedasticity
using the F-max test (Sokal and Rohlf 1969). The average hourly morning and
afternoon NP and R for equal periods of time preceding and following solar
noon on each sampling day were compared over the study using paired t-tests
(n = 19 days). Day-to-day variation in average hourly NP and R for the same
time periods on successive days were also compared using t-tests (n varied
from 5 to 14 measurements per day). Short-term changes in sediment
chl. concentrations over 2-12 day series each month were examined using one­
way analysis of variance. Variation of mean hourly metabolic rates as a
function of tidal condition were analyzed by comparing hourly NP and R
between dates with noon ± 2 hour high tides (n = 10) and days with mid-day
low tides (n = 7) using t-tests. Seasonal differences in average hourly NP
and R were examined using analysis of variance and Student-Newman-Keuls
(SNK) multiple range tests (n = 185). All statistical procedures are
described in Sokal and Rohlf (1969). When coefficients of variation (CV)
are reported for two samples, e.g. variation of mean NP on successive days,
an estimate of the standard deviation was made from the range (Wilcoxon and
Wilcox 1964).
The effect of extrapolating single monthly measurements of hourly NP and R to annual estimates was examined by randomly selecting a single measurement from the total measurements made in a given month. The annual rates were calculated by extrapolating the hourly rate to a daily rate by multiplying the hourly rate by the number of hours in the photoperiod. Monthly estimates were then made by multiplying the daily rate by the number of days per month. Monthly estimates were then summed to produce an annual estimate. Monthly rates for the January-February period were linearly interpolated using the March and December sampling periods, and the estimate for September was interpolated using the August and October sampling periods. Two curves derived using randomly selected monthly measurements were plotted and compared with a third curve derived from the mean of all available monthly data. The resulting seasonal plot and annual production estimate represented by the latter curve is based on 185 data points while the other two curves and production estimates are based on 12 data points.

Results and Discussion

Temperature and salinity ranged from 7.3-27.3 C and 13.5-21.5 ppt respectively during the study. Minimum and maximum water depths during the study were 0.22 and 1.32 m. The average hourly rates of GP, NP and R by sampling date are given in table 2.1. Over the study, coefficients of variation for mean hourly GP, NP and R over the photoperiod ranged from 23 to 296%, 41 to 1281% and 31 to 127% and averaged 90%, 231% and 75% respectively. High variability in metabolic rates occurred in all seasons and often differed markedly on sequential sampling days. For example, the
TABLE 2.1. Hourly rates of metabolism of the sand shoal. Mean ± standard deviation (mg O$_2$·m$^{-2}$·h$^{-1}$), (n) = sample size.

<table>
<thead>
<tr>
<th>DATE</th>
<th>GROSS PRODUCTION</th>
<th>NET PRODUCTION</th>
<th>RESPIRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 MAR</td>
<td>61.2 ± 49.57 (9)</td>
<td>44.1 ± 43.22 (9)</td>
<td>13.3 ± 11.17 (11)</td>
</tr>
<tr>
<td>5 MAR</td>
<td>54.6 ± 19.66 (14)</td>
<td>42.9 ± 20.59 (14)</td>
<td>10.2 ± 8.67 (16)</td>
</tr>
<tr>
<td>14 MAR</td>
<td>55.8 ± 33.48 (15)</td>
<td>28.2 ± 27.07 (16)</td>
<td>26.6 ± 25.00 (16)</td>
</tr>
<tr>
<td>15 MAR</td>
<td>70.2 ± 45.63 (12)</td>
<td>48.1 ± 38.48 (13)</td>
<td>18.1 ± 21.72 (12)</td>
</tr>
<tr>
<td>13 APR</td>
<td>48.6 ± 77.27 (16)</td>
<td>46.1 ± 76.53 (16)</td>
<td>2.5 ± 3.75 (17)</td>
</tr>
<tr>
<td>23 MAY</td>
<td>54.7 ± 38.29 (12)</td>
<td>22.9 ± 47.63 (22)</td>
<td>24.7 ± 20.01 (11)</td>
</tr>
<tr>
<td>26 MAY</td>
<td>51.8 ± 69.41 (9)</td>
<td>27.4 ± 55.35 (11)</td>
<td>28.3 ± 23.77 (9)</td>
</tr>
<tr>
<td>31 MAY</td>
<td>20.7 ± 61.69 (13)</td>
<td>-5.5 ± 70.46 (13)</td>
<td>26.2 ± 20.70 (13)</td>
</tr>
<tr>
<td>22 JUN</td>
<td>139.7 ± 118.75 (10)</td>
<td>52.9 ± 87.29 (11)</td>
<td>80.2 ± 72.98 (10)</td>
</tr>
<tr>
<td>23 JUN</td>
<td>121.6 ± 51.07 (6)</td>
<td>29.3 ± 37.50 (6)</td>
<td>74.9 ± 38.95 (7)</td>
</tr>
<tr>
<td>30 JUN</td>
<td>47.1 ± 87.14 (9)</td>
<td>23.7 ± 69.44 (9)</td>
<td>23.3 ± 25.16 (9)</td>
</tr>
<tr>
<td>28 JUL</td>
<td>91.3 ± 108.65 (9)</td>
<td>27.2 ± 74.26 (9)</td>
<td>64.1 ± 53.20 (9)</td>
</tr>
<tr>
<td>4 AUG</td>
<td>213.0 ± 83.07 (4)</td>
<td>151.9 ± 92.66 (4)</td>
<td>61.1 ± 56.21 (4)</td>
</tr>
<tr>
<td>29 AUG</td>
<td>40.7 ± 32.15 (6)</td>
<td>-2.9 ± 20.24 (6)</td>
<td>43.6 ± 20.49 (6)</td>
</tr>
<tr>
<td>30 AUG</td>
<td>72.8 ± 77.17 (5)</td>
<td>38.7 ± 92.49 (6)</td>
<td>61.3 ± 19.00 (5)</td>
</tr>
<tr>
<td>3 OCT</td>
<td>137.1 ± 57.58 (6)</td>
<td>83.8 ± 46.93 (6)</td>
<td>53.3 ± 35.71 (6)</td>
</tr>
<tr>
<td>4 OCT</td>
<td>114.7 ± 84.88 (4)</td>
<td>81.0 ± 64.80 (5)</td>
<td>30.4 ± 23.10 (4)</td>
</tr>
<tr>
<td>8 NOV</td>
<td>168.2 ± 70.64 (5)</td>
<td>141.6 ± 58.06 (5)</td>
<td>26.6 ± 19.95 (5)</td>
</tr>
<tr>
<td>9 NOV</td>
<td>89.5 ± 113.67 (4)</td>
<td>57.5 ± 109.25 (4)</td>
<td>31.9 ± 4.79 (4)</td>
</tr>
<tr>
<td>15 NOV</td>
<td>74.5 ± 38.00 (2)</td>
<td>33.2 ± 26.56 (2)</td>
<td>42.3 ± 12.27 (2)</td>
</tr>
<tr>
<td>8 DEC</td>
<td>99.9 ± 4.00 (2)</td>
<td>91.1 ± 0.91 (2)</td>
<td>8.8 ± 3.08 (2)</td>
</tr>
</tbody>
</table>
Coefficient of variation for the respiration measurements made on 8 November was 75%, while the coefficient of variation the following day was only 15%.

Average morning and afternoon NP and R are shown in fig. 2.2a. NP was greater in the morning on 16 of 19 sampling dates and R was higher in the afternoon on 11 of 19 sampling days. In data pooled over the study, NP was significantly higher in the morning, but there was no statistically significant difference in R. Over the study, there was no significant difference in the amount of light received by the benthic community between morning and afternoon. During sampling dates when light levels were lowest (March, April, and November) NP was higher in the morning even though light conditions were more favorable in the afternoon.

The relatively consistent temporal separation observed between peak hourly NP and R within the photoperiod suggest that the two processes are coupled over a short time frame and endogenous factors in addition to exogenous factors such as light or temperature, limits their magnitude. Motility in epipelic algae is well-known (Round 1971), and in muddy intertidal sediments in which photosynthesis is frequently light-limited, microalgae migrate to the surface during daytime low tides (Pomeroy et al. 1981). This behavioral response has a pronounced effect on photosynthesis (Gallagher and Daiber 1973; Darley et al. 1976). However in the sand shoal sediment, light conditions are generally favorable, potential wave erosion is greater at low tides, and the community is probably comprised of non-motile diatoms (Round 1971). Pamatmat (1968) found no evidence of a migrational rhythm for the algal community of his intertidal sandflat site, but did note tidally-related metabolic rhythms in both photosynthesis and respiration. If a tidally-related migrational rhythm were present in the shoal community, peak photosynthesis would occur about an hour later each
Figure 2.2. Net production and respiration (mg O₂ m⁻² h⁻¹), and photosynthetically active radiation (E m⁻² day⁻¹) over various time scales, except fig. (2.2a). Statistical results are examined at the 95% significance level. Fig. 2.2a. * denotes morning rates significantly different from afternoon rates. PAR is in E m⁻² per morning or afternoon period. Fig. 2.2b. * denotes a significant difference from the preceding day. Fig. 2.2c. * denotes high tide rates significantly different from low tide rates. Fig. 2.2d. * denotes a seasonal rate significantly different from the other three seasons.

Legend: ▲ Net production, ▼ Respiration, □ PAR.
day and net production would not have been consistently significantly
greater in the morning.

Endogenous rhythms also occur in the microalgal communities of
saltmarsh sediments. Photosynthesis is highest in the morning in both
intact cores and cell suspensions held continuously in the light (Gallagher
and Daiber 1973; Pomeroy et al. 1981). The apparent rhythm in intact cores
was much greater than that in cell suspensions (Pomeroy et al. 1981). Cell
suspensions would be expected to show only biochemical rhythms, whereas in
intact cores, both migrational and biochemical rhythms may be present.
Photosynthesis increased from 150 to 200 \( \mu g \ C \ m^{-2} h^{-1} \) in the morning in the

A morning peak productivity rhythm may allow the shoal community to
maximize morning photosynthesis, but the magnitude of this photosynthetic
maximum may be set by a coupled endogenous sediment respiratory rhythm. For
example, \( NP \) may become limited during the afternoon by lack of nutrients.
While the upper York River has been characterized as moderately nutrient-
enriched (Heinle et al. 1980), the lower reaches of the river, including
this study site are relatively unenriched. Water column concentrations of
ammonium were < 10 \( \mu g - at \ N \ l^{-1} \) on all but one sampling date, and phosphate
concentrations were always < 2 \( \mu g - at \ P \ l^{-1} \) (see following chapter). In any
case, the availability of water column nutrients to the benthic microflora
may be diffusion limited. Consequently, microfloral photosynthesis in the
surface sediment may depend on in situ heterotrophic nutrient regeneration.
Concomitant studies indicate that the release of ammonium from these
sediments is highly correlated with benthic respiration (see following
chapter). Benthic respiration on the other hand, may be limited by lack of
labile organic matter. Organic matter concentrations in the surface
centimeter of these sediments averaged 0.64% and reached a maximum of 1.63% in summer. These concentrations are similar to sediment carbon determinations made for other submerged sandy shoal sediments in the lower York River (assuming % carbon = 0.45 ash-free dry weight). Percent sediment carbon varied little with depth. Concentrations in the surface 15 cm, at five cm intervals were, on a dry weight basis, 0.29 ± 0.16% (standard deviation), 0.28 ± 0.14% and 0.28 ± 0.14% over ten monthly samples (Rizzo and Wetzel, unpub.), suggesting that much of the surface organic matter is refractory. The tendency for R to increase in the afternoon and temporally lag peak NP suggests microheterotrophic metabolism in the surface sediments relies on the release of labile dissolved photosynthate. Increased heterotrophic activity in turn would increase nutrient regeneration stimulating autotrophic productivity the following morning. Further investigation into this apparent daily cycle would be highly desirable, and may provide further insights into day-to-day variability in rate estimates.

Photorespiration may also have potential effects on the morning/afternoon difference in net production. Although the purpose of photorespiration in plants is not well-known, it occurs simultaneously with photosynthesis, and results in the consumption of oxygen. Photorespiration increases with increasing light, temperature, oxygen concentration and with decreasing carbon dioxide concentration (Tolbert 1980). The diurnal increases in light and temperature, and increases in cell oxygen concentrations during active morning photosynthesis may create favorable conditions for photorespiration, which would cause net production to be underestimated. Tolbert has estimated that photorespiration in macrophytes may be 20% of gross production, but adds that photorespiration in algae is minimal compared to the impact of this process in higher plants. Therefore,
while photorespiration may contribute to the apparent afternoon decrease in net production, its impact is probably small.

The average NP and R for the same sampling periods on consecutive days are shown in fig. 2.2b. The average coefficient of variation for the six two-day periods was 51% (2 - 164%) for NP and 21% (5 - 39%) for R. Mean hourly NP was significantly different (P=.05) over two day periods in four of the 6 tests, and R was significantly different in 2 of 6 tests. However, average hourly metabolic rates compared on successive days varied less than measurements compared over the photoperiod. Day-to-day sampling was limited to successive days that had similar environmental regimes (i.e. similar tidal, photoperiod, temperature, salinity and climatic conditions) which further suggests that endogenous cycles account for a significant source of variation within a daily period.

Relationships between daily variability in metabolism and other measured parameters are not readily apparent. As shown in fig. 1.2b, daily light reaching the sediment surface was nearly identical between days for each two-day period. The maximum temperature difference between days was 0.9 °C, a difference unlikely to result in significant changes in metabolic rates. The ANOVA's of the sediment chl. concentrations over 2-12 day periods (table 2.2) show that significant changes typically occur abruptly. Changes over periods of days were significant in all but one month. However, changes in chl. biomass do not offer compelling evidence for the changes shown in fig. 1.2b. For example, in June, chl. concentrations changed little (115 to 125 mg m⁻²) and NP was not significantly different between the two days. However, in August, chl. decreased (128 to 79 mg m⁻²) and was accompanied by a significant NP increase on the second day. In November a decrease in chl. (299 to 255 mg m⁻²) was accompanied by a
TABLE 2.2. Results of analyses of variance of the chlorophyll series. Mean ± standard deviation (mg m$^{-2}$). Sample size, N = no. of sampling days per month. * denotes significant difference among days (P=.05).

<table>
<thead>
<tr>
<th>MONTH</th>
<th>CHLOROPHYLL A</th>
<th>N</th>
<th>PROBABILITY OF F</th>
</tr>
</thead>
<tbody>
<tr>
<td>MARCH</td>
<td>33 ± 30</td>
<td>2</td>
<td>.025 *</td>
</tr>
<tr>
<td>APRIL</td>
<td>50 35</td>
<td>8</td>
<td>.002 *</td>
</tr>
<tr>
<td>MAY</td>
<td>86 40</td>
<td>11</td>
<td>.000 *</td>
</tr>
<tr>
<td>JUNE</td>
<td>121 34</td>
<td>12</td>
<td>.002 *</td>
</tr>
<tr>
<td>JULY</td>
<td>131 37</td>
<td>9</td>
<td>.000 *</td>
</tr>
<tr>
<td>AUGUST</td>
<td>136 53</td>
<td>7</td>
<td>.000 *</td>
</tr>
<tr>
<td>SEPTEMBER</td>
<td>208 33</td>
<td>3</td>
<td>.044 *</td>
</tr>
<tr>
<td>OCTOBER</td>
<td>176 46</td>
<td>2</td>
<td>.250</td>
</tr>
<tr>
<td>NOVEMBER</td>
<td>236 94</td>
<td>4</td>
<td>.001 *</td>
</tr>
<tr>
<td>DECEMBER</td>
<td>235 78</td>
<td>3</td>
<td>.002 *</td>
</tr>
</tbody>
</table>
significant decrease in NP, but a similar increase in chl. (151 to 202 mg m\(^{-2}\)) in October was not accompanied by any significant change in NP. It also seems doubtful that biomass changes could be responsible for the observed day-to-day significant differences in R, particularly in March, although there are no data on heterotrophic biomass so the possibility cannot be ruled out. Within time periods having relatively constant physical conditions, much of the variability in metabolic rates may result from physiological responses to the proposed endogenous cycles of autotrophy and heterotrophy. Unfortunately, interpretation of such day-to-day changes is hindered by the often rapid changes in the physical environment, by lack of information on time lags in community responses and by lack of information on prior community history.

Tidally-related changes in metabolic rates are shown in fig. 1.2c. Metabolic rates were higher on days with mid-day low tides, although only R was significantly higher (P=.05). Daily PAR at the sediment surface was significantly higher on days with mid-day low tides, and probably accounted for the higher NP. High variability in net production over the photoperiod probably obscured real differences in net production between tidal conditions. Marshall et al. (1971) also found that metabolism was higher on days with mid-day low tides in shoal sediments in Rhode Island. Since temperatures varied only a few degrees between tidal conditions (i.e. between weeks) the significant increase in R is probably a response to increased NP.

Fig. 2.2d shows the changes in average NP, R and PAR among seasons. NP was significantly different among seasons and SNK tests indicated that fall NP was significantly greater than NP during the other three seasons. Similarly, R was significantly different among seasons, with summer R
greater than other seasons. Although the peak in $R$ coincided with the seasonal peak in water temperature, a lag is apparent. Spring temperatures increased from ca. 12°C to over 20°C between April and May, but $R$ did not significantly increase until June (temperatures ≤ 28°C). Fall $R$ remained high until mid-November, even though water temperatures were similar to the spring period (ca. 20°C). $NP$ peaked in fall and lagged spring increases in PAR and water temperature. The apparent seasonal decoupling of net production and respiration actually represents a seasonal shift in heterotrophic to autotrophic dominance of community gross production. That is, gross production remains nearly constant between summer and fall, but is largely determined by community respiration in summer, whereas net production exerts more impact on gross production rate in fall.

Fig. 2.3 shows the results of plotting two curves derived from single, randomly chosen measurements of $NP$ and $R$ from each month compared to a third curve derived from the mean of all the monthly data. Annual estimates of $NP$ calculated from these data are 288, 232 and 230 g O$_2$ m$^{-2}$ year$^{-1}$ respectively, and for $R$ are 233, 230 and 287. The agreement of the annual estimates from curves 1 and 2 ($n = 12$) with curve 3 ($n = 185$) is striking. However, random sampling of a normally distributed population will tend to produce similar estimates if the sample size is large enough. Apparently a sample size of 12, evenly distributed over the year, will give the same estimate of annual metabolism as a much larger sample size. This is supported by the similarity among these three estimates and their general agreement with published values (Pomeroy, 1959; Pamatmat 1968; Marshall et al. 1971; Riznyk and Phinney 1972a; Cadee and Hegeman 1974; 1977; Gallagher and Daiber 1974; van Raalte et al. 1976; Joint 1978; Riznyk et al. 1978; Baillie and Welsh
Figure 2.3. Plots of net production (Fig. 2.3a) and respiration (Fig. 2.3b) in mg O$_2$ m$^{-2}$ h$^{-1}$, by month. Curve 1 (— — —) and curve 2 (— — —) are drawn from a single randomly selected measurement each month (total sample size = 12). Curve 3 (—— —) is drawn from a mean of all monthly measurements (total sample size = 185).
While short-term variability appears to have little impact on estimates of annual production, it has major impact on our perception of the seasonal changes in metabolism. In the plot of NP (fig. 2.3a) the monthly changes suggested by curves 1 and 2 based on 12 data points are much different from curve 3, each differing by an order of magnitude during one month (November and August). Curve 2 indicates net heterotrophy for the benthic community during most of the spring.

The respiration plots show similar differences. Each curve shows a different peak month for R, in September, March and July, for curves 1 to 3 respectively. Again, the differences among the points in most months are substantial, approaching an order of magnitude in September for curve 1.

Summary

While estimates of annual metabolic rates are very important, consideration of temporal distribution of metabolic rates is equally important in the overall functioning of estuaries and also for insight into controls on metabolic processes. The type of sampling design typically used in past studies (single, brief measurements, on a monthly schedule) appears to be adequate for estimation of annual rates, but is inadequate for assessing seasonal changes in metabolism or for providing insights into controls on metabolic processes on shorter time scales. As shown in this study, there is high variability in metabolic rates over the photoperiod, between consecutive days each month, and between tidal conditions, all imbedded in the changes in metabolism found on the seasonal scale.
Variation on the shorter time scales can markedly affect the shape of seasonal curves based on limited data. Adequate description of seasonal changes requires enough sampling to encompass variability occurring on these shorter time scales. At a minimum, multiple measurements over the photoperiod, and an estimate of daily and tidally-related variability within the month is required to improve descriptions of the seasonal changes in metabolism within estuarine communities.

Intensive sampling over the photoperiod and between successive days also revealed temporal patterns in autotrophic and heterotrophic metabolism which are not wholly explained by variation in exogenous variables such as light and temperature. On these scales metabolic variability most likely varies as a result of changes in the physiological state of the community as a function of its past history. Differences in metabolism over longer time scales are more explainable by variability in exogenous variables. NP increases during days with mid-day low tides as a result of improved light conditions. R increases are probably a response to greater availability of organic matter from in situ benthic primary production. Seasonal changes in NP and R are also reasonably interpretable in terms of the seasonal changes in the physical variables of light and temperature. The variability in metabolism over brief periods of time, and the factors which control it on these scales need further attention, and require sampling over extended periods of time, but perhaps at less frequent intervals.

Adequate estimates of the magnitude of community metabolism, the seasonal changes in community metabolism and the factors controlling community metabolism are essential for a better understanding of benthic community dynamics. Adequate assessments of seasonal change and the factors
important in controlling benthic community metabolism must take into account the metabolic changes occurring on shorter time scales
CHAPTER 3

COMMUNITY METABOLISM AND NUTRIENT DYNAMICS OF A SHOAL SEDIMENT IN A TEMPERATE ESTUARY
Temperate estuaries are ecosystems intermediate between the fresh water and salt water systems they separate. These productive ecosystems have become increasingly stressed by human populations, particularly in the Chesapeake Bay region. One impact associated with increasing human population is the addition of large quantities of nutrients to estuarine systems. Nutrient enrichment is related to a number of undesirable effects including decreased phytoplankton species diversity, massive algal blooms and die-offs, and development of anoxic conditions in the sediments and/or water column in summer (D'Elia et al. 1982). Declines in populations of fishes and other biota have also occurred, and may be related to nutrient enrichment (D'Elia et al. 1982).

Several different communities contribute to primary production in the Chesapeake Bay, including marsh grasses, seagrasses, phytoplankton, macroalgae and sediment microflora. While the primary production and nutrient dynamics of marshes, seagrasses and phytoplankton communities have received much attention (Axelrad 1974; McCarthy et al. 1974; 1975; Moore 1974; Haas 1975; Heinle and Flemer 1976; Wolaver et al. 1980; Wetzel et al. 1981; Gilbert 1982; Murray 1983; Orth and Moore 1984; Kemp et al. 1984), benthic areas dominated by microflora have received limited study. The annual benthic microfloral primary production of a subtidal sand sediment was estimated by Rizzo and Wetzel (1985), but the exchanges of nutrients between sediment and water in euphotic sediments of the Chesapeake Bay have not been studied.

There have been two fundamentally different approaches to studying the exchanges of nutrients between sediment and water. The first involves
calculation of fluxes from the concentration gradient of the constituent in
the interstitial water and the overlying water column (e.g. Billen 1978).
The second approach has been to measure nutrient flux rates directly. In
general, estimates of nutrient flux rates based on concentration gradients
have been of limited usefulness (see reviews by Zeitschel 1980; Nixon and
Pilson 1983). Factors such as bioturbation and wave and current disturbance
also influence nutrient exchanges, but most importantly, rapid
remineralization of recently deposited organic matter occurs virtually at
the sediment/water interface, and thus is not represented in typical pore-

Studies of the nutrient exchanges between estuarine sediments and the
water column have concentrated on aphotic subtidal sediments (Davies 1975;
Nixon et al. 1976; Nixon et al. 1980; Boynton et al. 1980; Raine and
Patching 1980; Klump and Martens 1981; Fisher et al. 1982; Blackburn and
Henriksen 1983; Boynton and Kemp 1985). In many estuaries and nearshore
coastal ecosystems the benthic area receiving sufficient light to support
photosynthesis comprises only a small part of the total benthos (Nixon and
Pilson 1983). However, in many parts of the Chesapeake Bay and its
tributaries (e.g. the York River), there are extensive shoals which support
photosynthesis as indicated by the historical abundance and distribution of
submerged aquatic macrophytes (Orth and Moore 1984). The exchanges of
nutrients between the sediment and the water column in shoal sediments may
differ considerably from exchanges between aphotic sediments and the water
column due to nutrient uptake by benthic microflora. The potential
difference in sediment/water nutrient exchanges between aphotic and euphotic
areas could have a substantial impact on the nutrient budget of an estuary
such as the York River, which has a large benthic area comprised by shoal
sediments. Extensive measurements of the exchanges of nutrients between sediment and water in areas supporting a microfloral community have been made only by Hartwig (1976). Only limited measurements (1–6 samples) have been made in a few other areas (Propp et al. 1980; Phoel et al. 1981; Rutgers van der Loeff et al. 1981).

This study was undertaken to determine the rates of community metabolism of a sand shoal ecosystem; to determine the exchanges of the major species of inorganic nitrogen and phosphorus between sediments and the water column; and to investigate the environmental factors regulating the oxygen metabolism and nutrient cycling processes in this system.

Materials and Methods

Field and laboratory procedures.

The procedures for the measurement of dissolved oxygen, chlorophyll a (chl. a), and organic matter were given in the previous chapter. For nutrient determination, duplicate 70 ml water samples were taken at three hour intervals from each dome section with plastic syringes, through sampling ports fitted with tygon tubing. Water removed during sampling was replaced with ambient river water through one-way valves in each dome section. The volume removed in sampling represented <2% of the total volume of the smallest dome section. Duplicate samples of the ambient surface water were also taken. Samples for ammonium analysis were processed immediately on sampling and followed the procedures in Grasshoff (1976). Samples for phosphate, nitrate and nitrite analysis were frozen immediately. These samples were stored at -15 to -20 °C and analyzed within three months.
The analytical procedures for the determination of dissolved inorganic phosphate are from Grasshoff (1976). Analytical methods for nitrate and nitrite determinations were those given by Kopp and McKe (1979) for automated nutrient analysis.

Temperature was recorded at the time of each oxygen determination. Determinations of salinity and water depth, and collections of water samples for analysis of suspended solids were made every 2-4 hours. Salinity was measured with a temperature compensated salinity refractometer (Model AO 10419 American Scientific Products, Washington, D.C.). Photosynthetically active radiation (PAR) reaching the sediment surface was measured using a LiCor 185A quantum radiometer (LiCor, Inc. Lincoln, NE) and continuously recorded. Surface water samples were analyzed for suspended solids by filtering 500-1000 ml of water onto pre-combusted (500 C for 4 hours) Gelman A/E glass fiber filters. Filters were dried to a constant weight at 60 C, combusted at 500 C for 4 hrs, and reweighed, to estimate organic matter content in the suspended solids. Wind data were taken from summaries for Norfolk International Airport (NOAA 1983).

Daily rates of net production were calculated by multiplying the average hourly rate by the daily photoperiod. Daily respiration was calculated by multiplying the hourly average by 24 h. Daily exchanges of nutrients were calculated as the sum of the mean hourly flux rate of the transparent domes multiplied by the photoperiod and the mean hourly flux rate of the dark domes multiplied by the night-time period. Values for the September and January-February periods were linearly interpolated. Annual rates were estimated by applying the average daily rate in a month to the entire month, and summing the monthly estimates.
Statistical procedures.

The data were tested for normality using the Kolmogorov-Smirnov test for goodness of fit (Hull and Nie, eds. 1981), and for homoscedasticity using the F-max test (Sokal and Rohlf 1969). The procedures for analysis of variance (ANOVA) and Student's t-tests were taken from Sokal and Rohlf (1969). Pearson product-moment correlations were calculated with programs described in Nie et al. (1975). Stepwise linear regression procedures are outlined in Hull and Nie (eds. 1981). All tests were analyzed at the 95% significance level unless otherwise stated.

Results and Discussion

During the study water temperatures and salinities ranged between 7.3 - 27.3°C and 13.5 - 21.5 ppt respectively (fig. 3.1a.). Salinities were lowest in late winter and early spring. Daily PAR at the sediment surface is shown in fig. 3.1b. In addition to seasonal changes, daily PAR varied between tidal conditions. The sediment surface received significantly more light on days with mid-day low tides (see previous chapter). Daily PAR increased sharply between April and May, and declined steadily after June, reaching August-September minima for both high and low tide conditions. In early fall PAR again increased sharply before declining in late fall. The rapid post-June decline and secondary fall peak in PAR at the sediment surface are largely caused by changes in water column suspended solids. Orth and Moore (1982) have shown that diffuse attenuation coefficients from June through September at Gloucester Point range from 1.5 to 2.5, with attenuation decreasing to .75 to 1.5 from October through November. Moore
Figure 3.1. A. Average monthly temperature and salinity of the water column during the study. B. Average daily photosynthetically active radiation received at the sediment surface by month and tidal condition (tides at noon ± 2 hours.)
(unpub.) computed a multiple linear regression showing that diffuse vertical attenuation measured at 5 sites in the York River every two weeks for more than a year, was significantly and inversely related to water column concentrations of filterable inorganic matter, filterable organic matter and chl. a. Two-thirds of the variance in diffuse attenuation coefficients was attributable to concentrations of filterable inorganic matter alone.

Community production

The annual production of the benthic community of the sand shoal ecosystem is similar to many other estuarine and nearshore areas (table 3.1). The annual primary production of the water column (186 g C m\(^{-2}\)) was only slightly less than the sediment microfloral production. This estimate agrees almost exactly with the average (190 g C m\(^{-2}\) y\(^{-1}\)) reported by Boynton et al. (1982) in summarizing 45 studies of estuarine phytoplankton production.

Average hourly net production and respiration are shown in fig 3.2a. for the sediment and fig. 3.2b for the water column. Over the study, the sediment net production averaged 50.6 mg O\(_2\) m\(^{-2}\) h\(^{-1}\) slightly more than mean water column production (40.7 mg O\(_2\) m\(^{-2}\) h\(^{-1}\)). Mean sediment respiration (35.8 mg O\(_2\) m\(^{-2}\) h\(^{-1}\)) was less than half the average water column respiration (96.7 mg O\(_2\) m\(^{-2}\) h\(^{-1}\)). Maximum net production (152 mg O\(_2\) m\(^{-2}\) h\(^{-1}\)) was the same for both communities, but the minimum net production of the water column (-237 mg O\(_2\) m\(^{-2}\) h\(^{-1}\)) was two orders of magnitude lower than minimum sediment net production (-6 mg O\(_2\) m\(^{-2}\) h\(^{-1}\)). Respiration of both communities was generally greater during summer. However, rates of water column respiration were much
Table 3.1. Estimates of annual production in estuarine benthic habitats (g C m\(^{-2}\)). Values in parentheses are based on \(^{14}\)C, others are based on oxygen changes.

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<td>(190)</td>
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<tr>
<td></td>
<td>Delaware</td>
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<td>(105)</td>
<td>van Raalte et al. 1976.</td>
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<td></td>
<td>California</td>
<td>271*</td>
<td>Zedler 1980.</td>
</tr>
<tr>
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<td>315**</td>
<td>Christian 1981.</td>
</tr>
<tr>
<td>Mudflat</td>
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<td>(31)</td>
<td>Leach 1970.</td>
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<td>83*</td>
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</tr>
<tr>
<td></td>
<td>Netherlands</td>
<td>(102)*</td>
<td>Cadée and Hegeman 1974.</td>
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<td>154*</td>
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</tr>
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<td>113</td>
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* Mean of several sites.

** Total system.
Figure 3.2. Average hourly net production and respiration (mg O$_2$ m$^{-2}$) of the shoal communities. A. Sediment. B. Water column.
more variable, with both minimum (22 mg O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}) and maximum (265 mg O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}) respiration occurring in March. Minimum sediment respiration (3 mg O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}) occurred in April. Maximum sediment respiration (80 mg O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}) occurred in June, and respiration remained high until mid-November.

In recent years there has been growing concern over the increasing extent of hypoxic and anoxic conditions in the sediment and bottom water of many estuaries during summer (Officer et al. 1984; Boesch 1985; Stanley et al. 1985), and concern that anoxic conditions may increase in spatial and temporal extent (Webb 1981). In this study, daily sediment gross production supplied an average of 202% (range = 48-1076%) of the daily sediment oxygen demand. Daily sediment respiration exceeded gross production on 5 of 21 days, (P:P < 1.0; table 3.2; 31 May, 28 July, 29-30 August and 15 November). Daily water column gross production averaged 101% (range = 0-381%) of the daily oxygen demand, but exceeded water column respiration on only 7 of 21 days, (table 3.2; 4-5 March, 31 May, 22-23 June, 29 August and 15 November). Excess daily gross production by the sediment community could have supplied 8-724% (mean = 108%; 52% with the maximum percentage deleted) of the water column oxygen deficits. These calculations are based on a 24 h period. Since sediment oxygen production is confined to the photoperiod only, daytime oxygen inputs to the water column may be greater than would be indicated by calculations made on a 24 h basis.

When total system oxygen production does not meet oxygen demand, dissolved oxygen concentrations over the shoal will decrease if there is little or no physical mixing, since atmospheric diffusion of oxygen is minimal. In a study of the Patuxent estuary, oxygenation due to atmospheric diffusion comprised only a small part (6-14%) of the diel dissolved oxygen flux (Kemp and Boynton 1980). Physical mixing is greatly affected by wind.
Table 3.2. Daily rates of net production and respiration (mg-at O m²) and nutrient flux (μg-at N or P m²). A. Sediment. B. Water column. Ratios are calculated from ammonium fluxes in the dark domes only, and only for periods when nutrient fluxes and respiration were simultaneously measured. Positive flux values denote release from the sediments or production within the water column.

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A wind speed of 5.0 m s\(^{-1}\) was determined to be the threshold value for measurable effects of wind stress on vertical mixing of surface water (Kullenberg 1976), and the wind speed value necessary to cause strong horizontal currents and physical turbulence in near-shore surface waters (Therriault and Platt 1981). The number of days each month with a resultant wind speed > 5.0 m s\(^{-1}\) (fig. 3.3) indicates minimal wind mixing from June - September. While local topography, direction of prevailing winds, fetch, and other factors affect mixing the lack of strong summer winds underscores the importance of biogenic oxygen production in the sediment. Sediment oxygen demand in aphotic sediments of the bay are 30-150 mg O\(_2\) m\(^{-2}\) h\(^{-1}\) in summer (Boynton et al. 1980; Kemp and Boynton 1981; Phoel et al. 1981; Callender and Hammond 1982; Boynton and Kemp 1985). Even though the summer oxygen demand of the shoal sediment was similar (fig. 3.2a), the shoal sediments were usually oxygen sources rather than oxygen sinks.

Factors controlling seasonal changes in production

The variability of net production and respiration over time scales shorter than seasons, and the potential factors causing the observed variability, were discussed in the previous chapter. This chapter presents a more detailed discussion of seasonal changes. A multiple linear regression of mean net production on mean light, temperature, and chl. a, over the study was computed. The stepwise procedure selected only chl. a concentration as the independent variable or combination of independent variables explaining more than 5% of the variance in net production (fig. 3.4). Other studies have also shown high correlations between autotrophic production and chlorophyll concentration (Leach 1970; Cadee and Hegeman
Figure 3.3. Number of days per month with resultant wind speeds $\geq 5.0$ meters per second.
Figure 3.4. Regression of average net production (mg O$_2$ m$^{-2}$ h$^{-1}$) on chl. a (mg m$^{-2}$). Net production = 0.32 chl. a + 9.99. ($r^2 = .33; P = .0061$).
The lack of significant impact of PAR in the regression is understandable since the community appears to be light saturated over much of the photoperiod, and on most days. By extrapolating published estimates of saturating irradiances to an hourly period, and using the recorded light data (from the first full hour of light to the last full hour of light), from 42 days of data collection, the amount of community light saturation can be estimated. Based on a range of light saturation for mudflat microalgae of 75–300 \( \mu \text{E m}^{-2} \text{s}^{-1} \) (Colijn and van Buurt 1975; Whitney and Darley 1983), saturating light was received by the sediment for 58 to 20% of the photoperiod hours respectively, (fig. 3.5). Based on a range of daily PAR required for light saturated growth of mudflat microalgae of 2.5–5.0 \( \text{E m}^{-2} \text{d}^{-1} \) (Admiraal 1977a), 81% and 64% respectively, of the daily PAR records showed that the sediment received sufficient light for light-saturated growth.

At saturating light, temperature could be expected to greatly affect net production. Between 15–30 °C, an average \( Q_{10} \) value of 1.7 was found for the increase in photosynthesis of a salt marsh microalgal community (Gallagher and Daiber 1973). The \( Q_{10} \) value was not significantly different between 17 and 103 klux, light levels reflecting the seasonal extremes in light received by the sediment community (Gallagher and Daiber 1973). Since water temperatures at the study site varied only 7 °C from May through October, a \( Q_{10} \) value of 1.7 indicates that temperature alone would account for only about 16% of the net production increase between May and the fall peak (3 October – November 9), explaining the statistically minor role of temperature in regulating net production. The minor role of temperature in
Figure 3.5. Number of total photoperiod hours with average PAR ≥ 75
and ≥ 300 μE m⁻² s⁻¹.
regulation of net production is also indicated by significantly higher fall
net production than all other seasons (see previous chapter) though
temperatures were less than or equal to those in spring and summer.

Grazing activity has been shown to limit microalgal biomass on an
intertidal mudflat (Pace et al. 1979). Grazing pressure was not assessed in
this study, and so could not be examined by regression analysis. However,
changes in grazer population dynamics could have significant impacts on the
autotrophic community.

The seasonal change in chl. a concentration over the study is shown in
(fig. 3.6a). Chl. concentrations varied from 7 mg m\(^{-2}\) on 15 March to 286 mg
m\(^{-2}\) on 8 November. In addition to the seasonal increase, chl. varied
greatly among days per month. Most monthly ranges of chl. concentrations
overlapped despite the large annual increase. There were significant
differences (P ≤ .05) in concentrations among days each month except in
October.

The seasonal changes in organic matter concentrations did not closely
follow those of chl. a, nor was the day-to-day variation as great (fig.
3.6b). Day-to-day changes in organic matter concentrations were significant
(P = .05) only in March, November and December. Changes in chl. and organic
matter were only weakly correlated (r = .33; P = .011; n=60). Assuming that
g C m\(^{-2}\) = .45 g organic matter m\(^{-2}\) and a 50:1 chl:carbon ratio (de
Jonge 1980), microfloral carbon comprised < 1% of the total sediment carbon
and did not account for the changes in organic matter. Organic matter
concentrations declined sharply after the initial sample, reaching a minimum
of .05% in April, and remained low until May, when they increased from .35%
to .71%. Concentrations increased rapidly in June reaching a maximum of
1.63%. Thereafter, concentrations decreased, remaining around .50% for the
Figure 3.6. A. Chlorophyll a concentrations (mg m$^{-2}$), and
B. Organic matter concentrations (X) over the study.
remainder of the study. The similarity between the initial value (.52% on 5 March) and the final value (.42% on 8 December) suggest that surface organic matter concentrations are in a steady-state over an annual cycle. The brief June peak in organic matter probably results from increases in heterotrophic biomass rather than deposition, since sediment respiration also reached maximum at this time.

Changes in chl. and to a lesser extent, organic matter have also been ascribed to changes in PAR and temperature (Cadee and Hegeman 1974; 1977). However, changes in chl. and organic matter concentrations were uncorrelated with either temperature or PAR for the shoal sediment.

Severe wind/wave related sediment resuspension was evident from personal observations, as wave conditions prevented or curtailed sampling on several occasions in April-May and late November-January. The sharp drop in chl. and organic matter concentrations between the 5 March and 15 March sampling dates (62 to 7 mg chl. a m⁻², and .52 to .25%) appeared to be storm related, and prompted the subsequent longer sampling series. Both monthly mean chl. concentration and the mean spatial variability of the chl. samples were significantly correlated with the frequency of winds with resultant speeds > 5.0 m s⁻¹ occurring during the chlorophyll sampling series (fig. 3.7). Chl. concentrations were inversely related to frequency of high winds, (r = -68; P=.029; n=10) while the CV for the chl. samples was directly correlated with frequency of high winds (r = .77; P=.014; n=9). As a result, decreases in chl. concentrations were accompanied by increases in chl. spatial variability (r = -.41; P = .005; n = 44). Neither organic matter concentration nor coefficient of variation of the organic matter samples were correlated with wind parameters. These differing results may be attributable to steeper concentration gradients of chl. relative to
Figure 3.7. Relative chlorophyll concentration ($l = 235$) and relative coefficient of variation of the chlorophyll samples ($l = 40\%$) as a function of the relative frequency of days with resultant wind speeds $\geq 5.0 \, \text{m s}^{-1}$ occurring during the chlorophyll sampling series each month ($l = 5 \, \text{days}$).
organic matter in the surface sediments, making chl. more susceptible to erosion. In sediments, incident light decreases to 1-10% of surface values at depths < .5 cm even in sand (Taylor 1964; Gargas 1970; Fenchel and Staarup 1971; Riznnyk and Phinney 1972a). Microalgae are also often concentrated in the top few millimeters of sediment (Gargas 1970; Leach 1970) especially in winter when light is often limiting (Gargas 1970), whereas organic matter is distributed more evenly through the surface sediments (Steele and Baird 1968; previous chapter).

Figure 3.3 shows that the frequency of disruptive winds (speeds > 5.0 m s\(^{-1}\)) occurred on half of the days from March through May. Frequent disruption of the sediment surface may partially negate the positive effects of spring increases in light, temperature and photoperiod on production of greater autotrophic biomass. Increased spring light could allow chl. concentrations to increase over a broader sediment depth range thus providing some protection from erosion for part of the community even though general wind conditions were adverse in spring. Wind conditions were favorable in June, and remained relatively favorable for the remainder of the study.

The influence of wind on the shoal ecosystem may be more important than the correlations would suggest since wind-related sediment resuspension is affected by many other factors. One of the primary factors is fetch, which influences wave formation (Gabrielson and Lukatelic 1985). Fetch is a function of local topography, wind direction and wind duration (Gabrielson and Lukatelic 1985). At the study site, winds from 300-320 degrees blow unimpeded over water for more than twice the distance as winds from any other direction, so that winds with speeds < 5 m s\(^{-1}\) may cause appreciable wave development and greater resuspension than stronger winds from other
directions. The duration of a given prevailing wind is also important in wave formation. A constant wind of a given speed produces greater wave action than variable winds with the same resultant speed and direction. However, days with light resultant winds may still be associated with significant surface sediment erosion if brief wind gusts and wind-wave formation occur at low tide. Also, the relationship between sediment resuspension and wind speed is non-linear. Gabrielson and Lukatelich (1985) found that sediment resuspension was a function of the third power of wind speed. As indicated by the chl. sample of 15 March (7 mg m$^{-2}$), virtually all the chlorophyll can be scoured from the sediment surface, implying that at some point, further increases in wind speeds will have little additional effect. Such a non-linear relationship would lower the correlation between chl. concentration and wind speed.

Community respiration

Sediment respiration as a function of temperature is shown in fig. 3.8. The best fit of the data showed that mean respiration increased linearly with temperature ($r^2=0.53; P=.0002$). Previous studies have suggested other empirical forms of the relationship between temperature and respiration. The respiration data also fit an exponential regression on temperature ($r^2 = 0.42; P=.0016$). A similar form proposed by (Nixon et al. 1976) is also shown in fig. 3.8. The great difference between the two exponential expressions probably results from differing heterotrophic biomass between the communities. A log temp. vs. log respiration form, suggested by Hargrave (1969) produced a slightly poorer fit than the untransformed data
Figure 3.3. Regressions of average respiration (mg O$_2$ m$^{-2}$ h$^{-1}$) on temperature. The linear regression is respiration = 2.33 temperature - 7.70 ($r^2 = .53; P = .0002$), the exponential regression (-----) is respiration = $e^{.08 \text{ temp.} + 1.82}$ ($r^2 = .42; P = .0016$). Also shown in an exponential expression (-----) given by Nixon et al. 1976, respiration = $e^{.15 \text{ temp.} + 2.09}$. 
(r^2 = .38, p = .0031).

Figure 3.8 points out the influence of other factors on sediment respiration. For example, the high short-term variability in sediment community respiration is unrelated to temperature (see last chapter). Residual variability may result from change in heterotrophic biomass and/or heterotrophic metabolism. The sharp decrease in respiration between 22-23 June and 30 June (fig. 3.2a; temperature change of only 25.6-24.8) for example, could result from reduced heterotrophic biomass, or a decrease in respiration coupled to a decrease in net production (fig. 3.2a), since P:R changed only slightly (table 3.2). Recent research has shown that sediment respiration is affected by the supply of organic matter to the benthos (see discussion in Kemp and Boynton 1981). In many benthic systems, organic matter supply is largely derived from sedimentation (Nixon et al. 1980; Boynton et al. 1980). The P:R ratios shown in table 3.2 indicate that both the water column and sediment communities are reasonably balanced with respect to production and consumption, suggesting that water column inputs to the sediment are small. In addition, excluding the high P:R value for the sediment on 13 April, daily P:R remains relatively constant despite large day-to-day and seasonal changes in metabolic rates. This indicates a close coupling between net production and respiration and suggests that sediment net production supplies most of the labile organic matter respired in the sediments.

Flux of nutrients between sediment and water

Average monthly concentrations of ammonium, phosphate, nitrate and nitrite in the water column are shown in fig. 3.9. Ammonium and phosphate
Figure 3.9. Average monthly water column concentrations of ammonium, phosphate, nitrate and nitrite (ug-at N or P l\(^{-1}\)).
concentrations were lowest in winter and early spring. Ammonium concentrations doubled between May and June, reached a maximum in early October, and declined thereafter. Phosphate concentrations reached a maximum in June, declined to spring levels by August and remained fairly constant through December. The seasonal variations in nitrate concentrations were typical of the Chesapeake Bay. However, they are about an order of magnitude less than concentrations in the upper bay (D'Elia et al. 1982). Nitrate concentrations were highest during spring, declined during summer, and increased again in fall. Nitrite concentrations were always ≤ 0.14 ug-at-N m⁻² h⁻¹ and varied little over the study.

The mean hourly flux rates of ammonium, phosphate, nitrate and nitrite between the sediment and the water column are shown in figures 3.10 a-d. As in most studies of aphotic sediments (see review by Nixon and Pilson 1983), ammonium was the dominant form of dissolved inorganic nitrogen exchanged between sediment and water averaging 84.6% (range = 37-100%) of the total dissolved inorganic nitrogen flux in the dark domes. The average rate of ammonium release to the water column was 112 ug-at-N m⁻² h⁻¹ over the study, similar to rates in other estuarine and coastal areas (table 3.2).

Within the transparent domes ammonium release was only 25% of the release occurring within the dark domes. The average flux rate was 28 ug-at N m⁻² h⁻¹, significantly less (P = .025) than release within the dark domes. Studies on nutrient exchanges between sediment and water occurring during photosynthesis of the sediment community have been few. Propp et al. (1980) measured oxygen and nutrient fluxes on six occasions, during both day and night. On a single spring date, net production was positive during the day, and associated with very low flux ammonium from the sediment (table 3.2). Net production was negative on the other five sampling dates. Ammonium was
Figure 3.10. Average hourly fluxes of nutrients between sediment and water (ug-at N or P m$^{-2}$) in transparent and dark domes. A. Ammonium. B. Nitrate. C. Nitrite. D. Phosphate. Positive values denote release from the sediment.
Table 3.3. Nutrient fluxes between sediment and water in estuarine and coastal marine ecosystems. A. Aphotic sediments or dark incubations. B. Euphotic sediments, net production (NP) positive (+) or negative (-). Rates are ug-at N or P m$^{-2}$ h$^{-1}$, release denoted by positive values, uptake by negative values. N indicates negligible or undetectable rates.

<table>
<thead>
<tr>
<th>A. Site</th>
<th>Ammonium</th>
<th>Nitrate</th>
<th>Phosphate</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Loch Thurnaig, UK (mud, 4% C)</td>
<td>&lt;1,76</td>
<td>N</td>
<td>ca. 7-12</td>
<td></td>
</tr>
<tr>
<td>2. South River, NC</td>
<td>0,267</td>
<td>0,6</td>
<td>-8,23</td>
<td>1-22</td>
</tr>
<tr>
<td>Neuse River, NC</td>
<td>71,454</td>
<td>0,6</td>
<td>-2,46</td>
<td></td>
</tr>
<tr>
<td>Newport River, NC (sand, shell)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3. Cape Lookout Bight, NC (mud)</td>
<td>22,796</td>
<td>N</td>
<td>-1,32</td>
<td>5-28</td>
</tr>
<tr>
<td>4. Tague Bay, VI (sand, .19-.59% C)</td>
<td>-90,372</td>
<td>-131,141</td>
<td>ca. 26</td>
<td></td>
</tr>
<tr>
<td>tidal river (sandy mud)</td>
<td>49,746</td>
<td>-68,57</td>
<td>-8,19</td>
<td></td>
</tr>
<tr>
<td>transition (mud)</td>
<td>-100,843</td>
<td>-42,8</td>
<td>1,56</td>
<td></td>
</tr>
<tr>
<td>lower estuary (mud)</td>
<td>36,821</td>
<td>-150,75</td>
<td>-5,40</td>
<td>May,Aug.</td>
</tr>
<tr>
<td>6. Patuxent River, MD (1.5-2.6% org.)</td>
<td>-105,1584</td>
<td>-674,100</td>
<td>1,295</td>
<td>3-29</td>
</tr>
<tr>
<td>7. Colne Pt. UK (saltmarsh mud)</td>
<td>18,58</td>
<td>1,3</td>
<td>20</td>
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</tr>
<tr>
<td>8. Chesapeake Bay, MD (1-7% C)</td>
<td>3,124</td>
<td>&lt;1,5</td>
<td>-15,5</td>
<td>2-16</td>
</tr>
<tr>
<td>Buzzards Bay, MA</td>
<td>8,128</td>
<td>-2,2</td>
<td>7,22</td>
<td>20</td>
</tr>
<tr>
<td>Eel Pond, MA</td>
<td>8,67</td>
<td>-1,6</td>
<td>4-18</td>
<td></td>
</tr>
<tr>
<td>10. Narragansett Bay, RI</td>
<td>-8,60</td>
<td>3-25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. Narragansett Bay, RI (1.5-4.5% C)</td>
<td>0,400</td>
<td>-30,110</td>
<td>3-25</td>
<td></td>
</tr>
<tr>
<td>12. coastal Georgia (.3% C)</td>
<td>165</td>
<td>5</td>
<td>37</td>
<td>28</td>
</tr>
<tr>
<td>13. Roskeeda Bay, Ireland</td>
<td>8,67</td>
<td>-1,6</td>
<td>4-18</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.3. Continued.

<table>
<thead>
<tr>
<th>Site Description</th>
<th>14. York River (16 m; mud)</th>
<th>14. York River (9 m; sand)</th>
<th>15. Vostok Bay (+NP day only)</th>
<th>15. Vostok Bay (-NP day only)</th>
<th>16. La Jolla, CA (+NP)</th>
<th>16. La Jolla, CA (dark enclosures)</th>
<th>17. Waddensea Netherlands (Sta. R)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288-511</td>
<td>162</td>
<td>22,97</td>
<td>191</td>
<td>.3</td>
<td>.1,2</td>
<td>-208.83</td>
</tr>
<tr>
<td></td>
<td>-47,11</td>
<td>18</td>
<td>734,936</td>
<td>7</td>
<td>.7</td>
<td>0,2</td>
<td>-208,0</td>
</tr>
<tr>
<td></td>
<td>25-26</td>
<td>26-27</td>
<td>274,936</td>
<td>2-4</td>
<td>.4</td>
<td>.1,5</td>
<td>-8.42</td>
</tr>
</tbody>
</table>

Site-Ammunium Nitrate Phosphate Temp

taken up during the day on one of those dates and on two other dates ammonium release was lower during the day than at night. However, simultaneous day-time measurements of respiration and nutrient fluxes were not made, so it cannot be determined whether these day/night differences were due to changes in respiration, or to changes in the activity of the autotrophic community during the day.

Phoel et al. (1981) made nutrient and oxygen flux measurements in August at one site in the York River sufficiently shallow (3 m) to support a benthic microflora. They found that release of ammonium from the sediment nearly doubled as the sediment became aphotic (table 3.2).

On an intertidal mudflat, ammonium uptake occurred regardless of the direction of oxygen flux, and against concentration gradients on two occasions (Rutgers van der Loeff et al. 1981). They concluded that ammonium was present far in excess of the photosynthetic requirements of the benthic microflora and attributed the observed fluxes to high densities of both nitrifying and denitrifying bacteria within the surface sediment, which apparently controlled ammonium exchanges on the mudflat through coupling of nitrification and denitrification processes.

Although the magnitude of sediment ammonium release differed significantly between the dome treatments, the seasonal pattern of change was similar (figure 3.10a). Ammonium release from the sediments occurred on nearly all sampling dates, and at maximum rates in summer. Slight ammonium uptake occurred on the final two half-day samples in late Nov. and Dec. in both dome treatments, and also in April within the transparent domes. In estuarine areas sediment ammonium release often peaks in summer and is low or negative (uptake) in colder weather (Fisher et al. 1982; Nixon et al. 1976; Boynton et al. 1980; Raine and Patching 1980; Boynton and Kemp 1985;
Klump and Martens 1981). Since respiration tends to be greater in the afternoon (previous chapter), had afternoon sampling been possible on the final two sampling days, the mean hourly ammonium flux may have shown release from the sediments on the final two sampling days as well. In addition, water column ammonium concentrations were still relatively high, such that during the final two sampling dates the absence of appreciable nutrient regeneration within the sediments may have resulted in low interstitial concentrations of ammonium and a diffusion gradient of ammonium into the sediment (fig. 3.9).

In contrast to the ammonium fluxes, phosphate fluxes were not significantly different between dome treatments ($P = .970$). The range for the dark domes was $-3.23$ to $75.61$ ug-at P m$^{-2}$ h$^{-1}$, and $-5.92$ to $79.72$ ug-at P m$^{-2}$ h$^{-1}$ for the transparent domes, agreeing well with other reported rates (table 3.2). The lack of significant differences in phosphate flux between dome treatments suggests that phosphate is generally present in excess of benthic microfloral photosynthetic demands in contrast to ammonium which is intensively recycled. This is in agreement with Propp et al. (1981) who also found no significant difference in phosphate release between day and night, suggesting little microfloral impact on phosphate fluxes.

Phosphate release peaked in summer while slight uptake occurred in November and December in both dome treatments, and on 4 March within the transparent domes. Fluxes of ammonium and phosphate were always in the same direction within the dark domes, and were in the same direction on 9 of 12 days within the transparent domes. Large summer releases of phosphate (Boynton et al. 1980; Klump and Martens 1981) and exchanges $\leq 0$, at temperatures $\leq 15$ C are typical findings for temperate estuaries (Nixon et
In many other studies nitrate and nitrite fluxes were extremely low comprising only a small percentage of the total inorganic nitrogen flux (Nixon et al. 1976; Raine and Patching 1980; Klump and Martens 1981; Hopkinson and Wetzel 1982; Fisher et al. 1982). However, in some areas of the upper Chesapeake Bay, spring fluxes of nitrate are an order of magnitude greater (Boynton et al. 1980; Boynton and Kemp 1985). Nitrite fluxes comprised less than 3% of the total dissolved inorganic nitrogen fluxes in both dome treatments (fig. 3.10c). Nitrate fluxes were also low, averaging only 13.0% of the total inorganic nitrogen flux in the dark domes, and 14.3% in the transparent domes. The maximum nitrate flux was 26.10 µg-at N m\(^{-2}\) h\(^{-1}\) in the dark domes and -44.97 µg-at N m\(^{-2}\) h\(^{-1}\) in the transparent domes. In the dark domes, nitrate was taken up by the sediment on 8 of 13 sampling days, but the largest exchanges were releases from the sediment in March-May resulting in an average flux out of the sediment over the study (fig. 3.10b). In contrast, nitrate uptake was observed on 9 of 13 sampling dates within the transparent domes, with only slight releases (< 2.10 µg-at N m\(^{-2}\) h\(^{-1}\)) occurring on four occasions.

Water column nutrient dynamics

The nutrient dynamics occurring within the water column are shown in fig. 3.11 a-d. In the dark domes, the average ammonium production of the water column was 109 µg-at N m\(^{-2}\) h\(^{-1}\), nearly equal to the sediment release, but was much more variable, (-107 to 444 µg-at N m\(^{-2}\) h\(^{-1}\)). Also, ammonium was removed from the water column in the dark on half of the summer sampling
Figure 3.11. Average hourly fluxes of nutrients within the water column (ug·at·m⁻²). A. Ammonium. B. Nitrate. C. Nitrite.
D. Phosphate. Positive values denote production of nutrient.
dates, while ammonium was always released by the sediments in the summer (figs. 3.10-3.11). In the transparent domes, the water column removed ammonium at an average rate of 85 ug-at N m$^{-2}$ h$^{-1}$, about equal to the average production of ammonium within the water column in the dark. Uptake was observed on 8 of 12 occasions, and was greatest during summer (fig. 3.11a).

Within the dark domes, phosphate fluxes were erratic, from -36 to 44 ug-at P m$^{-2}$ h$^{-1}$, had no evident seasonal pattern, and were generally smaller than the fluxes between sediment and water. Within the transparent domes, water column phosphate fluxes were greater, ranging from -41 to 66 ug-at P m$^{-2}$ h$^{-1}$. Phosphate uptake occurred on 5 of 7 spring/summer samples, and release on 5 of 6 fall/winter dates (fig. 3.11d).

Nitrate plus nitrite fluxes in the water column were of greater magnitude relative to the sediment fluxes, averaging 27% of the total dissolved nitrogen flux (range = 2-99%) in the dark domes and 34% (range = 4-88%) in the transparent domes. In the dark domes, nitrate was removed from the water on 62% of the sampling dates, including all sampling days from March through May (fig. 3.11b-c). In the transparent domes nitrate and nitrite were removed from the water column on 69% and 62% of all sampling dates, respectively. Within both dome treatments the magnitude of the combined nitrate + nitrite flux closely followed the seasonal pattern of ambient nitrate concentrations in the water column (fig. 3.9), comprising greater than 25% of the total inorganic nitrogen flux in March - May, and Nov - Dec.
Factors controlling nutrient exchanges between sediment and water

Sediment release of ammonium and phosphate increased significantly and exponentially with temperature, although the relationships were not strong ($r^2 = 0.20-0.34$; fig. 3.12a–b). Similar equations given by Nixon et al. (1980) and Nixon and Pilson (1983) are also shown.

Compared to temperature, variation in respiration rate explained much more variation in ammonium flux ($r^2 = 0.50$), and about equal amounts of the variation phosphate flux ($r^2 = 0.24$) (fig. 3.13a,b). The relatively stronger linear relationship between respiration and ammonium flux partially explains the relatively weak relationship between temperature and ammonium release. Since aerobic respiration dominates remineralization processes in these sediments, temperature exerts only a minor effect on ammonium release via other pathways, and since the exponential relationship between respiration and temperature (fig. 3.8) explained less than half the variation in mean respiration rate, the relationship between ammonium flux and temperature would not be expected to be stronger than that between respiration and temperature.

Consistent with the differences between the respiration/temperature exponential curve of Nixon et al. (1976) and that derived from this data (fig. 3.8), the differences in ammonium flux between the exponential curve of Nixon and Pilson (1983) and that shown in fig. 3.12 a–b, are of similar magnitude, and reflect the differences between the two systems in the degree of temperature dependence of both respiration and ammonium flux.

Ammonium and to a lesser extent phosphate release increase with both temperature and/or respiration. Regression coefficients ($r^2$) between .2 and .83 are reported for the relationship between ammonium release and
Figure 3.12. Hourly fluxes of ammonium and phosphate (ug-at N or P m\(^{-2}\)) between sediment and water as a function of temperature.

A. Ammonium flux, dark domes = \(e^{.17 \text{ temp.} - 0.02} (r^2 = .20; P = .0117)\). B. Phosphate flux, dark domes = \(e^{.13 \text{ temp.} - 1.12} (r^2 = .28; P = .0015)\). C. Ammonium flux transparent domes = \(e^{.20 \text{ temp.} - 1.46} (r^2 = .39; P = .0002)\). D. Phosphate flux, transparent domes = \(e^{.16 \text{ temp.} - 2.15} (r^2 = .34; P = .0004)\). Also plotted (solid lines) are exponential expressions for ammonium flux (NH = \(e^{.16 \text{ temp.} + 1.90}\) figures A and C) and phosphate flux (P = \(e^{.18 \text{ temp.} - 0.24}\) figures B and D) from Nixon and Pilson 1983 and Nixon et al. 1980, respectively. Positive values denote release from sediment.
Figure 3.13. Linear regressions of ammonium and phosphate flux (ug-at N or P m\(^{-2}\) h\(^{-1}\)) on respiration (mg O\(_2\) m\(^{-2}\) h\(^{-1}\)). A. Ammonium flux = 4.66 R - 43.03 (r\(^2\) = 0.50; P = 0.0000). B. Phosphate flux = 0.51 R - 5.42 (r\(^2\) = 0.24; P = 0.0055). Positive values denote nutrient release from the sediment.
temperature (Boynton et al. 1980; Raine and Patching 1980; Fisher et al. 1982; Nixon and Pilson 1983), and .2 to .94 for oxygen uptake vs. ammonium release (Boynton et al. 1980; Raine and Patching 1980; Nixon 1981; Fisher et al. 1982), although Rutgers van der Loeff et al. (1981) reported no correlation between oxygen uptake and ammonium release. A regression coefficient of .61 was reported for phosphate release vs. temperature by Nixon et al. (1980), while Fisher et al. (1982) found no relationship between respiration and phosphate release.

The extent to which ammonium release is controlled by temperature and/or respiration probably depends mostly on the oxygenation of the system, with respiration controlling ammonium and phosphate release in well-oxygenated systems and temperature controlling fluxes in fully reduced systems.

The low \( r^2 \) values for phosphate release as a function of both temperature and respiration indicate the degree of non-biological control exerted on phosphate release from the sediment. Under aerobic conditions, phosphate is bound to sediments in iron-manganese-phosphate complexes (Martens et al. 1978; Callender 1982; Callender and Hammond 1982; Klump and Martens 1981; Propp et al. 1980). Thus while active remineralization of phosphate may be occurring, it may not be reflected by equally high phosphate releases from the sediments, until the binding capacity of the sediments is exceeded. This would result in an apparently weaker relationship between phosphate release and both temperature and respiration compared to those relationships for ammonium. Large summer phosphate releases are often attributed to temporary late summer anoxic conditions in the lower water column and/or surficial sediments, resulting in dissolution of the iron-manganese-phosphate complexes adsorbed to sediments, and release
of phosphate (Callender 1982; Callender and Hammond 1982; Klump and Martens 1981; Propp et al. 1980). Klump and Martens (1981) measured phosphate releases of 198 ug-at P m\(^{-2}\) h\(^{-1}\) in experimental cores allowed to become anoxic, compared to uptake (17 ug-at P m\(^{-2}\) h\(^{-1}\)) while oxic conditions were maintained. Nixon et al. (1980) also observed greatly enhanced phosphate releases in cores experimentally subjected to anoxic conditions. Sediment cores from the shoal showed the presence of reduced iron only at depths greater than ca. 1.5 cm, indicating oxic conditions. Thus desorption reactions would not occur in the surface sediments during the daytime measurements. Oxygen concentrations greater than 2.0 mg l\(^{-1}\) were maintained in the dark domes on 22 June, when the largest phosphate releases were observed, precluding the possibility of large releases related to anoxic conditions. Since the maximum respiration rate was also measured on 22 June, high remineralization rates may have saturated the capacity of the sediments to bind phosphate.

Other factors also contribute to variation in ammonium and phosphate fluxes including bioturbation, tidal/wave pumping and organic matter input (Nixon et al. 1976; Boynton et al. 1980; Callender 1982; Callender and Hammond 1982; Klump and Martens 1981; Hopkinson and Wetzel 1982; Nixon and Pilson 1983). Bioturbation effects were not evaluated, nor were effects of tidal/wave pumping. While hydraulic effects could be important on this shoal, their effects were eliminated in this study by the dome enclosures. However, availability of labile organic matter may affect nutrient fluxes within the shoal sediments.

Although rates of ammonium release from sediments do not appear to be closely related to overall concentrations of sediment organic matter (table 3.3), short-term inputs of labile organic matter may be important in
providing a substrate for remineralization (Nixon et al. 1980; Fisher et al. 1982; Nixon and Pilsom 1983; Andersen 1986). In another shoal sediment, carbon concentrations remained constant with depth over the first 15 cm (previous chapter) suggesting that most of the sediment organic matter is refractory. Nixon et al. (1980) found that phosphorus regeneration was correlated with temperature most strongly during the winter/spring warming, and that fall regeneration was less than spring regeneration at the same temperatures. In their study, the sediment was aphotic and dependent on sedimentation for a source of labile organic matter. They postulated that stocks of labile organic matter are exhausted by fall, thus explaining their observations. Fisher et al. (1982) attributed their very low but significant correlations between temperature and phosphate release ($r^2 = - .2$ - .4) to partitioning between aerobic and anaerobic processes. Occasional large pulses of phosphate release were ascribed to rapid aerobic mineralization of sporadic inputs of organic matter at the sediment surface, while seasonal temperature effects on anaerobic metabolism deeper in the sediment produced lower, steadier releases of phosphate (Fisher et al. 1982).

In addition to in situ autotrophic production, short-term sedimentation of water column organic matter during slack water may provide additional sporadic inputs of labile organic matter to the sediment community (Jennes and Diineveld 1985). Roman (1978), Roman and Tenore (1978) and Baillie and Welsh (1980), have shown increases in water column suspended solids due to resuspension at low tide. The difference between high and low tide concentrations of suspended solids in the water column (fig. 3.14) suggest that such transient inputs also occur on this shoal. The balanced P:R ratios of the sediment and water column community (table 3.2) also suggest
Figure 3.14. Concentrations of suspended solids (mg l\(^{-1}\)) over the sampling period on selected sampling dates. A. 14 March. B. 31 May. C. 22 June. D. 30 June. The vertical reference line the time of predicted low tide.
that sediment net production provides the dominant input of labile organic matter to the sediment. Shallow systems with currents strong enough to prevent settling of organic matter and turbid enough to eliminate an autotrophic community may have limited substrates for mineralization. Lack of substrate may partly explain why nutrient fluxes were undetectable at Fisher et al.'s (1982) Newport River study site.

The dependence of ammonium release on respiration and net production, rather than temperature would better explain the observed seasonal pattern of ammonium release. In May (temp. = 20.8°C; NP = 15 and R = 26 mg O$_2$m$^{-2}$h$^{-1}$), ammonium release did not increase with increasing spring water temperatures, but did increase substantially in June (temp. = 25.4°C; NP = 41, R = 78), as respiration and net production increased threefold over May rates. In October, temperatures were similar to those in May, but net production and respiration were 2-6 times greater (temp. = 22.9°C; NP = 83; R = 42), and release of ammonium from the sediments remained high.

The seasonal changes in sediment release of ammonium are directly reflected in the seasonal changes in ambient water column concentrations of ammonium (fig. 3.9), although water column concentrations and mean ammonium flux were not correlated. The lack of correlation could be due to several factors: seasonal variation in direction of ammonium flux between the sediments and water, making correlations difficult to show; water column concentrations integrate ammonium inputs from many sources (e.g. aphotic sediments), dampening the effects of changes in release rate from the shoal sediment; and because changes in water column concentrations probably lag changes in sediment release rates. Although releases were lower than in the dark domes, the transparent domes nevertheless released ammonium from 31 May through 3 October at rates > 50 ug-at m$^{-2}$h$^{-1}$. This indicates day-time
ammonium production in excess of microfloral photosynthetic requirements during summer and early fall. Since water column net production during this period was accompanied by uptake of ammonium (except for the 22 June sampling date), the summer increase in ammonium concentrations in the water column appear to be largely controlled by sediment releases, as hypothesized by Nixon et al. (1976).

In contrast, water column nitrate concentrations are largely controlled by water column processes and/or anthropogenic inputs. While the magnitude of nitrate fluxes from the sediments within the dark domes (disregarding direction) was correlated with the seasonal maximum in water column nitrate concentrations (r = .81; P < .001), the direction of nitrate fluxes varied. Nixon et al. (1976) found no correlation between water column concentrations and nitrate fluxes, concluding that pelagic processes controlled nitrate dynamics in the estuary.

This is evident in the seasonal dynamics of water column nitrate in Chesapeake Bay. D'Elia et al. (1982) have shown that nitrate acts conservatively within the Chesapeake Bay, becoming progressively diluted with seawater from north to south. Winter nitrate concentrations are greater than 50 ug-at l^{-1} in the upper Chesapeake and the Patuxent estuary, but less than 5 ug-at N l^{-1} at the shoal site. The high nitrate concentrations in the mid to upper Chesapeake Bay and the Patuxent River of the upper bay, support high nitrate uptake by the sediment in May (Boynton and Kemp 1985). Sediment nitrate uptake decreases with increasing salinity, reaching zero near the mouth of the Rappahannock River, and was proportional to the water column nitrate concentrations. In August, nitrate fluxes were low at all their stations, and sediments generally released nitrate. The spring nitrate uptake at the upper Bay stations was attributed to coupled
nitrification/denitrification processes, whose rates and seasonal changes
(spring >> summer) were consistent with the observed uptake of nitrate
(Jenkins and Kemp 1984).

Anomalous nutrient ratios

The atomic ratios for oxygen consumption vs. nitrogen and phosphorus
release from the shoal sediments are shown in table 3.2. The expected O:N
ratio for the aerobic decomposition of organic matter in seawater varies
from 13.25:1 if nitrate is the end product, to 17.25:1 if ammonium is the
end product (Redfield et al. 1963). The average O:N ratios were 57.9 (NH$_4^+$-
N only) and 43.0 (total dissolved inorganic nitrogen), more than 3 times
higher than predicted. The ratios were ≥ 20 on all but two days. Ratios of
phosphate released vs. oxygen consumed by the sediments were also high. For
the entire study, using only data from days when phosphate flux was > 1.0
μg-at m$^{-2}$h$^{-1}$, the average ratio was 789.6, also nearly 3 times the expected
value (276:1).

While O:N ratios are typically higher than predicted (Boynton and Kemp
1985; Nixon et al. 1976; Boynton et al. 1980; Raine and Patching 1980;
Hopkinson and Wetzel 1982; Callender and Hammond 1982), O:P ratios are
usually near the expected ratio (Nixon et al. 1980; Fisher et al. 1982;
Hopkinson and Wetzel 1982), resulting in nitrogen and phosphorus release in
ratios less than the expected 16:1 (Nixon et al. 1976; Boynton et al. 1980;
Hopkinson and Wetzel 1982; Nixon et al. 1980). The ratios from these
studies indicate that based on rates of oxygen consumption, phosphorus is
released in expected quantities, but nitrogen is not.
A number of hypotheses have been advanced to account for the "missing" nitrogen. Nixon et al. (1976) postulated that the anomalously low nitrogen release resulted from unmeasured fluxes of nitrogen as $N_2$ or $N_2O$ gases derived from denitrification, or from large fluxes of dissolved organic nitrogen (DON) from the sediments. Nixon et al. (1976) found that DON fluxes were sufficiently large to account for the "missing" nitrogen. Boynton et al. (1980) also measured sediment/water fluxes of DON but found little nitrogen exchanged in this form. They attributed the anomalous O:N ratios to either denitrification or to diagenesis within the sediments leading to greater burial of nitrogen relative to phosphorus and/or carbon. Hopkinson and Wetzel (1982) found no evidence for selective burial of nitrogen (constant C:N ratios with depth in the sediment) and attributed the anomalous nutrient ratios to nitrification/denitrification processes within the sediment, based on the vertical profiles of interstitial water concentrations of nitrate and ammonium in the sediment. More recently, Boynton and Kemp (1985) have shown that selective burial of nitrogen occurs in some sediments of the upper Chesapeake Bay, but that nitrification/denitrification processes are largely responsible for the anomalous ratios. Significant rates of denitrification require nitrate either from the water column, or from nitrification within the sediment, an aerobic process. Boynton and Kemp (1985) concluded that denitrification was largely responsible for the anomalous O:N ratios they observed in May (185:1 $NH_4^+-N$ only; or 95:1 $NO_3^--N$ included), and that the required nitrate was supplied by sediment nitrification, supplemented by high uptake of nitrate at their uppermost bay stations, where winter and spring nitrate concentrations are typically high. In the upper bay, spring rates of nitrification and denitrification measured by Jenkins and Kemp (1984), were
about equal to the ammonium release from the sediment, and therefore sufficiently high to double the 0:N ratio (Boynton and Kemp 1985). In summer Jenkins and Kemp (1984) found that nitrification/denitrification rates were near zero. Boynton and Kemp (1985) suggested that summer 0:N ratios were more representative of the aerobic decomposition model because of the lack of nitrification/denitrification.

Since the York River study site always had low water column nitrate concentrations (< 5 umol l\(^{-1}\)), the water column is probably not as large a source of nitrate for sediment nitrification as it is in the upper bay. Nitrification within the shoal sediment probably supplies most of the nitrate necessary for denitrification to occur. Conditions would appear to be favorable for nitrification in May, when temperatures are relatively warm but before the period of peak sediment respiration reduces the depth of the oxidized zone of the sediment. The greatest 0:N anomalies (NH\(_4^+\)-N only) in this study also occurred in May and were of the same magnitude (124:1 and 223:1) as those reported by Boynton and Kemp (1985). The next highest ratio was 47:1 (14 March). In contrast to deeper, aphotic sediments which may experience periodic summer anoxia, both tidal action and autotrophic production would maintain an oxidized surface layer, at least during the day, allowing some nitrification/denitrification activity all year. Even if deeper aphotic sediments were oxidized, the depth of oxygenated sediment on the shoal is probably much greater, allowing greater nitrification. This could explain why summer 0:N ratios in this study, although much closer to the predicted Redfield ratios than in spring, remained relatively high.

The maintenance of oxic conditions in the surface sediment layer may also explain the anomalous 0:P ratios observed, through binding of phosphorus into iron-manganese complexes, which are sorbed to sediments.
preventing their release (Callender 1982; Callender and Hammond 1982; Klump and Martens 1981; Nixon et al. 1980). The high O:P ratios in the dark domes, the weak regression coefficient ($r^2 = .24$) for the relationship between phosphate release and respiration, and the non-significant difference in phosphate release between dome treatments all suggest significant influences on phosphate release by non-biological factors.

Based on the net production and respiration measurements, and Redfield ratios, daily autotrophic demand and heterotrophic supply of ammonium and phosphate can be estimated and compared with the actual daily ammonium and phosphate demand and supply (table 3.4). Based on the Redfield ratios, sediment respiration meets the sediment net production demand for nitrogen and phosphorus on 13 of 21 days (62%); water column respiration meets the water column net production demand on 17 of 21 days (81%), and the total system nitrogen demand is met by total system respiration on 18 of 21 days (86%) with relatively small deficits (7, 16 and 43%) on the other three days.

The measured daily fluxes of ammonium and phosphate show similar results to the calculations made from oxygen fluxes and Redfield ratios for the sediment, but not for the water column. Nutrient flux calculations show that sediment ammonium regeneration can supply the benthic microfloral nitrogen demand on 9 of 12 occasions (75%) and the phosphorus demand on 11 of 13 occasions (85%). Excess water column remineralization could have supplied the sediment deficit in both ammonium and phosphate on 15 November and 8 December, and 53% of the ammonium deficit on 13 April.

The water column regenerated sufficient ammonium for water column photosynthesis on 7 of 12 occasions (58%), and sufficient phosphorus on 6 of 12 dates (50%). The sediments could supply 21 - 3667% of the ammonium
Table 3.4. Comparison of daily nitrogen (as ammonium) and phosphorus demand and supply (ug-at N or P m⁻²) calculated from ratios given by Redfield et al. (1963) (negative demand indicates negative net production, and presumably no demand), and daily demand and supply estimated from measured rates of nutrient flux, where measured demand is the average flux in the transparent dome times the photoperiod (positive values denote release from sediments or accumulation within water column), and measured supply is the average flux within the dark domes times 24 h. A. Sediment and B. water column.

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deficits (mean = 837%), and 19 - 63% (mean = 32%) of the phosphate deficits. On the basis of the actual nutrient flux measurements the sediment component of the system is generally able to meet its nutrient needs. In addition the sediments could supply sufficient nitrogen to meet deficits in water column nitrogen regeneration, but only a fraction of the phosphorus deficits.

The total system is generally balanced in its nitrogen dynamics, but apparently requires an allochthonous phosphorus source, especially in the summer. While phosphorus may not limit water column production, it does appear to be much more tightly cycled, explaining why phosphorus concentrations do not show the large summer increase found for ammonium concentrations.

The metabolism of the shoal sediment can be represented by the simple model shown in fig. 3.15. The principal features represented are the high rates of microfloral net production which supports extensive heterotrophic activity and concomittant remineralization of ammonium and phosphate. Much of the remineralized ammonium is recycled in the sediment and much remineralized phosphate is trapped in the sediments through sorptive processes, by maintenance of oxic conditions in the sediment surface through microfloral photosynthesis.

Monthly and annual estimates of the day-time fluxes of oxygen, ammonium and phosphate can be calculated for the York River sediments weighted by photic characteristics, and compared to a hypothetical situation in which all the bottom area is considered aphotic. The results of these calculations are shown in table 3.5.

As shown in table 3.5, during the daylight hours, York River sediments would consume 85% more oxygen and release 31% more ammonium and 30% more phosphate than under the present euphotic conditions maintained in the shoal
Figure 3.15. A conceptual model of the major flows of matter/energy in the shoal sediment. Average rates of net production, respiration (mg O$_2$m$^{-2}$h$^{-1}$) and fluxes of nitrogen (ug-at NH$_4^+$-N m$^{-2}$h$^{-1}$) and phosphorus (ug-at PO$_4^{-3}$-P m$^{-2}$h$^{-1}$) over the study are also given. Fluxes within the dark domes are shown in parentheses. Positive values denote release from the sediments.
areas. Shoal sediments play an important role in oxygenation of the estuary and in limiting releases of ammonium and phosphate from the sediments. However, increasing eutrophication may limit the extent of euphotic shoal areas through increased turbidity, or decrease the oxygenation provided by the shoal areas through increased heterotrophic metabolism mediated by large allochthonous inputs of organic matter. Decreased sediment net production may result in less ammonium uptake by the shoal sediments and increased sediment anoxia. Increased sediment anoxia may also result in greater releases of phosphate from the sediments. Relative to other types of subtidal sediments, shoal areas are readily accessible for study. Continual monitoring of the nutrient exchanges and oxygen dynamics of shoal sediments may allow early detection of eutrophication impacts. Comparison of the community metabolism of shoal sediments in relatively unenriched areas like the York River to more impacted areas may also yield new information on the consequences of estuarine nutrient enrichment.
CHAPTER 4

SUMMARY AND CONCLUSIONS
Summary and Conclusions

Hourly estimates of oxygen metabolism varied significantly over diurnal, day-to-day, tidal and seasonal scales. Some of the factors important to metabolism (e.g. temperature, and light) were not significantly different between morning and afternoon, or day-to-day, and other important factors (e.g. chl. and grazing) varied only slightly over such brief periods. Variability over short-term scales is most likely related to endogenous metabolic cycles between mutually-dependent autotrophic and heterotrophic communities, and to physiological changes related to the history of the communities.

Variability in oxygen metabolism over longer time scales, e.g. tidal and seasonal scales were related to changes in exogenous variables. On a tidal scale, mean hourly net production was higher on days with mid-day low tides. Although this difference was not significant, a real difference was probably obscured by the high variability in net production found on diurnal and day-to-day scales. PAR and respiration were both significantly greater during mid-day low tides. Improved light conditions probably caused the increase in net production found on days with mid-day low tides and respiration probably increased in a coupled response to the increased net production.

On a seasonal scale, respiration was significantly related to temperature, and net production was directly related to chl. concentration, which was significantly correlated with frequency of severe winds. Thus, the exogenous variables of PAR, temperature and wind (through impacts on chl.), controlled oxygen metabolism by the sediments in this study, but only
over time scales greater than one week. On shorter scales endogenous metabolic changes control variability in oxygen metabolism.

The high variability on short-term scales, the lack of control by exogenous variables on short-term scales, and the interaction between these factors and typical sampling designs (monthly, brief incubations) were found to have a number of implications:

1. A relatively few samples are required to estimate annual changes in production. Samples tend to "average out" and yield similar annual estimates, and a significantly increased sampling effort (order of magnitude) did not improve the annual estimate of oxygen metabolism, but

2. Sampling designs which do not incorporate short-term variability in oxygen metabolism show very different seasonal patterns of change than designs incorporating variability in imbedded time scales.

3. Real effects of exogenous variables may be obscured by high endogenous variability in in situ situations. For example, regressions of individual oxygen metabolism measurements on instantaneous values of exogenous variables may show non-significant, or significant but weak relationships between the variables.

If annual gross production is calculated for the microfloral communities of the shoal sediments in the York River, and for the water column (assuming a 2 m euphotic zone) using the annual estimates from this study, and the areal estimates given in the study site section, the shoal sediments supply 15%, and the shoal water column 14% of the total annual microfloral primary production of the York River. By way of comparison, submerged aquatic vegetation contributes only 8% of the benthic microfloral production based on recent estimates of SAV abundance in the York River (238
ha; Orth et al. 1984), and the annual production estimate of Penhale (1977; 330 g C m$^{-2}$ y$^{-1}$).

Daily sediment community gross production exceeded respiration on more than 75% of the sampling dates, while autotrophic on only 33% of all sampling dates. In many estuaries, sediments represent an oxygen sink, but the shoal sediments represent a significant source of oxygen to the estuary, even in summer, when biogenic oxygen production is especially important because wind mixing is reduced.

Concomitant with oxygen production in the transparent domes, ammonium and phosphate were also generally released. However, the rate of ammonium release was significantly less than that within the dark domes. This difference was probably due to microfloral uptake. Release rates of ammonium within the dark domes were similar to those reported for other aphotic sediments. However, O:N ratios indicated less ammonium was released from the dark domes than expected on the basis of respiration. This may in part by due to coupled nitrification/denitrification processes.

Nitrification would be favored by oxic conditions in the surface sediments, and sediment P:N ratios indicate that oxic conditions could be maintained by microalgal photosynthesis over a 24 h scale on most days. In addition to inflation of O:N ratios, maintainance of an oxic surface layer also results in trapping of phosphate into iron-manganese-phosphorus complexes sorbed to sediments. Since there was no significant difference in release rates of phosphate between transparent and dark domes, the high O:P ratios observed are probably due to trapping of phosphate in the sediment. While sediment trapping of phosphate in aphotic, oxic sediments is well known, aphotic sediments also often experience periods of anoxia in summer, accompanied by large episodic releases of phosphate from the sediment.
The shoal sediments of the York River differ markedly from aphotic estuarine sediments in fluxes of oxygen, ammonium and phosphate. They are generally oxygen sources rather than sinks, due to the presence of the microfloral community. Potential releases of ammonium and phosphate, represented by dark dome flux rates, are similar to rates measured in aphotic areas, but because of the presence of an autotrophic community, much of the remineralized ammonium is taken up by the microflora. Also due to sediment oxygenation by the microflora, much of the remineralized phosphate is trapped within the sediment.

If nutrient enrichment increases in the York River, turbidity may increase to the point where the sediment microfloral communities of the shoals are reduced or eliminated, and/or organic matter inputs to the sediments may increase heterotrophic biomass and metabolism relative to rate of autotrophic production (P:R ratios), resulting in decreased oxygenation of the shoal sediments. In addition to affecting the oxygen dynamics of the estuary, elimination or reduction in the extent of the microfloral community of the shoal sediments of the York River would have significant impacts on the sediment/water exchanges of ammonium and phosphate, and subsequent impacts on the nutrient dynamics of the entire estuary.
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