

## The biogeochemical cycling of dissolved organic nitrogen in estuarine sediments

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### Abstract

Benthic fluxes and pore-water profiles of dissolved organic nitrogen and carbon (DON and DOC, respectively) were determined in seasonal studies at contrasting sites in Chesapeake Bay. Pore-water dissolved organic matter (DOM) concentrations were elevated over bottom-water values, generally increased with depth, and ranged from 15 to  $\sim 160 \mu\text{M}$  for DON and  $\sim 200\text{--}2000 \mu\text{M}$  for DOC. Pore-water DOM concentrations and the C:N ratio of this material showed spatial (depth) and temporal changes that varied among the sites studied. These trends appeared to be related to differences in the types of sediment organic matter (SOM) undergoing remineralization, as well as differences in the biogeochemical processes occurring in the sediments (e.g., the presence or absence of bioturbation and bioirrigation). Measured DON fluxes ranged from essentially zero to  $\sim 0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ , and together with benthic DOC fluxes were coupled to seasonal trends in temperature and SOM remineralization rates. On an annual basis, benthic DON fluxes were a small fraction ( $\sim 3\%$ ) of benthic inorganic nitrogen fluxes. At an anoxic nonbioturbated site measured DON fluxes were essentially identical to calculated diffusive DON fluxes, whereas at a bioturbated and bioirrigated site, measured DON fluxes were much greater than calculated fluxes. The molar ratios of DOC to DON benthic fluxes ranged from  $\sim 2$  to 6 and were lower than those of pore-water DOM, which were  $> \sim 10$ . This implies that DOM accumulating in these sediment pore waters was carbon-rich compared with the DOM that was either remineralized or escaped the sediment as a benthic flux. These measured benthic DON fluxes and estimated DON fluxes from continental margin sediments combine to yield a lower limit for the integrated sediment DON flux to the oceans that is similar to a value estimated previously. These net DON inputs to the oceans are small compared with internal oceanic DON cycling rates, although sediment DON fluxes and riverine DON inputs are roughly of the same order. At the same time, our results also suggest that the DON escaping from these sediments may not be inherently refractory because of its observed low C:N ratio. This implies that estuarine sediments (and perhaps marine sediment in general) may not be a major source of “refractory” DON to the oceans.

Dissolved organic nitrogen (DON) can be a significant component of the dissolved nitrogen pool in the oceans (Sharp 1983), although little is known about its biogeochemical behavior. This is because of methodological problems involved with making the DON measurement (Walsh 1989; Hansell 1993; Hopkinson et al. 1993) and because a significant fraction of the DON in seawater cannot be characterized in terms of known biochemicals such as urea, amino acids, or aliphatic amines (Sharp 1983; Lee 1988; Antia et al. 1991). Much of the DON in the water column has historically been presumed to be refractory, although all evidence in the literature does not necessarily support this assumption (*see* discussions in Jackson and Williams 1985, Walsh 1989, Antia et al. 1991, and Bronk et al. 1994).

DON is a heterogeneous class of organic compounds that ranges from well-defined biochemicals such as urea or amino acids to more complex (and poorly characterized) compounds such as humic and fulvic acids (*see* Walsh 1989, Antia et al. 1991, and references therein). Much of the nitrogen functionality in DON appears to be in the amide form ( $-\text{NH}_2$ ; McCarthy et al. 1997), although heterocyclic nitrogen compounds (pyrroles and pyridines) have also been de-

tected in seawater and in sediment organic matter (SOM; Antia et al. 1991; Patience et al. 1992). In sediment pore waters, DON compounds such as dissolved amino acids can be produced as intermediates in the SOM remineralization (Burdige and Martens 1990), whereas other types of more refractory DON may be end products produced from the partial remineralization or oxidation of SOM (Hatcher and Spiker 1988; Amon and Benner 1996; Burdige and Gardner 1998). Refractory DON can also be produced by abiotic condensation reactions that are generally referred to as geopolymerization or humification reactions (Tissot and Welte 1978; Hedges 1988).

Concentrations of DON in marine sediment pore waters are generally elevated over bottom-water values (Heggie et al. 1987; Lomstein et al. 1998; Landén-Hillemyr 1998; Cifuentes and Morse unpubl. data), predicting the occurrence of DON fluxes out of sediments. It has been suggested that these benthic fluxes may be a source of refractory DON to the oceans (Hedges 1992) and that these fluxes may also be an important component of some sediment nitrogen budgets (Blackburn et al. 1996; Landén-Hillemyr 1998; *also see* discussions in Bender et al. 1989 and Cowan and Boynton 1996). In part, the significance of these fluxes in oceanic processes and the marine nitrogen cycle is similar to that which has been discussed for benthic fluxes of dissolved organic carbon (DOC) and the marine carbon cycle (Burdige et al. 1992; Chen et al. 1993; Bauer et al. 1995; Burdige et al. unpubl. data). However, because nitrogen can be a limiting nutrient in marine ecosystems (Carpenter and Capone 1983), and because marine phytoplankton can use DON as their nitrogen source (Jackson and Williams 1985; Antia et

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al. 1991; Bronk et al. 1994), there is additional interest in understanding the role of sediments as a source of DON to the water column.

In this article, we describe studies of DON cycling in contrasting sediments of Chesapeake Bay, along with parallel studies of sediment DOC cycling. This work involved seasonal pore-water studies and direct benthic flux measurements. These results will be used to quantify the role of benthic DON fluxes in nitrogen cycling in these sediments, as well as to examine the controls on pore-water dissolved organic matter (DOM) concentrations and the role of this material in SOM preservation and remineralization (Burdige and Gardner 1998).

### Study sites

The field sites for this study were three contrasting sites in Chesapeake Bay (*see* maps in Burdige and Homstead 1994, Burdige and Gardner 1998). The biogeochemical characteristics of these sediments are summarized below and in a number of previous articles (Burdige and Homstead 1994, Burdige et al. 1995, Cowan and Boynton 1996, Skrabal et al. 1997, Burdige and Gardner 1998, Marvin-DiPasquale and Capone 1998). Site N3 is in the northern Bay where bottom-water salinities range from  $<0.1$  to  $\sim 10$  psu. Site M3 is in the mesohaline portion of the Bay (bottom-water salinities are  $\sim 10$ – $20$  psu) where seasonal anoxia (or low-oxygen conditions) generally occurs in the bottom waters during the summer months (Smith et al. 1992). However, during our sampling times (March 1995, July 1995, October 1995, March 1996, August 1996, and October 1996) bottom-water anoxia was only observed at this site in August 1996. Site S3 is in the southern Bay, has bottom-water salinities that range from  $\sim 20$  to  $30$  psu, and is well oxygenated year-round. Water depths at all three sites range from  $\sim 10$  to  $15$  m.

The sediments at site M3 are fine-grained, sulfidic sediments in which sulfate reduction dominates organic matter remineralization. The sediments here are organic-rich (total organic carbon [TOC]  $>3\%$ ; total nitrogen [TN]  $\sim 0.5$ – $1\%$ ) and have a C:N ratio of  $\sim 6$ – $10$  (all TOC and TN data discussed here are from Burdige and Homstead 1994, Burdige et al. 1995, and Cowan and Boynton 1996). Bioturbation is virtually absent in these sediments, although a few bivalve spat and polychaete worms inhabit the upper  $\sim 5$  cm of sediment in the early spring (Kemp et al. 1990).

The sediments at site S3 are silty sands with a lower organic matter content (TOC  $\sim 0.6$ – $0.8\%$ ; TN  $\sim 0.04$ – $0.06\%$ ; solid-phase C:N  $\sim 12$ – $16$ ). These sediments are bioturbated and bioirrigated by large suspension-feeding tube worms and other benthic macrofauna (Schaffner 1990).

The sediments at site N3 are clay dominated, iron rich, and contain a diverse community of polychaetes and bivalves (Marvin-DiPasquale and Capone 1998). The sediments contain  $\sim 2$ – $4\%$  TOC and  $\sim 0.2$ – $0.3\%$  TN, and the C:N ratio of the sediments ranges from  $\sim 12$ – $22$ . Consistent with these high C:N ratios, the organic matter in these sediments appears to be largely terrestrially derived, on the basis of its low  $\delta^{13}\text{C}$  value ( $< -25\%$  versus  $\sim -21$  to  $-22\%$  at

the other two sites; J. Cornwell unpubl. isotope data cited in Marvin-DiPasquale and Capone 1998).

### Methods

*Pore-water and water-column sample collection*—Sediment cores were collected by box core and subcored for sediment pore-water and benthic flux studies (sediment subcores used at sites M3 and N3 were 7-cm interior diameter [ID], and the pressurized core barrels used at site S3 had a 9-cm ID; cores used for benthic flux studies had a 14-cm ID). Pore waters were extracted from sediments by either core sectioning under an inert atmosphere and subsequent centrifugation (sites M3 and N3) or by the use of a modified pressurized core barrel technique (site S3). This latter technique was used at site S3 to avoid artifacts associated with pore-water collection via centrifugation from bioturbated sediments (for details, *see* Martin and McCorkle 1993; Burdige and Gardner 1998; Alperin et al. unpubl. data). Both pore-water collection techniques are described in detail in Burdige and Gardner (1998). At sites M3 and N3, sediments were generally sectioned in 1-cm depth intervals down to 4 cm, at 2-cm depth intervals to 4–8 cm, and at 3-cm intervals at greater depths. The pressurized core barrels we used have discrete sampling ports every 1 cm down to 30 cm, although samples were only drawn from selected ports (roughly matching the sampling distribution used at the other sites).

Pore waters collected by either technique were filtered through  $0.45\text{-}\mu\text{m}$  Gelman Acrodisc filters. Samples for organic analyses were then placed into cleaned glass vials, quick-frozen in an aluminum block placed in a standard freezer, and stored frozen until analyzed. Samples for DOC analysis were acidified to a pH of  $\sim 2$  with 6 M HCl before freezing, whereas aliquots for DON analyses were frozen unacidified. Pore-water samples for other analyses (e.g., sulfate,  $\Sigma\text{CO}_2$ ) were stored until analyzed as described previously (Burdige 1991; Burdige and Homstead 1994; Burdige and Gardner 1998).

Samples for water-column DOC and DON analyses were collected from Niskin bottles mounted on a rosette. An all-polypropylene syringe was placed directly into the nipple of the bottle, and the syringe was rinsed three times with water from the bottle before a water sample was collected. These water-column samples were then processed (under ambient air) as described above.

*Benthic flux determinations*—Immediately after collection, sediment subcores for benthic flux studies were sealed with plastic caps and stored in a darkened water bath at in situ temperatures. The water over the core was periodically flushed with bottom water until the flux experiment was started (to prevent oxygen depletion). The water overlying the core was then flushed with 5 volumes of fresh bottom water, and the height of the water overlying the core was set at 9–13 cm. At this point, flux studies were carried out in the laboratory at in situ temperatures using the procedures described by Burdige and Homstead (1994), although here all fluxes were determined with single flux measurements made with three replicate cores (as opposed to making repeated flux measurements with the same core).

As in our previous work, these flux determinations were run as open flux measurements in that the tops placed on the core tubes were not sealed to avoid contact with the overlying air. For experiments run under normoxic conditions (i.e., when the bottom waters contained dissolved oxygen), moistened air was bubbled through the water overlying the core at a bubbling rate of 1 bubble every 4–5 s, to prevent oxygen depletion in this water (*see* Aller et al. 1985). Our past work has demonstrated that this approach maintains oxygen concentrations in the water overlying the cores at near-constant values that are similar to those in the bottom waters at the time of collection. Control experiments have also shown that the loss of CO<sub>2</sub> by this bubbling process accounts for <1% of measured benthic ΣCO<sub>2</sub> fluxes. For the one flux determination run under anoxic conditions (August 1996 with site M3 sediments) N<sub>2</sub> gas, rather than air, was bubbled through the water over the cores. Nitrogen gas was also blown across the headspace of these anoxic cores (i.e., between the lid placed on the core tube and the surface of the water overlying the core) at a gas flow rate much higher than the water bubbling rate to further maintain anoxic conditions in this flux measurement (*see* Burdige and Homstead 1994 for details).

During flux studies, samples of the water overlying the core were periodically removed, filtered, and stored for later analysis (*see above*). At each sampling time, an equivalent amount of bottom water was added back to the water overlying the core. This recharge water came from a parallel control experiment carried out in the dark at in situ temperatures in a clean glass bottle (anoxic control experiments were run by placing these bottles in a N<sub>2</sub>-filled anaerobic jar). Samples from these control experiments were also periodically taken, filtered, and stored as described above for analysis later.

Benthic fluxes were determined with these data as follows. Concentration data from the water overlying the cores were first corrected to account for the sequential dilution of the water overlying the core caused by the addition of recharge bottom water when each time point was taken. The slope of the best-fit line through the control data was then subtracted from the slope of the best-fit line through the corrected concentration data, to account for any in situ production or consumption of analytes in the water overlying the core. Benthic fluxes were then determined by multiplying this corrected slope by the volume: surface area ratio of the water overlying the core (*see* Burdige and Homstead 1994 and Berelson et al. 1996 for details).

Flux determinations were run for ~100 up to 300 h to obtain good time courses for the changes over time in DON concentrations in the water over the flux cores (*see the section Comparison of our benthic nitrogen fluxes...* for further details on the rationale for this approach). Such long-term flux measurements are prone to potential problems (*see* discussions in Blackburn 1986; Devol 1987; Bender et al. 1989; Berelson et al. 1996), although in most cases these problems express themselves as nonlinear concentration changes during the later parts of a flux core incubation. Thus, we calculated benthic fluxes using only data that showed a linear concentration increase with time from  $t = 0$  and that also

resulted in a best-fit y-intercept that equalled ( $\pm 1 \sigma$ ) the initial ( $t = 0$ ) concentration in the water overlying the core.

*The analysis of DON and nitrate plus nitrite*—The concentration of DON is generally obtained by determining total dissolved nitrogen (TDN) and then subtracting from this value the concentration of dissolved inorganic nitrogen (DIN, i.e., the sum of ammonium, nitrate, and nitrite). In our work we remove ammonium from the sample before its analysis so that DON is determined as the difference between TDN and nitrite plus nitrate (N+N). By removing one concentration term from the calculation of DON, we obtain a more accurate DON concentration, because we have to propagate one less concentration error into the calculation (*see* Hansell 1993 for details). This procedure also improves the accuracy of the DON measurement in sediment pore waters, in which N+N concentrations are generally very low compared with DON, and in which dissolved ammonium concentrations may be as much as one order of magnitude higher than DON concentrations. In the absence of this procedure, the DON concentration in sediment pore waters would be determined as the small difference of two large numbers (i.e., TDN minus ammonium concentrations) and would therefore be subject to large uncertainties in both an absolute and a relative sense (Hansell 1993).

The ammonium removal procedure used here was modified from that originally described by Burdige and Martens (1990) for the removal of ammonium before the analysis of dissolved free amino acids in sediment pore waters. Although this process was shown to not affect the concentrations of amino acids (which generally have low volatility), it is possible that more volatile DON compounds (e.g., short-chain aliphatic amines such as methylamine) could also be lost from a sample during ammonium removal. However, the concentrations of most of these amines in pore waters are generally less than ~1–2 μM and often times are at least one order of magnitude lower (e.g., Wang and Lee 1990; Yang et al. 1993; Burdige et al. 1995). Thus, if there is any loss of these compounds during this stripping process it likely has a minimal effect on the pore-water DON concentrations observed here (which ranged from ~20 to >100 μM).

In this process, the pH of a sample is first raised to ~10 using 1 M NaOH (to convert all ammonium to NH<sub>3</sub>(g)), and moist, ammonia-free N<sub>2</sub> is bubbled through the sample for 30 min at 75°C (gas flow rate = 250 ml min<sup>-1</sup>) to strip off this ammonia. To dissolve precipitates that form in seawater samples that have been basified, after degassing the sample is acidified to a pH of ~2 with 1 M HCl. Finally, before analyzing these samples, any water lost during ammonia removal is added back with deionized distilled water (DDW). With each set of samples a DDW sample was also run through the procedure and used as a procedural blank. After this ammonium removal process, ammonium concentrations in samples were generally less than 0.2 μM, a value that is small compared with most TDN concentrations we have determined.

Concentrations of TDN and N+N in these samples were determined using a Dohrmann DN-1900 dual-channel nitrogen analyzer, modified as shown in Figure 1. For the deter-

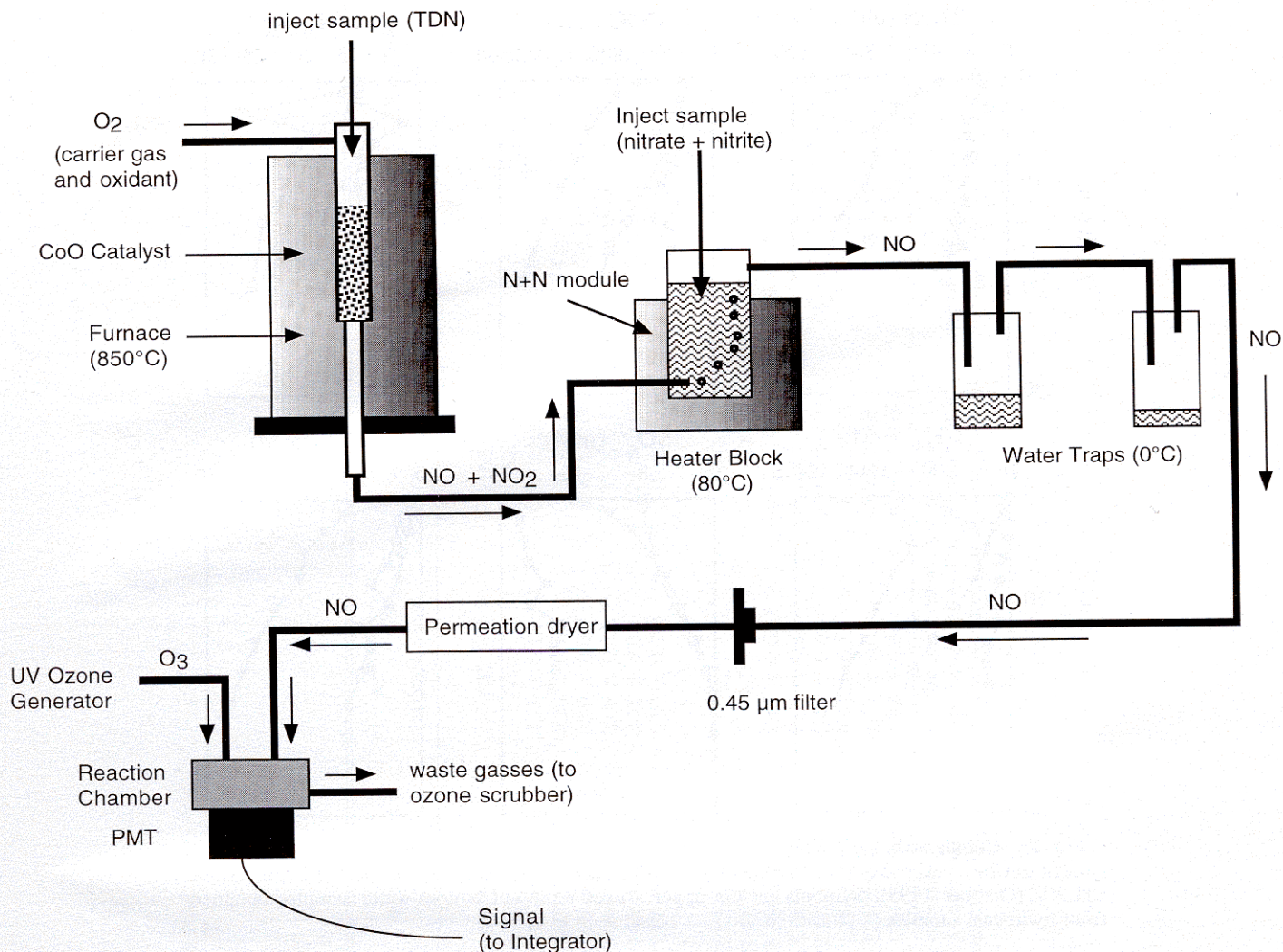


Fig. 1. A schematic of the DN-1900 analyzer used to determine DON. Note that injecting a sample directly into the furnace determines TDN (i.e., DON plus N+N), whereas injecting a sample into the N+N reaction chamber bypasses the furnace and measures only N+N. Because we remove ammonium from our samples before analysis (see text for details), the concentration of DON is determined as the difference between these two quantities.

mination of TDN, a sample (up to 40  $\mu\text{l}$  in low DON waters) is injected into a gas stream of ultra-pure oxygen (200  $\text{ml min}^{-1}$ ) in an 850°C vertical combustion tube containing cobalt oxide on alumina as a catalyst. Here, TDN is converted to a mixture of NO plus  $\text{NO}_2$ , which then passes through the heated (80°C) N+N reaction chamber that contains a 1% solution of  $\text{VCl}_3$  in 40% sulfuric acid. In this solution the nitrogen oxides produced by the combustion process are completely converted to NO. The exiting gas is partially dried in a series of two 0°C water traps and then passed through a 0.45- $\mu\text{m}$  filter. This removes aerosol particles from the gas stream that appear to be produced by the combustion of seawater samples and are apparently not removed by either the water traps or the aqueous solution in the N+N chamber. The gas is finally dried using a permeation dryer, and the NO is then reacted with ozone and quantified by chemiluminescence. Nitrate plus nitrite can also be determined with this instrument by directly injecting a water sam-

ple (up to 200  $\mu\text{l}$  in low N+N waters) into the N+N reaction chamber. This then bypasses the combustion furnace and converts only these inorganic nitrogen compounds to NO (Garside 1982).

Standardization was carried out using sodium nitrate in distilled water, and we have not observed a significant difference in the slopes of calibration curves determined in either seawater or distilled water. All samples were analyzed in triplicate, and the relative standard deviation was usually less than 5% at 3  $\mu\text{M}$  TDN or N+N. Using this modified DN-1900, we have obtained recoveries for a wide range of organic and inorganic nitrogen compounds that are comparable to those obtained by an ultraviolet oxidation technique or a similar high-temperature oxidation technique with a different instrument (Walsh 1989; and our results not shown here). To date, our recovery of antipyrine (a recalcitrant N-containing compound) has been  $96 \pm 2\%$  ( $n = 25$  sets of triplicate analyses).

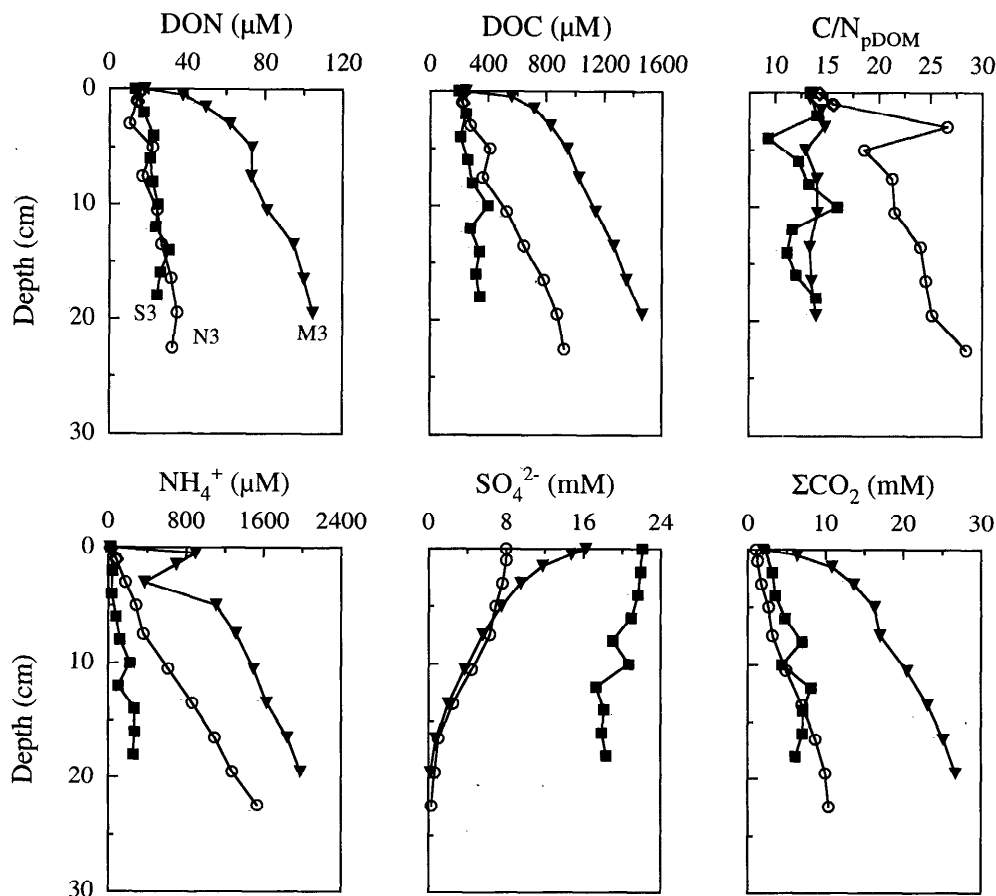


Fig. 2. Comparative pore-water profiles of organic and inorganic constituents at the three sites studied in Chesapeake Bay (N3 =  $\circ$ ; M3 =  $\blacktriangledown$ ; S3 =  $\blacksquare$ ). These cores were collected during cruise CH XV (October 1995). Symbols on the upper x-axes represent bottom-water samples obtained from hydrocast samples.

**Other analytical procedures**—Ammonium and  $\Sigma\text{CO}_2$  were determined by flow injection techniques (Hall and Aller 1992; Lustwerk and Burdige 1995), and sulfate was determined by ion chromatography. DOC was determined by a high-temperature catalytic oxidation technique using a Shimadzu TOC-5000 total carbon analyzer (Burdige and Homstead 1994; Burdige and Gardner 1998). All glassware and plasticware were cleaned as described previously (Burdige and Homstead 1994).

## Results

**General sediment pore-water profiles**—Figure 2 shows sediment pore-water profiles from all three sites for cores collected in October 1995. These profiles illustrate the basic differences among the three sites. Concentrations of DOC and DON were higher at site M3 than they were at the other two sites, possibly because of the higher rates of SOM remineralization at this site (*see below*). The C:N ratio of the DOM in the pore waters ( $[\text{DOC}]/[\text{DON}] = \text{C}/\text{N}_{\text{pDOM}}$ ) is generally higher at site N3 than at the other two sites, presumably reflecting the source of organic matter to the upper Bay sediments (i.e., nitrogen-poor, terrestrially derived material).

Pore-water  $\Sigma\text{CO}_2$  and ammonium concentrations are highest in site M3 pore waters, consistent with the high remineralization rates in these sediments. At sites M3 and S3,  $\Sigma\text{CO}_2$  benthic fluxes for the time period of this study predicted integrated annual average sediment carbon oxidation rates ( $C_{\text{ox}}$ ) of  $7.2 \pm 0.7$  and  $4.4 \pm 1.0$  mol  $\text{m}^2 \text{yr}^{-1}$ , respectively (Table 1). At site S3 this value is similar to that measured during an earlier time period (August 1991–July 1992; Burdige and Homstead 1994), although the integrated annual average value of  $C_{\text{ox}}$  reported here for site M3 is  $\sim 30\%$  lower than that observed during this earlier period. We have not directly measured  $C_{\text{ox}}$  using benthic  $\Sigma\text{CO}_2$  fluxes at site N3, although modeling of pore-water  $\Sigma\text{CO}_2$  profiles (Martens and Klump 1984; Burdige and Homstead 1994) predicts an integrated annual average value of  $C_{\text{ox}}$  that is  $0.8 \pm 0.4$  mol  $\text{m}^2 \text{yr}^{-1}$ .

Sulfate pore-water gradients at site S3 are much smaller than they are at site M3, despite the fact that measured sulfate reduction rates in site S3 sediments are  $\sim 60\%$  of those in site M3 sediments (Marvin-DiPasquale and Capone 1998). This presumably results from the bioturbation and bioirrigation of site S3 sediments and the accompanying oxidation of sulfide back to sulfate. Consistent with this expla-

Table 1. Summary of measured benthic fluxes.

Cruise	Date	BW temp.* (°C)	DOC	$\Sigma\text{CO}_2$ (= $\text{C}_{\text{org}}$ )	DON	N+N	$\text{NH}_4^+$	DON/DIN (%)
Site M3								
CH XII	Mar 95	6	0.67 ± 0.16	8.79 ± 5.79	ND	ND	ND	
CH XIV	Jul 95	22	1.65 ± 0.13	15.86 ± 0.91	ND	ND	ND	
CH XV	Oct 95	20	0.66 ± 0.26	20.98 ± 3.45	0.18 ± 0.10	-0.31 ± 0.04	4.78 ± 1.37	3.9
CH XVI	Mar 96	4	1.05 ± 0.29	7.40 ± 2.02	0.20 ± 0.12	-0.46 ± 0.17	2.74 ± 0.10	8.6
CH XVII	Aug 96	22	1.06 ± 0.08	47.76 ± 2.01	0.19 ± 0.07	0.00 ± 0.00	10.06 ± 0.52	1.8
CH XVIII	Oct 96	18	0.86 ± 0.10	10.99 ± 3.26	0.08 ± 0.02	-0.35 ± 0.11	4.52 ± 0.47	1.8
Integrated annual average†			1.03 ± 0.19 (0.37 ± 0.07)	19.64 ± 2.01 (7.17 ± 0.73)	0.18 ± 0.07 (0.07 ± 0.02)	-0.29 ± 0.08 (-0.10 ± 0.03)	5.38 ± 0.47 (1.96 ± 0.17)	3.5
Site S3								
CH XII	Mar 95	6	0.20 ± 0.08	1.32 ± 2.03	ND	ND		
CH XIV	Jul 95	22	0.63 ± 0.22	21.03 ± 5.23	ND	ND		
CH XV	Oct 95	20	0.22 ± 0.10	8.36 ± 2.83	0.13 ± 0.08	-0.17 ± 0.16	4.29 ± 6.10	3.3
CH XVI	Mar 96	4	0.37 ± 0.06	7.79 ± 3.02	-0.01 ± 0.03	-0.12 ± 0.03	1.06 ± 0.17	-1.0
CH XVII	Aug 96	22	0.85 ± 0.15	17.11 ± 4.18	0.18 ± 0.08	0.13 ± 0.04	7.18 ± 1.45	2.5
CH XVIII	Oct 96	18	0.39 ± 0.32	17.25 ± 6.35	0.42 ± 0.13	0.22 ± 0.20	2.66 ± 1.23	14.5
Integrated annual average†			0.46 ± 0.10 (0.17 ± 0.04)	12.01 ± 2.71 (4.38 ± 0.99)	0.11 ± 0.05 (0.04 ± 0.02)	-0.03 ± 0.06 (0.01 ± 0.02)	3.65 ± 1.73 (1.33 ± 0.63)	3.1

All fluxes  $\text{mmol m}^{-2} \text{d}^{-1}$ , except integrated annual averages in parentheses, which are  $\text{mol m}^{-2} \text{yr}^{-1}$ . Positive fluxes are out of the sediments.

\* BW = bottom water; DIN = ammonium plus N+N benthic fluxes; ND = not determined. All cruises were designated by CH (Chesapeake Bay) and a sequential Roman numeral.

† Integrated annual averages were obtained by integrating under the curve of measured benthic fluxes versus time by trapezoidal approximations and then dividing by the time period of integration.

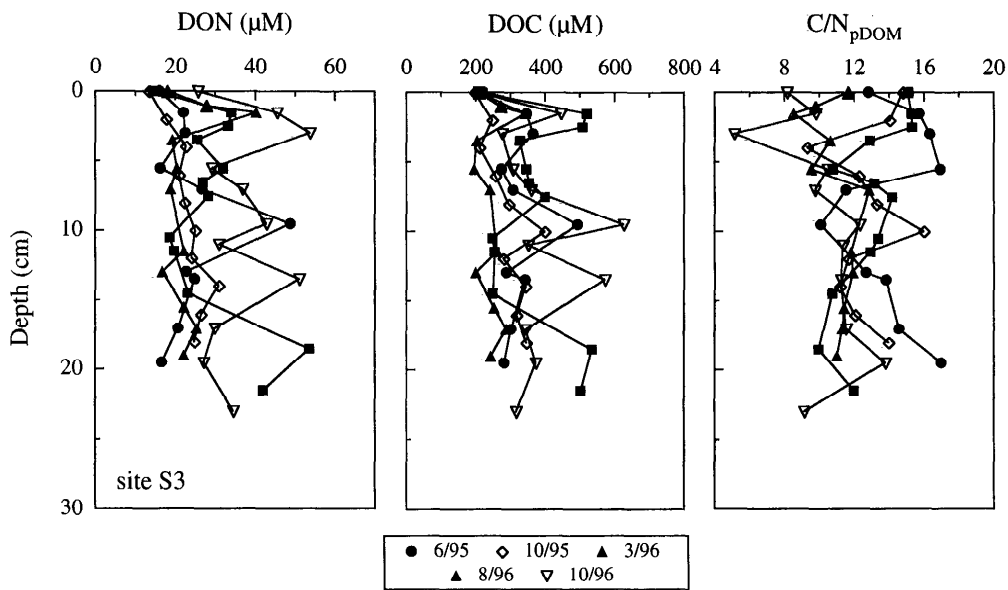


Fig. 3. Seasonal pore-water profiles of DOC, DON, and  $C/N_{pDOM}$  at site S3 in the southern Chesapeake Bay. Symbols on the upper x-axes represent bottom-water samples obtained from hydrocast samples.

nation, dissolved sulfide in site S3 pore waters is generally undetectable ( $< \sim 0.2 \mu\text{M}$ ; Skrabal et al. unpubl. data), and very small benthic sulfate fluxes have been measured at this site (Burdige and Homstead 1994).

*DON profiles in sediment pore waters*—Figures 3 and 4 show seasonal DON pore-water profiles from sites M3 and S3, along with DOC and  $C/N_{pDOM}$  profiles. Figure 5 shows two sets of similar profiles from site N3 (for logistical rea-

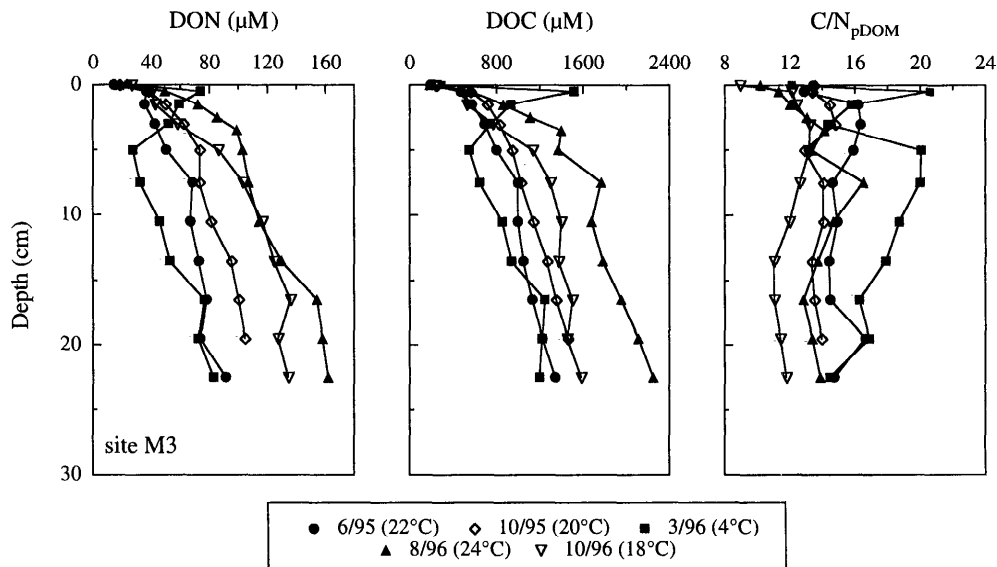


Fig. 4. Seasonal pore-water profiles of DOC, DON, and  $C/N_{pDOM}$  at site M3 in the mesohaline mid-Chesapeake Bay. Symbols on the upper x-axes represent bottom-water samples obtained from hydrocast samples. With the exception of the core collected in June 1995, pore-water DOC and DON concentrations appeared to be positively correlated with bottom-water temperatures (see Fig. 6) and SOM remineralization rates (as inferred by the strong correlation between sediment temperature and  $C_{ox}$  and benthic ammonium fluxes shown in Fig. 9). Also note that DOM concentrations and  $C:N_{pDOM}$  appear to vary in opposite directions (i.e., are out of phase with one another), at least in the upper 10–15 cm of sediments (see Fig. 6 and text).

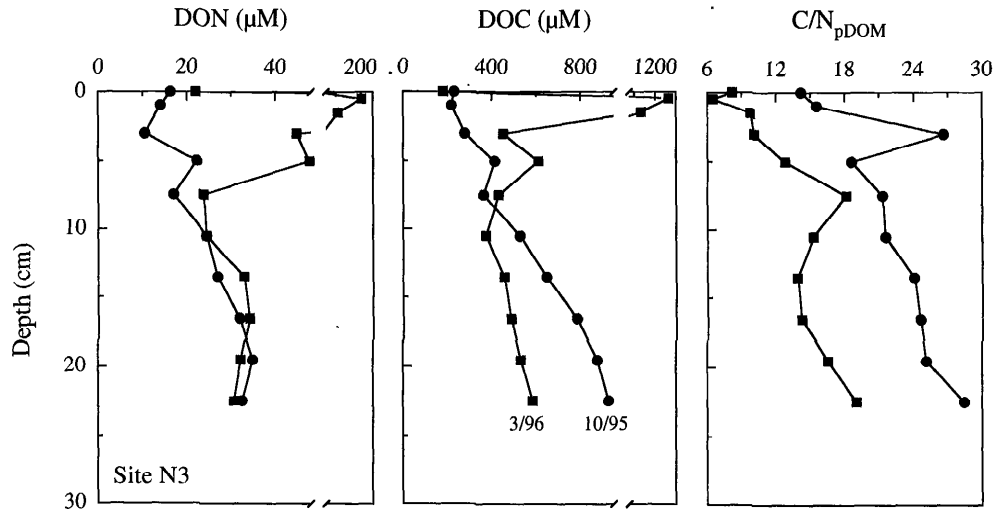


Fig. 5. Pore-water profiles of DOC, DON, and  $C/N_{pDOM}$  at site N3 in the northern Chesapeake Bay collected on two different sampling dates. Symbols on the x-axes represent bottom-water samples obtained from hydrocast samples.

sons we were only able to visit this site twice, precluding seasonal DOM studies). At all sites, pore-water DON concentrations were higher than bottom-water values, generally increased with depth, and ranged from 15 to  $\sim 160 \mu M$ . Concentrations of DOM (both DOC and DON) in site M3 pore waters were much higher than those observed at the other sites and increased with depth in an exponential fashion. Pore-water concentrations of DOM at site M3 also showed temporal variations that with the exception of the core collected

in June 1995 appeared to be closely coupled to bottom-water temperatures (Figs. 4, 6), and by inference to SOM remineralization rates, given the strong correlation between temperature and  $C_{ox}$  values and benthic ammonium fluxes (*see next section*). We speculate that the reason the June 1996 core does not follow this general trend is that bottom-water temperatures may have been changing rapidly in the time period during which we collected this core, and sediment temperatures (and, therefore, sediment processes) may not

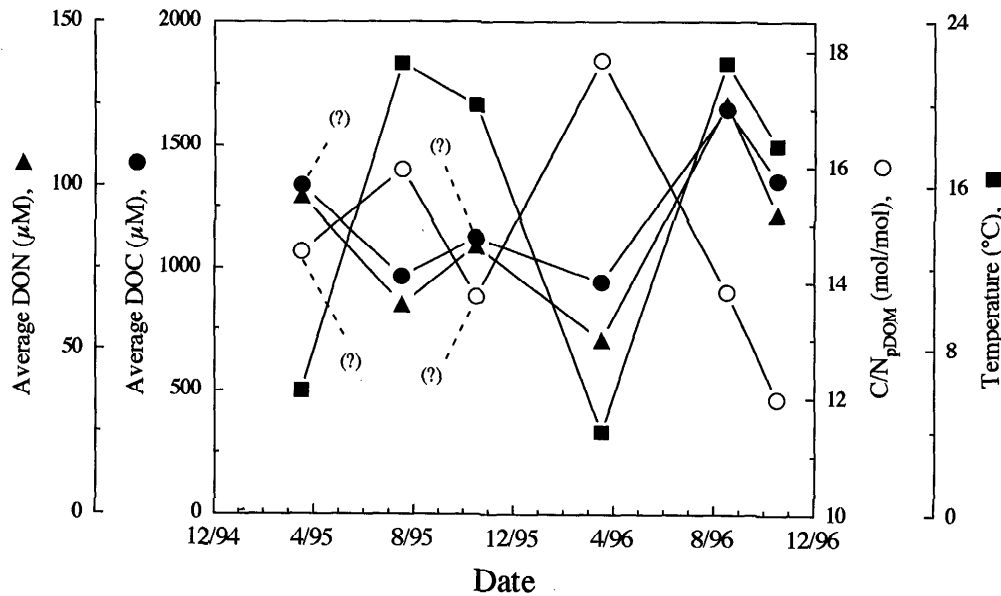


Fig. 6. Temporal changes at site M3 in bottom-water temperature (■), depth-weighted average DOC (●) and DON (▲) concentrations, and  $C/N_{pDOM}$  (○), further illustrating the temporal (seasonal) changes in these quantities. These depth-weighted values were calculated for the upper 20 cm of sediment using the formula  $(\sum \Delta x_i C_i)/20$ , where  $\Delta x_i$  is the thickness of each sediment section and  $C_i$  is either the DOC or DON pore-water concentration or the value of  $C/N_{pDOM}$  in that sediment slice. The dashed lines are meant to indicate that the June 1995 core does not appear to follow the general trends of this data and to suggest the trend they might be expected to follow (*see text*).

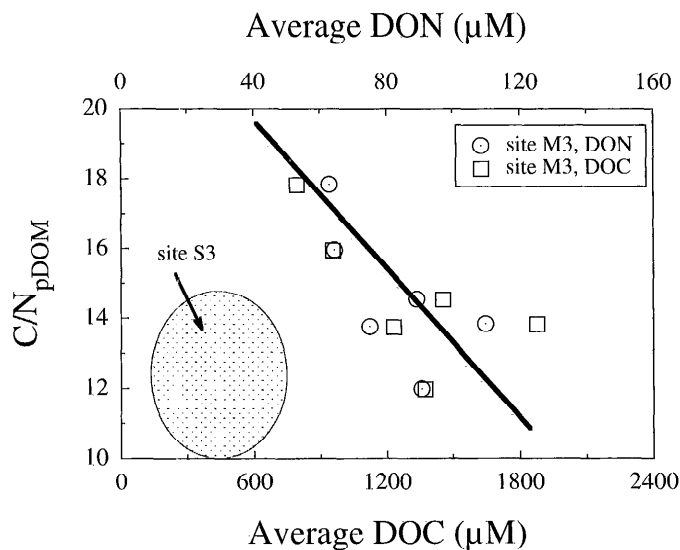


Fig. 7. The depth-weighted average DOC and DON concentrations versus the depth-weighted average value of  $C/N_{pDOM}$ , all for the upper 20 cm of site M3 sediments. These depth-weighted values were calculated as described in the caption to Figure 6. The line shown here is meant to indicate the inverse relationship between average DOM concentrations and the average value of  $C/N_{pDOM}$  (i.e., that their seasonal changes are out of phase with one another).

yet have equilibrated with bottom-water temperatures. At sites S3 and N3, DOM concentration gradients were generally much smaller than they were at site M3 (also see Fig. 2). Pore-water DOM profiles at site S3 showed no obvious seasonal variability (Fig. 3).

The  $C/N_{pDOM}$  ratio was generally highest at site N3 ( $\leq 25$ ) and lowest at site S3 ( $\sim 12$ ). At site N3 this ratio clearly increased with depth (Fig. 5). At site S3 this ratio showed no significant depth variation and no seasonal variability (Fig. 3). At site M3,  $C/N_{pDOM}$  ranged from  $\sim 12$ – $18$  and at some times of the year showed a pronounced decrease with depth. Despite the fact that  $C/N_{pDOM}$  values tended to converge to a constant value at depth year-round in these sediments ( $\sim 12$ – $14$ ; Fig. 4), significant seasonal differences in  $C/N_{pDOM}$  in the upper  $\sim 10$ – $15$  cm of these sediments led to seasonal changes in the average  $C/N_{pDOM}$  value at this site that were out of phase with seasonal changes in DOM concentrations (Figs. 4, 6). Cores with higher DOM pore-water concentrations (e.g., October 1996 or August 1996) showed lower  $C/N_{pDOM}$  values, whereas cores with lower DOM concentrations (e.g., March 1996) had higher ratios (see Fig. 7). Note that  $C/N_{pDOM}$  values in Chesapeake Bay sediment pore waters were higher than the Redfield ratio (6.6) and were generally similar to (S3), or higher than (N3 and perhaps M3), the C:N ratio of DOM in the bottom waters (Figs. 2–5).

**Benthic flux determinations**—Results from a typical benthic flux determination are shown in Figure 8, and all of our flux data are summarized in Table 1 and Figure 9. As in other coastal sediments (e.g., Martens and Klump 1984; Cowan and Boynton 1996), sediment  $C_{ox}$  values and benthic ammonium fluxes showed seasonal variations that were

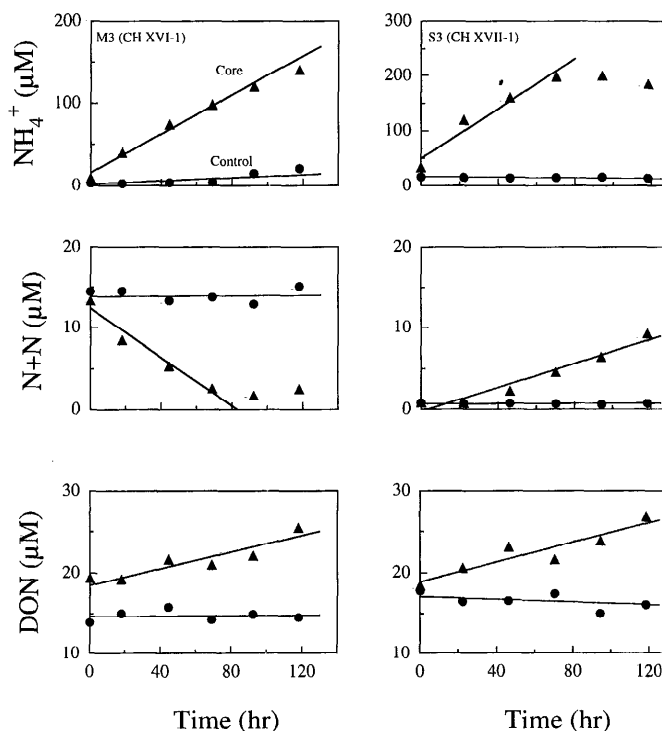


Fig. 8. Concentrations of DON, N+N, and ammonium, all versus time, in selected flux experiments with site M3 sediments (core 1, CH XVI, March 1996; left panels) and site S3 sediments (core 1, CH XVII, August 1996; right panels). The data for the water overlying the flux core ( $\blacktriangle$ , labeled “Core”) have been corrected as described in the text for the sequential sample dilution that results from replacing the water collected for each time point with an equivalent amount of recharge water. The best-fit lines through the initial linear portions of this corrected data and the best-fit lines through the recharge water data ( $\bullet$ , labeled “Control”) were used to calculate benthic fluxes as described in the text. The results of all flux experiments are shown in Table 1.

closely coupled to sediment temperature (Fig. 9). Seasonal variations in benthic DOM fluxes are discussed below. The benthic DOC fluxes and  $C_{ox}$  values in Figure 9 are also generally similar to those observed at these sites during an earlier period (Burdige and Homstead 1994; also see above).

Measured DON fluxes from site M3 sediments ranged from  $0.08$ – $0.2$   $\text{mmol m}^{-2} \text{d}^{-1}$ , and from essentially 0 to  $0.42$   $\text{mmol m}^{-2} \text{d}^{-1}$  at site S3 (Fig. 9). At site S3, benthic DOM fluxes (both DON and DOC) were coupled to seasonal trends in temperature and SOM remineralization rates. In contrast, seasonal trends in benthic DOM fluxes appeared to be less tightly coupled to these parameters at site M3. At site M3, measured DON fluxes were essentially identical to calculated diffusive DON fluxes (Table 2). Measured DON fluxes were much greater than calculated diffusive fluxes at site S3, presumably because of the bioturbation and bioirrigation of these sediments (Berner 1980; Aller 1982). In both sediments, the molar ratio of DOC: DON benthic fluxes ( $\sim 2$ – $6$ ) was lower than that of the average value of  $C/N_{pDOM}$  (which was greater than  $\sim 10$ ; see Fig. 10).

Inorganic nitrogen fluxes from these sediments were dominated by ammonium fluxes, which ranged from  $\sim 2.5$ – $10$

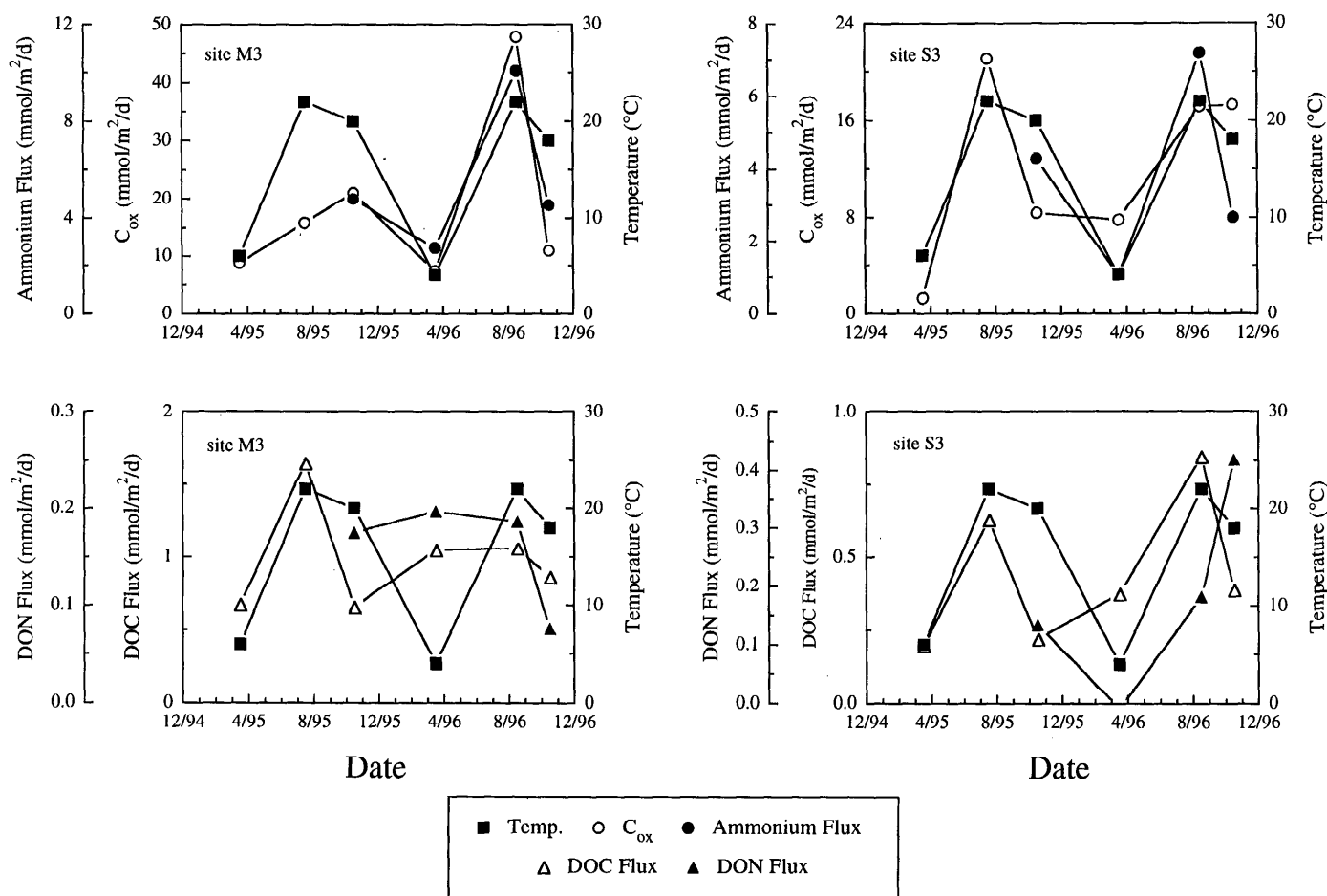


Fig. 9. Upper graphs show temporal changes at sites M3 (left) and S3 (right) in bottom-water temperature (■), C<sub>ox</sub> (○), and benthic ammonium flux (●). Lower graphs show temporal changes in bottom-water temperature (■), benthic DOC (△), and DON fluxes (▲).

Table 2. Comparison of calculated and measured benthic DON fluxes.

Cruise	Calculated flux*	Measured flux	Measured/Calculated†
<b>Site M3</b>			
CH XV (Oct 95)	0.03 ± 0.01	0.18 ± 0.10	5.7 ± 4.0
CH XVI (Mar 96)	0.08 ± 0.03	0.20 ± 0.12	2.5 ± 1.9
CH XVII (Aug 96)	0.05 ± 0.02	0.19 ± 0.07	3.8 ± 2.1
CH XVIII (Oct 96)	0.02 ± 0.01	0.08 ± 0.02	3.5 ± 1.6
Average			3.9 ± 1.3
<b>Site S3</b>			
CH XV (Oct 95)	0.0005 ± 0.0002	0.13 ± 0.08	271 ± 190
CH XVI (Mar 96)	0.003 ± 0.001	-0.01 ± 0.03	
CH XVII (Aug 96)	0.001 ± 0.001	0.18 ± 0.08	140 ± 85
CH XVIII (Oct 96)	0.003 ± 0.001	0.42 ± 0.13	137 ± 70

All fluxes are mmol m<sup>-2</sup> d<sup>-1</sup>, and positive fluxes are out of the sediments.

\* These fluxes were calculated as described earlier (Burdige et al. 1992; Burdige and Homstead 1994) using the pore-water data in Figures 3 and 4 and Fick's first law of diffusion ( $J = -\phi_0 D_s dC/dz_0$ ) assuming that: (1) the DON concentration gradient across the sediment-water interface ( $dC/dz_0$ ) can be approximated by  $\Delta C/\Delta z$ , where  $\Delta C$  is the difference between the DON concentration in the bottom waters and the first sediment sample, and  $\Delta z$  is the depth of the mid-point of this sediment sample; and (2) the average molecular weight (MW) of pore-water DON is between 1,000 and 10,000 and that there is an inverse cube root relationship between MW and the free solution diffusion coefficient for an organic compound. Recent DOC (Burdige and Gardner 1998) and DON (Burdige and Zheng unpubl. data) MW data support this assumption about the average MW of Chesapeake Bay pore-water DOM. See Table 1 for explanation of cruise designations.

† The ratio of measured to calculated DON fluxes.

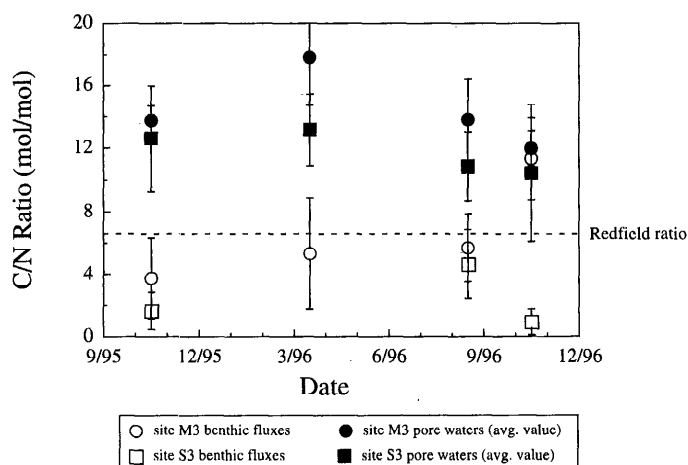


Fig. 10. Temporal changes at sites S3 and M3 in the depth-weighted average value of  $C/N_{pDOM}$  (see Fig. 6) and the C/N ratio of the DOM escaping from the sediments (i.e., the ratio of the DOC benthic flux to the DON benthic flux).

$\text{mmol m}^{-2} \text{d}^{-1}$  (Table 1). Benthic N+N fluxes were much smaller, less than  $0.4 \text{ mmol m}^{-2} \text{d}^{-1}$  in magnitude. These fluxes were almost always into the sediments at site M3. In contrast, N+N fluxes into and out of site S3 sediments were observed. Integrated annual averages suggest that there is a net flux of N+N into site M3 sediments and effectively no N+N flux either into or out of site S3 sediments (Table 1). A comparison of inorganic and organic nitrogen fluxes shows that measured benthic DON fluxes were a small fraction ( $\sim 3\%$ ) of the DIN fluxes from these sediments. Thus, like benthic DOC fluxes and sediment carbon oxidation (Burdige and Homstead 1994), benthic DON fluxes appeared to represent a similar small fraction of nitrogen remineralization in these Chesapeake Bay sediments.

## Discussion

*Comparison of our pore-water profiles with other reported profiles*—The DON concentrations reported here were similar to those observed in previous studies of pore-water DON in coastal and nearshore sediments (Enoksson 1993; Sloth et al. 1995; Lomstein et al. 1998; Cifuentes and Morse unpubl. data; Landén-Hillemyr 1998). In studies in which pore-water DOC concentrations were also measured (Lomstein et al. 1998; Landén-Hillemyr 1998), similar  $C/N_{pDOM}$  values have been observed.

Several of these pore-water profiles were obtained in studies of the effects of anoxia and organic matter additions on SOM remineralization and benthic fluxes. Because sites S3 and M3 have natural differences in these parameters (and more similar types of organic matter input to the sediments than does site N3), we can use these results to begin to examine the controls on pore-water DON concentrations. Pore-water DON (and DOC) concentrations were generally higher at site M3 than they were at S3, as were the amounts of organic matter input to the sediments and the degree of sediment anoxia. In the aforementioned studies, the addition of reactive organic matter to experimental sediment cores

generally increased pore-water DON concentrations (Enoksson 1993; Sloth et al. 1995), consistent with our pore-water results. These observations are also consistent with pore-water data from a wide range of coastal and continental margin sediments that show that there is a positive relationship between pore-water DOC concentrations and  $C_{ox}$  values over a  $\sim 100$ -fold range in sediment carbon oxidation rates (Burdige unpubl. data).

In contrast, water-column oxygenation (or anoxia) appears to have differing effects on pore-water DON concentrations. In one study (Hansen and Blackburn 1991), anoxic conditions in the water overlying experimental cores led to an increase in pore-water DON concentrations, whereas in other studies it led to a decrease in pore-water DON concentrations (Enoksson 1993; Hansen and Blackburn unpubl. data in Hansen and Blackburn 1991). Based on their results, Hansen and Blackburn (1991) reached the “tentative conclusion” that the mineralization of DOM may be less efficient under anoxic conditions, which would also be consistent with our pore-water results. This possibility is discussed below in more detail (see the section *Controls on Pore Water Concentrations*).

*Comparison of our benthic nitrogen fluxes with other reported values*—The ammonium and N+N benthic fluxes reported here are similar to values reported for these same sites during an earlier period (Cowan and Boynton 1996). At site M3 the integrated annual average DIN flux we determined ( $1.9 \pm 0.2 \text{ mol m}^{-2} \text{yr}^{-1}$ ) also agreed with that of this earlier study ( $\sim 1.5 \text{ mol m}^{-2} \text{yr}^{-1}$ ). Similar agreement was seen at site S3 between our value for the integrated annual average DIN flux and that reported by Cowan and Boynton (1996) ( $1.3 \pm 0.6$  versus  $\sim 0.8 \text{ mol m}^{-2} \text{yr}^{-1}$ ).

A comparison of our measured benthic DON fluxes with those observed previously at these same sites in the Bay by Cowan and Boynton (1996), and those observed in other coastal and estuarine sediments, is shown in Table 3. The previously reported benthic DON fluxes cited in this table show quite a tremendous range, both in absolute magnitude and direction (into and out of the sediments). However, at sites at which repeated (or seasonal) studies were carried out, mean or annual averages generally suggest that benthic DON fluxes are small, usually out of the sediments, and a small percentage of the benthic fluxes of total dissolved reactive nitrogen. These particular observations are consistent with our results. The data for Forleague-Atchafalaya Bay (Teague et al. 1988) appear to be an exception to this observation and are discussed below.

At the same time, poor agreement is seen when our results are compared with similar studies of benthic DON fluxes carried out several years ago at these same sites in the Bay (Cowan and Boynton 1996). Furthermore, Cowan and Boynton (1996) generally observed DON fluxes into site M3 sediments, where we observed DON fluxes out of the sediments. They observed DON fluxes both into and out of site S3 sediments (as we did), although their measured fluxes were much greater than ours.

In an attempt to reconcile these differences we note that many of the DON fluxes reported previously were based on short-term incubations ( $< 12 \text{ h}$ ), and as Nixon (1981) ob-

Table 3. Comparison of measured benthic DON fluxes from different estuarine and coastal sediments.

Site	DON flux	% TDN flux*	Inc. time†	In situ
La Jolla Bight, CA, USA‡	-0.08 (-1.3 to +1.3)		~6	Yes
Pautuxent R. estuary, MD, USA§	-10.3 to +5.2		1-3 h	Yes
Narragansett Bay, RI, USA	~0.3 (0.1 to 0.4)	13	24 h	No
Georgia Bight, USA¶	+0.2 (-2 to +6)	12	4 h	Yes
Forleagu/Atchafalaya Bay, LA, USA#	-17 (upper bay) 7.3 (lower bay) (-116 to +107)		3-5 h	Yes
Tomales Bay, CA, USA**	-0.3 ± 0.9 (-3.5 to +0.1)		~24 h	Yes
Laholmm Bay, Sweden††	~0.1 to 0.4	~40	Continuous flow expts. over 30 d	No
Chesapeake Bay, USA‡‡	-0.6 to +13.2		10-12 h	No
Chesapeake Bay, USA§§	0.11 (S3) 0.18 (M3) (-0.01 to +0.42)	~3 (S3) ~4 (M3)	~100 h (up to ~300 h)	No

Inc. = incubation; R. = River; expts. = experiments. All fluxes are in  $\text{mmol m}^{-2} \text{d}^{-1}$ , and positive fluxes shown here are out of the sediments.

\* Benthic DON fluxes as a percentage of total dissolved reactive nitrogen fluxes (i.e., DON plus DIN fluxes). These percentages are based on integrated annual averages or mean values of these fluxes.

† Approximate incubation time used to determine the benthic flux.

‡ From Hartwig (1976). The reported value is the mean value observed at the site, whereas the value in parentheses is the observed range of values.

§ From Boynton et al. (1980).

|| From Nixon et al. (1976), Nixon (1981), and Nixon and Pilson (1983). The reported value is the integrated annual average value, whereas the value in parentheses is the observed range of values.

¶ From Hopkinson (1987). The reported value is the mean annual average at this site, whereas the value in parentheses is the observed range of values in temporal studies over an annual cycle.

# From Teague et al. (1988). The reported values are the mean annual fluxes at two different sites in this bay. The value in parentheses is the observed range for individual flux measurements made at both sites. As discussed in the text, the errors associated with these individual measurements are quite large; therefore, the errors associated with these mean annual averages may be as large as the averages themselves.

\*\* From Dollar et al. (1991). The reported value is a whole bay average, whereas the value in parentheses represents the mean of three different stations in the bay over the period June 87-May 89.

†† From Enoksson (1993). Fluxes were determined from the difference between the concentration of inflowing and outflowing water overlying a sediment core (the residence time of the water overlying the core was not given). Fluxes were determined approximately daily over the ~30-d period of the experiment.

‡‡ From Cowan and Boynton (1996). The fluxes were measured at the same three sites in the bay at which we measured DOM fluxes and pore-water profiles, although they were determined during a different period (April 89-September 89).

§§ Results from this study. The reported values for each site are the integrated annual averages (taken from Table 1), whereas the value in parentheses is the overall range of observed fluxes at both sites (again from Table 1).

served, it is very difficult to measure benthic DON fluxes during such short-term incubations. Consistent with this observation, Cowan and Boynton (1996) reported that 30% of their DON flux measurements could not be interpreted (and were therefore not reported in their article), because the observed concentration changes in the water overlying the cores were "analytically significant but erratic." We also note that in the study of DON fluxes from Forleagu-Atchafalaya Bay sediments (Teague et al. 1988) the individual flux measurements generally have uncertainties (1 standard error) that are in many cases equivalent in magnitude to (or larger than) the fluxes themselves. The majority of these fluxes may therefore be indistinguishable from zero, suggesting that the large mean annual benthic DON fluxes into and out of these sediments (reported in the Teague et al. [1988] article with no error estimates) are also highly uncertain.

Based on these observations, we suggest that the use of short-term core incubations to measure DON fluxes may be subject to some sort of artifact associated with, for example, setting up benthic chambers in situ or collecting sediment cores for laboratory or shipboard incubations. These may then lead to the disruption of near-surface pore-water DON concentration gradients because of changes in the balance

between sediment DON production and consumption (which then allow anoxic nonbioturbated sediments to temporarily become sinks for DON from the water column), or because of stresses to benthic macrofauna living in the sediments (which lead to their excretion of DON compounds). In contrast, our more long-term flux measurements may allow the sediments being studied to re-equilibrate after these disturbances, and the benthic fluxes that are subsequently measured may be more representative of their actual value.

At the present time we cannot provide additional information on this possible artifact and its relationship to the discrepancy between our measured DON fluxes and those of Cowan and Boynton (1996). In partial support of our measured DON fluxes we note that at site M3, other organic (e.g., DOC) and inorganic benthic flux studies suggest that molecular diffusion is the dominant mechanism for benthic fluxes from these sediments (Burdige and Homstead 1994; Cornwell and Boynton unpubl. data). The fact that our measured DON fluxes at M3 essentially agree with calculated diffusive fluxes, which were based on pore-water profiles (Table 2), is also consistent with this observation. This leads us to conclude that our measured fluxes at site M3 represent a reasonable estimate of the DON flux from these sediments. In the remainder of this discussion we will also assume that

our measured benthic DON fluxes at site S3 are reasonable estimates of this flux, recognizing that further studies are needed to more clearly resolve these differences.

*Controls on pore-water DON concentrations*—In attempting to understand the controls on pore-water DON concentrations in these sediments, we will build on the recently proposed pore-water DOC size-reactivity (PWSR) model (Burdige and Gardner 1998). There are two key points of the model that are most relevant to the discussion here. The first is that the remineralization of SOM to  $\Sigma\text{CO}_2$  and ammonium occurs through the production of DOM intermediates of increasingly smaller molecular weights. The second is that along with the remineralization of SOM to inorganic nutrients there is also some small net production of relatively low-molecular-weight DOM (referred to here as polymeric low-molecular-weight DOM, or pLMW-DOM). This pLMW-DOM is presumed to be much less reactive than other high- and low-molecular-weight DOM intermediates produced and consumed during organic matter remineralization (see Santschi et al. 1995 and Amon and Benner 1996, for a discussion of similar processes in the water column). Therefore, in sediments the net production of refractory low-molecular-weight (not high-molecular-weight) DOM leads to both an imbalance between DOM production and consumption, and to a first order then, the accumulation of DOM with depth in sediment pore waters (see Burdige and Gardner 1998 for further details).

A wide range of published data on the biogeochemical properties of DOC in sediment pore waters and in the water column can be explained using the PWSR model (see references cited in Burdige and Gardner 1998). The PWSR model is also consistent with recent pore-water DOC molecular-weight data (Burdige and Gardner 1998) that show that ~90% of the DOC in the pore waters of these Chesapeake Bay sediments (and ~60–70% of the DOC in continental margin sediment pore waters) is of relatively low molecular weight (<~3 kDa; note that Burdige and Gardner [1998] discuss the reasons why the vast majority of the DOC in the <3-kDa-molecular-weight fraction likely has biogeochemical properties consistent with those defined for pLMW-DOM). Finally, consistent with this model is the fact that ~90% of the DON in these Chesapeake Bay sediment pore waters also has a molecular weight less than ~3 kDa (Burdige and Zheng unpubl. data).

A common feature of many pore-water DOM profiles is that they approach asymptotic concentrations at depth (see Figs. 2–5 and discussions in Burdige and Gardner 1998). In the context of the PWSR model, this may occur in two possible ways. The first simply involves a balance between low rates of DOM production (from SOM) and consumption of pLMW-DOM (Alperin et al. 1994). Second, DOM production may go to zero with depth, and processes (biotic or abiotic) that affect pLMW-DOM may continually decrease the overall reactivity of this material. The end result of this scenario will therefore be that the pLMW-DOM found at depth is essentially nonreactive on early diagenetic time scales (e.g., Hatcher and Spiker 1988; Amon and Benner 1996). At the same time, recent studies have also shown that DOM adsorption to sediment particles affects pore-water

DOM concentrations (Hedges and Kiel 1995; Henrichs 1995). Pore-water DOM concentrations at depth may therefore also be buffered by reversibly adsorbed DOM in equilibrium with the pore waters (Thimsen and Keil 1998). In the following sections we will use the pore-water data from these sediments to more carefully examine the possible occurrence of all of these phenomena.

*Site M3*—At this site pore-water DOM seasonally grew in and out, presumably in response to sediment temperatures and rates of SOM remineralization (Figs. 4, 6). Such trends are similar to those that have been observed for DOC concentrations in the anoxic sediments of Cape Lookout Bight (Alperin et al. 1994). As was also shown for these sediments, this suggests that on seasonal time scales DOM concentrations at depth in site M3 sediments are controlled by a balance between DOM production and consumption.

The inverse relationship between average pore-water DOM concentrations at site M3 and  $\text{C}/\text{N}_{\text{pDOM}}$  values (Figs. 6, 7) further suggests that the net selectivity of these processes varies with the overall rate of SOM remineralization. During periods of low remineralization, the processes appeared to be more selective, leading to the preferential net utilization of N-rich DOM (and thus to an increase in the value of  $\text{C}/\text{N}_{\text{pDOM}}$ ). In contrast, the opposite appeared to be the case during periods when remineralization rates were more rapid, leading to the accumulation of N-rich DOM (i.e., low  $\text{C}/\text{N}_{\text{pDOM}}$  material).

Superimposed on the more pronounced seasonal differences in  $\text{C}/\text{N}_{\text{pDOM}}$  near the sediment surface and seasonal changes in total DOM concentrations is the observation that  $\text{C}/\text{N}_{\text{pDOM}}$  values at depth tend to converge to a constant value of ~14–15 (Fig. 4). This suggests some similarity in the chemical composition of pore-water DOM at depth in these sediments. Equilibrium reactions with DOM adsorbed to mineral surfaces may play a part here (Thimsen and Keil 1998; also see above), although this material also likely represents low C:N ratio pore-water DOM produced at depth during the summer months that is then partially retained in the sediments during the remainder of the year. During periods of low remineralization rates (e.g., winter months) the overall net utilization of DOM produced earlier in the year, coupled with the general decrease with depth in the rates of sediment remineralization processes (e.g., Klump and Martens 1989; Roden and Tuttle 1996), likely leads to enhanced consumption of low C:N ratio DOM near the sediment surface (in a way similar to that described above). This would then lead to the observed decrease in  $\text{C}/\text{N}_{\text{pDOM}}$  with depth during this time of the year (Fig. 4). Diffusion limitations on the upward transport of N-rich DOM produced at depth in the sediments during the summer months may also contribute to these observed depth trends in  $\text{C}/\text{N}_{\text{pDOM}}$  during the winter months.

The observed depth variations in  $\text{C}/\text{N}_{\text{pDOM}}$  at site M3 contrasts with that of the C:N ratio of the SOM undergoing remineralization in estuarine sediments, which generally increases with depth, from values close to the Redfield ratio (6.6) to values >25 (Burdige 1991). It also contrasts with that of the C:N ratio of the bulk SOM at this site (~6–10), which is enriched in nitrogen as compared with pore-water

DOM ( $C/N_{pDOM} > 12$ ). This suggests an uncoupling of the C:N ratios of these different organic matter pools, depending on the exact mechanism or mechanisms that control  $C/N_{pDOM}$  values and how these elemental ratios are modified during SOM remineralization and the production of refractory pore-water DOM (i.e., pLMW-DOM).

*Site N3*—DOM concentration profiles here show that there is a significant increase in  $C/N_{pDOM}$  with depth (Fig. 5), which is not seen in the sediments from sites S3 and M3. In these site N3 sediments in which there is a more significant input of terrestrially derived organic matter, the refractory pore-water DOM accumulating in the sediments becomes increasingly depleted in nitrogen with depth. In the context of the discussion above regarding the PWSR model, this suggests that in these sediments the accumulation of pore-water DOM at depth may result from the accumulation of material that is refractory on early diagenetic time scales (based on the assumption that high C:N ratio DOM will, in general, be more refractory).

Because at least some of the SOM undergoing remineralization in site M3 and S3 sediments also has a C:N ratio consistent with that of terrestrial organic matter ( $C:N > 25$ ; Burdige 1991), these  $C/N_{pDOM}$  values from site N3 pore waters are somewhat surprising. The reasons for these differences are not well understood, although as discussed above they suggest that there may not be a tight coupling between the C:N ratio of the SOM undergoing remineralization and that of its DOM intermediates (or its refractory end products, e.g., pLMW-DOM). Kristensen and Blackburn (1987) observed that the C:N ratio of SOM undergoing remineralization is not always a good indicator of its reactivity, a fact that could explain the differences between the site N3 results and those at sites M3 and S3. More detailed studies of the organic geochemistry of the SOM undergoing remineralization in these different sediments, and its relationship to the pathways of SOM and DOM diagenesis in these different sediments (i.e., marine or estuarine versus low salinity or freshwater) will be needed to further examine this problem.

*Site S3*—Compared with sites M3 and N3, DOM concentrations at site S3 were lower, showed very little gradient with depth, and had no obvious seasonal variability (Figs. 2, 3). The  $C/N_{pDOM}$  ratio at site S3 also showed little depth or temporal variability and was very close to the C:N ratio of the SOM. In contrast to these other sites, the relationship between the PWSR model and pore-water DOM concentrations at site S3 is not as clear. Rather, it appears that the extensive bioturbation and bioirrigation of these sediments has a more significant role in controlling pore-water DOM concentrations and properties. If the mineralization of DOM is indeed less efficient under anoxic conditions (Hansen and Blackburn 1991), the more oxidizing conditions of site S3 sediments (as compared with site M3) could explain these observations. Enhanced remineralization of SOM under alternating redox conditions such as those found in these bioturbated sediments (Aller 1994) may also lead to lower pore-water DOM concentrations. Other factors that may have a role in affecting site S3 pore-water DOM concentrations in-

clude the following: enhanced microbial activity associated with macrofaunal burrows, perhaps leading to greater net DOM consumption (Aller and Yingst 1985; Alongi 1985), and direct utilization of pore-water DOM by benthic macrofauna (O'Dell and Stephens 1986).

Because pore-water DOM concentrations and  $C/N_{pDOM}$  ratios at site S3 were similar to those observed in bottom waters (Figs. 2, 3), the mixing of bottom waters into the pore waters caused by sediment irrigation may have a role in determining the composition of pore-water DOM at this site. However, pore-water profiles of other inorganic constituents at this site (e.g., ammonium,  $\Sigma CO_2$ , and  $Mn^{2+}$ ) clearly show evidence of SOM remineralization reactions, demonstrating that these reactions and bioturbation and bioirrigation control pore-water concentrations at this site (see Fig. 2 and Burdige 1993; Burdige and Homstead 1994; Burdige et al. 1995).

At the same time, though, if we compare pore-water DOM concentrations and  $C/N_{pDOM}$  values from site S3 with those from site M3 (Fig. 7) we see that the site S3 data fall below the site M3 trend line. Given the low concentrations of pore-water DOM at site S3, this material appears to be enriched in nitrogen compared with site M3 pore-water DOM. The same factors discussed above that may lead to lower DOM concentrations in bioturbated sediments may also similarly affect the C:N ratio of this material and lead to the observed DOM composition differences at the two sites. In addition, the presence of specific low C:N ratio organic compounds in site S3 pore waters may affect the concentration and composition of pore-water DOM at this site. Glycine ( $C:N = 2$ ) is an abundant amino acid in many benthic invertebrates (Awapara 1962; Henrichs 1980) and is also found at high levels in pore waters of Cape Lookout Bight surface sediments when they were temporarily colonized by polychaete worms (Burdige and Martens 1990). In bioturbated and bioirrigated sediments in the Gulf of Mexico, Cifuentes and Morse (unpubl. data) have observed that urea ( $C:N = 0.5$ ) is roughly 25% of the pore-water DON. Studies of bioturbated sediments on the Bering Sea shelf (Lomstein et al. 1989) have also shown that urea is found in the pore waters of these sediments and that it is a significant component of nitrogen cycling in these sediments.

Although we did not measure glycine or urea in site S3 pore waters, their presence here at relatively low levels could lower the  $C/N_{pDOM}$  value at site S3 from the trend line shown in Fig. 7 for site M3 pore waters to that actually observed at this site. In the next section, we also show that urea production in site S3 sediments is consistent with the C:N ratio of the DOM passing from these sediments. Whether the presence of urea in the pore waters at this site is a result of the macrofauna themselves (Boucher and Boucher-Rodoni 1988, Lomstein et al. 1989, Antia et al. 1991) or of the bacteria associated with the macrofauna or their burrows (e.g., Jørgensen et al. 1997) requires further study. However, it does reinforce previous observations about the potential significance of urea in sediment and water-column nitrogen cycling in environments containing bioturbated sediments (Lomstein et al. 1989).

*The C:N ratio of DOM benthic fluxes*—At sites S3 and M3, the C:N ratio of the DOM passing from the sediments

(~4–6 for site M3 fluxes, ~2–4 for site S3 fluxes) is substantially lower than that of the average value of  $C/N_{pDOM}$  in the pore waters (which is greater than ~10; Fig. 10). This implies that the DOM accumulating in the sediment pore waters is carbon rich compared with the more N-rich DOM that either escapes the sediments as a benthic flux or is remineralized near the surface sediments (assuming that the C:N ratio of the SOM undergoing remineralization in the surface sediments is close to the Redfield ratio, 6.6; see Burdige 1991). Thus, there appears to be a fractionation between the DOM that passes from the sediments and that which accumulates in the sediment pore waters, leading to N-depleted pore-water DOM.

Similar trends have been reported for other sediments (Blackburn et al. 1996; Landén-Hillemyr 1998) and have been explained as being caused by diffusional loss of low C:N ratio DOM produced during the initial hydrolysis of fresh (i.e., low C:N ratio) detrital organic matter near the sediment surface. This suggestion is also consistent with discussions in Burdige and Gardner (1998) regarding the spatial separation in sediments between the hydrolytic processes that produce the initial high-molecular-weight intermediates of SOM remineralization and the processes responsible for the production of refractory DOM in sediment pore waters (i.e., pLMW-DOM; see Chen and Burdige 1998 and manuscript in prep., in which these ideas are developed in more detail using pore-water DOM fluorescence data).

The very low C:N ratios of the DOM escaping from site S3 sediments are also consistent with the possibility that a significant amount of this material is urea. Although some of this urea may accumulate in the pore waters (see Lomstein et al. 1989 and the discussion above), it must also be directly input into the waters used to irrigate (or flush) sediment burrows to account for the extremely low C:N ratios of the site S3 DOM benthic fluxes. Some studies have observed that urea fluxes from bioturbated continental margin (Lomstein et al. 1989) and coastal (Boucher and Boucher-Rodoni 1988) sediments represent a significant fraction of the dissolved nitrogen benthic fluxes. In contrast, however, Cowan and Boynton (1996) observed that urea (and primary amines) was a small fraction (<5%) of the total DON fluxes they determined at site S3. As discussed above, additional studies are needed to resolve these discrepancies.

Given the low C:N ratios for site S3 and M3 DOM benthic fluxes, these results also imply that the DOM passing from these estuarine sediments could be more reactive in the water column than has been previously suggested (cf. Hedges 1992). This is certainly the case if a significant fraction of the DON passing from bioturbated sediments is urea. If this is so, it suggests that some of the DOM escaping from these sediments may not escape the estuary and become incorporated into the oceanic DOC and DON cycles. Resolution of this question is clearly important because it has ramifications on whether or not DOM benthic fluxes represent a significant source of refractory DON to the oceans (Cifuentes and Morse unpubl. data; also see discussion below), and whether benthic fluxes have a major role in controlling the concentration and  $^{14}C$  age of DOC in the deep ocean (compare discussions in Burdige et al. 1992, Bauer et al. 1995, and Guo et al. 1996).

Table 4. Annual sediment nitrogen budget for site M3.

Process	Annual average (mol m <sup>-2</sup> yr <sup>-1</sup> )
Net nitrogen input	
TN deposition minus long-term burial (I)*	2.4 (2.3–2.5)
Nitrogen outputs	
Benthic ammonium flux (II)†	2.0 (± 0.2)
Benthic nitrate + nitrite flux (III)‡	–0.1 (± 0.03)
Benthic DIN flux (II+III)	1.5‡, 1.9 (± 0.2)§
Benthic DON flux (IV)†	0.07 (± 0.02)
Denitrification (V); (i.e., loss of nitrogen as a benthic N <sub>2</sub> flux)	0.3–0.5   0.5–0.9¶ 0.4# 0.4–0.7**

\* The upper limit is calculated with data from Kemp et al. (1990), whereas the lower limit is based on data for POC deposition minus burial (Roden et al. 1995), assuming that the organic matter being remineralized (which is what this difference represents) has a C:N ratio equal to the Redfield ratio (e.g., see Burdige 1991).

† This work (Table 1).

‡ From Cowan and Boynton (1996).

§ From this work.

|| Calculated using the data listed above, assuming a steady-state sediment nitrogen budget (i.e., I = II + III + IV + V).

¶ Calculated assuming denitrification is 15–30% of the TN input (Boynton et al. 1995); data for TN input taken from Kemp et al. (1990).

# An estimate based on a similar closure of a sediment nitrogen budget (see note || above) for a nearby mid-Bay site (Kemp et al. 1990).

\*\* Calculated with measured ammonium benthic fluxes and an estimate of sediment ammonium production based on sediment organic carbon profiles (from Cowan and Boynton 1996).

*Benthic DON fluxes and sediment nitrogen budgets*—Interest in benthic DON fluxes also stems from a desire to better understand the relative importance of denitrification versus benthic DON fluxes in sediment nitrogen budgets (Nixon 1981; Boynton and Kemp 1985; Bender et al. 1989; Blackburn et al. 1996). This consideration is important in continental margin sediments because denitrification in these sediments is generally thought to be an important (and perhaps the major) sink for combined nitrogen in the entire marine environment (see, most recently, Codispoti 1995 and references therein). However, the relative importance of sediment denitrification compared with benthic DON fluxes is not well constrained in most sediments in general (e.g., Bender et al. 1989; Kemp et al. 1990). With the results of this study we can begin to examine this problem for the estuarine sediments of Chesapeake Bay.

Results of the calculation of a sediment nitrogen budget for site M3 are shown in Table 4. Although there is a range in the different estimates of sediment denitrification rates at this site, these results suggest that unless we have significantly underestimated benthic DON fluxes (see above), these fluxes represent ~20% or less of the denitrification rates in site M3 sediments. Similar calculations are not possible for site S3 because data on sediment nitrogen deposition, burial, and denitrification are not available. However, an examination of the flux data in Table 1 also suggests that on annual time scales benthic DON fluxes are not a significant component of the sediment nitrogen cycle at this site.

As discussed by Boynton et al. (1995), denitrification rates

in Chesapeake Bay sediments appear to be low compared with values for other coastal ecosystems. In Bay sediments denitrification is equal only 15–30% of the total nitrogen (TN) inputs to Chesapeake Bay sediments compared with 40–55% of the TN inputs for other sedimentary environments (Seitzinger 1988). Because much of this denitrification is fueled by coupled nitrification–denitrification (Jenkins and Kemp 1984; Seitzinger and Giblin 1996), increased denitrification will also lead to a concomitant decrease in benthic ammonium fluxes. Presuming that changes in denitrification do not significantly affect pore-water DON profiles or decrease DON benthic fluxes, this would imply that in sediments with higher denitrification rates DON could represent a higher fraction of the total dissolved reactive nitrogen (i.e., non-N<sub>2</sub> gas) that escapes from sediments. Thus, in some estuaries sediment DON fluxes could have a more significant role in the transformation of DIN to DON observed within estuaries (e.g., López-Veneroni and Cifuentes 1994).

On annual time scales, these results suggest that benthic DON fluxes are not a significant component of the sediment nitrogen cycle at these Bay sites. As discussed above (*see Table 3 and above, Comparison of Our Benthic Nitrogen Fluxes With Other Reported Values*), the relative importance of benthic DON fluxes in nitrogen cycling in these Chesapeake Bay sediments appears to differ somewhat from that observed in other sediments (*see Blackburn et al. 1996 and Landén-Hillemyr 1998*). The reasons for these differences require further study. At the same time, however, we also note that on time scales that are shorter than annual cycles relatively large benthic DON fluxes from sediments can be observed (e.g., for short time periods immediately after the deposition of fresh detrital material at the sediment surface; *see discussions in Sloth et al. 1995 and Blackburn et al. 1996*).

*Benthic DON fluxes and the oceanic nitrogen cycle*—Using pore-water DON profiles from shelf and slope sediments from the Gulf of Mexico, Cifuentes and Morse (unpubl. data) made a first estimate of the global significance of benthic DON fluxes to the oceanic nitrogen cycle. Their estimated DON fluxes are similar to those we have measured in Chesapeake Bay (Table 1) and have estimated from pore-water profiles for mid-Atlantic continental margin sediments (Zheng and Burdige 1997). Our results therefore yield a similar lower limit for the integrated sediment DON flux to the oceans (~1.6 Tmol N yr<sup>-1</sup> versus 0.1–0.6 Tmol N yr<sup>-1</sup> as noted by Cifuentes and Morse unpubl. data). As is also the case for oceanic DOC cycling (e.g., Chen et al. 1993), these net inputs of DON are small in comparison to internal nitrogen cycling rates (Cifuentes and Morse unpubl. data), although sediment DON fluxes and riverine inputs (= 3.6 Tmol N yr<sup>-1</sup>; Walsh 1991) are roughly of the same order.

At the same time, however, our results suggest that DON passing from marine sediments may not be inherently refractory, and sediments (at least not estuarine sediments) may not be a major source of refractory DON to the oceans, as suggested by Cifuentes and Morse (unpubl. data). This observation further points out the importance of characterizing not only the sources of DON to the oceans but the reactivity of this material as well.

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