

Benthic metabolism and nitrogen cycling in a subtropical east Australian estuary (Brunswick): Temporal variability and controlling factors

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Abstract

We examined temporal variability in benthic metabolism and nitrogen (N) cycling in the subtropical Brunswick Estuary, Australia from December 2000 to December 2002. Benthic metabolism was tightly coupled to the production of labile carbon (C) in the water column (phytodetritus) and temperature, both of which increased in summer, resulting in increased rates of benthic metabolism and a shift to sulfate reduction. C:N ratios of remineralized material showed a consistently low return of N relative to “Redfield”-type material over the 2-yr study period (up to 84:1 and averaging 31:1). The highest remineralized C:N ratios occurred at a sediment CO₂ productivity/respiration of ~0.4, which corresponds to maximum respiration and maximum productivity, and also when water-column dissolved inorganic nitrogen concentrations were lowest, reflecting potential N limitation. The “missing N” was most likely assimilated by heterotrophic bacteria and autotrophic benthic microalgae (BMA). Extracellular organic carbon extruded by the BMA and subsequently decomposed may also account for some of the high remineralized C:N ratios. Net N₂ effluxes were controlled by a complex interaction between the supply of NO₃⁻ from the water column and nitrification, the supply and decomposition of labile C, benthic productivity, and macrofauna abundance. A N mass balance for the sediment over the 2-yr study period showed that a significant proportion of the mineralized nitrogen may have been removed from the microbial loop and passed up to the metazoan levels of the food chain. About 22% of the remineralized N was permanently removed via denitrification. This active competition for limited N resources between heterotrophs, autotrophs, and chemoautotrophs appears to be a mechanism by which N-limited oligotrophic subtropical estuaries tightly recycle and conserve N.

The metabolism of benthic communities is a central component of the nutrient cycling and overall productivity of shallow coastal ecosystems. Much of the carbon decomposition in shallow coastal ecosystems occurs in bottom sediments through heterotrophic-mediated processes (Hammond et al. 1985), and the associated release of nutrients can provide a large proportion of the nitrogen and phosphorus required by pelagic communities (Boynton and Kemp 1985; Cowan and Boynton 1996). Bottom sediments can also be a sink for nutrients through the burial of carbon (C), nitrogen (N), and phosphorus; the loss of carbon through CO₂ efflux; and the loss of N through denitrification. Denitrification (the reduction of NO₃⁻ through NO₂⁻ to nitrous oxide [N₂O] and dinitrogen gas [N₂]) is a key pathway in the N budgets of coastal ecosystems, because it permanently removes fixed N and, as such, may help alleviate nutrient overenrichment. Sediment autotrophic processes, in particular benthic microalgal production, are an important source of new C in shallow coastal ecosystems (Underwood and Kromkamp 1999), can act as a sink for nutrients (Cercio and Seitzinger 1997), and can modify heterotrophic processes by modifying the sediment redox status (Risgaard-Petersen et al. 1994) and through competition for limited nutrients (Risgaard-Petersen

2003). The net balance of sediment productivity and respiration appears to be an important control on the overall role of sediments as a source or sink of C and N (Eyre and Ferguson 2002).

The importance of benthic metabolism and N cycling pathways (e.g., denitrification) in shallow coastal ecosystems is usually quantified by scaling up individual rate measurements (e.g., Boynton et al. 1995; Eyre and McKee 2002). These scaled rates are, in turn, often used to drive models that will determine the allocation of management resources. However, a good understanding of the spatial and temporal variability in benthic metabolism and N cycling pathways is required if the scaled up rates are to give reliable whole-ecosystem estimates. An understanding of temporal variability will also give some insight into the factors important in controlling and maintaining benthic metabolism and N-cycling pathways in shallow coastal ecosystems. Although a number of studies have examined temporal variability in benthic metabolism and N cycling in temperate systems (e.g., Banta et al. 1995; Cowan et al. 1996; Giblin et al. 1997; Norwicki et al. 1997), similar studies in tropical and subtropical estuaries are rare (e.g., Ferguson et al. 2003, in press).

Previous work in subtropical estuaries has highlighted the importance of episodic events in delivering nutrients (Eyre 2000; Eyre and Pont 2003). The subsequent internal recycling of these nutrients within subtropical estuaries is primarily controlled by freshwater residence times (Ferguson et al. 2003, 2004, in press). For example, in the subtropical Brunswick Estuary, the recycling of dissolved inorganic N (DIN) to the water column, as opposed to assimilation by benthic microbes and denitrification, was controlled by the rate of organic matter (OM) supply to the sediments (Fer-

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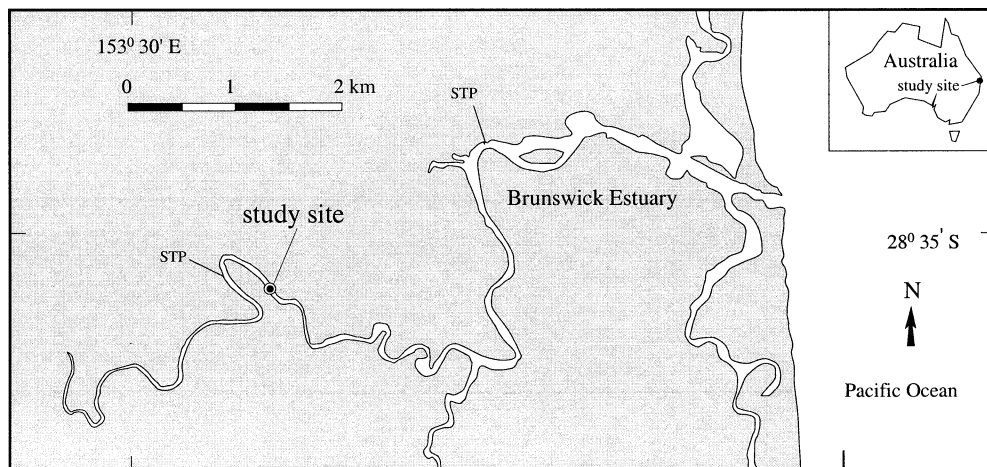


Fig 1. Location of the Brunswick Estuary, the study site and the STPs.

guson et al. 2003, in press). Hence, during the growth phase of large phytoplankton blooms after nutrient inputs to the system, the benthic metabolism was dominated by anaerobic mineralization, and the sediments acted primarily as a source of NH_4^+ to the water column. As residence times increased and the OM supply waned, secondary productivity in the benthos increased the grazing of microbial biomass, and N tended to be retained within the sediments and passed up the metazoan food chain. The immobilization of N appeared to increase as the net benthic metabolism productivity/respiration (p/r) became more autotrophic, which was, in turn, related to the OM supply and light attenuation (Ferguson et al. in press). However, previous work in the Brunswick Estuary (e.g., Ferguson et al. 2003, in press) was limited to four sample collections over 1 yr and only one measurement of net N_2 efflux (denitrification). The present study aimed to expand this previous work by measuring dark and light benthic fluxes of CO_2 , O_2 , alkalinity, NH_4^+ , NO_3^- , dissolved organic N (DON), and N_2 every 1–2 months over a 2-yr period, allowing diurnal, seasonal, and interannual scales of variability and their controlling factors to be assessed. Of particular interest was the coupling between benthic and pelagic systems and the pathways of N transfer after C decomposition, including benthic fluxes, benthic microalgae, and macrofaunal assimilation and denitrification.

Materials and methods

Study area—The Brunswick River is located on the northern coast of New South Wales (NSW), Australia (Fig. 1). The climate is controlled by two major influences: the subtropical high-pressure belt during winter and spring (July–October) bringing clear, mainly dry conditions, and easterly monsoonal trade winds during summer and autumn (November–May) bringing warm, humid conditions. Tropical cyclones may affect the region between January and April, bringing heavy rainfalls (up to 400 mm d^{-1}) and flooding. Major rainfall events may also occur due to the occurrence of intense low-pressure systems off the NSW coast (east coast lows). The region experiences the highest annual rain-

fall in NSW, with a summer-autumn maximum (wet season) and the lowest rainfall occurring during the winter-spring transition (dry season). There is high interannual variation in rainfall due to the influence of the Southern Oscillation on climate in the region: lower than average annual rainfalls occur during El Niño years (atmospheric pressure at Darwin $>$ Tahiti), whereas greater than average rainfalls occur during La Niña years (atmospheric pressure at Darwin $<$ Tahiti). Cyclone genesis tends to move east during El Niño years, resulting in generally less cyclonic influence on the region's climate. Freshwater flows to the Brunswick Estuary are dominated by large episodic, short-lived inputs during summer and very low flow in winter (Eyre 2000).

The Brunswick Estuary forms the main arm of the system, and up to 75% of the catchment has been cleared for agriculture and grazing; 75% of the estuary shoreline has been modified. The main arm of the Brunswick Estuary receives direct effluent discharges from two sewage treatment plants (STPs): one at Mullumbimby in the upper estuary (10.5 km from the estuary mouth) and one at Ocean Shores in the lower estuary (3 km from the estuary mouth). The relative importance of STP loadings increases during low flow conditions.

Selection of sample site—One site was selected in the upper Brunswick Estuary (Fig. 1) and was the same site as the upper estuary site (site RW) sampled by Ferguson et al. (2003). This site was chosen to represent the upper extent of extensive subtidal shoals (and, hence, OM deposition) within the Brunswick Estuary. Upstream of this site, the sediments are dominated by coarse gravel beds and rock substrate. The site was located on subtidal littoral shoals with a mean depth of $1 \pm 0.75 \text{ m}$ and was therefore euphotic for most of the time, excluding high flow events when suspended sediment loads were high. The study site is situated $\sim 1 \text{ km}$ downstream of the Mullumbimby STP and therefore is heavily influenced by elevated nutrients and phytoplankton blooms associated with effluent discharges. Peak phytoplankton biomass along the estuary generally occurs within 1 km upstream or downstream of the STP discharge at high

tide. It was therefore expected that the study site would represent the area of maximum phytodetritus deposition along the estuary. This site is fairly representative of the upper sections of other subtropical eastern Australian estuaries, where similar zones of maximum phytoplankton biomass occur at the head of the estuary (Eyre 2000).

Sample collection—The one site was sampled every 1–2 months (16 samplings in total) between December 2000 and December 2002 (Fig. 1). Additional weekly collections were undertaken after a flood event; however these data will be reported elsewhere. Three to five undisturbed cores were collected using a surface-operated hand corer. The plexiglass core liner (95 mm inner diameter) was inserted into the sediment so as to retain ~1,000 ml of water overlying a 20-cm sediment core, and a gas tight (on the timescale of the incubations) plexiglass plate was placed on the bottom of the core after it was brought to the surface. A 20-liter sample of water was also collected from the site and physicochemical parameters (dissolved oxygen, salinity, and temperature) were measured at the sample site using a Horibia U-10 multiprobe and a sample collected for nutrient and chlorophyll *a* analysis (collection and preservation techniques outlined below). Incident radiation (2 pi) was measured at the top and bottom of the water column at the sample site using a Li-Cor 250 light meter to determine light attenuation.

Benthic flux incubations—After collection, the cores for benthic flux measurements were individually shaded to in situ light conditions ($\pm 5.0\%$) using shade cloth, capped with a gas-tight plexiglass plate, placed in a floating cradle in the estuary, and equilibrated at in situ light ($\pm 5.0\%$) and temperature ($\pm 2^\circ\text{C}$) conditions for ~24 h, to ensure steady-state concentration profiles. The water in the cores was continuously exchanged over the 24-h preincubation period from a large reservoir of site water, also equilibrated at in situ light ($\pm 5.0\%$) and temperature ($\pm 2^\circ\text{C}$) conditions, to maintain in situ oxygen and nutrient concentrations. Each core was stirred at a rate just below the threshold for sediment resuspension. This was considered to be the most appropriated stirring rate, because bottom sediments in the estuary are regularly resuspended by wind waves and currents. All stoppers, replacement water lines, and other incubation materials were also carefully preincubated, to avoid the introduction of any new surfaces for Ar and N₂ absorption/desorption (Eyre et al. 2002).

The cores were incubated at in situ light ($\pm 5.0\%$) and temperature ($\pm 2^\circ\text{C}$) conditions over a 24-h dark:light cycle. Dissolved oxygen concentrations ($\pm 0.01 \text{ mg L}^{-1}$) and pH ($\pm 0.001 \text{ pH units}$) were measured electrochemically, and alkalinity, nutrient, and N₂ samples were collected at 0, 3, 6, and 13 h during the dark cycle and at 0, 4, and 8 h during the light cycle. To avoid bubble formation during the light cycle, which may result in an underestimate of benthic production (Dalsgaard et al. 2000) and will interfere with the N₂:Ar concentrations (Eyre et al. 2002), the partial pressure and concentration of O₂ was lowered by always running the dark incubation before the light incubation (Eyre and Ferguson 2002). Dissolved oxygen typically only decreased by ~20% over the course of the dark incubation. Nutrient and

alkalinity samples were withdrawn with a plastic syringe and transferred to 10-ml acid-rinsed and sample-rinsed polyethylene vials. As a sample was withdrawn, an equal amount was replaced from a gravity-feed reservoir of estuary water. To minimize the introduction of bubbles, N₂ samples were collected in triplicate by allowing water to flow, driven by the reservoir head, directly into 7-ml gas-tight glass vials with glass stoppers filled to overflowing. The replacement water was withdrawn from a sealed collapsible reservoir bag, also equilibrated at in situ light ($\pm 5.0\%$) and temperature ($\pm 2^\circ\text{C}$) conditions, to maintain constant Ar concentrations (Eyre et al. 2002). All nutrient samples were immediately frozen at -20°C . N₂ samples were poisoned with 20 μl of 5% HgCl₂ and stored submerged at ambient temperature. Alkalinity samples were kept cold at 4°C. One core (blank) with only water was preincubated and incubated and sampled as above.

Sediment solid phase and macrofauna—At completion of the flux incubations, the top 2 cm of each sediment core was sampled for total organic C and total N, and the top 2 mm of each sample core was sampled for Chl *a* analysis. The sediment samples were placed in a 30-ml polyethylene vial, and these were immediately frozen at -20°C . The Chl *a* samples were immediately extracted in 90% acetone in 10-ml polyethylene vials, wrapped in aluminum foil, and frozen at -20°C . The remaining sediment from each core (~20 cm long) was wet sieved (200 μ), and the macrofauna were stored in ethanol until identified to species level. Macrofauna sampling started in July 2001.

Analytical techniques—Analytical procedures, abbreviations, and errors are summarized in Table 1. All nutrient analyses were carried out colorimetrically using Lachat flow injection analysis. Analytical errors were determined as the average percentage coefficient of variation (%CV) of the triplicates. Because the variance of the analytical procedures propagates additively, the variance associated with the nutrient forms calculated by difference was estimated as the sum of the variances of the two measured nutrient forms used in the calculation (Eyre 1995). Analytical accuracy for nutrient analysis was maintained using standard additions of certified laboratory standards in both Milli-Q and low-nutrient seawater. ΣCO_2 data are not available for January and February 2001 because of the alkalinity samples being frozen.

Benthic flux calculations—Fluxes across the sediment-water interface were calculated by linear regression of the concentration data, corrected for the addition of replacement water and changes in the blank, as a function of incubation time, core water volume, and surface area. Only the linear portions of the concentration versus incubation time curve were used in the flux calculations. Dark flux rates were calculated using concentration data from the first 12 h of the incubation, and light flux rates were calculated using concentration data from the second 12 h of the incubation. Net flux rates are the average of the dark and light flux rates. Benthic production was calculated as

Table 1. Analytical procedures, abbreviations, and analytical errors.

Parameter	Abbreviation	Method	Source	Error (%)
Total nitrogen	TN	Persulfate digestion	Valderrama 1981	4.3
Particulate nitrogen	PN	TN-TDN		7.3
Total dissolved nitrogen	TDN	Persulfate digestion	Valderrama 1981	4.1
Dissolved organic nitrogen	DON	TDN - (NO ₃ + NH ₄)		19.6
Oxidized nitrogen	NO _x	Cadmium reduction	Lachat 1994	3.6
Nitrate	NO ₃	NO _x - NO ₂		5.6
Nitrite	NO ₂	Sulphanilamide	Lachat 1994	2.8
Ammonium	NH ₄	Hypochlorite/phenolate	Lachat 1994	5.1
Dissolved inorganic nitrogen	DIN	(NO ₃ + NH ₄)		7.2
Di-nitrogen gas	N ₂	N ₂ : Ar ratios—modified membrane inlet mass spectrometry with O ₂ removal	Eyre et al. 2002	0.01
Alkalinity	Alkalinity	Gran titration	Grasshoff et al. 1983	1.0
Carbon dioxide	ΣCO ₂	Alkalinity and pH (±0.001)	Grasshoff et al. 1983	1.2
Chlorophyll <i>a</i>	Chl <i>a</i>	90% acetone extraction	Strickland and Parsons 1972	—

Benthic oxygen production (positive, efflux)

$$= \text{Light O}_2 \text{ flux (positive)} - \text{Dark O}_2 \text{ flux (negative)}$$

Benthic carbon fixation (negative, uptake)

$$= \text{Light } \Sigma\text{CO}_2 \text{ flux (negative)} - \text{Dark } \Sigma\text{CO}_2 \text{ flux (positive)}$$

Results

Hydrology, salinity, and flushing characteristics—Three high-flow events occurred during the 2-yr study period (Fig.

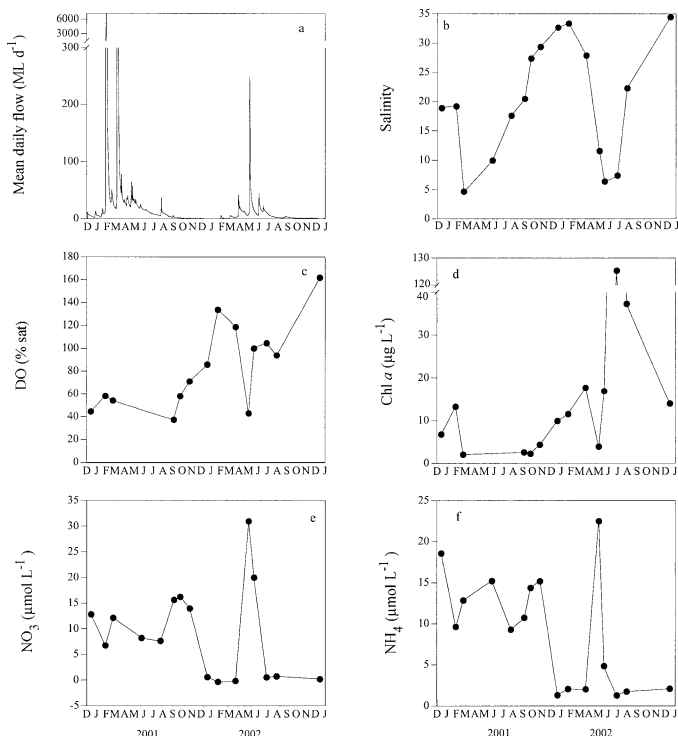


Fig. 2. Temporal variability in physicochemical parameters over the 2-yr study period.

2a). The resulting large narrow hydrograph peaks, separated by long low base-flow periods, were typical of the episodic nature of this system (Eyre 2000). Salinity at the study site was strongly related to river flow, dropping to 0.4 (weekly sampling; data not shown) after the early 2001 flow events and then increasing to 33.4 in January 2002, dropping again to 6.4 after the smaller April 2002 flow event and again recovering to 34.5 in December 2002 (Fig. 2b). By the time the monthly cores were collected after the early 2001 flow events, the salinity had already recovered to 4.7 (Fig. 2b). Flushing times (fraction of freshwater method; Eyre 2000) were also strongly related to river flow, with rapid flushing (<1 d) immediately following the early 2001 flow events, increasing to 59 d in January 2002, dropping again to 3 d after the smaller April 2002 flow event, and again increasing to 11 d in December 2002.

Water-column parameters—Water-column temperatures ranged from a maximum of 29.0°C in January 2001 and 2002 (summer) to a minimum of 15.3°C in July 2002 (winter). Dissolved oxygen was supersaturated in a number of summer months, including February 2001 and January, February, and December 2002 (Fig. 2c) and depressed (<50% saturation) in December 2000, January and September 2001, and April 2002. Dissolved oxygen concentrations were strongly influenced by phytoplankton production, as is illustrated by the positive correlation between dissolved oxygen and Secchi depth ($r^2 = 0.60$; $p < 0.01$) and Chl *a* ($r^2 = 0.38$; $p < 0.05$); increased phytoplankton production results in decreased Secchi depth because of shading by phytoplankton biomass in the water column. Chl *a* concentrations in the water column were <0.1–125.4 $\mu\text{g L}^{-1}$ (Fig. 2d), with the highest concentrations recorded during winter 2002. NO₃⁻ concentrations in the water column were <0.1–31.0 $\mu\text{mol L}^{-1}$ (Fig. 2e). STP loads contributed to NO₃⁻ concentrations during lower flows, but the highest NO₃⁻ concentrations occurred after the April 2002 flood event. Almost complete NO₃⁻ removal from the water column occurred during periods of low flow. The removal of NO₃⁻ typically corresponded with increased Chl *a* concentrations, which suggests

uptake by phytoplankton (Eyre 2000). The removal of NO_3^- was not strictly seasonal, with low concentrations found in both summer and winter, but was more closely related to lack of supply and enhanced utilization between episodic runoff events. Ammonium concentrations in the water column were <0.1 – $22.5 \mu\text{mol L}^{-1}$ (Fig. 2f) and followed a similar pattern to NO_3^- , with removal during periods of low flow and increasing concentrations following runoff events. STP loads also contributed to ammonium concentrations during lower flows. DIN concentrations were negatively correlated ($r^2 = 0.45$; $p < 0.01$) with Chl *a* concentrations, which is consistent with uptake by phytoplankton. DON concentrations in the water column were <0.1 – $42.2 \mu\text{M}$ (data not shown) and were negatively correlated with DIN concentrations ($r^2 = 0.51$; $p < 0.01$) and positively correlated with Chl *a* concentrations ($r^2 = 0.45$; $p < 0.01$). Increased DON concentrations during periods of DIN uptake by phytoplankton (i.e., elevated Chl *a*) suggests that DON was released during grazing of phytoplankton (Glibert et al. 1991) and/or is the hydrolysis product from freshly deposited phytodetritus (Eyre and Ferguson 2002). Particulate M (PN) concentrations were 4.0 – $22.5 \mu\text{mol L}^{-1}$ (data not shown) and were positively correlated ($r^2 = 0.75$; $p < 0.001$) with Chl *a* concentrations, indicating that the main source of PN was algal biomass.

Macrofauna—Polychaeta was the dominant class of macrofauna, with wet biomass of 0 – 11.0 g m^{-2} and averaging 5.9 g m^{-2} (Fig. 3a). Bivalvia was the next most dominant class of macrofauna with wet biomass of 0 – 11.3 g m^{-2} but only averaging 1.9 g m^{-2} (Fig. 3b). Crustacea were only recorded on four occasions, and the wet biomass was always $<0.9 \text{ g m}^{-2}$ (Fig. 3c).

Benthic metabolism—Dark ΣCO_2 fluxes (respiration) showed a distinct seasonal pattern during the study period, with maximum rates of $3,628$ – $4,879 \mu\text{mol m}^{-2} \text{ h}^{-1}$ in summer and minimum rates of $1,318$ – $2,531 \mu\text{mol m}^{-2} \text{ h}^{-1}$ in winter (Fig. 4). Interannual variability in respiration was low, with a %CV of 14% between the same summer months (i.e., December 2000, 2001, and 2002) and a %CV of 10% between the same winter months (i.e., May 2001 and 2002). There was a distinct diurnal variation in dark ΣCO_2 fluxes, with an efflux in the dark and an uptake or reduced efflux in the light. Benthic ΣCO_2 fixation also showed a seasonal pattern, with maximum rates of $2,371$ – $3,938 \mu\text{mol m}^{-2} \text{ h}^{-1}$ in summer and minimum rates of 0 – $1,945 \mu\text{mol m}^{-2} \text{ h}^{-1}$ in winter (Fig. 4). Interannual variability in ΣCO_2 productivity was higher than respiration, with a %CV of 22% between the same summer months and a %CV of 250% between the same winter months. Although net ΣCO_2 fluxes showed a similar seasonal pattern to respiration, the greater ΣCO_2 fixation in summer and associated greater uptake of ΣCO_2 dampened the seasonal pattern compared with respiration. Net ΣCO_2 efflux had an interannual %CV of 22% between the same summer months (i.e., December 2000, 2001, and 2002) and a %CV of 63% between the same winter months (i.e., May 2001 and 2002). Dark O_2 fluxes showed a less distinct seasonal pattern than ΣCO_2 effluxes because of enhanced O_2 consumption in winter (Fig. 4). Respiratory quo-

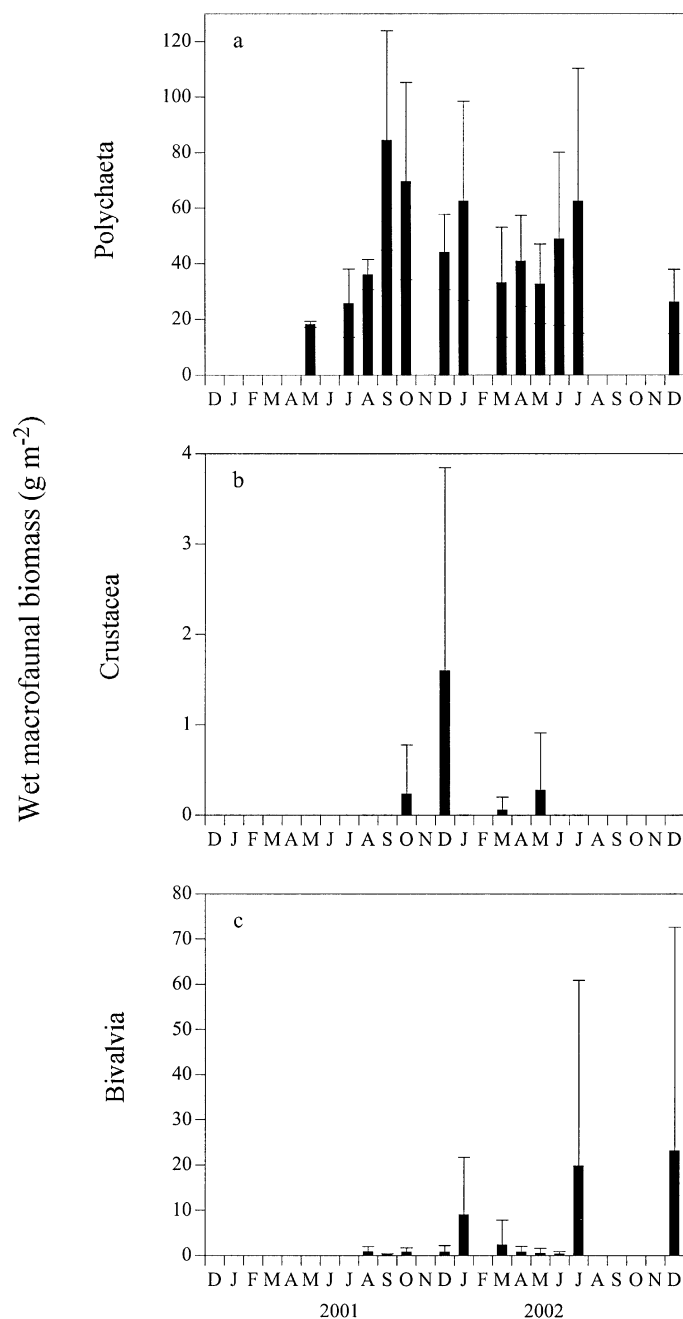


Fig. 3. Temporal variability in macrofaunal class biomass over the 2-yr study period.

tients ($\text{RQ} = \text{dark } \Sigma\text{CO}_2 \text{ efflux} / \text{dark } \text{O}_2 \text{ consumption}$) showed a distinct seasonal pattern during the study period, with $\text{RQs} > 1$ occurring in summer and $\text{RQs} < 1$ occurring in winter. Dark RQs had an interannual %CV of 30% between the same summer months and an interannual %CV of 25% between the same winter months. Net RQs showed a similar seasonal pattern to dark RQs but were higher because of the larger production of O_2 in the light than associated uptake of ΣCO_2 . Benthic O_2 productivity was 856 – $6,011 \mu\text{mol m}^{-2} \text{ h}^{-1}$, but unlike benthic ΣCO_2 , productivity rates were generally lower in summer and highest in spring.

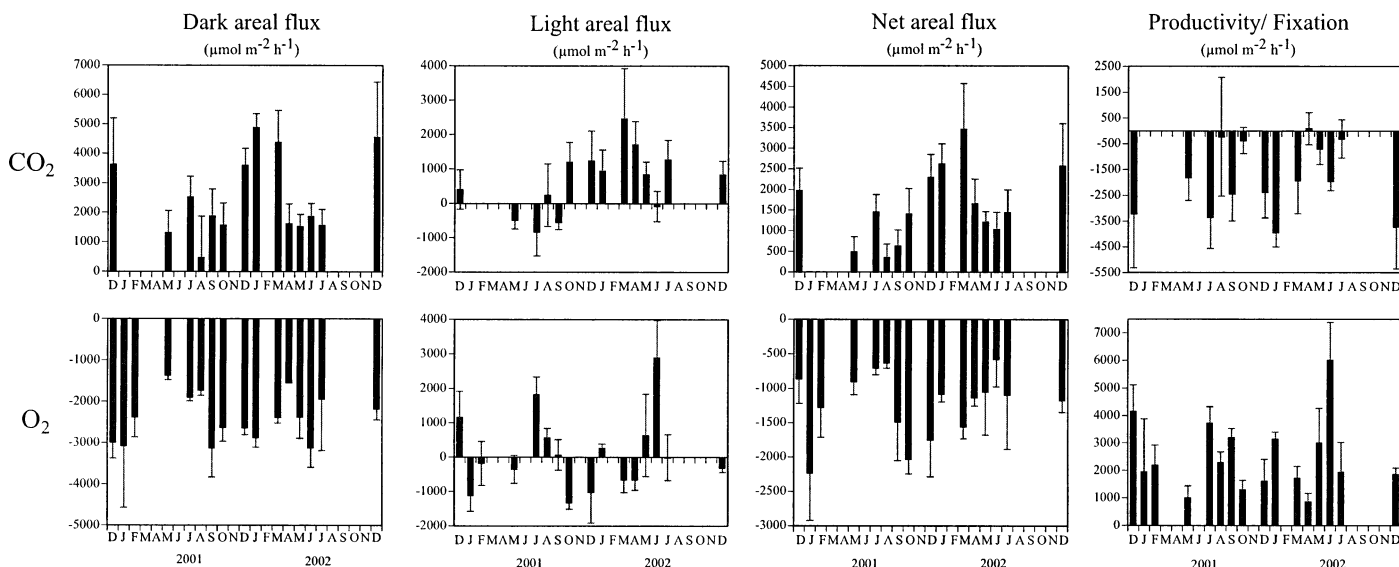


Fig. 4. Temporal variability in average (\pm SD; $n = 3$ –5) benthic ΣCO_2 and O_2 fluxes over the 2-yr study period.

Nitrogen fluxes—Dark NH_4^+ fluxes were -13 – $205 \mu\text{mol m}^{-2} \text{h}^{-1}$ and showed no seasonal pattern (Fig. 5). Interannual variability in dark NH_4^+ effluxes was high between the same summer months (%CV = 92%) and lower between the same winter months (%CV = 29%). There was a distinct diurnal variation in NH_4^+ fluxes, with an efflux in the dark (one exception in June 2002, when there was a small uptake) and an uptake or reduced efflux in the light (Fig. 5). Net NH_4^+ fluxes ranged from -33 to $164 \mu\text{mol m}^{-2} \text{h}^{-1}$, showed no seasonal pattern, and had a larger interannual variability than the dark effluxes, with a %CV of 124% between the same summer months and 141% between the same winter months (Fig. 5).

Dark NO_3^- fluxes showed a distinct but nonseasonal pattern of periods of large uptakes (up to $-155 \mu\text{mol m}^{-2} \text{h}^{-1}$) separated by periods of small uptake or efflux (Fig. 5). Interannual variability in dark NO_3^- fluxes was high (%CV = 150%) between the same summer months but much lower (%CV = 3%) between the same winter months. There was a distinct diurnal variation, with dark NO_3^- effluxes decreased or changed to an uptake and dark NO_3^- uptakes either reduced or enhanced in the light. Net NO_3^- fluxes were -130 – $64 \mu\text{mol m}^{-2} \text{h}^{-1}$ and showed a very similar pattern to dark NO_3^- fluxes and similar interannual variability.

Dark DON fluxes ranged from -106 to $199 \mu\text{mol m}^{-2} \text{h}^{-1}$ during the study period (Fig. 5). There was no seasonal pattern in dark DON fluxes, with both uptakes and effluxes occurring in summer and winter. Interannual variability in dark DON fluxes was high (%CV = 223%) between December 2000 and 2001 and 2002 but much lower (%CV = 23%) between December 2000 and 2001. The influence of light on DON fluxes was highly variable (Fig. 5), but, overall, there was generally a greater efflux of DON in the light. Net DON fluxes ranged from -94 to $112 \mu\text{mol m}^{-2} \text{h}^{-1}$ and showed a similar pattern to dark DON fluxes (Fig. 5).

Dark N_2 fluxes were 3 – $58 \mu\text{mol m}^{-2} \text{h}^{-1}$ and showed no seasonal pattern (Fig. 5). Interannual variability of dark N_2 fluxes was high (%CV = 79%) between the same summer

months and was much lower (%CV = 9%) between the same winter months. There was a distinct diurnal variation in dark N_2 fluxes, with light rates typically reduced by 40–50% (Fig. 5). However, on five occasions, dark N_2 fluxes were enhanced in the light by 1.1–1.8 times. Net fluxes were 4 – $39 \mu\text{mol m}^{-2} \text{h}^{-1}$ and showed an almost identical pattern to dark N_2 fluxes and similar interannual variability (Fig. 5).

Discussion

Controls on benthic respiration—Dark ΣCO_2 fluxes (respiration) showed a distinct seasonal pattern over the 2-yr study period. Much of this seasonal variation was related to temperature changes, as illustrated by the strong positive linear correlation between temperature and respiration ($r^2 = 0.95$; $p < 0.001$; Fig. 6a). An 8.8°C increase in temperature from winter to summer resulted in a fivefold increase in sediment respiration rates ($1,000$ – $5,000 \mu\text{mol m}^{-2} \text{h}^{-1}$). Strong relationships between temperature and sediment respiration rates in coastal systems have been well documented (Kemp and Boynton 1981; Hopkinson et al. 1999) but, in contrast to this study, are typically nonlinear (Middelburg et al. 1996). However, temperature influences not only molecular diffusion and microbial metabolic rates but other factors important in controlling sediment respiration rates. The most important of these is the delivery of labile C to the sediment surface (Banta et al. 1995; Cowan et al. 1996; Giblin et al. 1997). Sediment dark and net respiration both show a strong positive correlation with water-column Chl *a* concentrations ($r^2 = 0.76$; $p < 0.001$ and 0.88 ; $p < 0.001$, respectively; excluding the winter bloom), which reflects the delivery of phytodetritus to the sediments (Fig. 6b). The better correlation between water-column Chl *a* and net respiration probably reflects algae that remain viable once they reach the sediment surface and contribute to benthic production rather than benthic respiration.

The importance of labile C loads on sediment respiration

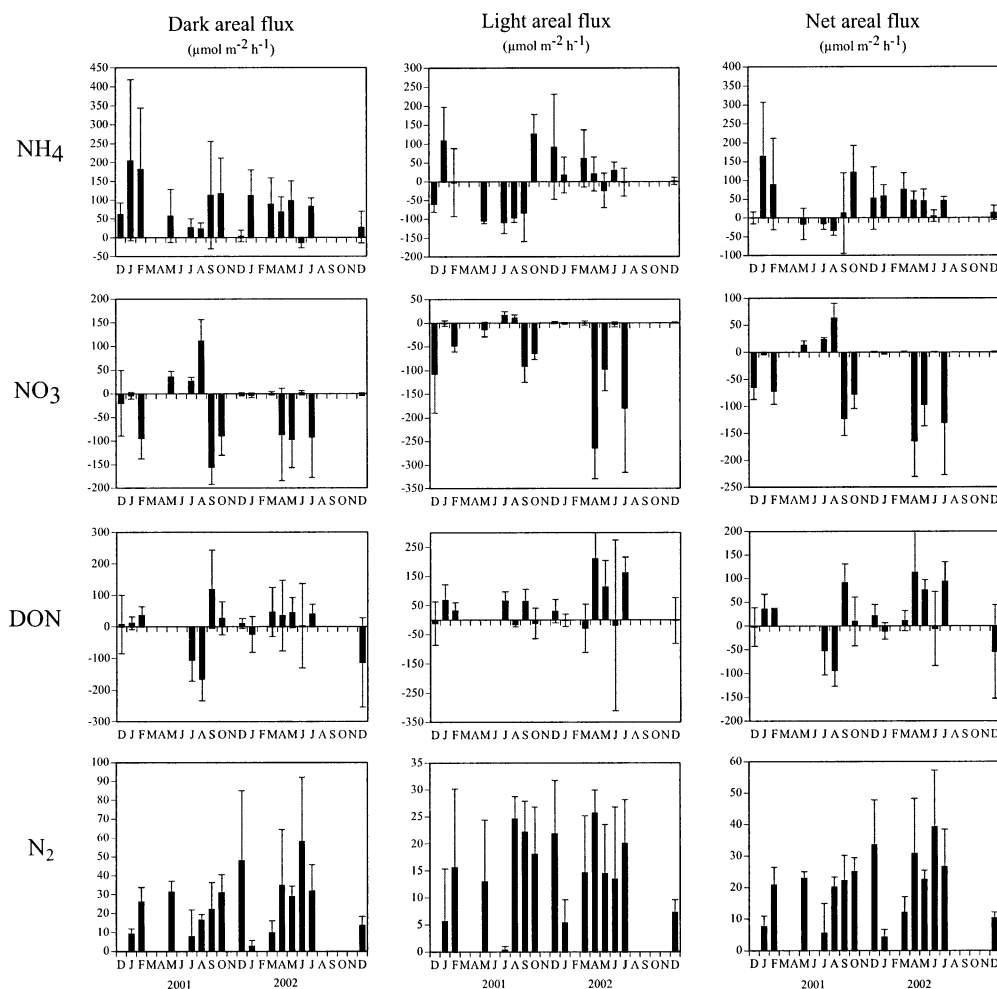


Fig. 5. Temporal variability in average (\pm SD; $n = 3-5$) benthic NH_4 , NO_3 , DON, and N_2 fluxes over the 2-yr study period.

rates is further highlighted by the outliers in Fig. 6b. These outliers represent net respiration rates measured during a winter phytoplankton bloom in 2001 (i.e., Chl *a* concentrations of 17, 37, and 125 $\mu\text{g L}^{-1}$) that was associated with drought conditions, a small runoff event that delivered DIN (Fig. 2), and long flushing times. Net respiration rates were clearly enhanced by the delivery of labile C from the bloom, despite low winter temperatures. Similar rapid increases in sediment respiration associated with an increased supply of labile C, above what would have been expected for the given temperature, have also been seen in temperate and polar coastal systems (Banta et al. 1995; Rysgaard et al. 1998). As such, sediment microbial communities across a range of coastal systems all appear to be poised to utilize labile C when it becomes available, independent of temperature. Lower respiration rates for a given water-column Chl *a* concentration (Fig. 6b) suggests that the available C is not as rapidly used at lower temperatures, which, in turn, may be associated with lower rates of sulfate reduction (see below) or lower metabolic efficiency.

RQs and alkalinity can give some insight into the pathways of OM decomposition (Eyre and Ferguson 2002). There was a distinct seasonal pattern in RQs during the study

period, with RQs >1 in summer and RQs <1 in winter. An RQ >1 occurs when reduced equivalents are stored (most likely because of enhanced C decomposition through sulfate reduction), and an RQ <1 occurs when accumulated reduced equivalents are oxidized (most likely sulfide). Consistent with increasing anaerobic respiration with increasing RQ (i.e., summer) was the positive correlation between nutrient-corrected dark alkalinity fluxes, which are a proxy for sulfate reduction (Berelson et al. 1996), and RQs ($r^2 = 0.71$; $p < 0.001$). Similar seasonal cycles of enhanced sulfate reduction and associated sulfide accumulation in summer and enhanced sulfide oxidation in winter have been seen previously in the Brunswick Estuary (Ferguson et al. 2003) and in the sediments of a number of other shallow coastal systems (Zimmerman and Benner 1994; Panutrakul et al. 2001). Enhanced O_2 consumption in winter via sulfide oxidation (i.e., greater than CO_2 efflux) also explains the less-distinct seasonal pattern in dark O_2 fluxes compared with dark ΣCO_2 effluxes. This also highlights the problem of using O_2 fluxes as a measure of benthic metabolism because of oxygen's interaction with the sulfur cycle and resultant uncoupling from the C cycle.

The strong coupling of benthic and pelagic processes in

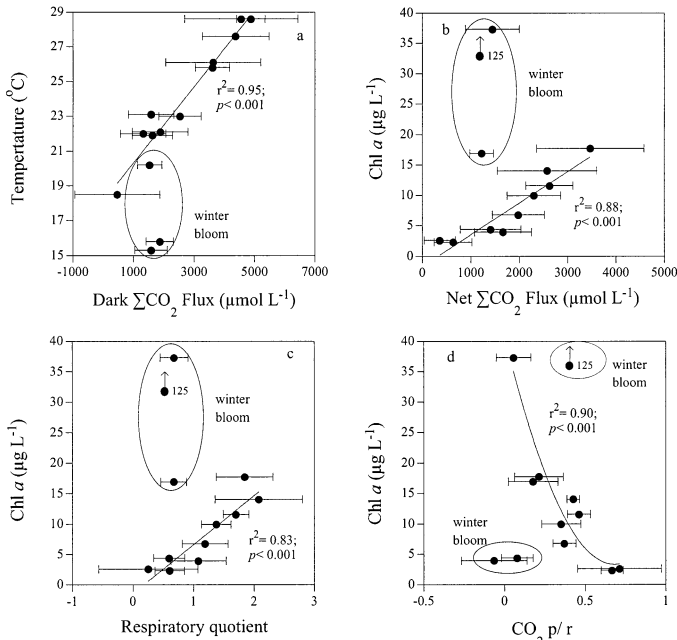


Fig. 6. Plots showing some of the major controls on benthic metabolism (a) dark ΣCO_2 flux as a function of temperature, (b) net ΣCO_2 flux as a function of water-column Chl *a* concentrations, (c) respiratory quotient (dark ΣCO_2 /dark O_2) as a function of water-column Chl *a* concentrations, and (d) ΣCO_2 p/r as a function of water-column Chl *a* concentrations.

the Brunswick Estuary is further illustrated by the strong positive correlation between water-column Chl *a* concentrations and sediment RQs ($r^2 = 0.83$; $p < 0.001$). Similar couplings of benthic and pelagic processes have been demonstrated in many shallow coastal systems (e.g., Cowan and Boynton 1996). Increasing pelagic C production results in increasing benthic C decomposition via sulfate reduction (Fig. 6c). Laboratory experiments have also demonstrated an increase in C decomposition via sulfate reduction after the deposition of algal bloom material (Hansen and Blackburn 1992). The Chl *a*/RQ relationship (Fig. 6c) suggests that above a Chl *a* concentration of $\sim 6 \mu\text{g L}^{-1}$, C deposition rates (i.e., $>2,200 \mu\text{mol } \Sigma\text{CO}_2 \text{ m}^{-2} \text{ h}^{-1}$) will exceed the capacity of the sediments in this system to decompose the C via aerobic pathways. The exception occurred during the winter 2001 phytoplankton bloom, when despite higher C deposition and decomposition rates (i.e., high Chl *a* and ΣCO_2 effluxes for the given temperature) RQs remained <1 , most likely because of low temperatures.

Net benthic metabolism and nitrogen cycling—Sediment CO_2 p/r appears to be a good indicator of the overall benthic metabolism of the Brunswick Estuary. It has an advantage over O_2 p/r, which has been used previously as a measure of benthic metabolism in shallow coastal systems (Rizzo et al. 1996; Eyre and Ferguson 2002; Ferguson et al. in press) because it is not complicated by interaction with the sulfur cycle. However, in more marine systems sediment CO_2 p/r may be complicated by the carbonate cycle (authors' unpubl. data). Similar to respiration, the sediment CO_2 p/r is strongly

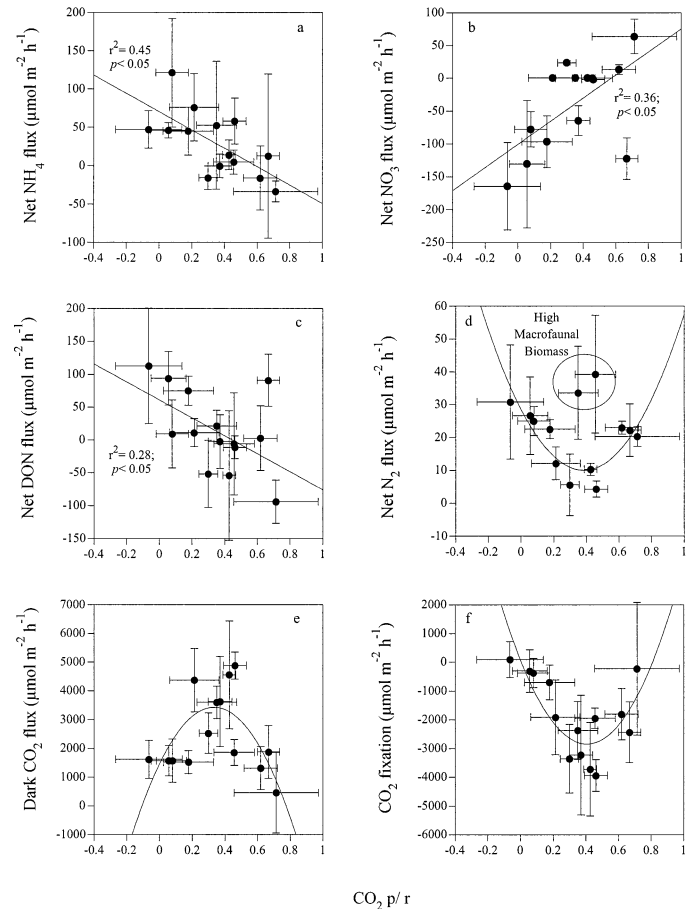


Fig. 7. Plots showing the overall control of sediment CO_2 p/r on benthic N cycling.

correlated with water-column Chl *a* concentrations ($r^2 = 0.90$; $p < 0.001$; excluding winter bloom outliers). However, the relationship is not linear, most likely because, at higher Chl *a* concentrations, apparently some of the algae remain viable once they reach the sediment surface and contribute to benthic production which increases the sediment p/r (Fig. 6d). This is consistent with one of the outliers, which has a very high p/r for the given Chl *a* concentrations, probably because the bloom occurred during winter and the settled algae contributed more to benthic productivity (highest recorded) than they did to sediment respiration rates, most likely due to the low temperatures. The other two outliers had low CO_2 p/r values for the given Chl *a*, both due to low benthic productivity. One of the outliers had the highest biomass of polychaeta, which suggests that the low productivity may be due to grazing of the benthic microalgae (BMA). It is unknown why the other outlier had low rates of benthic productivity.

Sediment CO_2 p/r also appears to be an overall control on the benthic cycling of nitrogen in the Brunswick Estuary (Fig. 7). As the sediments become more heterotrophic due to increased loadings of labile C (i.e., phytodetritus), more N is released as NH_4^+ and DON, and NO_3^- is consumed by bacteria decomposing carbon. An increase in sediment au-

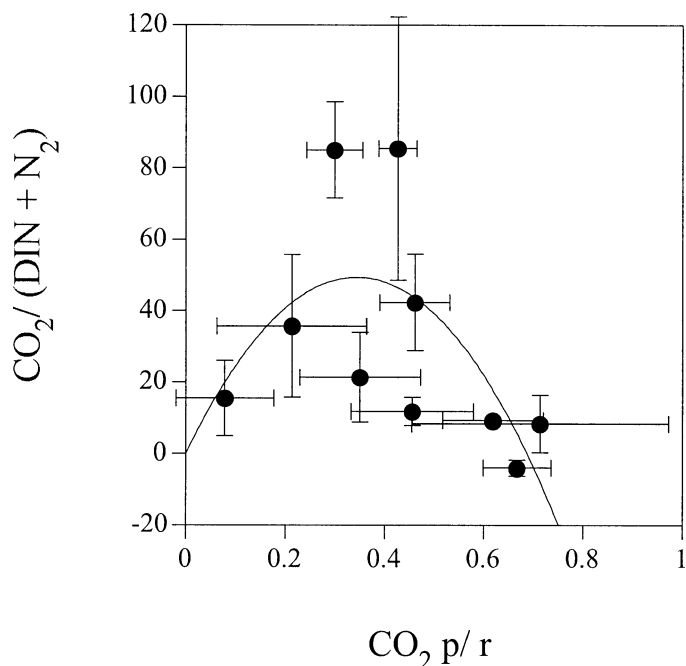


Fig. 8. Sediment ΣCO_2 p/r as a function of the remineralized C:N ratio ($\text{CO}_2/\text{DIN} + \text{N}_2$).

trophy results in an uptake of NH_4^+ and DON and a release of NO_3^- . Net N_2 effluxes are more complex because of a number of competing controls, increasing from a p/r of ~ 0.4 as the sediments become both more heterotrophic and autotrophic. They are also two distinct outliers in the net N_2 efflux p/r relationship that may be due to the overriding influence of macrofauna; these two sample runs had the highest biomass of macrofauna. The presence of macrofauna has also been shown to override the influence of BMA on NH_4^+ release from sediments (Sunback et al. 1991) and the influence of temperature on N_2 effluxes (Nowicki et al. 1997). Maximum respiration and productivity occur around a CO_2 p/r of 0.4 (Fig. 7), resulting in maximum competition for N resources among autotrophs, chemoautotrophs (e.g., nitrifiers), and heterotrophs. This competition maximum is reflected in the N fluxes, which are all near zero, and the remineralized C:N ratios, which are highest (84:1), around p/r = 0.4 (Fig. 8). The theoretical peak in competition should occur at p/r = 1, when all fixed C is respired (Ferguson et al. 2003), but it occurred at p/r = 0.4 at this site in the Brunswick Estuary, most likely because of allochthonous inputs of C from phytodetritus and terrestrial sources.

Controls on denitrification—Temporal variability in net N_2 fluxes appeared to be controlled by a complex interaction between the supply of NO_3^- to the denitrifiers from the water column and sediment nitrification, the supply and decomposition of labile C, benthic productivity, and macrofauna abundance. Water-column NO_3^- concentrations as a function of N_2 effluxes showed two distinct trends (Fig. 9a). When water-column NO_3^- concentrations were $>1 \mu\text{mol L}^{-1}$, they showed a strong positive relationship ($r^2 = 0.74$; $p < 0.001$), with net N_2 effluxes reflecting the direct uptake and denitri-

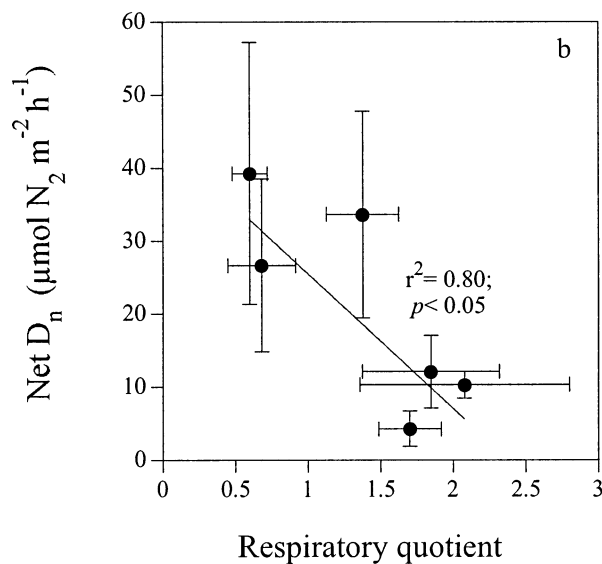
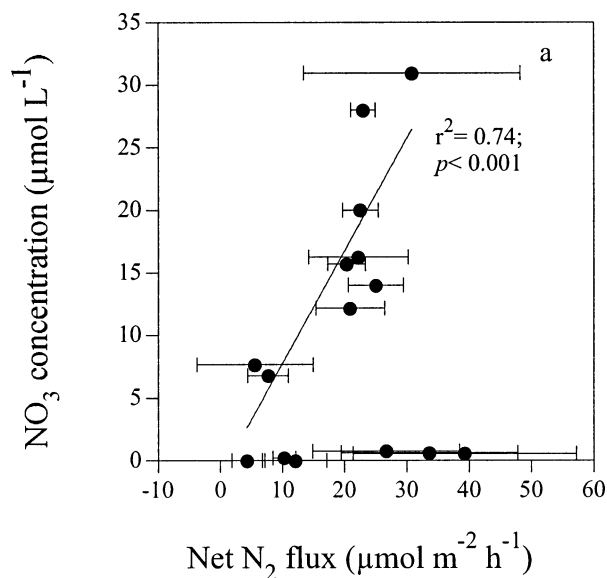


Fig. 9. Plots showing some of the major controls on benthic N cycling (a) Net N_2 efflux as a function of water-column NO_3^- concentrations and (b) RQ (dark $\Sigma\text{CO}_2/\text{dark O}_2$) as a function of net D_n .

fication of water-column NO_3^- (D_w). A number of recent studies have reported similar relationships, highlighting the importance of water-column NO_3^- concentrations in controlling N_2 effluxes (see Kana et al. 1998; Dong et al. 2000). However, dark N_2 effluxes up to $58.2 \mu\text{mol m}^{-2} \text{h}^{-1}$ (the highest recorded) were also measured when water-column NO_3^- concentrations were near zero reflecting the importance of coupled nitrification-denitrification. D_n (i.e., N_2 efflux rates when water-column NO_3^- concentrations were near zero) was negatively correlated with sediment RQs ($r^2 = 0.80$; $p < 0.05$; Fig. 9b), reflecting the control of sediment redox conditions on nitrification. Furthermore, D_n was also

strongly negatively correlated with dark alkalinity effluxes ($r^2 = 0.79$; $p < 0.05$), which are a proxy for sulfate reduction (Berelson et al. 1996, 1998); exposure to sulfides has been shown to reduce nitrification rates (Joye and Hollibaugh 1995). Alternatively, some of the N_2 may have been removed by via N fixation by sulfate reducers (Kristensen et al. 1998). In contrast to D_n , D_w was positively correlated with sediment RQs ($r^2 = 0.77$; $p < 0.05$). This may reflect a decrease in the distance between the water-column NO_3^- and the zone of denitrification at the oxic/anoxic boundary as sediments become more anoxic and/or an increase in the supply of labile C to the denitrifiers. However, there was also some covariation between sediment RQs and water-column NO_3^- concentrations.

Net N_2 effluxes were generally lower in the light than the dark. Depressed D_n values are most likely due to competition for NH_4^+ and NO_3^- by BMA (Risgaard-Petersen 2003), and depressed D_w values are most likely due to oxygen production by BMA increasing the distance between the water-column NO_3^- and the zone of denitrification at the oxic/anoxic boundary (Risgaard-Petersen et al. 1994). This is most clearly illustrated by the negative correlation between benthic CO_2 fixation and net N_2 efflux ($r^2 = 0.57$; $p < 0.01$), excluding two sampling periods with high macrofauna biomass. Although benthic production decreased net N_2 effluxes, the influence of macrofauna appears to override this control because of their stimulatory effect (Kristensen 2000). However, in January and March 2002 (summer), N_2 effluxes were stimulated in the light 1.9 and 1.5 times, respectively. Summer 2002 was characterized by low water-column NO_3^- concentrations and associated low net N_2 effluxes derived from D_n , high productivity rates, and high sediment RQs. When sediments are highly reducing (i.e., high RQs) D_n appears to be stimulated by benthic productivity because of the enhancement of nitrification. Although the sediments were also highly reducing in summer 2001 and benthic productivity was similar to 2002, a similar enhancement was not seen because net N_2 effluxes were derived from D_w (see below). Similarly, D_n was not enhanced by benthic productivity at other times of the year, presumably because of low sediment RQs, but were depressed because of competition for N substrate.

Interannual differences in net N_2 effluxes are due to differences in the factors that control water-column NO_3^- concentrations and the supply of labile carbon to the sediments (i.e., phytodetritus). Water-column NO_3^- concentrations remained elevated through much of 2001 because of freshwater inputs. As such, net N_2 effluxes during much of 2001 were directly related to water-column NO_3^- concentrations (D_w) (Fig. 9a). In contrast, during 2002, water-column NO_3^- concentrations were lower because of smaller freshwater inputs and extended flushing times and associated removal by phytoplankton, and net N_2 effluxes were mainly supported by coupled nitrification-denitrification (D_n). As such, net N_2 effluxes were lower in late summer 2002 compared with 2001, probably because of the suppression of coupled nitrification-denitrification by the more reduced sediment conditions (i.e., high RQs) associated with the high summer C loading to the sediments (phytodetritus). However, net N_2 effluxes were higher in winter 2002 com-

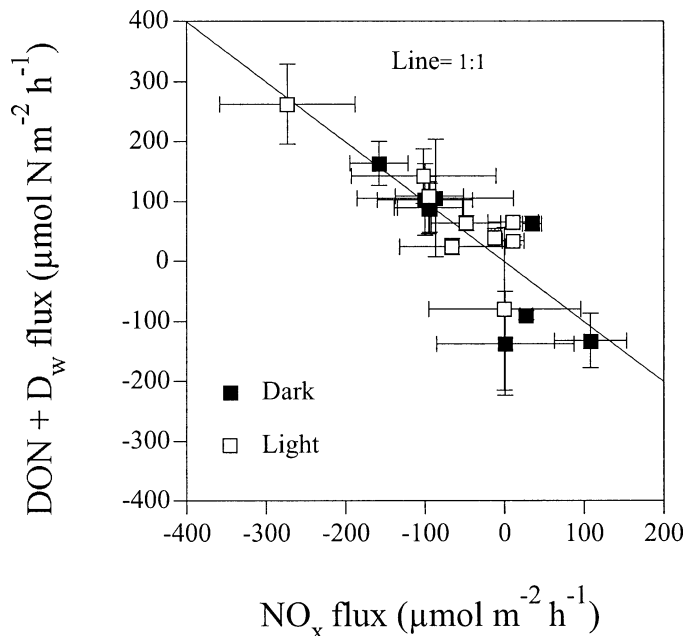


Fig. 10. NO_x flux as a function of $DON + D_w$ flux.

pared with 2001 because of high rates of coupled nitrification-denitrification probably associated with a high C loading to the sediments (phytodetritus from winter bloom) combined with oxic sediment conditions (i.e., low RQs). The lack of a consistent seasonal signal in net N_2 effluxes in the Brunswick Estuary may be typical of subtropical Australian estuaries, which are characterized by a high degree of variability in nutrient (NO_3^-) delivery and phytoplankton growth (Eyre 2000) because of their variable hydrology. This contrasts with the temperate Boston Harbor, which shows a more consistent seasonal denitrification signal (Nowicki et al. 1997).

N transformation and assimilation—Despite N_2 effluxes (i.e., D_w) being strongly related to water-column NO_3^- concentrations, the net uptake of NO_x cannot be accounted for by the net efflux of N_2 (D_w), which indicates that other processes must also be involved. NO_x can be converted to N_2O and N_2 (denitrification), NH_4^+ (dissimilatory nitrate reduction to ammonium [DNRA]), or DON. The only combination of these end products that can quantitatively account for the net uptake of NO_x is N_2 (D_w) and DON (Fig. 10). The conversion of NO_x to N_2 is easily explained via denitrification; the conversion of NO_x to DON is not so straightforward. In pelagic systems, NO_3^- uptake by phytoplankton results in the release of DON via “sloppy feeding” by zooplankton, excretion, and cell lysis (Sharp 1977), which suggests the DON efflux may be associated with the assimilation of NO_x by BMA. However, autotrophic processes are unlikely, because NO_x uptake and DON efflux increase as the sediments become more heterotrophic (Fig. 7), and the slope of the relationship between NO_x and $DON + D_w$ in the dark and light are similar, which indicates a similar causative process. If BMA were directly involved, a greater uptake in the light would

be expected. The DON efflux may be hydrolysis products of fresh phytodetritus (Burdige and Zheng 1998). Blackburn et al. (1996) suggested that the loss of DON with a low C:N from sediment may increase the C:N ratio of the remaining OM, resulting in the uptake of N by bacteria due to N limitation of the microbial decomposition. The hydrolysis of phytodetritus can still result in a DON efflux even when mineralized N is assimilated by sediment bacteria (Lomstein et al. 1998). Although this would also explain our findings, we are not completely satisfied with this explanation, because it is unclear why bacteria would allow N-rich OM to escape, resulting in N limitation and then have to uptake NO_x to overcome this N limitation. However, DON efflux and NO_x uptake only occurs when water-column NO_3^- is freely available ($>1 \mu\text{mol L}^{-1}$), probably because inorganic N is preferred by the bacteria. In contrast, when water-column NO_x concentrations are low, the sediments take up DON (as discussed above). Some of the NO_x may have been converted to NH_4^+ via DNRA, which has previously been suggested for this site (Ferguson et al. in press); $\text{N}_2 + \text{NH}_4^+$ do not quantitatively account for the uptake of NO_x , but this may be due to the assimilation of NH_4^+ by bacteria and/or N fixation, which would consume some of the N_2 (Eyre et al. 2002). Experimental work is required to further investigate the controls on NO_x uptake and a corresponding DON efflux, which have also been seen in the sediments of other subtropical systems (Cook et al. 2004b; unpubl. data).

A comparison of net ΣCO_2 fluxes (C mineralization) and net DIN + N_2 fluxes (N mineralization) shows a consistently low return of N during the study period. C:N ratios of remineralized material averaged 31:1, were as high as 84:1, and were nearly always greater than expected from the decomposition of Redfield material (6.6:1). Negative ratios were also recorded on four occasions because of the net uptake of DIN. This contrasts with many temperate systems, where remineralized C:N ratios are often lower than the sediment C:N ratio because of the preferential mineralization of N (Zimmerman and Benner 1994; Kristensen and Hansen 1999). The highest remineralized C:N ratios occur at a sediment CO_2 p/r of ~ 0.4 (excluding the winter bloom, where there was a net uptake of DIN associated with a low p/r), which corresponds to maximum respiration and maximum productivity rates (see Figs. 7, 8). This suggests that there may be two controls, one heterotrophic and one autotrophic, competing for N and resulting in the high remineralized C:N ratios. N limitation of the microbial decomposition of OM results in the uptake and accumulation of N by bacteria (Tupas and Koike 1991; van Duyl et al. 1993; Lomstein et al. 1998). Several types of bacteria can assimilate NH_4^+ , including sulfate reducers and fermentative bacteria (Koike and Sumi 1989). Consistent with sulfate reducers as the likely bacteria assimilating N was the positive linear relationship between remineralized C:N ratios and nutrient-corrected dark alkalinity fluxes ($r^2 = 0.67$; $p < 0.001$). The highest remineralized C:N ratios also tended to occur when water-column DIN concentrations were lowest, reflecting N limitation. There was a strong negative relationship between net DON fluxes and the C:N ratio of remineralized material ($r^2 = 0.85$; $p < 0.001$), with DON effluxes decreas-

ing and progressing to an uptake as the remineralized C:N ratio increased. Heterotrophic marine bacteria have been shown to assimilate urea (Jahns 1992), and marine microbial mats have been shown to assimilate DON (Paerl et al. 1993; Rondell et al. 2000). This suggests that the DON may be utilized by bacteria under N-limited conditions and the associated DOC may be an additional source of labile C for benthic metabolism.

The combination of a net uptake of DIN on some occasions and the highest remineralized C:N ratios corresponding to maximum benthic productivity suggests that some of the missing nitrogen may also have been assimilated by BMA. Furthermore, extracellular organic carbon (EOC) with a high C:N extruded by BMA and subsequently decomposed may also account for the high remineralized C:N ratios (Cook et al. 2004a,c, unpubl. data). Up to 73% of the total primary production (TPP) of BMA can consist of EOC (Goto et al. 1999), and the EOC:TPP ratio is likely to be highest at times of nutrient limitation (Staats et al. 2000; Engel et al. 2002). These exudates decouple the C and N cycles and, as such, act as a "carbon sink" and probably provide a mechanism for BMA to conserve N under conditions of N limitation. Phytoplankton have a higher percentage release of EOC in tropical systems than in temperate systems (Gomes et al. 1991), which suggests release of EOC from BMA, and subsequent decomposition by sediment heterotrophs may also be more important in benthic tropical systems than benthic temperate systems.

Immobilization and transfer of N—A considerable amount of N appears to have been immobilized in BMA and bacterial biomass. BMA production:biomass ratios (P:B) show that BMA biomass was turned over up to >8 times d^{-1} (average, 2 times d^{-1}) over the 2-yr study period, most likely because of grazing by macrofauna. This is consistent with the weak correlation ($r^2 = 0.46$; $p < 0.05$) between macrofaunal biomass and P:B, which is reasonable, considering that macrofaunal biomass at this site is more likely controlled by the supply of phytodetritus and not BMA production. The macrofaunal biomass was better correlated with water-column Chl *a* from the previous sample run ($r^2 = 0.55$; $p < 0.01$) than the corresponding sample run ($r^2 = 0.38$; $p < 0.05$), indicating that it takes some time for the macrofaunal biomass to build up after the supply of a new food source. This was most clearly illustrated after the winter phytoplankton bloom in June 2002, when the highest Chl *a* concentrations during the 2-yr study were recorded ($125 \mu\text{g L}^{-1}$) and the highest macrofaunal biomass (17.4 g m^{-2}) was recorded 1 month later. Most of the available food in marine sediments is consumed by micro- and meiofauna, which are then grazed by macrofauna (Kemp and Boynton 1981; Heip et al. 1995). Bacterial biomass is also likely to have been turned over rapidly and stimulated ("microbial gardening") in the presence of high meiofaunal grazing pressure (Kemp and Boynton 1981; Montagna 1984) removing N from the microbial loop and passing it up to metazoan levels of the food chain (Ferguson et al. in press).

The pathways of N transfer following C decomposition during the study period are shown in Table 2. The pathways considered (benthic fluxes, BMA, and macrofauna

Table 2. Pathways of nitrogen transformation during the 2-yr study period. BMA and macrofaunal assimilation and net N₂ efflux pathways are expressed as a percentage of the total available dissolved nitrogen (N mineralization – TDN flux). All pathways are given as $\mu\text{mol N m}^{-2} \text{d}^{-1}$.

Sample period	DIN mineralization*	TDN flux†	DIN mineralization TDN flux	BMA assimilation‡ (%)	Macrofaunal assimilation§ (%)	Net N ₂ efflux (%)
Dec 2000	13,021	-1,593	14,614	5,102 (35)	NA	NA
Jan 2001	6,528	4,788	1,741	2,461 (141)	NA	369 (21)
Feb 2001	8,521	1,265	7,256	3,842 (53)	NA	1,002 (14)
May 2001	4,733	0	4,733	2,866 (61)	NA	1,103 (23)
Jul 2001	3,842¶	-1,092	4,933	2,717 (55)	969 (20)	267 (5)
Aug 2001	1,662	-1,580	3,242	382 (12)	2,832 (87)	974 (30)
Sep 2001	6,747	534	7,280	4,430 (61)	19,687 (270)	1,066 (15)
Oct 2001	5,658	1,188	4,470	533 (12)	6,566 (147)	1,201 (27)
Dec 2001	5,692¶	1,774	3,918	4,551 (116)	-6,916 (-177)	1,614 (41)
Jan 2002	17,512	1,083	16,429	8,040 (49)	9,823 (60)	206 (1)
Mar 2002	8,970¶	2,109	6,861	3,254 (47)	7,353 (-107)	581 (8)
Apr 2002	2,108¶	-221	2,328	0 (0)	-417 (-18)	1,479 (64)
May 2002	5,489	459	5,030	1,099 (22)	3,684 (73)	1,082 (21)
Jun 2002	6,690	-24	6,713	2,934 (44)	3,137 (47)	1,885 (28)
Jul 2002	5,656	119	5,537	492 (9)	24,419 (441)	1,280 (23)
Dec 2002	5,927¶	-947	6,874	7,019 (102)	-2,051 (-30)	495 (7)

* Dark hourly ΣCO_2 flux $\times 24 \times 16/106$.

† Net daily DIN + DON flux.

‡ Net hourly ΣCO_2 fixation $\times \text{h of light} \times 16/106$.

§ Average daily change in macrofaunal biomass from last sample period/C:N of 10:1.

|| Dark hourly O₂ flux $\times 24 \times 16/106$.

¶ Dark hourly ΣCO_2 flux/sediment C:N $\times 24$.

assimilation and denitrification) provide a reasonable mass balance of the remineralized N (excluding three outliers; Fig. 11) considering that there was some “double accounting” (i.e., some of the BMA biomass will have counted toward the macrofauna biomass via grazing) and the errors

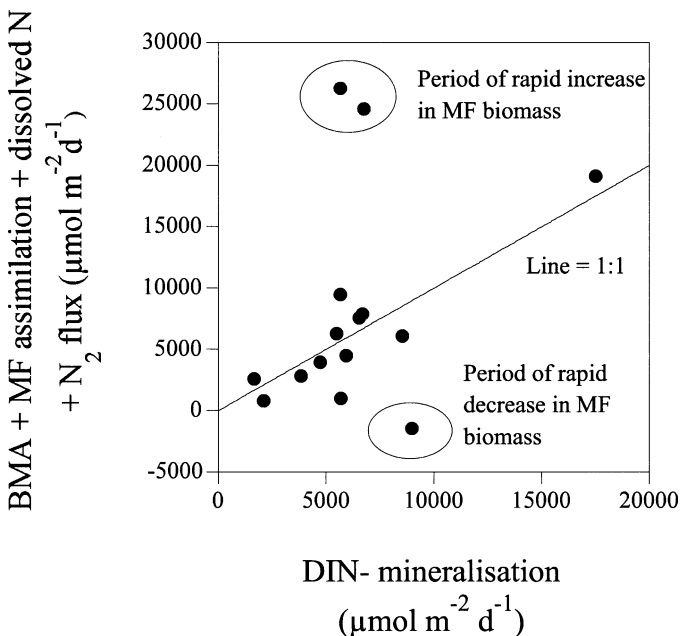


Fig. 11. N mineralization calculated from ΣCO_2 respiration as a function of BMA and macrofauna (MF) assimilation plus measured dissolved N and N₂ fluxes.

involved in such calculations. However, rather than providing a tightly constrained N budget, Table 2 is more intended to simply show the relative magnitude of the most important N pathways. All three of the outliers followed large increases or decreases in macrofaunal biomass, suggesting that our monthly to bimonthly samplings may have missed N losses and uptakes associated with these rapid changes. Mineralized N was calculated using the sediment C:N ratio (data not shown) and not the C:N for phytodetritus for five sample periods because it provided a better mass balance for N (Fig. 11). This was considered to be appropriate because all five periods had decreasing macrofaunal biomass, suggesting a diminishing food source (i.e., degraded phytodetritus). Assimilation into the macrofaunal biomass was the largest N sink for most of the sampling periods. BMA uptake was the largest sink of N when the macrofauna biomass was decreasing. However, assimilation into BMA and macrofauna (via bacteria and meiofauna) biomass is only a transient storage of N, because there is no long-term build up of biomass. The assimilated N must be either passed up to higher trophic levels of the food chain, which is unlikely to be 100% efficient, so there must also be large periodic releases of N from the sediments as the biomass decomposes (missed by our monthly sampling), or some of the N must be buried (Eyre and Ferguson 2002; Ferguson et al. in press). The low remineralized C:N ratio of 5.1 in May 2001 may represent one of these periodic releases of N as bacterial biomass decomposes. About 22% of the remineralized N is permanently removed via denitrification. Assimilation by heterotrophs and autotrophs and the

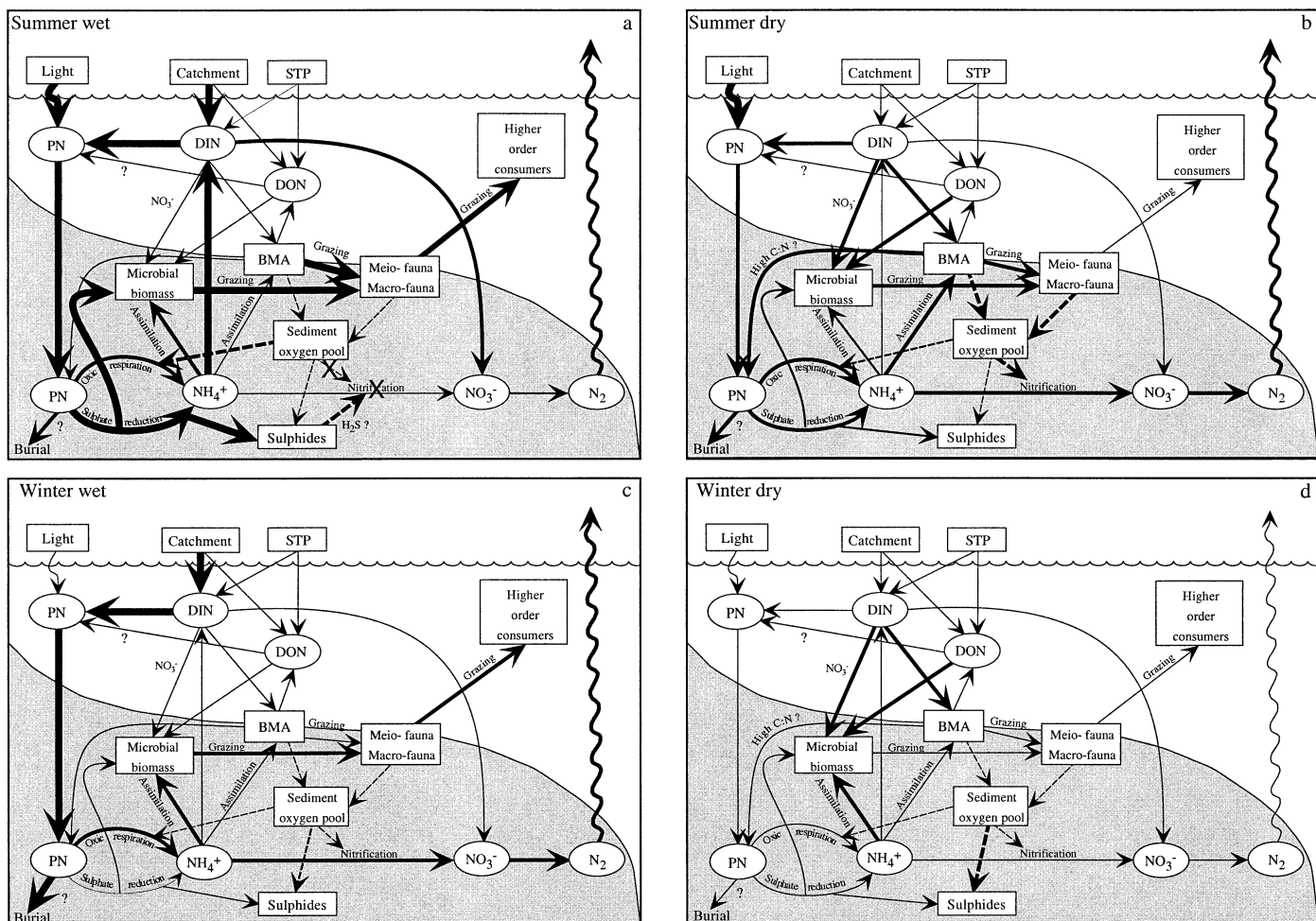


Fig. 12. Conceptual models of N cycling in the subtropical upper Brunswick Estuary during (a) a wet summer, (b) a dry summer, (c) a wet winter, and (d) a dry winter. Ovals represent N pools. Boxes and dashed lines represent controlling factors. The line thickness represents the relative importance of the various N-cycling pathways.

associated flow of N up the food chain results in little N being returned to the water column via dissolved effluxes and little N being available for denitrification. This active competition for limited N resources in the sediments appears to be a mechanism by which N-limited oligotrophic subtropical estuaries (Eyre 2000) tightly recycle and efficiently conserve N. “Missing N” has also been reported in sediments from a number of shallow arctic, temperate, and tropical coastal systems (Blackburn et al. 1996; Lomstein et al. 1998; Rysgaard et al. 1998; Anderson et al. 2003), but removal up to the metazoan food chain was not quantified, which suggests that this pathway of N removal may not just be restricted to subtropical estuaries.

Conceptual model and synthesis—The major pathways of N transfer and transformation and the factors controlling these transfers and transformations in the upper Brunswick Estuary are summarized in Fig. 12. This conceptual model builds on a previous model of nutrient cycling in the Brunswick Estuary (Ferguson et al. 2004) by capturing the extremes of the important drivers and providing more detail

on the benthic system. N cycling is primarily driven by episodic inputs of N from the catchment and the supply of labile C to the sediments (phytodetritus), which in turn is driven by light, temperature, and N supply. The four model scenarios represent conditions under which the extremes of these drivers, in combination, occur: summer wet reflects high light, temperature, and N supply (Fig. 12a); summer dry reflects high light and temperature but low N supply (Fig. 12b); winter wet reflects low light and temperature but high N supply (Fig. 12c); and winter dry reflects low light, temperature, and N supply (Fig. 12d). Scenarios a and c are equivalent to the enhanced recycling-recovery scenario of Ferguson et al. (2004) that occurs after high flow events. However, they separate out the extremes of the different N-cycling pathways after runoff events by including summer and winter. Scenarios b and d are equivalent to the tight recycling-low flow scenario of Ferguson et al. (2004) but also separate out the extremes of the different N-cycling pathways during low flow periods by including summer and winter.

Summer wet—Diffuse catchment runoff stimulates phytoplankton production and the delivery of labile C to the sediments (phytodetritus). The capacity of the sediments to decompose this labile C via oxic respiration is exceeded, and much of the C is processed via sulfate reduction under anoxic conditions. The release of NH_4^+ from the sediments to the water column is enhanced further stimulating phytoplankton production. Some of the remineralized NH_4^+ is also assimilated into the microbial biomass. The sediment oxygen pool is reduced because of high rates of C decomposition inhibiting coupled nitrification-denitrification. Hydrogen sulfide from sulfate reduction may also contribute to the decline in coupled nitrification-denitrification. The oxic/anoxic interface moves closer to the sediment surface under anoxic conditions, increasing D_w because of a decrease in the length of diffusion path for water-column NO_3^- . Meio- and macrofaunal biomass increases due to the increased supply of labile C, and the enhanced grazing of microbial and BMA biomass results in N being passed up the food chain.

Summer dry—The system is N limited because of the lack of diffuse catchment inputs. Phytoplankton production becomes N limited, resulting in less labile C being delivered to the sediments. With less labile C decomposing, there is a larger sediment oxygen pool available to stimulate coupled nitrification-denitrification. BMA production also contributes to the sediment oxygen pool and enhances coupled nitrification-denitrification. Most of the remineralized NH_4^+ is assimilated mostly into BMA biomass, resulting in little NH_4^+ being released from the sediments. DIN and DON from the water column are also assimilated into the BMA biomass. Grazing of BMA biomass results in some N being passed up the food chain; however, macrofauna may become food limited because of the lack of C supply. Under the N-limited conditions of this scenario, N is very tightly cycled and conserved within the sediments.

Winter wet—Despite less light and lower temperatures, phytoplankton production is still stimulated by diffuse N inputs increasing the delivery of labile C to the sediments (phytodetritus). However, in contrast to summer, when the sulfate reduction is important, most of this labile C is decomposed via oxic respiration, probably because of the lower temperatures. As such, there is sufficient sediment oxygen available to stimulate coupled nitrification-denitrification. Most of the remineralized NH_4^+ is assimilated into the microbial biomass. Meio- and macrofaunal biomass increases dramatically because of the increased supply of labile C, and the enhanced grazing of microbial biomass results in most of the remineralized N being passed up the food chain.

Winter dry—Under the nitrogen limited conditions of this scenario, N is very tightly cycled and conserved within the sediments.

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