Comparison of carbon production and decomposition, benthic nutrient fluxes and denitrification in seagrass, phytoplankton, benthic microalgae- and macroalgae-dominated warm-temperate Australian lagoons

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ABSTRACT: The influence of marine plants representing different stages of eutrophication on carbon decomposition and production, benthic nutrient fluxes and denitrification was examined in 4 shallow warm-temperate Australian lagoons. Differences in carbon production and decomposition across the lagoons were the main regulators of the quantity and quality of benthic nutrient fluxes and the relative proportion of nitrogen lost through denitrification. For example, the efficiency with which the lagoon sediments recycled nitrogen as N_2, (i.e. denitrification efficiency: $N_2\text{-N}/(N_2\text{-N} + DIN)$), decreased as carbon decomposition rates increased. C:N ratios of the remineralised organic matter in some of the plant-sediment systems were much higher than expected from the stoichiometry of the dominant carbon supply. Dark DON fluxes were also very high in all the plant-sediment systems (30 to 80 % of the total nitrogen flux). We offer 2 alternative explanations for the observed sediment and benthic flux characteristics: (1) The low dark C:N ratios of the remineralised organic matter may have been due to dark uptake by benthic microalgae and possibly other plants. The large DON effluxes were either the hydrolysis product of freshly produced *in situ* organic material or/and associated with the grazing of benthic microalgae. This explanation has important implications regarding the importance of benthic microalage as a sink for nitrogen. (2) Alternatively, the high C:N ratios of the remineralised organic matter may have been directly related to the large dissolved organic nitrogen (DON) effluxes; large DON effluxes with a low C:N ratio increase the C:N ratio of organic matter in the surface sediments, which in turn causes an uptake and accumulation of nitrogen by bacteria due to N-limitation of the microbial decomposition. Production by all the plant groups had a significant influence on benthic nutrient fluxes, with a typical pattern of an efflux during the dark cycle and an uptake during the light cycle. As such, the sediment productivity/respiration (*p/r*) ratio was one of the major controls on (best indicators of) net benthic inorganic and organic nutrient fluxes and appears to be one of the key changes which occur in shallow coastal lagoons as these become eutrophic. This has important management implications, demonstrating the need to maintain the balance of benthic autotrophy and heterotrophy. The robustness of the denitrification efficiency and sediment *p/r* relationships across such a diverse range of plant-sediment systems that represent the different stages of eutrophication suggests that these may be useful in synthesising denitrification and benthic flux data across shallow coastal systems and in defining suitable carbon loading rates.

KEY WORDS: Coastal lagoon · Production · Decomposition · Benthic fluxes · Denitrification · Eutrophication

INTRODUCTION

Shallow coastal lagoons are particularly susceptible to nutrient enrichment because of limited tidal and freshwater flushing. General conceptual models have been proposed that show the typical lagoon response to nutrient enrichment as a sequential change in the dominant primary producers (Nienhuis 1992, Castel et

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al. 1996, Raffaelli et al. 1998). Benthic primary producers such as seagrasses and benthic microalgae decrease, epiphytes build up and are in turn replaced by pelagic primary producers such as phytoplankton and fast-growing floating macroalgae. Accompanying and enhancing these shifts in the primary producers are changes in benthic metabolism, benthic nitrogen fluxes and sediment denitrification. For example, lagoons dominated by phytoplankton and macroalage often show large diurnal changes in oxygen concentrations associated with high sediment production and respiration rates (Sand-Jensen & Borum 1991, Viaroli et al. 1995). These rapid changes in benthic metabolism are enhanced by the composition of the primary producers. Fast-growing plants such as macroalgae and phytoplankton decompose more quickly due to their high nutrient and low fibre content and low N:C and P:C ratios (Enriquez et al. 1993). The deposition and decomposition of this labile carbon may lead to the temporary disappearance of dissolved oxygen from the water column, resulting in benthic effluxes of free-sulphide known as 'dystrophic crises' (Pugnetti et al. 1992, Viaroli et al. 1996).

Changes in the dominant primary producers associated with nutrient enrichment also modify the chemical and physical conditions of the surface sediments, leading to changes in nitrogen and phosphorus cycling. Seagrasses and other rooted plants and benthic microalgae oxygenate the upper sediment layers, which may enhance coupled nitrification-denitrification (Caffrey & Kemp 1990, Christensen et al. 1990, Risgaard-Petersen & Jensen 1997, although this effect in seagrasses has recently been questioned by Ottosen et al. 1999) and trap phosphorus in oxidised iron compounds (Graneli & Sundback 1985, Carlton & Wetzel 1988). Rooted plants may also indirectly enhance denitrification by the release of dissolved organic carbon

through their roots and by the trapping of particulate carbon in their above-ground biomass (Christensen & Sørensen 1986, Hemminga et al. 1991). Benthic nutrient fluxes are typically low, due to the low nitrogen and phosphorus content of the decomposing organic matter and efficient recycling within the plant-sediment system (Hansen et al. 2000). In contrast, macroalgae can reduce denitrification by physically separating the denitrifiers from water-column nitrate, by efficient assimilation of water-column nitrate, and by suppression of nitrification through anoxia below the algal mats (Krause-Jensen et al. 1999). Deposition of large quantities of phytoplankton detritus may also result in sediment anoxia. A combination of reduced denitrification and decomposition of large quantities of organic matter enhances benthic ammonium fluxes and anoxia releases phosphorus from oxidised iron compounds (Owens & Stewart 1983, Sfriso et al. 1987, Lavery & McComb 1991). Increased benthic nitrogen and phosphorus fluxes in turn stimulate further primary production in the lagoon (Sfriso et al. 1987).

Information on how changes in benthic metabolism, benthic nutrient fluxes and sediment denitrification accompany and enhance shifts in the primary producers is important for understanding how shallow coastal lagoons respond to nutrient enrichment. There have been a number of field and laboratory studies that have examined the effect of production and decomposition of individual plant-sediment systems representing different stages of eutrophication on benthic nutrient fluxes and denitrification, including seagrasses (Jørgensen et al. 1981, Johnson & Johnstone 1995, Risgaard-Petersen et al. 1998, Pedersen et al. 1999, Hansen et al. 2000), benthic microalgae (Christensen et al. 1990, Enoksson 1993, Risgaard-Petersen et al. 1994), and macroalgae (Owens & Stewart 1983, Hansen & Blackburn 1991, Lavery & McComb 1991,
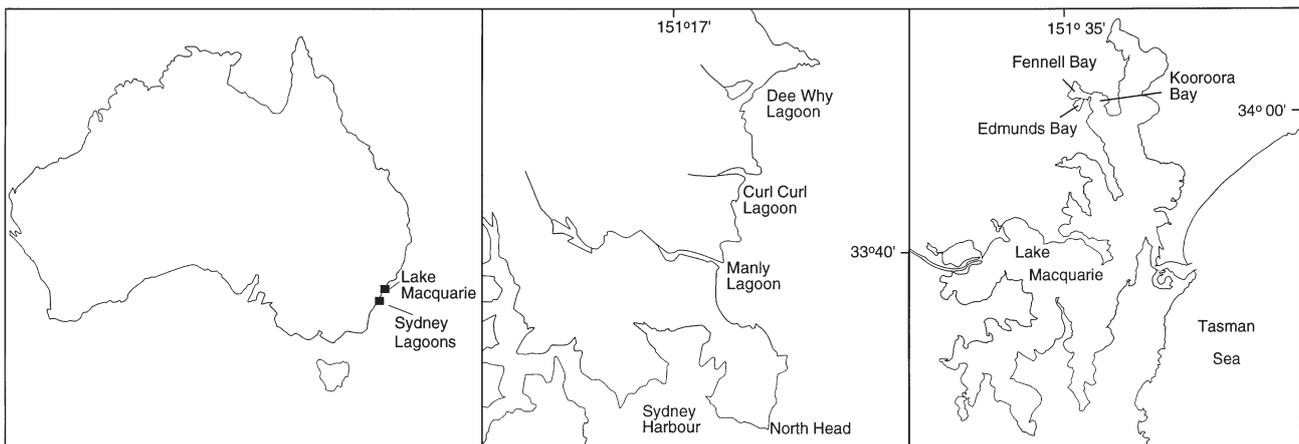

Fig. 1. Locations of study sites

McGlathery et al. 1997). However, to our knowledge, there have been relatively few comparative sediment biogeochemical studies of shallow coastal lagoons at different stages of eutrophication (i.e. different dominant primary producers), and these few studies have all been restricted in the parameters they have examined, and all are for the one geographical region. Rysgaard et al. (1996) compared nitrification, denitrification and nitrate ammonification processes in 2 coastal lagoons of southern France: a less eutrophic area of Bassin d'Arcachon dominated by seagrasses *Zostera noltii* and the more eutrophic Etang du Prevost characterised by floating macroalgae *Ulva rigida*. In a separate study Viaroli et al. (1996) compared benthic fluxes of oxygen, sulphide, nitrogen and phosphorus, also in the Etang du Prevost and a seagrass area of the Bassin d'Arcachon, but included a third environment, the fishponds of Certes (Bassin d'Arcachon) covered by macroalgae *Ruppia cirrhosa*. Finally, Bartoli et al. (1996) compared benthic oxygen respiration and fluxes of ammonium and phosphorus in seagrass and macroalgal areas of the Bassin d'Arachon, Etang du Prevost and the coastal lagoon Sacca di Goro (Italy).

This study was undertaken to evaluate the influence of different primary producers on carbon decomposition and production, benthic nutrient fluxes and sediment denitrification. We measured benthic metabolism using both oxygen and carbon dioxide fluxes, denitrification using direct N_2 fluxes, and benthic fluxes of alkalinity and organic and inorganic forms of nitrogen and phosphorus in 4 shallow warm-temperate Australian lagoons: Manly Lagoon, where primary production is dominated by benthic and pelagic microalgae; Curl Curl Lagoon, which is periodically covered with the green macroalgae *Enteromorpha* sp.; Dee Why Lagoon, which is covered with the red macroalgae *Gracilaria* sp.; and 3 bays in Lake Macquarie which have extensive *Zostera capricorni* seagrass beds, with and without epiphytes. These lagoons/bays represent the different stages of eutrophication (Nienhuis 1992), and we expected that associated differences in carbon production and decomposition would control the relative proportion of nitrogen lost through denitrification and regulate benthic nutrient fluxes.

MATERIALS AND METHODS

Study area. Manly, Curl Curl and Dee Why lagoons are on the northern shore of the Sydney metropolitan region (Fig. 1) on the east coast of Australia. Lake Macquarie is also on the east coast of Australia, about 100 km north of Sydney. Manly, Curl Curl and Dee Why lagoons are shallow barrier-built estuaries, and in their natural state would be closed to the sea for most of the year, only opening during floods. All 3 lagoons are heavily disturbed and receive runoff from urban and industrial areas. The physical and chemical characteristics of each lagoon/bay are summarised in Table 1. Manly Lagoon has minor seagrass beds, no macroalgae and little riparian vegetation and in the deeper areas on the lagoon the sediments are covered with a layer of phytodetritus several centimetres thick, suggesting that primary production is dominated by phytoplankton. NH_4 and NO_3 concentrations in the water column of Manly Lagoon are elevated, and dissolved oxygen concentrations are under-saturated. Curl Curl Lagoon is periodically covered with a 10 cm-thick layer of the green macroalgae *Enteromorpha* sp., which results in high productivity and super-saturated dissolved oxygen concentrations in the water column. Curl Curl lagoon has the highest water column NH_4 and NO_3 concentrations of all the systems studied. Dee Why Lagoon is covered with the red macroalgae

Table 1. Physical and chemical characteristics of the Manly, Curl and Dee Why lagoons and Fennell, Edmunds and Kooroora bays

Characteristic during sampling period	Manly Lagoon	Curl Curl Lagoon	Dee Why Lagoon	Fennell Bay	Edmunds Bay	Kooroora Bay
Open water area (km^2)	0.09	0.06	0.24	1.04	0.63	0.23
Seagrass (% coverage)	<5%	0	15%	95%	30%	30%
Macroalgae (% coverage)	0	100%	85%	5%	5%	0
Average depth (m)	1.0–2.0	0.5	1.0–2.0	0.5	1.0–3.0	1.0–4.0
Salinity	35.5	17.6	8.3	41.4	38.6	42.0
Temperature (°C)	25.9	24.7	24.7	26.1	26.1	25.9
Dissolved O$_2$ (μM) (% saturation)	160.4(77)	330.1(141)	264.4(107)	176.5(88)	166.7(82)	158.4(79)
NH$_4$ (μM)	2.25	6.17	0.39	0.60	0.75	0.70
NO$_3$ (μM)	7.27	10.26	0.26	0.43	0.66	0.28
DON (μM)	13.84	32.64	27.82	11.23	33.82	7.22
DIP (μM)	0.23	0.24	0.15	0.19	0.43	0.53

Gracilaria sp., and has the lowest NH_4, NO_3 and DIP concentrations of all the systems studied. The mouths of all 3 lagoons are unvegetated sand, except for a cover of benthic microalgae. In Lake Macquarie, sampling was undertaken in Edmunds, Fennell and Kooroora bays in the north-west corner of the lake (Fig. 1). Edmunds Bay is very shallow (typically <0.5 m), and has extensive *Zostera capricorni* seagrass beds with a thick coating of epiphytes, and some macro-algae, that cover most of the bottom sediments in the bay. Fennell Bay is deeper (about 0.5 to 2.0 m) and has extensive *Z. capricorni* seagrasses beds, also with a thick coating of epiphytes, and some macroalgae in the shallow water around its perimeter. Kooroora Bay is the deepest of the 3 bays (up to 4 m), and has extensive *Z. capricorni* seagrass in the shallower water around its perimeter. Water quality in all 3 bays is similar, with NH_4 and NO_3 concentrations falling between the elevated concentrations in Manly and Curl Curl lagoons and the low concentrations in Dee Why Lagoon.

Sampling and core incubations. Six sediment-plant types (*Enteromorpha* sp. [E], phytoplankton detritus [P], seagrass + epiphytes [SE], seagrass [S], *Gracilaria* sp. [G], benthic microalgae [B]) reflecting the different stages of eutrophication were sampled in late summer (February) to represent the stationary phase (Malta 2000) when both active production and decomposition were occurring. Fluxes of ΣCO_2, O_2, DON, NH_4, NO_3, DOP, DIP and alkalinity between the sediment and overlying water column were measured using undisturbed cores collected in 95 (diam.) × 500 mm (length) clear acrylic pipe. Triplicate cores were collected for each sediment-plant type, including the plants, but the spacing between cores varied. In Manly (P), Curl Curl (E) and Dee Why (G) lagoons, the triplicate cores were separated by about 100 m. Three sets (separated by about 100 m) of triplicate cores separated by <1 m were collected from Edmunds and Fennell Bays (SE). One set of triplicate cores separated by <1 m was collected in Kooroora Bay (S). One core from sandy sediments at the mouths of each of the Manly, Curl Curl and Dee Why lagoons were pooled to give a triplicate of the benthic microalgae sediment (B).

The core was inserted into the sediment so as to retain about 1000 ml of water overlying the sediment, and a gas-tight (on the time scale of the incubations) Plexiglas plate was placed on the bottom of the core. A 40 l sample of water was also collected from each lagoon and bay, and physico-chemical parameters (dissolved oxygen, salinity, temperature) were measured at each sample site using an Horibia U-10 multi-probe. Incident radiation (2 pi) was measured at the top and bottom of the water column at each of the sample sites using a Li-Cor 250 light meter to determine light attenuation.

After collection, the cores were drained and replaced with water from each site that had been passed through a 60 µm mesh. The water was passed through the 60 µm mesh to homogenise the replacement water, as we had previously noted that the presence of 1 or 2 large zooplankters in 1 or 2 of the cores can significantly increase the variability in fluxes between triplicates. The cores were then individually shaded to mimic *in situ* light conditions (±5.0%) using shade cloth, placed in a floating cradle in the estuary, and equilibrated at *in situ* light (±5.0%) and temperature (±2°C) conditions for approximately 24 h. Immediately before the beginning of the flux experiments, the water overlying the sediment cores was again replaced with water from each site that had been passed through 60 µm mesh. The cores were then sealed gas-tight by a top Plexiglas plate that had a sample port and a Teflon stir bar mounted on its underside. The cores were incubated over a 24 h dark/ light cycle in *in situ* light (±5.0%) and temperature (±2°C) conditions. To avoid bubble formation during the light cycle the O_2 gas pressure in the water column was lowered by consistently running the dark incubation before the light incubation. Each core was stirred at a rate just below the threshold for sediment resuspension. This was considered the most appropriated stirring rate, as bottom sediments in these lagoons/bays were observed to be regularly resuspended by wind waves and currents. Dissolved oxygen concentrations (±0.01 mg l^{-1}) and pH (±0.001 pH units) were measured using an electrode, and alkalinity, nutrient and N_2 samples were collected every 4 to 6 h. 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-fed reservoir of 60 µm mesh-filtered lagoon/bay water. To minimise the introduction of bubbles, N_2 samples were collected by allowing water to flow (driven by the reservoir head) directly into 7 ml gas-tight glass vials with glass stoppers, which were filled to overflowing. All nutrient samples were immediately frozen at –20°C, except the alkalinity samples which were keep cold at 4°C. N_2 samples were poisoned with 20 µl of 5% $HgCl_2$ and stored submerged at ambient temperature. Three extra cores (blanks) from Edmunds, Fennell and Kooroora bays, and 1 extra core (blank) from Manly, Curl Curl and Dee Why lagoons with only filtered water (60 µm mesh) were pre-incubated, incubated and sampled as above.

The top 2 cm of each sediment core, including large pieces of organic detritus, was sampled for total organic carbon, total nitrogen and total phosphorus analysis, and the top 2 mm of each sample core, excluding large pieces of organic detritus, was sampled for

Table 2. Analytical procedures, nutrient forms, abbreviations, detection limits, and analytical errors

Parameter	Abbreviation	Method	Detection limit	Error (%)	Source
Total dissolved phosphorus	TDP	Persulfate digestion	0.16 µM	3.5	Valderrama (1981)
Dissolved inorganic phosphorus	DIP	Ascorbic acid	0.03 µM	2.3	Lachat (1994)
Dissolved organic phosphorus	DOP	TDP–DIP		5.1	
Total dissolved nitrogen	TDN	Persulfate digestion	0.7 µM	4.1	Valderrama (1981)
Dissolved organic nitrogen	DON	TDN–(NO_2 + NO_3 + NH_4)		19.6	
Nitrite	NO_2	Sulphanilamide	0.07 µM	2.8	Lachat (1994)
Nitrate	NO_3	Cadmium reduction	0.07 µM	3.6	Lachat (1994)
Ammonium	NH_4	Hypochlorite/phenolate	0.35 µM	5.1	Lachat (1994)
Dissolved inorganic nitrogen	DIN	NO_2 + NO_3 + NH_4		7.2	
Dissolved nitrogen gas	N_2	Membrane inlet mass spectrometry	–	0.05	Modified from Kana et al. (1994); see Eyre et al. (in press)
Alkalinity	Alkalinity	Gran titration	–	1.0	Grasshoff et al. (1983)
Carbon dioxide	ΣCO_2	Alkalinity and pH (±0.001)	–	–	Grasshoff et al. (1983)
Chl a (sediment)	–	90% acetone extraction	0.1 µg l^{-1}	4.1	Strickland & Parsons (1972)
Total organic carbon (sediment)	TOC	High temperature combustion	–	–	LECO (1996)
Total nitrogen (sediment)	TN	High temperature combustion	–	–	LECO (1996)
Total phosphorus (sediment)	TP	550°C combustion /HCl extraction	–	–	Eyre (1993)

chlorophyll a (chl a) analysis. The sediment samples were placed in a 30 ml polyethylene vials, and these were immediately frozen at –20°C. The chl a samples were immediately extracted with 90% acetone in 10 ml polyethylene vials, wrapped in aluminum foil, and kept cold at 10°C.

Analytical techniques. Analytical procedures, abbreviations, and analytical errors are summarised in Table 2. All nutrient analyses were carried out colourmetrically using Lachat^{TM} flow-injection analysis. Analytical errors were determined as the average %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 2 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.

Denitrification. Denitrification was estimated by directly measuring N_2 fluxes obtained from N_2:Ar ratios using the method and instrumentation of Kana et al. (1994) with the following modifications. Gases were detected with a Balzers QMS422 quadrupole mass spectrometer, and a water bath (±0.01°C) was used to stabilise sample temperature in the waterline upstream of the membrane. Both these modifications improved stability of the mass signal and precision of the measured N_2:Ar ratios (up to %CV <0.01). With this improved precision we observed that the O_2 concentration of the sample significantly effected the mea-

sured N_2:Ar ratios; an effect that was not seen by Kana et al. Measured NO concentrations also increase with increasing O_2 concentrations most probably due to O_2 combining with the sample N_2 within the mass spectrometer to form NO (Jensen et al. 1996), thus decreasing the N_2 signal and decreasing the N_2:Ar ratio. This effect was corrected by making a standard curve of O_2 concentration (0 to 100% saturation) against N_2:Ar ratios using a water standard made from the incubation water equilibrated at constant temperature. All N_2:Ar ratios were then corrected back to the O_2 concentration at the start of the incubation so that N_2 concentrations were comparable over the course of the benthic flux incubation. The use of an O_2 correction curve to correct N_2:Ar ratios increases the variability between replicates and may under- or overestimate actual rates due to a lower precision in the N_2/Ar analysis and the propagation of errors (Eyre et al. in press).

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. Net flux rates are the average of the dark and light flux rates. Benthic production was calculated as:

Benthic oxygen production (positive, efflux) =
  light O_2 flux (positive) – dark O_2 flux (negative)

Benthic carbon production (negative, uptake) =
  light ΣCO_2 flux (negative) – dark ΣCO_2 flux (positive)

Productivity/respiration (*p/r*) ratio = (hourly productivity
  × daylight period)/(hourly respiration × 24 h)

The errors associated with the calculated flux rates are due to the analytical precision of the measured concentration data and the fit of the data to a linear function. The given errors include the standard deviation between the triplicate measurements at each site and the measurement errors of the individual rates.

Statistical analysis. Correlations between benthic fluxes and environmental factors were analysed using a Pearsons correlation matrix (2-tailed test) undertaken using SPSS 7.0 software. Data normality was assessed using a Kolmogorov-Smirnov goodness-of-fit test. Further details of the statistical methods and software used can be found in Norusis (1994).

RESULTS

Sediment characteristics

The highest TOC concentrations were found in the P sediments (Fig. 2). TOC concentrations were also much higher in the E and SE sediments than in the S, G and B sediments. TN and TP concentrations showed a similar pattern to that of TOC with higher concentrations in the E, P, and SE sediments and lower concentrations in the S and G sediments. TN and TP concentrations were not determined for the B sediments because of analytical problems. Sediment TN and TP concentrations reflect the composition of dominant plants with higher TN and TP concentrations in the faster-growing micro- and macroalgae sediments and lower concentrations in the rooted plant sediments (Atkinson & Smith 1983, Enriquez et al. 1993).

Chl *a* was found in the top 2 mm of all the sediment types, indicating that all the plant-sediment systems contained some benthic microalgae. As such, each sediment type should be considered a plant-benthic microalgae-sediment community. Very high chl *a* concentrations (90.8 µg g^{-1}) (MacIntyre et al. 1996) were found in the B sediment, most probably reflecting the very shallow water (<0.5 m), sheltered environment, and lack of competition for light from other primary producers. High chl *a* concentrations were also found in the macroalgae sediments, and the lowest chl *a* concentrations were found in the seagrass sediments. The P sediments still had fairly high chl *a* concentrations despite only receiving 5% of the incident surface light.

The molar C:N ratios were highest in the E and G sediments and lower, but very similar, in the P, SE and S sediments. Molar C:N ratios in the E and G sediments were much higher than typical macroalgae and phytoplankton molar C:N ratios (Atkinson & Smith 1983, Enriquez et al. 1993). In contrast, the molar C:N ratios of the S and SE sediments were similar to typical molar C:N ratios of seagrasses (Enriquez et al. 1993).

The molar C:P ratios were highest in the P sediments and lowest in the S sediments. Molar C:P ratios in the P sediments were much higher than the Redfield ratio suggesting preferential release of phosphorus. In contrast, the molar C:P ratios in the other sediments were much lower than typical molar C:P ratios of seagrasses and macroalgae (Atkinson & Smith 1983, Enriquez et al. 1993), suggesting an accumulation of phosphorus.

Dissolved oxygen fluxes

All the plant-sediment systems showed diurnal variations in O_2 fluxes, with O_2 consumption in the dark and O_2 production in the light (Fig. 3). The highest O_2 consumption occurred in the G sediments (–1821 ± 891 µmol m^{-2} h^{-1}), although these rates were only slightly higher than in the SE, S, and G sediments. The lowest O_2 consumption occurred in the B sediments (–525 ± 86 µmol m^{-2} h^{-1}). O_2 production was remarkably similar across all the plant-sediment systems (around 1000 µmol m^{-2} h^{-1}) with the exception of the G sediments. The G sediments had significantly higher, but much more variable, O_2

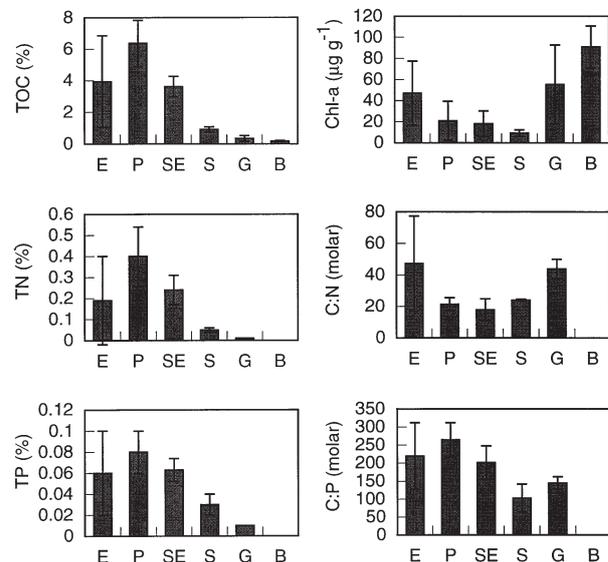
Fig. 2. Sediment characteristics for the 6 plant-sediment systems (means ± SD, n = 3, except SE n = 9). E: *Enteromorpha* sp.; P: phytoplankton; SE: seagrass + epiphytes; S: seagrass; G: *Gracilaria* sp.; B: benthic microalgae; TOC: total organic carbon; TN: total nitrogen; TP: total phosphorus

production rates (3498 ± 1564 µmol m^{-2} h^{-1}). This variability reflects a combination of the typical spatially heterogeneous biogeochemistry of macroalgae mats (Malta 2000) and the sampling strategy used (i.e. cores spaced 100 m apart); clearly, patches of actively growing and decomposing *Enteromorpha* sp. were sampled. This spatial variability in the G sediment is also reflected in a number of the other parameters.

Net O_2 fluxes in the P, SE, S and G sediments were net-respiratory, indicating that at the time of sampling they were decomposing more organic carbon than they were producing and/or oxidising reduced compounds (e.g. sulphides). Excess organic carbon was most probably produced during an earlier growth phase. Excess reduced compounds would have been produced during an earlier phase of carbon decomposition probably following an earlier growth phase. Net O_2 fluxes in the E and B sediments were balanced, but highly variable between sites.

Carbon dioxide and alkalinity

All the plant-sediment systems showed diurnal variations in ΣCO_2 fluxes, with an efflux in the dark and an uptake in the light (Fig. 3). ΣCO_2 effluxes exceeded O_2 consumption in the E, P, SE and S sediments and balanced O_2 consumption in the G and B sediments. The highest ΣCO_2 efflux rate (carbon oxidation rate) occurred in the S sediments (4290 ± 1922 µmol m^{-2} h^{-1}). There was a correspondingly high dark-alkalinity efflux in the S sediments, suggesting that sulphate reduction played a major role in the oxidation of organic matter. The lowest ΣCO_2 efflux occurred in the G and B sediments.

The general pattern of ΣCO_2 uptake (carbon production) was similar to that of O_2 production, with high uptake in the E and SE sediments and low uptake in the P and B sediments. ΣCO_2 uptake in the S sediment was highly variable (3364 ± 4404 µmol m^{-2} h^{-1}), ranging from an efflux to a high uptake. Net ΣCO_2 effluxes in all the plant-sediment systems except the B sediment were net-respiratory, indicating that at the time of sampling they were decomposing more organic carbon than they were producing.

Nutrients

Nutrient fluxes showed a variety of patterns over the 24 h dark-light cycles. The most typical pattern was a diurnal variation with an efflux in the dark and a reduced efflux (or uptake) in the light. However, NH_4, NO_3 and DOP were sometimes taken up in the dark, and DON, DIP and DOP were sometimes effluxed in the light.

DON dominated the nitrogen fluxes in all the plant-sediment systems (Fig. 4), highlighting the importance of including DON in benthic nitrogen-flux measurements. Dark DON fluxes ranged from 341 ± 117 µmol m^{-2} h^{-1} in the B sediment to 50 ± 81 µmol m^{-2} h^{-1} in the SE-sediment. The E, P and B sediments showed a DON efflux in the light, and the SE, S and G sediments showed a DON uptake in the light. However, all the plant-sediment systems showed a net efflux of DON. All the plant-sediment systems, except the B sediments, showed an NH_4 efflux in the dark and an NH_4 uptake in the light (Fig. 4). NH_4 was the second largest of the dark nitrogen fluxes in the P and SE sediments. A very high dark NH_4 efflux also occurred at 1 of the E sediment sites (410 µmol m^{-2} h^{-1}), but the other 2 sites
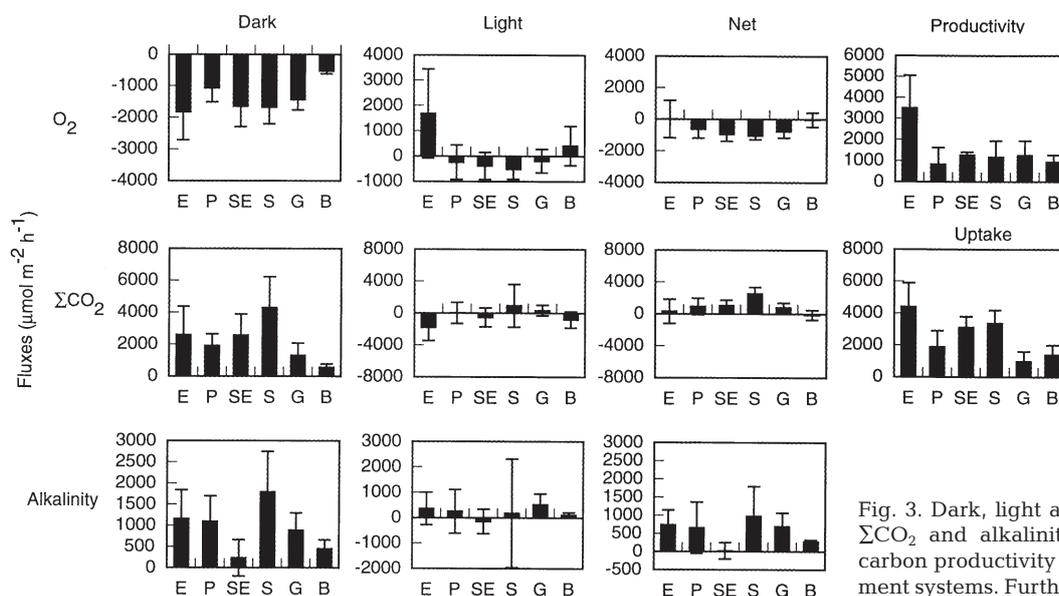

Fig. 3. Dark, light and net fluxes of O_2, ΣCO_2 and alkalinity and oxygen and carbon productivity for the 6 plant-sediment systems. Further details as in Fig. 2

showed dark NH$_4$ uptakes resulting in a low, but highly variable, average dark NH$_4$ efflux. The S, G and B sediments all had low NH$_4$ effluxes in the dark. The pattern of net NH$_4$ fluxes was quite variable across the plant-sediment systems, with the SE and S sediments showing a net efflux, the E and B sediments showing a net uptake, and the P and G sediments showing a net balanced flux. The E, G and B sediments all showed large dark, light and net uptakes of NO$_3$. In contrast, the P, SE and S sediments had very low NO$_3$ fluxes.

All the plant-sediment systems showed dark DIP effluxes, with rates varying from 4 µmol m^{-2} h^{-1} in the G sediments to <1 µmol m^{-2} h^{-1} in the G sediments

(Fig. 4). The pattern of light DIP fluxes was quite variable across the plant-sediment systems with the S sediments showing an efflux, the E, P, G and E sediments an uptake, and the SE sediments a balanced DIP flux. Net DIP fluxes ranged from net effluxes in the E, S, SE, B, and sediments to net uptakes in the P and G sediments. Dark DOP fluxes were of a similar magnitude but different direction to the DIP fluxes, ranging from −3 µmol m^{-2} h^{-1} in the S sediments to 1 µmol m^{-2} h^{-1} in the SE sediments. Similar to DIP, the pattern of light DOP fluxes was quite variable across the plant-sediment systems, with the P and SE sediments showing an efflux, the E, G, and B sediments an uptake, and the S sediments a balanced DIP flux. Net DOP fluxes ranged from net effluxes in the P and SE sediments to net uptakes in the E, S, G and B sediments.

Di-nitrogen gas (denitrification)

N$_2$ fluxes in the dark ranged from 69 µmol m^{-2} h^{-1} in the B sediments to 8 ± 5 µmol m^{-2} h^{-1} in the SE sediments (Fig. 4). N$_2$ was the second largest of the dark nitrogen fluxes in the E, S, G and B sediments, indicating that these plant-sediment systems are efficient at removing nitrogen through denitrification. Light N$_2$ fluxes increased in the E, P and SE sediments. Net N$_2$ fluxes showed an almost identical pattern across the plant-sediment systems to that of the dark fluxes.

DISCUSSION

Carbon and oxygen stoichiometry

The stoichiometry of the dark ΣCO_2, O$_2$, alkalinity, nitrogen and phosphorus fluxes gives some insight into the type of organic matter undergoing heterotrophic respiration (diagenesis) and the decomposition pathways in the different plant-sediment systems. When carbohydrate-rich organic plant matter decomposes, the molar ratio between the amount of O$_2$ consumed and the amount of ΣCO_2 produced in the presence of oxygen is dependent on the C:N ratio of the material (Anderson et al. 1986) and the end product. Aerobic respiration (oxic diagenesis) of organic
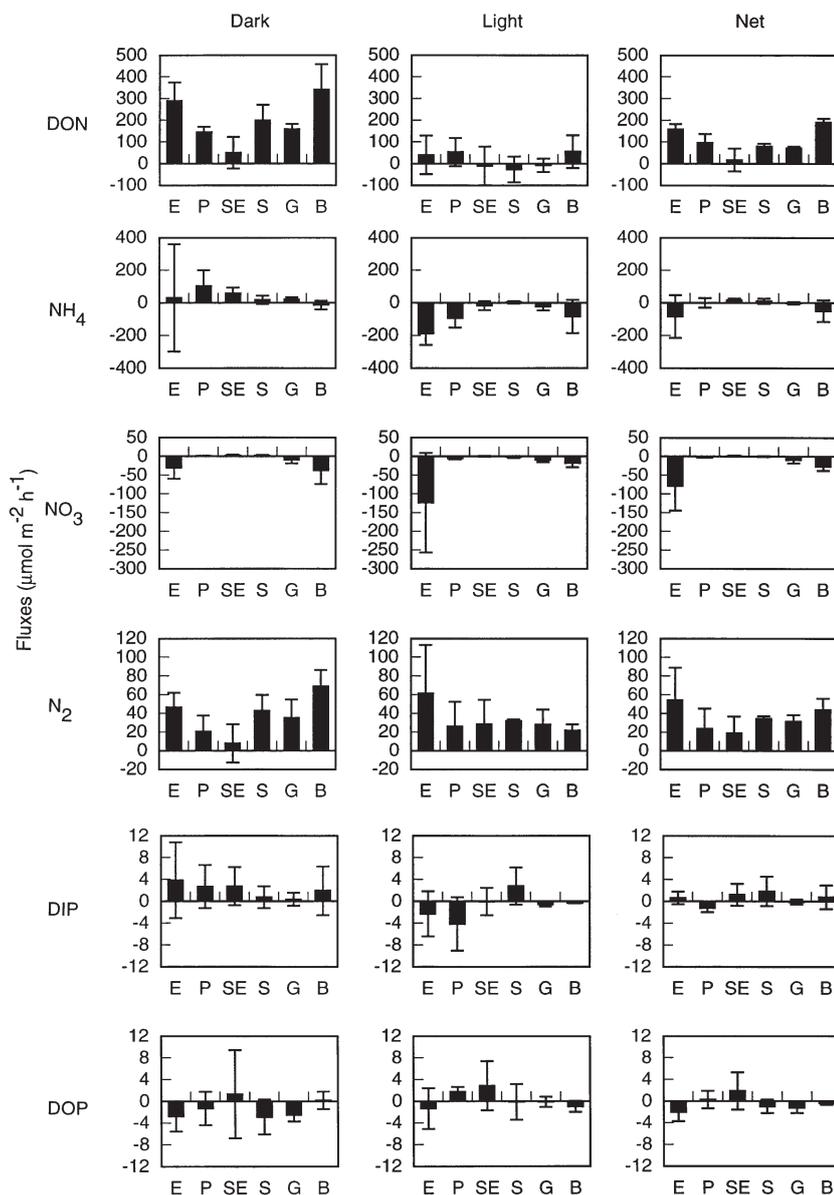

Fig. 4. Dark, light and net fluxes of DON, NH$_4$, NO$_3$, N$_2$, DIP and DOP for the 6 plant-sediment systems. Further details as in Fig. 2

matter with C:N ratios between 6.6 (Redfield type material) and 27 (seagrasses), and with NH_4 as the end product, results in $O_2:\Sigma CO_2$ molar ratios of between 1.02 and 0.92, respectively. In the presence of nitrification and subsequent denitrification the $O_2:\Sigma CO_2$ molar ratios may be as high as 1.23. The precipitation of calcium carbonate, the chemical oxidation of reduced species (such as sulphides), and the consumption of CO_2 by chemo-autotrophic bacteria will also drive the ratio higher.

The G and B sediments had dark $O_2:\Sigma CO_2$ molar ratios between 1.23 and 0.92, indicating a dominance of aerobic respiration (Fig. 5a). Consistent with limited anaerobic respiration were small alkalinity fluxes (present Fig. 3; and Berelson et al. 1996, 1998). In contrast, the E, P, SE, and S sediments all had dark O_2:ΣCO_2 molar ratios less than 0.92 to 1.23 (Fig. 5a), indicating either a dominance of anaerobic respiration processes such as sulphate reduction, or alternatively calcium carbonate dissolution. Consistent with anaerobic respiration and/or calcium carbonate dissolution were large alkalinity fluxes (Fig. 3; and Berelson et al. 1996, 1998). However, the SE and S sediments still had an excess ΣCO_2 efflux (about 20%) that cannot be explained by the alkalinity data (Fig. 5b; see Berelson et al. 1996 and 1998 for details on correcting and applying alkalinity data). Hammond et al. (1999) also found an alkalinity-free source of ΣCO_2 in pore waters in the Northern Adriatic Sea, and offered 7 possible explanations. The most likely of these explanations for the alkalinity-free ΣCO_2 found in the SE and S sediments is the oxidation of Fe^{2+} or sulphides which consumes alkalinity and O_2. Consistent with the oxidation of sulphides in the SE and S sediments were the thick black sediment layers near the surface in the cores, indicating a large supply of FeS and FeS_2, and the high sulphur content of the sediments (data not shown). Further, some of the individual flux measurements in the SE sediments had negative alkalinity fluxes that were masked by averaging the triplicates. Based on the negative alkalinity fluxes, up to 20% of the O_2 consumption in individual cores may have been due to the oxidation of reduced sulphides. Alternatively some of the excess ΣCO_2 may have been due to seagrass respiration which would alter the dark flux $O_2:\Sigma CO_2$ molar ratios from that expected for decomposing organic matter.

Nitrogen stoichiometry

The ratio of the dark ΣCO_2 flux to dark total dissolved inorganic nitrogen flux $(DIN+N_2)$ should have a 1:6.6 stoichiometry if the organic matter undergoing decomposition is phytoplankton detritus (i.e. Redfield-type material), a stoichiometry around 1:27 if the or-
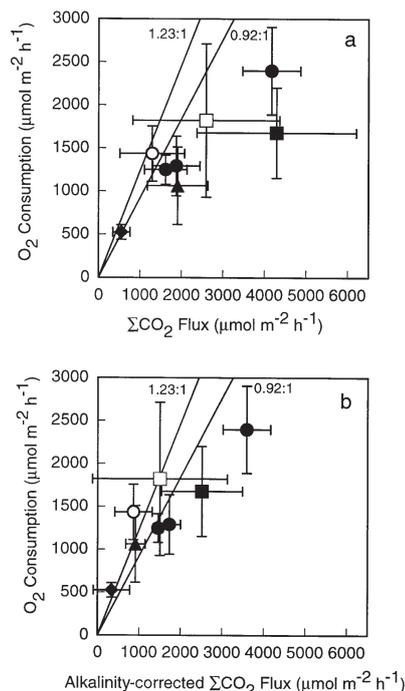

Fig. 5. (a) Dark O_2 fluxes versus dark ΣCO_2 fluxes and (b) dark O_2 fluxes versus alkalinity corrected dark ΣCO_2 fluxes for the 6 plant-sediment systems (means ± SD, n = 3). Lines represent a range in the molar ratio between the dark O_2 flux and the dark ΣCO_2 flux that indicates aerobic respiration (oxic diagenesis) in the absence of nitrification (i.e. ammonium is end product) and in the presence of nitrification and subsequent denitrification. (□) *Enteromorpha* spp.; (▲) phytoplankton; (●) seagrass + epiphytes; (■) seagrass; (○) *Gracilaria foliifera*; (◆) benthic microalgae

ganic matter undergoing decomposition is seagrass or red macroalgae, and a stoichiometry around 1:10 if the organic matter undergoing decomposition is green macroalgae (Atkinson & Smith 1983; see also later discussion of light uptake of DIN vs benthic production). The dark C:N ratios of the remineralised organic matter in the G and B sediments and 2 of the SE sediments were consistent with the above ratios, indicating a complete return of remineralised nitrogen (Fig. 6). In contrast, the dark C:N ratios of the remineralised organic matter and the C:N ratios of the surface sediment in the E, P and S sediments and one of the SE sediments was much higher than the expected stoichiometry (cf. Figs 6 & 2). Dark DON fluxes were also very high in all the plant sediment systems (30 to 80% of the total nitrogen flux). We offer 2 alternative explanations for the observed sediment and flux characteristics:

Firstly, the low dark C:N ratios of the remineralised organic matter may be due to dark uptake by benthic microalgae (Andersen & Kristensen 1988, Rysgaard et al. 1995) and possibly other plants. The large DON

Table 3. Pearson correlations between dark, light and net fluxes and sediment parameters. *p/r*: productivity/respiration ratio. *p < 0.1; **p < 0.01; all other cases significant at p < 0.05

	C:N	TN	TOC	TP	Chl *a*	*p/r*
DO						
Dark						
Light	0.398*					0.922**
Net	0.460					0.881**
CO_2						
Dark	−0.426*			−0.476		
Light						−0.680**
Net	−0.394*				−0.460	−0.705**
NH_4						
Dark	−0.556**	0.553	0.483	0.550	−0.375*	−0.471
Light						−0.458
Net	−0.779**				−0.501	−0.758**
NO_3						
Dark				−0.406*		
Light						−0.724**
Net					−0.690*	
DIN						
Dark	−0.624**	0.571**	0.538**	0.548	−0.469	−0.619*
Light	−0.383*					−0.662**
Net	0.565**				0.665**	
DON						
Dark	0.575**				0.533**	0.630**
Light						
Net	0.382*				0.569**	0.529**
N_2						
Dark	0.485	−0.399*	−0.489		0.404*	0.440
Light	0.597**					0.395*
Net	0.665**	−0.405*	−0.377*			0.535**
DIP						
Dark	−0.435*	0.488	0.417	0.445		
Light		−0.595**	−0.564**			
Net						
DOP						
Dark						
Light		−0.531	0.423*	0.389*		
Net	−0.568**	0.498				

gen by Sundback & Miles (2000). However, only inorganic nitrogen was studied by Sundback & Miles, so much of the inorganic nitrogen uptake may have been returned to the water column as DON, decreasing the role of benthic microalgae as a sink. The correlation between sediment chl *a* and DIN and DON fluxes was weaker than that with the sediment *p/r* ratio (Table 3), indicating that the whole plant-sediment system had a greater influence on benthic fluxes than the benthic microalgae alone.

Alternatively, these sediment and flux characteristics may be described by Blackburn et al. (1996) for sediments in Svalbard, Norway. Large effluxes of DON with a low C:N ratio increase the C:N ratio of organic matter in the surface sediments (Blackburn et al. 1996). The high C:N ratio of the remaining organic material results in the uptake and accumulation of nitrogen by the bacteria due to N-limitation of the microbial decomposition (Tupas & Koike 1991, van Duyl et al. 1993, Blackburn et al. 1996, Rivera-Monroy & Twilley 1996, Lomstein et al. 1998, Pedersen et al. 1999), and hence there is little efflux of inorganic nitrogen. Several types of bacteria can metabolise ammonium, including sulphate-reducers and fermentative bacteria (Koike & Sumi 1989). To maintain a steady-state low C:N ratio, organic matter must then be buried (Blackburn et al. 1996) and/or there must be periodic low C:N ratio effluxes when the bacteria die and decompose.
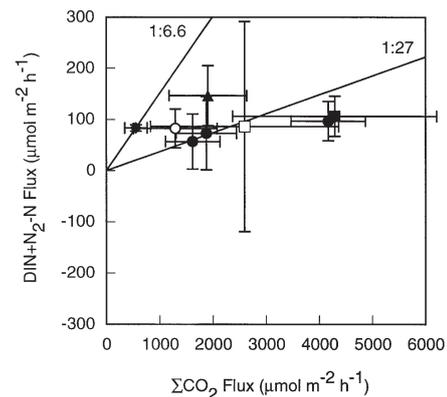
effluxes are most likely to have been the hydrolysis product of fresh organic matter (Blackburn et al. 1996, Burdige & Zheng 1998), and the strong positive correlation with sediment *p/r* ratios (Table 3) suggests that the DON was from freshly produced *in situ* organic material (see later discussion and Fig. 12). Dark DON fluxes were positively correlated with sediment chl *a* and DIN fluxes were negatively correlated with sediment chl *a*, (Table 3), which also supports the role of benthic microalgae in the uptake of inorganic nitrogen and efflux of organic nitrogen. DON release from benthic microalgae may also be associated with grazing, as has been seen in pelagic microalgae (Glibert et al. 1991). This has important implications regarding the importance of benthic microalgae as sinks of nitrogen in shallow coastal systems. Benthic microalgae have recently been identified as an important sink of nitro-

Fig. 6. Dark total dissolved inorganic nitrogen ($DIN + N_2$-N) flux versus dark ΣCO_2 flux for the 6 plant-sediment systems (means ± SD, n = 3). Lines represent the relationship between $DIN + N_2$-N and ΣCO_2 if Redfield-type material (1:6.6) or seagrass material (1:27) was decomposing. Symbols as in Fig. 5

Denitrification efficiency

The relative percentages of the different forms of nitrogen effluxing from the sediments to the water column was quite variable between the plant-sediment systems; this has important implications for the trophic status of coastal lagoons. For example, nitrogen returned as N_2 (denitrification) is lost from the system, which helps to ameliorate the effects of nutrient enrichment. In contrast, nitrogen returned as NH_4 and DON may further stimulate productivity in the water column, resulting in the delivery of more organic matter to the sediments and leading to greater decomposition and oxygen consumption. If anoxia occurs through the mineralisation of excess organic matter, nitrification-denitrification may be inhibited, and thus more nitrogen may be recycled back into the water column as ammonium, further stimulating primary production (Kemp et al. 1990).

The denitrification efficiency is the percentage of the total inorganic nitrogen released as N_2 during organic matter decomposition (N_2-N/(DIN + N_2-N) $\times$ 100%: modified from Berelson et al. 1998). The rate of carbon decomposition (which can be considered a proxy for carbon loading) appears to be an important control on the efficiency with which the plant-sediment systems (excluding the S sediments) recycle nitrogen as N_2 (Fig. 7a). At carbon decomposition rates above ~1500 μmol CO_2 m^{-2} h^{-1} there is a large decrease in the denitrification efficiency with most of the nitrogen returned to the water column as ammonium. Berelson et al. found a similar drop in the denitrification efficiency of Port Phillip Bay sediments above a carbon decomposition rate of ~1250 μmol CO_2 m^{-2} h^{-1}. The low denitrification efficiencies are most probably due to either the inhibition of nitrification by exposure to sulphide (Kemp et al. 1990, Joyce & Hollibaugh 1995) or to a lack of oxygen for nitrification. In an experimental system, Caffrey et al. (1993) found that an increased organic load resulted in a decrease in nitrification and denitrification. They postulated that this was also due to a decrease in oxygen supply and inhibition by sulphide. Alternatively, as the organic matter loading increases, dissimilatory nitrate reduction to ammonium may become quantitatively more important (Kaspar et al. 1988, Gilbert et al. 1997, Christensen et al. 2000).

Despite a high carbon decomposition rate, the S sediments still had high denitrification efficiencies due to small effluxes of ammonium (Fig. 5). Seagrass beds are known to be very efficient at recycling inorganic nitrogen (Hansen et al. 2000) and this appears to occur even under high carbon loadings. However, if DON effluxes are included, the S sediments have denitrification efficiencies comparable to their high carbon decomposi-

tion rates (Fig. 7b). Including DON in the denitrification efficiency term gives a similar, albeit poorer, relationship to carbon decomposition as the N_2-N/(DIN + N_2-N) term. Fig. 7b also suggests that there will be a significant return of DON to the water column even at low carbon decomposition rates, reflecting the hydrolysis of freshly deposited organic matter. Inclusion of DON in the denitrification efficiency term is warranted when benthic DON effluxes are high because (1) the efflux of DON with a low C:N may be an important control on the efflux of inorganic nitrogen including N_2 (see also Blackburn et al. 1996), and (2) the return of nitrogen to the water column as DON may also be important for stimulating further production (Bronk et al. 1994). Despite the importance of benthic DON fluxes, these have only been measured in a few studies of shallow coastal waters (e.g. Burdige & Zheng 1998 and references therein; Rondell et al. 2000). The robustness of the denitrification efficiency relationship (Fig. 7) across such a diverse range of plant-sediment systems representing different stages of eutrophication suggests that it may provide a useful approach for synthesising denitrification data across shallow coastal systems and for defining suitable carbon loading rates. Further, because the denitrification efficiency relationship is exponential, it suggests that mangers will be rewarded with greater return (i.e. increased denitrification for natural removal of nitrogen) for effort (i.e. reducing carbon loading rates) in
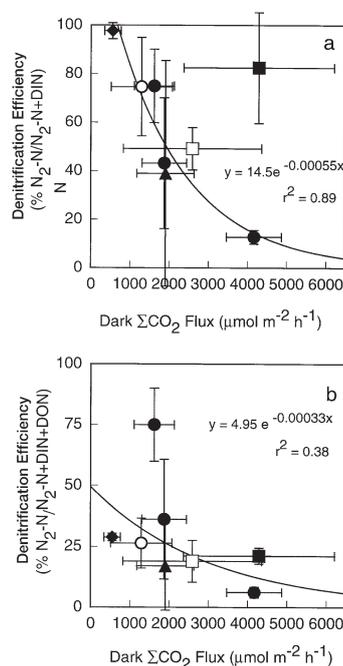

Fig. 7. Lines of best fit for (a) denitrification efficiency N_2-N/(N_2-N + DIN) and (b) denitrification efficiency N_2-N/(N_2-N + DIN + DON), versus dark ΣCO_2 flux for the 6 plant-sediment systems (means ± SD, n = 3). Symbols as in Fig. 5
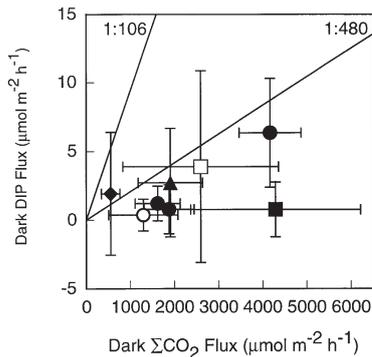
Fig. 8. Dark dissolved inorganic phosphorus (DIP) flux versus dark ΣCO_2 flux for the 6 plant-sediment systems (means ± SD, n = 3). Lines represent the relationship between DIP and CO_2 if Redfield-type material (1:106) or seagrass (1:480) was decomposing). Symbols as in Fig. 5

the early stages of eutrophication. Further work is required to test these relationships in different shallow coastal systems and to determine what causes the decrease in denitrification efficiency. For example, does the relationship hold in estuaries with high nitrate concentrations where denitrification may not be cou-
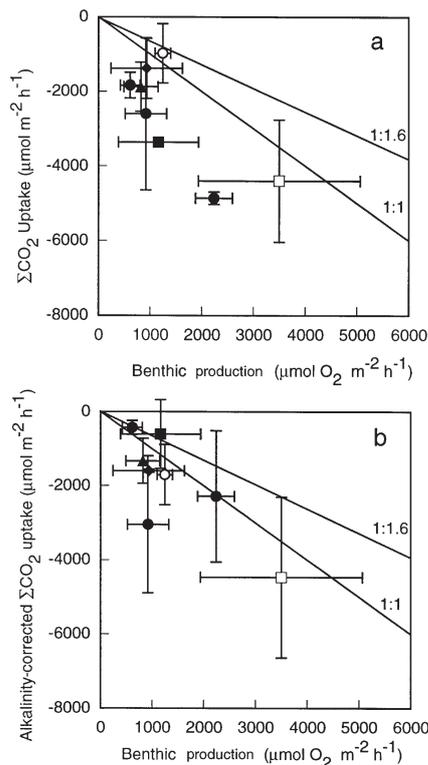
Fig. 9. ΣCO_2 uptake versus O_2 production (a) and alkalinity-corrected ΣCO_2 uptake versus alkalinity-corrected O_2 production (b) for the 6 plant-sediment systems (means ± SD, n = 3). Lines represent the relationship between nitrogen uptake from the water column and O_2 production during photosynthesis depending on the source of nitrogen (i.e. ammonium or nitrate) and the type of carbon produced (i.e. carbohydrate or lipid synthesis). Symbols as in Fig. 5

pled to nitrification, and does dissimilatory nitrate reduction to ammonium increase under high organic loadings?

Phosphorus stoichiometry

The ratio of the dark ΣCO_2 flux to dark DIP flux in all the plant-sediment systems was less than the 1:106 to 1:480 stoichiometry expected from decomposition of Redfield-type material and seagrass and macroalgal material (Fig. 8). This probably reflects the trapping of phosphorus in the oxidised upper sediment layers by iron oxy-hydroxides, probably enhanced through the injection of oxygen by benthic productivity. Consistent with this are the much lower C:P ratios in the sediment, which reflect an accumulation of the trapped phosphorus (Fig. 2). This has important management implications because, if the surface sediments become reducing (anoxic), large quantities of phosphorus may be released into the water column.

Influence of benthic production on benthic fluxes

Photosynthesis by benthic producers assimilates ΣCO_2 and releases O_2 in the ratio of ~0.6 to 1, depending on the source of nitrogen (i.e. ammonium or nitrate) and the type of carbon produced (i.e. carbohydrate or lipid synthesis) (Valiela 1995). A plot of light ΣCO_2 uptake versus O_2 production shows that most of the plant-sediment systems fall above a ratio of 1 (Fig. 9a). One of the major problems in estimating benthic production from ΣCO_2 or O_2 fluxes is the extrapolation of dark respiration rates to the light period, because O_2 production may modify the dark O_2 consumption and ΣCO_2 production rates through photorespiration, enhanced bacterial respiration due to release of DOC from phototrophs (Bauld & Brock 1974, Glud et al. 1999), enhanced nitrification (Risgaard-Petersen et al. 1994), and perhaps through changes in sulphate reduction.

Changes in alkalinity from dark to light can be used to correct for some of these changes in O_2 consumption and ΣCO_2 production from dark to light, since changes in nitrification and sulphate reduction will result in a change in the alkalinity flux. When the alkalinity-corrected light ΣCO_2 uptake is plotted against alkalinity-corrected O_2 production, most of the plant-sediment systems fall close to the ratio 1:1, indicating that benthic production is the dominant control on ΣCO_2 and oxygen fluxes during the light cycle (Fig. 9b). The scatter in the $\Sigma CO_2:O_2$ plot may be associated with the dissolution of calcium carbonate or photorespiration, which is not accounted for by the
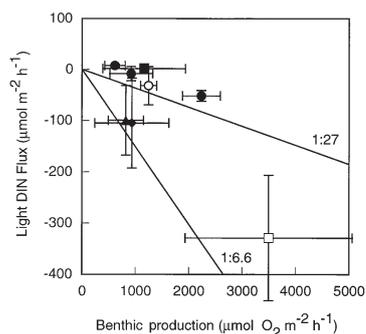
Fig. 10. Dissolved inorganic nitrogen (DIN) uptake versus O_2 production for the 6 plant-sediment systems (means ± SD, n = 3). Symbols as in Fig. 5. Line represents the relationship between benthic production and DIN uptake by seagrass (1:27) and benthic microalgae (1:6.6)

alkalinity flux. Consumption of ΣCO_2 by chemoautotrophic bacteria (nitrification) should have little impact on the ΣCO_2 flux because they only assimilate 1 mol of bicarbonate for every 5 mol of ammonium oxidised (Gunderson & Mountain 1973).

The optimum stoichiometric ratio of C:N:P for benthic microalgae is 119:17:1, slightly higher than the Redfield ratio (106:16:1) (Hillebrand & Sommer 1999), and for seagrasses and macroalgae it is around 480: 27:1. A plot of the light DIN flux versus benthic productivity shows that the SE and G sediments fall around the optimum ratio for seagrass and macroalgae and the P and B sediments around the optimum ratio for benthic microalgae (Fig. 10). This suggests that nitrogen uptake in these plant-sediment systems is dominated by the major plant group and that this group is obtaining much of its nutritional requirements by direct assimilation of nitrogen from the water column. The uptake of nutrients by the seagrass + epiphytes, macroalgae and benthic microalgae was so great that it changed the sediments from a nutrient source to a nutrient sink, as has been seen in a number of other systems (e.g. Nilsson et al. 1991, Sundback et al. 1991, Rysgaard et al. 1995, Risgaard-Petersen et al. 1998). Seagrasses, macroalgae and benthic microalgae can source nutrients from both the water column and sediment porewaters (Calton & Wetzel 1988, Lee & Dunton 1999, Hansen et al. 2000). The water column was clearly an important source of nutrients for benthic microalgae and seagrasses + epiphytes and *Gracilaria* sp. in the present study, and the uptake in Redfield and 1:27 (C:N) proportions respectively indicates that nitrogen was not limiting. Rizzo et al. (1992) suggested that the most efficient way for benthic microalgae to overcome nutrient limitation is by using water column nutrients; diffusional gradients and the development of microzones of nutrient limitation may preclude the use

of sediment-porewater nutrients. The DIN uptake: benthic production ratio was very low for the E sediment (1:10) suggesting luxus uptake and storage of nitrogen, which is common for macroalgae (Rosenberg & Ramus 1982, Fong et al. 1994). In contrast, there was benthic production in the S sediments, but no uptake of DIN, suggesting that the seagrasses at this site were obtaining much of their nutrient requirements from the sediments, which is consistent with the results of other studies (e.g. Zimmerman et al. 1987, Pedersen & Borum 1992, Hansen et al. 2000).

One of the SE sediments was obtaining most of its phosphorus requirements from the water column, as indicated by the uptake ratio of 1:480 (Fig. 11). The E and P sediments appeared to be obtaining about half their phosphorus requirements from the water column, as indicated by uptake ratios of 1:200 and 1:1500 respectively. The remaining plants showed little phosphorus uptake, and were most probably obtaining most of their phosphorus from pore water in the upper sediment layers.

Sediment factors controlling benthic fluxes and denitrification

A Pearson correlation was used to help identify some of the sediment factors that may be controlling the differences in dark, light and net benthic fluxes and denitrification between sediment-plant systems (Table 3). Sediment C:N ratios were correlated with a number of the benthic fluxes and denitrification. Most importantly, sediment C:N ratios were negatively correlated with dark DIN effluxes and were positively correlated with dark DON effluxes. An increase in the DON efflux and a decrease in the DIN efflux associated with
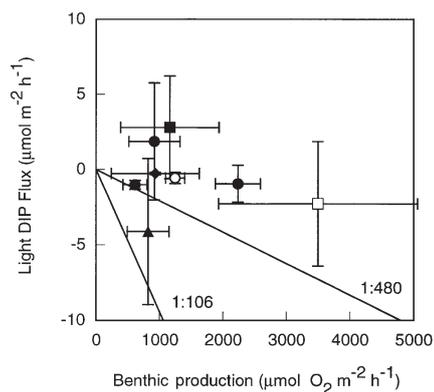

Fig. 11. Dissolved inorganic phosphorus (DIP) uptake versus O_2 production for the 6 plant-sediment systems (means ± SD, n = 3). Symbols as in Fig. 5. Line represents the relationship between benthic production and DIP uptake by seagrass (1:27) and benthic microalgae (1:6.6)
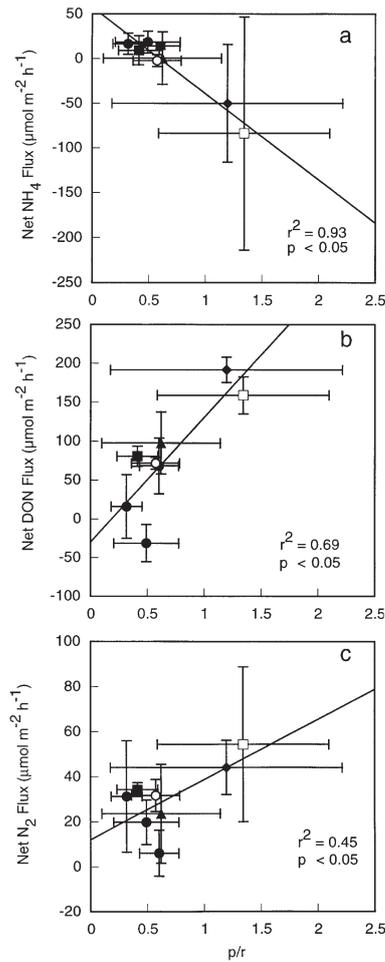
Fig. 12. Lines of best fit for (a) net NH$_4$ flux, (b) net DON flux and (c) net N$_2$ flux, i.e. denitrification versus the sediment *p/r* ratio for the 6 plant-sediment systems (means ± SD, n = 3). Symbols as in Fig. 5

an increase in sediment C:N ratios is consistent with low C:N ratios and DON effluxes increasing the C:N ratio of organic matter which, in turn, causes an uptake and accumulation of inorganic nitrogen by bacteria. The bulk sediment composition parameters (TOC, TN, TP) were all positively correlated with dark DIN effluxes, reflecting an increase in inorganic nitrogen effluxes with increasing carbon and nitrogen concentrations in the sediment. The correlation between TP and dark DIN effluxes most probably reflects the co-variance of TP and TN concentrations in the sediments. Denitrification was positively correlated with TOC concentrations, as has also been found for other coastal sediments (Norwicki et al. 1997).

Chl *a* is positively correlated with dark DON effluxes and negatively correlated with dark DIN fluxes, suggesting that some of the dark DON effluxes and DIN uptakes may be associated with benthic microalgae. Interestingly, there was no correlation between chl *a* and any of the light fluxes, indicating that the other

plants dominated the benthic fluxes in the light. In Chesapeake Bay sediment, chl *a* was a good indicator of dark benthic fluxes (e.g. Cowan & Boynton 1996), whereas this was not so in the sediments of the present study. This is presumably related to the different origins of the sediment chl *a* in the 2 systems. In the deep Chesapeake Bay, sediment chl *a* is a good indicator of the amount of labile material (phytodetritus) reaching the sediments. In contrast, in the shallow systems of the present study, sediment chl *a* is an indicator of the biomass of benthic microalgae. Chl *a* was positively correlated with dark denitrification rates, most probably through increased oxygen penetration from benthic production which would enhance coupled nitrification-denitrification (Risgaard-Petersen et al. 1994). Despite an increase in light N$_2$ fluxes in the E, P and SE sediments, there was no relationship between light denitrification rates and chl *a*; this probably reflects a dominance of oxygen production by other plants. N$_2$ fluxes decreased in the S, G and B sediments during the light, most probably through increased competition for NO$_3$ by plants (Rysgaard et al. 1995, 2000).

One of the major controls (best sediment indicators) on many of the dark, light and net benthic fluxes across the plant-sediment systems was the *p/r* ratio of the sediments (Table 3). When the *p/r* is >1, the sediments are net autotrophic and more carbon is produced than is respired; when the *p/r* is <1, the sediments are net heterotrophic and more carbon is respired than is produced; and when the *p/r* = 1, respiration and production are balanced. Net autotrophic sediments should assimilate inorganic nutrients to support productivity, net heterotrophic sediments should release inorganic nutrients through respiration, and sediments with a balanced *p/r* should have no net flux. This was clearly illustrated in the plant-sediment systems. For example, when the *p/r* ratio was >1 there was a net uptake of NH$_4$, when the *p/r* ratio was <1 there was a net release of NH$_4$, and at a *p/r* of close to 1 there was no uptake of efflux of NH$_4$ (e.g. Fig. 12a). Similar patterns were also shown by the other inorganic nutrients. Interestingly, net DON fluxes were positively correlated with *p/r* ratios, reflecting the release of DON from freshly produced organic material (Fig. 12b). This further highlights the importance of benthic primary producers in controlling the flux of inorganic and organic nutrients across the sediment-water interface. The positive relationship between net N$_2$ fluxes (denitrification) and *p/r* ratios (Fig. 12c) most probably reflects enhanced coupled nitrification-denitrification (Risgaard-Petersen et al. 1994) with increasing benthic production. Counteracting enhanced coupled nitrification-denitrification is increased competition for NO$_3$ by plants (Rysgaard et al. 1995, 2000), which is most probably reflected by its poorer relationship with *p/r* ratios compared to NH$_4$

and DON. Sediment *p/r* ratios have important management implications for coastal lagoons, demonstrating the need to maintain the balance of benthic autotrophy and heterotrophy. We have also observed similar relationships between sediment *p/r* ratios and benthic fluxes in other estuaries (unpubl. data), suggesting that the *p/r* ratio of sediments may provide a useful approach for synthesising benthic flux data across shallow coastal systems.

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