Macroalgae Mediation of Dissolved Organic Nitrogen Fluxes in a Temperate Coastal Lagoon

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The activity of the benthos, including benthic plants, is important in driving the overall system dynamics in shallow lagoons, due to the high ratio of sediment surface area relative to water volume. In Hog Island Bay, benthic macroalgae appear to be a key regulator of DON dynamics, both while alive and following senescence. We investigated the role of macroalgae in mediating water column concentrations and sediment-water column fluxes of DON across a nutrient gradient in Hog Island Bay, a shallow macroalgal-dominated back-barrier lagoon located on the Virginia Coast. Sediment-water column exchanges of DON, urea and DIN were measured in sediment cores with and without macroalgae (*Ulva lactuca*) at three subtidal sites from the mainland to the barrier islands in the fall of 1997 and the spring and summer of 1998. The summer sampling dates bracketed a large macroalgal bloom in the mid-lagoon. Dissolved organic nitrogen was an important component (52-98%) of the total dissolved nitrogen pool in Hog Island Bay waters and made up the majority of the sediment N flux to the water column. Macroalgae impacted benthic-pelagic coupling by preventing diffusion of DIN from the water column to the sediments and by intercepting urea fluxes from the sediment to the water column. Closest to the mainland and closest to the barrier islands, at sites with low macroalgal biomass, sediment-water column fluxes of DIN and urea-free DON were negligible or directed into the sediments. Fluxes of urea from the sediment to the water column were significant at both sites, and may play an important role in satisfying macroalgal N demand, especially at the low N island site. Urea was 32% of the mean DON flux from the sediments to the water column. Fluxes of urea-free DON were highest in the mid-lagoon, where macroalgal biomass was highest. The highest overall flux rates of DON (>38 mmol m⁻² d⁻¹) and DIN (>33 mmol m⁻² d⁻¹) were measured following an isolated crash of a large macroalgal mat. These release rates were not sustained for long, however, and we estimated that the majority of the N contained in the decomposing macroalgal tissues disappeared in <2 weeks. In addition to release of organic N following senescence, macroalgae ‘leak’ DON into the water column during active growth; release of DON increased by 250% in cores incubated with *U. lactuca* relative to cores with sediment only. These algae function as a conduit whereby water-column DIN and sediment urea are taken up and released to the water column as DON over relatively short (hours) time scales. This conversion of bioavailable dissolved N to PON and DON by macroalgae is likely to be important to overall system metabolism and to the retention of N within the lagoon.

**Keywords:** macroalgae; lagoons; sediment-water interface; nitrogen; organic matter; dissolved organic compounds; urea; Virginia Coast

Introduction

Dissolved organic nitrogen (DON) makes up a large fraction of the total nitrogen (N) in marine systems (Sharp, 1983). Coastal systems receive inputs of DON from allochthonous sources (Meybeck, 1982; Hopkinson, 1998) including atmospheric deposition (Paerl et al., 1990; Cornell et al., 1995; Paerl, 1995) and autochthonous production. In lagoonal systems with little riverine input the majority of new DON most likely comes from autochthonous production or from enriched groundwater. Because they are usually shallow, lagoons are for the most part littoral zone systems. As such, shallow lagoons tend to be dominated by benthic primary producers, such as seagrasses, macroalgae and benthic microalgae rather than by phytoplankton. Fast-growing species of macroalgae are at a competitive advantage over slow-growing seagrasses and perennial macroalgae under conditions of increased nutrient loading (Duarte, 1995) so that anthropogenically impacted lagoons typically display increased growth of opportunistic macroalgae (Lee & Olsen, 1985; Sfriso et al., 2001).
source of organic matter to the sediments (Nixon, 1981; Nixon, 1991). Thus in anthropogenically impacted lagoonal systems the remineralization of macroalgae contributes significant amounts of DON.

In deeper estuaries, some studies have shown DON to be an important component of the overall N flux (Lomstein et al., 1989; Enoksson, 1993; Blackburn et al., 1996; Cowan & Boynton, 1996), while others have shown that DON fluxes were either insignificant (Nixon, 1981; Burdige & Zheng, 1998) or only seasonally important (Boynton et al., 1980). Few studies have examined sediment fluxes of DON in shallow systems, even though the high sediment surface area to water volume ratio of lagoons increases the relative importance of sediment-water column interactions (Nowicki & Nixon, 1985; Sand-Jensen & Borum, 1991). The magnitude of sediment nutrient fluxes is generally related to the magnitude of primary production in the system, as primary production is the source of organic matter to the sediments (Nixon, 1981). Duarte (1995) described that in macroalgal-dominated systems nutrient cycling may be accelerated in comparison to systems dominated by vascular plants because macroalgae, which have little structural material and decompose rapidly (Buchsbaum et al., 1991), have the potential to contribute significantly and rapidly to sediment fluxes following senescence. For example, the addition of dead algal material to sediment cores has been shown to significantly increase fluxes of ammonium (NH$_4^+$) and DON to the water column (Hansen & Blackburn, 1992; Enoksson, 1993). In extreme cases, such as in the Sacci di Goro, Italy, massive blooms of Ulva rigida periodically crash, releasing significant amounts of dissolved and particulate organic matter and leading to severe dystrophic crises (Sfriso et al., 1992; Viaroli et al., 1995).

Nutrients regenerated in the sediments and released to the water column are thought to support a significant portion of primary production in coastal ecosystems (e.g. Nixon, 1981; Fisher et al., 1982; Koop et al., 1990; Cowan & Boynton, 1996). Macroalgal uptake of dissolved inorganic nitrogen (DIN) influences the flux of DIN between the sediment and the overlying water column, and may limit phytoplankton growth (Valiela et al., 1992; Thybo-Christesen et al., 1993; McGlathery et al., 1997). Because some species of macroalgae can take up specific DON compounds in addition to DIN (Nasr et al., 1968; Hanisak, 1983; Chisholm et al., 1996), they may influence water column concentrations and sediment fluxes of DON as well. However, the impact of living macroalgae on sediment fluxes of DON has not been investigated.

Dissolved organic nitrogen is a collective term for a variety of compounds that can differ substantially in molecular weight and bioavailability, from small, highly bioavailable, low C:N compounds like amino acids and urea to very large, refractory, high C:N polyphenolic compounds. Previous studies have indicated that a substantial fraction of the sediment DON flux is comprised of low C:N compounds, such as urea and amine compounds (Boucher & Boucher-Rodoni, 1988; Lomstein et al., 1989; Burdige & Zheng, 1998), which generally are more labile and available to water column organisms. Knowledge of the concentration of biologically important components of the DON pool, such as urea, is important in understanding overall system dynamics.

We investigated the role of macroalgae in regulating DON fluxes and transformations in Hog Island Bay, a shallow macroalgal-dominated lagoon located on the Virginia Coast. The specific objectives of this study were to characterize the importance of DON in the water column total dissolved nitrogen (TDN) pool and to determine the influence of the macroalga Ulva lactuca on water column concentrations and sediment-water column fluxes of DON, urea and DIN during active growth and following senescence. The study presented here represents one of the first attempts to characterize DON fluxes in temperate lagoons.

**Methods**

**Site description**

Hog Island Bay (Figure 1), a shallow coastal lagoon situated off of the Delmarva Peninsula, is part of the Virginia Coast Reserve (VCR) Long Term Ecological Research site (LTER). The VCR is comprised of 13 barrier islands, and numerous shallow shoals, deep channels, mudflats, marsh islands, fringing marshes, and tidal creeks extending westward from the Peninsula. Due to the small catchment area and lack of fluvial inputs, the primary sources of allochthonous N to Hog Island Bay are most likely seepage of nutrient enriched groundwater (Lee & Olsen, 1985; Reay et al., 1992), and atmospheric deposition (Paerl et al., 1990). There is a gradient of organic matter and nutrient inputs across Hog Island Bay from the mainland to the islands, with the highest concentrations of dissolved N and sediment organic matter found closest to the mainland (McGlathery et al., unpublished data). Within Hog Island Bay, N is transformed by algal and bacterial uptake, remineralization, nitrification and denitrification. Seagrasses here have been locally extinct since the 1930s and macroalgae are the dominant primary producers. Dominant macroalgal species include *U. lactuca*, *Gracilaria tikvahiae* and...
Cladophora sp. Benthic microalgae also may be important primary producers but phytoplankton production is low throughout the year.

We established a transect across Hog Island Bay with sites representing the three subtidal habitat types: a mainland tidal creek (Creek), two mid-lagoon shoals (Shoal 1 and Shoal 2), and a back-barrier island embayment (Hog) (Figure 1). The water depth at all sites is <1 m at mean low water and the tidal range is approximately 1-2 m at Hog Island and 1.5 m at the mainland (Santos, 1996). Atlantic Ocean water enters the lagoon through Machipongo Inlet at the southern tip of Hog Island. The Creek site is a small tidal creek (approx 5 m across) bordered by Spartina alterniflora marsh. The sediments are fine-grained and silty and often coated with a well-developed microalgal turf. Macroalgal biomass is generally low (<20 g dw m⁻², McGlathery et al., in press), and often partially buried in the sediment, although large floating mats of Ulva lactuca and G. tikvahiae were observed ephemerally during the summer of 1998. The Shoal sites in the mid-lagoon border remnant oyster reefs and the sediments are fine-grained sands. Substantial macroalgal mats develop at specific locations in the Shoal region of the mid-lagoon, with the peak biomass occurring in June/July (>450 g dw m⁻² at Shoal 1 and >650 g dw m⁻² at Shoal 2, McGlathery et al., in press). In early July 1998, the algal populations at Shoal 2 crashed, probably as a result of high temperatures and self-shading within the algal mat. No crash was observed at Shoal 1. The Hog Island site is a shallow embayment with coarser-grained sandy sediments. Algal biomass here is typically low (5-15 g dw m⁻², McGlathery et al., in press) and relatively constant throughout the year.

**N flux measurements**

Sediment–water column N fluxes were measured on 30 October 1997 and 4 May, 8 July and 18 August 1998. Six sediment cores (8 cm I.D., 12 cm sediment, 18 cm water column), water and Ulva lactuca were collected at each of the sites. The cores were returned to the laboratory and held overnight in outdoor flowing seawater tables to maintain ambient field temperatures. Experimental treatments were: sediment only and sediment+algae. Ulva lactuca and water from each site were used with the respective sediment. Parallel water blanks were used to correct for concentration changes in the overlying water column. In July 1998 additional cores from Shoal 2 were collected in order to measure fluxes immediately following the crash of the macroalgal bloom.

Prior to initiation of the experiment, the overlying water was drained using a siphon and carefully replaced, without disturbing the sediment surface. Ulva lactuca was added to the sediment+algae cores, large air bubbles were removed and the cores were sealed with a rubber stopper. Ulva lactuca density (equivalent to 100–200 g dw m⁻²) simulated moderately dense patches in the lagoon. The overlying water was stirred with a magnetic stir bar (approximately 60 rpm) throughout the experiment to prevent build-up of concentration gradients that may interfere with diffusion across the sediment-water and thallus-water interfaces. Fluxes were measured over a 12-h period (6 h light, 6 h dark). Surface irradiance during the light treatment ranged from 700 to 1200 μmol photons m⁻² s⁻¹ and was similar to that measured in situ (McGlathery et al., unpublished data). The water depth in the cores (17–20 cm) approximates low tide water levels in the field so that light reaching the water-sediment or water-algae interface within the cores was likely similar to low tide conditions. Samples for ammonium (NH₄⁺) and nitrate+nitrite (NO₃⁻ + NO₂⁻) were collected at 2-h intervals; samples for urea and total dissolved nitrogen (TDN)
were collected at 6-h intervals. All samples were filtered immediately (Gelman Supor, 0.45 μm) and frozen, with the exception of NH₄⁺ samples, which were analysed within 3 h of collection.

Ammonium was measured using the phenol-hypochlorite method (Solorzano, 1969). Nitrate+nitrite was measured using an Alpkem ‘Flow Solution’ Autoanalyzer (Perstorp, 1992). Urea was measured using a modification of the methods described by Mulvenna and Savidge (1992) and Goeyens et al. (1998). Total dissolved nitrogen was measured as NO₃⁻ following alkaline persulfate digestion in pre-combusted sealed ampoules (modified from Koroleff, 1983), and DON was calculated by difference between TDN and DIN (NH₄⁺ + NO₃⁻ + NO₂⁻). Several additional organic nitrogen standards were used to examine the recovery efficiency of the method (Table 1). The percent recovery was 95–100%, with the exception of ATP (85%). The limits of detection for the TDN method were 0.6 μM (calculated as two times the standard deviation of the blanks, n=10, as defined by Willason & Johnson, 1986).

### Elemental analysis

Following each experiment, the algae used in each core were rinsed with deionized water, patted dry and frozen. They were later freeze-dried and ground to homogeneity with a mortar and pestle. Small sediment cores (4 cm I.D.) were collected from each site at the time of the experiment, sectioned (0–2, 2–5, 5–10 cm), freeze-dried and ground with a mortar and pestle. Sediment samples were acidified with 20% HCl to remove carbonates. C and N content of sediment and algae were measured on a Carlo Erba NA 2500 Elemental Analyzer.

### Results

#### Site characteristics

Water column TDN ranged from 16–33 μM and was, in general, highest at the Creek site and lowest at the Hog site, with intermediate levels at the Shoal site throughout the seasons (Figure 2). Dissolved organic nitrogen represented 52–98% of the TDN pool, and ranged from 11–30 μM at Creek, 9–22 μM at Shoal 1,

**Table 1. Percent recovery of 20 μM organic nitrogen standards**

<table>
<thead>
<tr>
<th>LEU</th>
<th>HUM</th>
<th>GLY</th>
<th>NIC</th>
<th>UREA</th>
<th>ATP</th>
<th>EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.9 ± 0.3</td>
<td>95.8 ± 0.2</td>
<td>98.1 ± 0.5</td>
<td>100.7 ± 0.5</td>
<td>100.5 ± 0.2</td>
<td>84.8 ± 0.1</td>
<td>95.2 ± 0.3</td>
</tr>
</tbody>
</table>

Abbreviations are: LEU, leucine; HUM, humic acid; GLY, glycine; NIC, nicotinic acid; UREA, urea; ATP, adenosine triphosphate; EDTA, ethylenediaminetriacetic acid. Percent recovery noted in italics above bars. n=2 for HUM & EDTA; n=4 for all others.

**Flux calculations**

Fluxes were estimated based on the slope of the change in concentration over time using the equation:

\[
J = \frac{dC}{dt} \frac{V}{A}
\]

where J is the flux rate in μmol m⁻² h⁻¹, A is the core area, V is the water volume, C is the concentration and t is time. Sediment and sediment+algae fluxes were corrected for changes in the water blanks. Uptake and release by *U. lactuca* were calculated by subtracting the mean fluxes measured in sediment only chambers for that site from the sediment+algae chambers, and is expressed per gram dry weight of algae. Daily sediment flux and algal uptake rates were obtained by multiplying the measured hourly rate by the actual number of daylight or dark hours for that date.

**Figure 2.** Water column concentrations of DON (urea free), urea and DIN (NO₃⁻ + NO₂⁻ + NH₄⁺) from May, July and August 1998 and October 1997. DON (urea free), ■ urea, □ DIN.
and 12–20 μM at Hog. Highest values occurred in July. At all sites, DIN was highest and made up a greater proportion of TDN in October than in other months. Urea was generally lower in October and May (<1 μM) and higher in July and August at all sites (up to 2 μM), comprising a maximum of 9% of the TDN pool at Shoal 1 in August.

As with water column N, sediment %N and %C were highest at Creek, intermediate at Shoal 1, and lowest at Hog (Table 2). At Hog, the %N was consistently around 0.01%. The C:N in these sandy sediments was approximately 9 in May and July, declined in August, and rose in October, due mainly to changes in C content. Although the overall %N was higher, a somewhat similar pattern was seen in the C:N at Shoal 1 where there was a rise in October due to decreased %N. Following the crash of the macroalgal bloom in early July at Shoal 2, the sediment %N was 0.4% and %C was 2.5%, yielding a C:N of 7.2. Three weeks later the sediment N and C had dropped back down to values approaching those of Shoal 1, and the C:N had increased to 11.3. The Creek site had the highest C:N in the summer months of July and August, and lowest in May and October.

Mean macroalgal tissue N content was 2.5 ± 0.4, 2.0 ± 0.3 and 1.1 ± 0.2% for Creek, Shoal 1 and Hog macroalgae, respectively (Figure 3). Variations in tissue N content indicate a gradient of high to low N availability from the mainland seaward, echoing the patterns seen in the water column N and sediment N. There was a weak relationship (P=0.07; SPSS for Windows version 8.0, linear regression function) between macroalgal N and water column DIN. At all sites the highest values occurred in October.

### Table 2. Seasonal surface sediment %N, %C (carbonate-free) and C:N. Values are from top 2 cm section of each sediment core. Errors are the standard error of the mean

<table>
<thead>
<tr>
<th></th>
<th>%N</th>
<th>%C</th>
<th>C:N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Creek</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 May</td>
<td>0.12 ± 0.01</td>
<td>1.07 ± 0.09</td>
<td>10.7 ± 0.1</td>
</tr>
<tr>
<td>30 July</td>
<td>0.14 ± 0.02</td>
<td>1.93 ± 0.33</td>
<td>16.1 ± 1.0</td>
</tr>
<tr>
<td>18 August</td>
<td>0.09 ± 0.00</td>
<td>1.24 ± 0.14</td>
<td>15.5 ± 1.8</td>
</tr>
<tr>
<td>30 October</td>
<td>0.11 ± 0.00</td>
<td>1.05 ± 0.05</td>
<td>11.4 ± 0.9</td>
</tr>
<tr>
<td>Shoal 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 May</td>
<td>0.04 ± 0.00</td>
<td>0.35 ± 0.03</td>
<td>11.8 ± 0.2</td>
</tr>
<tr>
<td>30 July</td>
<td>0.02 ± 0.00</td>
<td>0.17 ± 0.02</td>
<td>9.4 ± 0.5</td>
</tr>
<tr>
<td>18 August</td>
<td>0.04 ± 0.01</td>
<td>0.26 ± 0.11</td>
<td>7.9 ± 1.3</td>
</tr>
<tr>
<td>30 October</td>
<td>0.02 ± 0.01</td>
<td>0.26 ± 0.04</td>
<td>19.0 ± 4.9</td>
</tr>
<tr>
<td>Shoal 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 July</td>
<td>0.40 ± 0.11</td>
<td>2.47 ± 0.64</td>
<td>7.2 ± 0.2</td>
</tr>
<tr>
<td>30 July</td>
<td>0.09 ± 0.00</td>
<td>0.87 ± 0.01</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td>Hog</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 May</td>
<td>0.01 ± 0.00</td>
<td>0.07 ± 0.01</td>
<td>8.9 ± 0.4</td>
</tr>
<tr>
<td>30 July</td>
<td>0.01 ± 0.00</td>
<td>0.10 ± 0.01</td>
<td>9.3 ± 0.4</td>
</tr>
<tr>
<td>18 August</td>
<td>0.01 ± 0.00</td>
<td>0.03 ± 0.01</td>
<td>3.4 ± 0.5</td>
</tr>
<tr>
<td>30 October</td>
<td>0.01 ± 0.00</td>
<td>0.10 ± 0.00</td>
<td>14.3 ± 4.1</td>
</tr>
</tbody>
</table>

### Flaxes

The concentration of DIN in all cores incubated with algae declined to a constant concentration close to zero within a few hours after the initiation of the experiment due to rapid DIN uptake by *U. lactuca*. This results in light flux rates that represent only the initial surge uptake and dark flux rates of zero. Since only the light values for macroalgal DIN uptake are interpretable, and even these are not representative of the potential uptake rate, the DIN fluxes for the sediment + algae cores are not discussed at length.

The DIN sediment flux rates at the Creek were not significantly different from zero (Figure 4) except during October when there was substantial uptake of
DIN, most likely as a result of high initial concentrations. The mean urea flux to the water column (188 μmol m⁻² d⁻¹) was 60-fold greater than the mean urea-free DON flux (3 μmol m⁻² d⁻¹) at the Creek site (Table 3). The highest overall urea flux was measured in August (Figure 4). Fluxes for the rest of the DON pool were not significantly different from zero, with the exception of August, when the net flux was negative at this site. In contrast, U. lactuca in these cores released DON into the water in all months with the exception of August (Figure 5). The urea released from the sediments was taken up immediately by the algae, except for July when the uptake rate was not significantly different from zero.

The Shoal sites exhibited the most dynamic fluxes of both DON and DIN (Figure 4). In May,fluxes of all dissolved N compounds were not different from zero at Shoal 1. Even though the macroalgae did not exhibit an episodic crash at Shoal 1, the summer DON fluxes were two-fold higher than those measured at Hog or Creek at any time. At Shoal 2 in July, the 5–10 cm layer of decomposing macroalgae at the sediment surface resulted in a large efflux of DON and DIN. The net TDN flux, >70 mmol m⁻² d⁻¹, was an order of magnitude greater than at any other site. The mean urea flux at Shoal 1 was negative, in contrast to positive mean fluxes at the other sites (Table 3). Shoal macroalgae took up urea only in October and DON only in August (Figure 5). Dissolved organic nitrogen was released in all other months, with highest rates in July.

In May, the Hog Island sediments demonstrated the only positive flux of DIN aside from post-crash Shoal 2 (Figure 4). In all other months DIN was either taken up by these sediments (August and October) or showed an insignificant flux (July). The sediments released urea in all months and DON in August, but took up DON in October. Macroalgal uptake rates for urea were significant in May, July and October (Figure 5). The DON release rates by macroalgae, although positive in all months except May, were so variable that we were unable to discern any patterns.

Overall, there was an inverse relationship between sediment C:N and net sediment TDN fluxes (∙0.06; SPSS for Windows version 8.0, linear regression function). Macroalgal DON release rates did not appear to be proportional to tissue N content (∙0.62; SPSS for Windows version 8.0, linear regression function). Macroalgal releases of DON appeared to occur primarily in the light, although light-dark differences were not significantly different due to high variability (Table 4). No significant differences in algal uptake or sediment release were seen for urea in light versus dark comparisons. Sediment release of DON occurred significantly more in the light than in the dark (Table 4). Dissolved inorganic nitrogen uptake by sediments was significantly higher in the light than in the dark.


### Table 3. Mean daily sediment fluxes of total DON (including urea), urea-free DON, urea and DIN from all experiments. A positive number indicates a flux from the sediment to the water column. Shoal 2 fluxes are not included in the overall mean. Units are μmol N m⁻² d⁻¹; errors are the standard error of the mean, n=12

<table>
<thead>
<tr>
<th>Treatment</th>
<th>TDON (μmol N m⁻² d⁻¹)</th>
<th>DON (urea free)</th>
<th>Urea</th>
<th>DIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Creek</td>
<td>72.9 ± 82.0</td>
<td>3.0 ± 75.3</td>
<td>188.1 ± 53.2</td>
<td>-166.1 ± 90.2</td>
</tr>
<tr>
<td>Shoal 1</td>
<td>367.8 ± 174.6</td>
<td>417.6 ± 201.2</td>
<td>-67.7 ± 67.5</td>
<td>-304.4 ± 165.2</td>
</tr>
<tr>
<td>Hog Island</td>
<td>583.0 ± 289.2</td>
<td>690.9 ± 284.0</td>
<td>-91.9 ± 59.1</td>
<td>-322.4 ± 130.9</td>
</tr>
<tr>
<td>Overall</td>
<td>1066.9 ± 268.9</td>
<td>1325.3 ± 323.4</td>
<td>-146.6 ± 51.6</td>
<td>-596.8 ± 235.3</td>
</tr>
</tbody>
</table>

### Discussion

Dissolved organic nitrogen is an important component of the total dissolved nitrogen pool in Hog Island Bay, comprising 58–95% of water column TDN. While river-dominated estuaries often have substantial allochthonous inputs of DON (Meybeck, 1982; Hopkinson, 1998), the DON in this system appears to come from autochthonous macroalgal production within the lagoon in addition to enriched groundwater. In spite of the variation in measured fluxes across the different habitat-types in the lagoon, the relative proportions of DON, DIN and urea remain relatively constant between sites, suggesting that the lagoon is very well mixed. Benthic macroalgae also appear to act as a conduit whereby DIN and some DON compounds (urea) are taken up during production, and subsequently released to the water column as different DON compounds during active growth. In addition, particulate organic nitrogen (PON) is provided to the sediments following senescence. The input of DON to the water column from decomposing organic matter in the sediments and from living macroalgae on the sediment surface has important consequences for the metabolism of heterotrophs and autotrophs capable of DON uptake. The uptake of bioavailable dissolved N compounds and conversion to PON and DON by macroalgae adds an additional step in the processing of N as it moves across the land-sea interface and may prolong its retention within the lagoon.

A proportion of the nutrient demand for estuarine primary production is often supported by nutrients recycled within the sediments and released to the water column (e.g. Nixon, 1981; Fisher et al., 1982; Koop et al., 1990; Cowan & Boynton, 1996). Indeed, in other coastal ecosystems, it has been shown that macroalgal uptake intercepts N released from the sediments (Valiela, 1992; Bierzychudek et al., 1993; McGlathery et al., 1997). However, the sediments of Hog Island Bay were not a source of DIN to the water column, with the exception of Shoal 2 following the crash of the algal bloom and Hog in May. As such, it appears that the macroalgae instead may prevent the downward diffusion of water column DIN to the sediments, especially because U. lactuca takes up N more rapidly than the sediments in the lagoon.

While sedimentary fluxes of DIN do not appear to be a significant component of macroalgal nutrition in Hog Island Bay, sediment-derived urea may be important. In using organic N directly, the algae effectively bypass the complete mineralization of organic N to inorganic N. Not all species of macroalga are capable of urea uptake and under conditions of low DON:urea availability, those species that can are at a competitive advantage. Recent evidence suggests that urea may be a more important source of N for primary producers than originally thought. For example, Cho et al. (1996) demonstrated that bacterial production of urea-N in the water column of the Southern California Bight was sufficient to supply 35–91% of the daily phytoplankton N demand. While sediment release of urea is likely to be closely coupled to macroalgal productivity in Hog Island Bay, at this point we do not know enough about the N demand of the macroalgal population to determine the relative importance of urea. Other, as yet unidentified, DON compounds, such as amino acids, may also play an important role in meeting algal N demand. Because macroalgae may serve as an indicator of an integrated measure of N availability, the high tissue N near the mainland suggests that terrestrial and groundwater N, entering at the land-water interface, are important to the overall N budget. This also lends support to the idea that the lagoon is well mixed, because higher concentrations of N in the water column are not consistently observed close to the mainland. Overall
mean macroalgal uptake rates for DIN and urea calculated from our flux incubations were 1·2 ± 0·5 and 0·6 ± 0·2 μm gdw⁻¹ d⁻¹. Maximum uptake rates (V_max) of 138 ± 78 μmol gdw⁻¹ h⁻¹ for ammonium (Fujita, 1985) and 11·7 ± 0·6 μmol gdw⁻¹ h⁻¹ for urea (Tyler, unpublished data) have been measured under non-limiting conditions, which are significantly higher than those reported here. However, N availability was relatively low at our sites and the rates obtained in this study may be a more realistic estimate of the impact that algae have on DIN and urea from water column and sediment sources in the lagoon.

In addition to the uptake of urea and DIN from the sediments and water column, respectively, living macroalgae also have a substantial impact on the net DON release from the benthos to the water column. The mean total DON flux in cores with algae was 331 μmol m⁻² d⁻¹ higher than the fluxes in the sediment only cores (Table 3; using urea-free DON flux the difference is 450 μmol m⁻² d⁻¹). Like phytoplankton (Bronk et al., 1994), the macroalga U. lactuca, appears to 'leak' DON into the water during active growth. Over relatively short time scales, DIN, urea, and possibly other small DON compounds are taken up, transformed and subsequently released to the water column as DON. Release was higher in the light than the dark, indicating a possible association with photosynthesis.

In dense patches, living macroalgae may be a more important source of DON for the water column than the sediments. Given the mean release rate of urea free DON by U. lactuca (3·5 ± 0·9 μm gdw⁻¹ d⁻¹) and the range of macroalgal biomass found at the sites used in this study (0 to >650 g dw m⁻²) there is the potential for the release of more than 2 mmol N m⁻² d⁻¹ from actively growing algae to the surrounding water (assuming all species have similar release rates). Dissolved organic nitrogen release by macroalgae has not been reported in the literature, however DOC release has been documented previously, with a wide range in the values reported (e.g. Khailov & Burlakava, 1969; Brylinsky, 1977; Moebus & Johnson, 1974). While the bioavailability of this released organic matter is as yet unknown, these inputs are likely to fuel heterotrophic metabolism in the water column (Brylinsky, 1977; Valiela et al., 1997).

Our measurements of macroalgal uptake and release of dissolved N are based on an estimate of the net change between cores incubated with and without algae. However, the macroalgae may have important indirect effects on nitrogen dynamics that were masked by our methods. For example, macroalgal chlorophyll a is generally low across the lagoon (1–8 μg cm⁻²; McGlathery et al., in press), however the light-dark difference in DIN uptake by sediments suggests that benthic microalgae were responsible for DIN uptake in the light. Uptake of water column NH₄⁺ by benthic microalgae has been shown to limit coupled nitrification-denitrification in the sediments (Rysgaard et al., 1995), which would in turn prolong...
the retention of N within the lagoon by slowing the loss as N₂. Where macroalgae are present in sufficient biomass, they will outcompete the macroalgae for water column nutrients and, by shading the sediment surface, for light. Further, over the diurnal cycle, macroalgal production and consumption of O₂ may alter the redox status at the sediment surface (Lavery & McComb, 1991), which may in turn affect sediment fluxes of DIN and DON (Kristensen & Blackburn, 1987; Hansen & Blackburn, 1991; Miller-Way et al., 1994) and may affect coupled nitrification-denitrification (Krause-Jensen et al., 1999).

Delivery of organic matter to the sediment surface from decomposing macroalgal tissue is an additional source of DON to the sediments and water column. Our data show clearly that in a macroalgal-dominated lagoon such as Hog Island Bay, DON was a major component of the TDN flux from the sediment to the overlying water column. This is consistent with the conclusion of Bartoli et al. (1996) who inferred high DON fluxes from sediment porewater profiles in the Lagoon of Venice. The mean total DON and urea sediment fluxes measured at the individual sites in this study fall within the range of reported values for a variety of coastal ecosystems (Table 5). In Hog Island Bay, macroalgal biomass peaks in mid-summer and rapidly declines (McGlathery et al., in press). In spite of this decline, the benthos (including macroalgae) remained net autotrophic during the study period (McGlathery et al., in press), with the exception of Shoal 2. The net uptake of DIN and release of DON observed at Hog, Shoal 1 and Creek are consistent with a net autotrophic metabolism.

The flux of nutrients from sediments is generally thought to be proportional to the amount of organic matter delivered to the sediment surface (Nixon, 1981). Kelly and Nixon (1984) and Kelly et al. (1985) demonstrated a positive relationship between sediment nutrient regeneration and primary production in experimental mesocosms and many others have reported increases in sediment DIN, DON and/or urea fluxes with the addition of organic material to the sediment surface both in situ (Jensen et al., 1990) and experimentally (Enoksson, 1993; Sloth et al., 1995; Therkildsen et al., 1996). The Shoal sites in Hog Island Bay had the highest N flux rates throughout the year, suggesting that sediment N release was related to macroalgal biomass. The ratio of C:N in sediments, often an indicator of the lability or age of the sediment organic matter, also may be related to sediment N fluxes (e.g. Kristensen & Blackburn, 1987; Caffrey, 1995; Hall et al., 1996). Low C:N values in the summer at both Shoal sites were most likely to be indicative of the input of fresh organic matter from macroalgal senescence, and were linked to large fluxes of DON. This is concordant with the observations of Hansen and Blackburn (1992) who observed both an increase in the magnitude of the DON flux as well as an increase in the proportion of the TDN flux made up by DON following the simulated deposition of an algal bloom. The magnitude of the summertime DON fluxes following the macroalgal decline at Shoal 2 rivals the highest values reported for coastal systems (Table 5). At both the Creek and Hog sites, where inputs of macroalgal detritus were low, the sediments were not a net source of N to the water column, even though urea release was high. The Creek site, closest to the mainland and with muddy sediments, had the highest sediment N content and also the highest C:N, probably reflecting the salt marsh sources of refractory organic material with a relatively high C:N. In contrast, the sandy, low-N sediments at Hog had

### Table 4. Light and dark fluxes of DON (urea free), urea and DIN. A positive number indicates release from the sediment or *U. lactuca* to the water column. Numbers represent pooled data from all experiments (n=36), except for Shoal 2 in July 1998. Errors are the standard error of the mean. Significance based on *t*-test between light and dark, equal variances not assumed. Units are μm gdw⁻¹ hr⁻¹ for macroalgal uptake/release and μm m⁻² hr⁻¹ for sediment fluxes.

<table>
<thead>
<tr>
<th></th>
<th>Light</th>
<th>Dark</th>
<th><em>P</em></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Urea lactuca</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DON (urea free)</td>
<td>0.23 ± 0.10</td>
<td>0.06 ± 0.10</td>
<td>0.206</td>
</tr>
<tr>
<td>Urea</td>
<td>0.00 ± 0.03</td>
<td>−0.06 ± 0.03</td>
<td>0.148</td>
</tr>
<tr>
<td>DIN</td>
<td>−0.13 ± 0.04</td>
<td>0.02 ± 0.01</td>
<td>0.003</td>
</tr>
<tr>
<td><strong>Sediment</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DON (urea free)</td>
<td>21.84 ± 12.43</td>
<td>−11.58 ± 9.11</td>
<td>0.034</td>
</tr>
<tr>
<td>Urea</td>
<td>4.35 ± 2.53</td>
<td>1.35 ± 2.89</td>
<td>0.437</td>
</tr>
<tr>
<td>DIN</td>
<td>−13.79 ± 4.36</td>
<td>−3.91 ± 1.49</td>
<td>0.038</td>
</tr>
</tbody>
</table>
Table 5. Comparison of sediment-water column DON fluxes from selected coastal systems. Comparison was limited to studies that directly measured fluxes, rather than estimations based on pore-water profiles. All measurements in mmol m\(^{-2}\) d\(^{-1}\).

<table>
<thead>
<tr>
<th>System</th>
<th>DON flux</th>
<th>Urea flux</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>Narragansett Bay, RI, U.S.A.</td>
<td>0.2–0.7</td>
<td>0.3</td>
<td>range: Nixon et al., 1976, mean: Nixon and Pilson, 1983</td>
</tr>
<tr>
<td>Patuxent River Estuary, MD, U.S.A.</td>
<td>−0.7–0.4</td>
<td></td>
<td>Boynton et al., 1980</td>
</tr>
<tr>
<td>Georgia Bight, GA, U.S.A.</td>
<td>−1.9~5.9</td>
<td>0.20</td>
<td>Hopkinson, 1987</td>
</tr>
<tr>
<td>Bay of Pampoul, France</td>
<td>−116–107</td>
<td>17.00 upper bay</td>
<td>2.1 Boucher and Boucher-Rodoni, 1988</td>
</tr>
<tr>
<td>Atchafalaya-Fourleague Bay, LA, U.S.A.</td>
<td>−3.5–0.1</td>
<td>0.3</td>
<td>Teague et al., 1988</td>
</tr>
<tr>
<td>Northern Bering Shelf</td>
<td></td>
<td></td>
<td>0.7 Lomstein et al., 1989</td>
</tr>
<tr>
<td>Tomales Bay, CA, U.S.A.</td>
<td></td>
<td></td>
<td>Dollar et al., 1991</td>
</tr>
<tr>
<td>Aarhus Bight, Denmark</td>
<td></td>
<td></td>
<td>Hansen et al., 1991</td>
</tr>
<tr>
<td>Svalbard, Norway</td>
<td>0.3–2.1</td>
<td>0.93</td>
<td>0.05–0.11 0.01 Blackburn et al., 1996</td>
</tr>
<tr>
<td>Chesapeake Bay, MD, U.S.A.</td>
<td>−6.0–13.2</td>
<td>0.18 middle bay</td>
<td>Cowan &amp; Boynton, 1996</td>
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<tr>
<td>Chesapeake Bay, MD, U.S.A.</td>
<td>−0.01–0.42</td>
<td>0.11 south bay</td>
<td>Burdige and Zheng, 1998</td>
</tr>
<tr>
<td>Young Sound, Greenland</td>
<td>−0.01–1.07</td>
<td>0.21</td>
<td>0.03 Rysgaard et al., 1998</td>
</tr>
<tr>
<td>Hog Island, VA, U.S.A.</td>
<td>38.89</td>
<td></td>
<td>0.07 This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>post-macroalgal crash</td>
</tr>
</tbody>
</table>
insignificant fluxes in May and July followed by a large flux of DON when the sediment C:N dropped in August. This release, which suggests a greater relative availability of high N organic material, coincided with a period of macroalgal decline at this site (McGlathery et al., in press).

Fast growing, opportunistic species of macroalgae have ‘boom and bust’ life cycles, little structural material, and rapid decomposition following senescence relative to vascular plants (Buchsbaum et al., 1991; Duarte, 1995; Bourgues et al., 1996). The labile fractions of macroalgal-derived organic matter disappear within days to weeks (Buchsbaum et al., 1991; Enriquez et al., 1993). The pulse of organic material at both Shoal 1 and Shoal 2 appeared to be utilized by October, when the C:N value more than doubled and flux rates decreased. The increase in C:N also indicates that N was metabolized and removed from the sediments more quickly than C. Given the biomass measured at Shoal 2 in June of 1998 and the measured flux rates, all of the N contained in the previously living macroalgae would have been released to the water column within approximately 13 days (this estimate is based on the N content of all algal species found at the site and ignores losses by denitrification). This is in agreement with the increased C:N measured 3 weeks after the crash. The release of nutrients following the macroalgal decline was thus an ephemeral occurrence that accelerated nutrient cycling, as has been shown in other systems (Buchsbaum et al., 1991; Duarte, 1995; Viaroli et al., 1996). A sudden increase in oxygen demand is also typically associated with such events (Valiela et al., 1992; Duarte, 1995; Viaroli et al., 1995).

In contrast to the substantial net DON flux at the Shoal site, the urea component of this flux was negligible. However, at the Creek and Hog sites, urea made up the majority of the N flux to the water column. This may indicate a highly developed infaunal community at the Creek and Hog sites in comparison to the Shoal site (Lomstein et al., 1989) and is consistent with Sundback et al. (1990) who demonstrated an impoverished infaunal community below macroalgal mats. Across all the sites, urea was a very important component of the N flux, comprising 32% of N released from the sediments. This is consistent with other studies that also have shown urea to be an important component of the sediment N flux: 36–70% in northern Bering Shelf sediments (of urea+NH\(_4^+\)+NO\(_2^-\)+NO\(_3^-\), Lomstein et al., 1989) and ~30% in the Bay of Pampoul, France (of urea+NH\(_4^+\), Boucher & Boucher-Rodoni, 1988). Likewise, Burdige and Zheng (1998) have suggested that the low C:N of benthic DOM fluxes in Chesapeake Bay intimates the potential importance of labile compounds such as urea and amino acids. Our data suggest that while net sediment-water column DON fluxes are related to macroalgal biomass, flux rates of specific DON compounds may be controlled by a more complex set of factors.

Short-term (hours) flux measurements such as ours tend to be more variable than those from longer-term incubations (days–weeks) (Nixon, 1981; Teague et al., 1988; Cowan & Boynton, 1996; Burdige & Zheng, 1998). However, in longer term experiments, DON released from the sediments may be mineralized in the water column to CO\(_2\) and DIN, causing an underestimate of DON fluxes and an overestimate of DIN fluxes. In some cases, we observed large differences between replicates which meant that making corrections for water column and sediment activity occasionally required subtracting a highly variable number from another highly variable number. For example, the August macroalgae+sediment DON flux measurement for the Hog site yielded a mean of 5.6 ± 4.8 \(\mu\)mol m\(^{-2}\) d\(^{-1}\); the mean sediment flux was used to calculate this. If the range of sediment flux values had been used, we would have calculated algal DON release/uptake rates ranging from −4.4 to +19.7 \(\mu\)mol m\(^{-2}\) d\(^{-1}\). This variability sometimes made trends in the data less significant. However, the release of DON from mid-lagoon shoal sediments in July was significant in spite of the variability, and was likely to have had an effect on overall system metabolism in the lagoon. We measured the highest water column DON concentrations across the lagoon in July, perhaps as a result of the massive release of DON from the decomposing algal mat. Further, water column chlorophyll \(a\) more than doubled following the crash at Shoal 2, suggesting the stimulation of phytoplankton production by the release of nutrients (McGlathery et al., in press). In this study, we were only able to address diffusive fluxes from the sediments. Advection by tidal forcing and the upwelling of N-rich groundwater may add substantially to the amount of dissolved N crossing the sediment-water interface.

**Conclusions and future research directions**

Our results clearly show that macroalgae play an important role in the uptake of DIN from the water column and urea from the sediments, and that other DON compounds are released to the water column during active growth as well as following senescence. Where decaying macroalgal biomass was deposited on the sediment surface, as at Shoal 1 and Shoal 2, it appears that mineralization was incomplete, as most...
of the N flux from the sediment occurred as DON rather than DIN (or N$_2$). In the absence of advection of DON directly from the system, mineralization to DIN in the water column adds an additional step to the processing of N as it moves across Hog Island Bay. DIN in the water column adds an additional step to the processing of N as it moves across Hog Island Bay.

In lumping together the individual compounds into ‘DON’, the dynamics of individual compounds are masked. When comparing the urea fluxes with the DON fluxes measured in this study, for example, it is evident that in many cases urea is behaving differently than the remainder of the DON pool. Discrepancies such as this underscore the importance of measuring fluxes of specific DON compounds, especially highly bioavailable compounds such as urea and amino acids. Future studies in this system will address DON fluxes on a compound specific basis in all seasons and will relate this to macroalgal biomass and productivity throughout the lagoon.

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