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Dissolved organic matter in Chesapeake Bay sediment pore waters

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Abstract

Results of recent studies of dissolved organic matter (DOM) in Chesapeake Bay sediment pore waters are summarized here, to gain further insights into the controls on the composition and reactivity of estuarine pore water DOM. This analysis shows that much of the DOM accumulating in sediment pore waters appears to be refractory and of relatively low molecular weight (less than ~3 kDa), consistent with recent water column DOM studies. Comparative analyses of pore water DOM data from bioturbated/bioirrigated sediments versus anoxic (i.e. non-bioturbated/bioirrigated) sediments indicate that differences in the physical and biogeochemical processes in these sediments lead to distinct differences in DOM concentrations and composition. The causative factors here appear to be both the presence/absence of macrofauna in the sediments, as well as differences in sediment redox conditions (more strictly anoxic vs. “mixed” redox conditions). These observations further suggest that differences in DOM composition and reactivity as a result of varying sediment redox conditions might also play a role in how sediment redox conditions affect overall sediment carbon preservation. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Dissolved organic matter (DOM) plays a major role in many biogeochemical processes in estuarine sediments. Many DOM compounds are produced and consumed during sediment particulate organic matter (POM) remineralization (e.g. Henrichs, 1995; Burdige and Gardner, 1998), and nutrient (N and P) regeneration during sediment POM remineralization can provide a significant amount of the nutrients required to fuel estuarine primary productivity (Klump and Martens, 1983; Cowan and Boynton, 1996). Estuarine, coastal and continental margin sediments also represent the major sites of carbon remineralization and burial in the oceans (Bernier, 1989; Hedges and Keil, 1995; Middelburg et al., 1997), and pore water DOM is an important intermediate in several proposed models for sediment

carbon preservation (Welte, 1973; Krom and Westrich, 1981; Mayer, 1994; Collins et al., 1995; Hedges and Keil, 1995; Burdige et al., 1999).

Biogeochemical processes in estuarine sediments have the potential to show great variations due to several factors, including: differing contributions of marine versus terrestrial organic matter to the sediments; salinity variations and their effect on the occurrence of anoxic sediment remineralization processes (e.g. the occurrence of sulfate reduction versus methanogenesis); the presence of benthic macrofauna in these sediments and their effect on sediment redox conditions. As a result, the concentrations, composition and reactivity of pore water DOM likely vary along estuarine gradients.

For the past several years, we have been studying pore water DOM at three sites along an estuarine transect in the mainstem of the Chesapeake Bay. In this article I will review our results, with reference to the general controls on pore water DOM cycling in these sediments. In particular, given the contrasting characteristics of two of the sites that have been examined in greatest detail, these results will be used to examine the role that benthic macrofaunal processes and varying

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sediment redox conditions play in affecting pore water DOM concentrations and composition.

1.1. Pore water size/reactivity model

Before beginning this discussion I want to briefly describe a model for DOM cycling in sediments that will be referred to throughout this paper. The pore water size/reactivity model (PWSR), first described as a conceptual model in Burdige and Gardner (1998), is based on traditional models for carbon cycling in anoxic sediments and the size reactivity continuum model for water column DOM cycling (Amon and Benner, 1996).

In the PWSR model the degradation of sediment POM to inorganic nutrients through DOM intermediates is thought of as a series of hydrolytic, oxidative, fermentative and eventually respiratory processes that produce and consume pore water DOM compounds with increasingly smaller molecular weights. Although this process likely leads to a continuum of DOM intermediates (in terms of molecular weights), the model assumes that there is an initial class of high molecular weight DOM compounds (HMW-DOM) containing biological polymers such as dissolved proteins and polysaccharides which result from the initial hydrolysis or oxidative cleavage (depolymerization) of sediment POM (see discussions in Laanbroek and Veldkamp, 1982; Capone and Kiene, 1988; Henrichs, 1992; Alperin et al., 1994; Arnosti et al., 1994; Burdige et al., 2000). Most HMW-DOM is further hydrolyzed and fermented to monomeric low molecular weight DOM compounds (mLMW-DOM) such as acetate, other small organic acids, and individual amino acids, that are then utilized in terminal respiratory processes in sediments such as denitrification or sulfate reduction.

In addition to these processes, some small fraction of the HMW-DOM pool is also broken down to a group of “polymeric” low molecular weight compounds (pLMW-DOM) that are proposed to be much less reactive than the HMW-DOM compounds. The pool of pLMW-DOM is believed to be recalcitrant because structural and/or chemical changes decrease its bioreactivity (see Santschi et al., 1995, and Amon and Benner, 1996, for discussions of similar phenomena in the water column). The accumulation of DOM with sediment depth in pore waters then occurs predominantly in the form of pLMW-DOM, since both HMW-DOM and mLMW-DOM represent reactive DOM pools that turn over rapidly.

The existence of these different DOC pools (with different reactivities) is consistent with our DOC molecular weight data discussed in Section 3.1 (Burdige and Gardner, 1998) and our recent DOM fluorescence data described in Section 3.3 (Burdige et al., 2001). It also explains pore water concentration data for acid volatile and nonvolatile DOC in the anoxic sediments of Cape

Lookout Bight, NC (Alperin et al., 1994) and is consistent with the results of polysaccharide (Arnosti et al., 1994) and lignocellulose degradation studies (Hodson and Moran, 1995). Finally, the PWSR model and the proposed production of refractory pore water pLMW-DOM may also help explain the fact that colloidal (> 1 kDa) organic matter desorbed from continental margin sediments is substantially older than the bulk sediment organic matter (~3000 vs. 700 years, respectively; Guo and Santschi, 2000). This is based on the fact that recent studies have shown that sorption of DOC to sediment particles plays some role in affecting pore water DOC concentrations (e.g. Hedges and Keil, 1995), and that pore water DOC concentrations may be “buffered” by reversibly-sorbed DOC in equilibrium with the pore waters (Thimsen and Keil, 1998). If this is indeed the case, the relatively refractory nature of the bulk pore water DOC pool (\approx pLMW-DOM) would then aid in the ageing process of this sorbed organic matter.

2. Chesapeake Bay field sites

The geochemical characteristics of the sediments from the three contrasting sites in Chesapeake Bay that will be discussed here are summarized below and in Table 1 (data taken from Kemp et al., 1990; Schaffner, 1990; Burdige and Homstead, 1994; Burdige et al., 1995, 2000,

Table 1
General site characteristics

Parameter/site ^a	N3	M3	S3
Average water depth (m)	10	15	12
Bottom water salinity (psu) ^b	<0.1–10	10–20	20–30
Sfc. Sediment POC (mg C/gdw)	~20–40	> 30	6–8
Sediment C/N ratio	12–22	6–10	12–16
PCHOs (% of POC) ^c	8±2%	9±2%	6±1%
C _{ox} (mol C/m ² /year) ^d	0.8±0.4	7.2±0.7	4.4±1.0
Pore water DOC (μM) ^e	200–900	400–2500	200–500
Pore water DON (μM) ^e	10–50	30–160	10–50
Pore water DCHO (μM) ^{e,f}	30–50	40–150	30–80

^a See Fig. 1 for a map showing site locations.

^b Seasonal ranges.

^c Average particulate (sediment) carbohydrate concentrations (as a percentage of sediment POC).

^d Depth-integrated sediment carbon oxidation rates. Values for sites S3 and M3 are based on integrated annual averages of measured \sum CO₂ benthic fluxes made during temporal studies at these sites (time period 3/95–10/96; data in Burdige and Zheng, 1998). The value at site N3 is based on modeling of \sum CO₂ pore water profiles, using procedures described in Burdige and Homstead (1994).

^e Ranges for the upper ~20–30 cm of sediment.

^f Concentrations of DCHOs are expressed on a per-mol-carbon basis, allowing for a direct comparison with DOC concentrations (see Burdige et al., 2000, for further details).

2001; Cowan and Boynton, 1996; Skrabal et al., 1997; Burdige and Gardner, 1998; Burdige and Zheng, 1998; Marvin-DiPasquale and Capone, 1998; also see the map in Fig. 1). Site N3 is in the northern Bay near the mouth of the Susquehenna River, one of the major sources of fresh water to the Bay. Site M3 is in the mesohaline portion of the Bay where seasonal anoxia (or low oxygen conditions) generally occurs in the bottom waters during summer months. Site S3 is in the southern Bay and is well-oxygenated year-round.

The sediments at site M3 are fine-grained, organic-rich and sulfidic, with sulfate reduction dominating organic matter remineralization. Redox potentials are very negative in the upper 10 cm of these sediments ($E_h \approx -120$ mV). Bioturbation is virtually absent, although a few bivalve spat and polychaete worms inhabit the upper ~ 5 cm of sediment in the early spring.

The sediments at site S3 are silty sands that are bioturbated and bioirrigated by large tube worms and

other benthic macrofauna. Site S3 sediments have a lower organic matter content than site M3 sediments, and have what can be considered mixed (or oscillating) oxic/anoxic sediment redox conditions (e.g. Aller, 1994). Evidence for this includes: minimal pore water sulfate gradients compared to site M3 (Fig. 2) in spite of measured sulfate reduction rates at site S3 that are $\sim 60\%$ of those measured at site M3; positive (oxidizing) redox values in the upper 10 cm of sediment ($E_h \approx 113$ mV) along with the presence of significant (~ 10 – 100 μM) pore water concentrations of reduced constituents such as ammonium and Mn^{2+} .

The sediments at site N3 are clay dominated, iron-rich, and contain a diverse community of polychaetes and bivalves. The upper 10 cm of sediments have positive E_h values (≈ 71 mV), and the organic matter here appears to be largely terrestrially-derived, based on its high C/N ratio (~ 12 – 22) and low $\delta^{13}\text{C}$ value (less than -25‰ at site N3, compared to ~ -21 to -22‰ at the

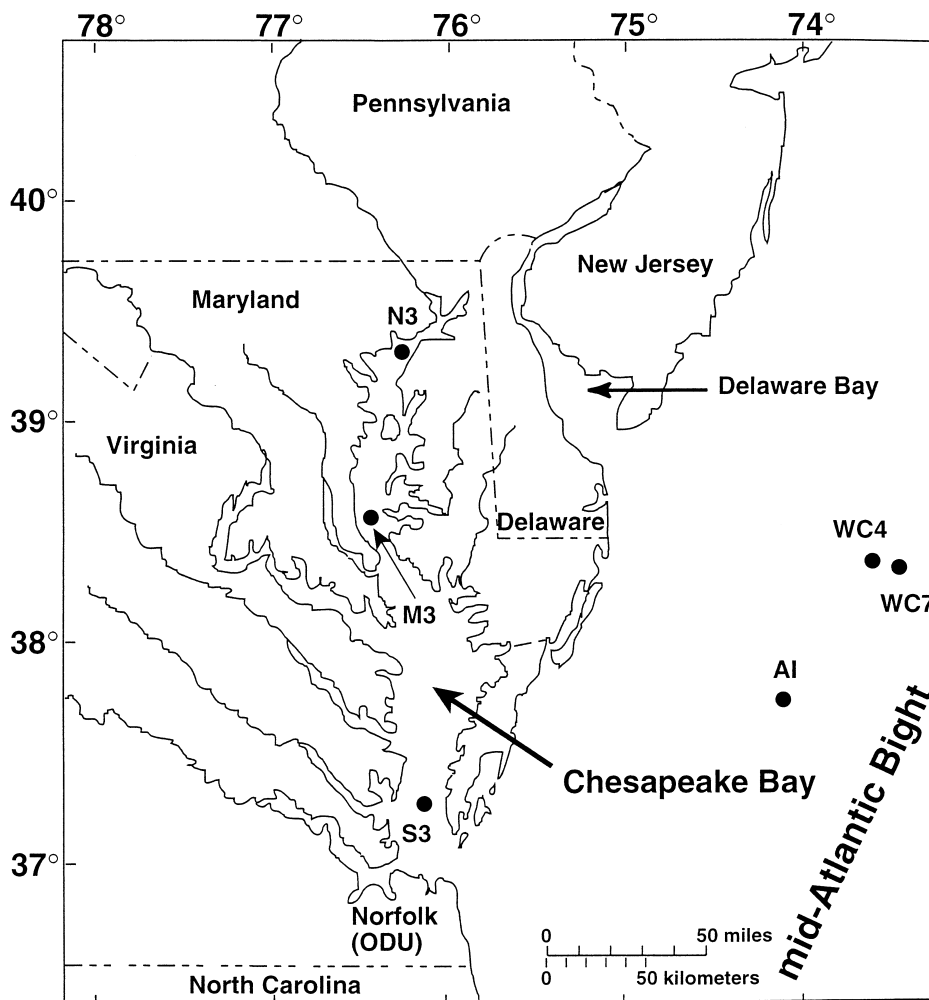


Fig. 1. Map showing the three Chesapeake Bay field sites (from Burdige and Gardner, 1998).

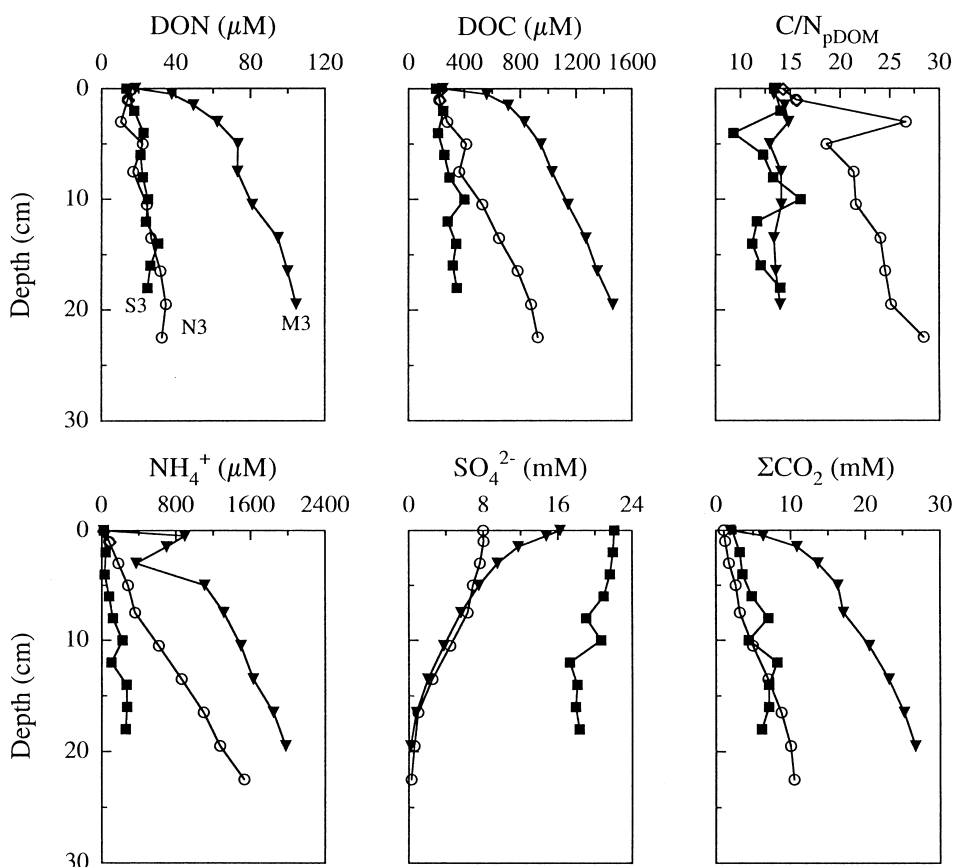


Fig. 2. Comparative inorganic and DOM pore water profiles collected in October 1995 at the three Chesapeake Bay sites. Symbols on the upper *x*-axes represent bottom water samples collected by hydrocasts (data and figure from Burdige and Zheng, 1998).

other two sites; J. Cornwell, unpub. isotope data cited in Marvin-DiPasquale and Capone, 1998). At the same time, there appear to have been recent temporal changes in organic matter deposition to site N3 sediments, as inferred by a decrease with depth in the sediment C/N ratio and an increase with depth in absolute particulate carbohydrate concentrations (Burdige et al., 2000, 2001).

In these sediment pore waters we have examined total DOC and DON (Burdige and Homstead, 1994; Burdige and Zheng, 1998), DOC and DON molecular weights (Burdige and Gardner, 1998), dissolved carbohydrates (Burdige et al., 2000) and DOM fluorescence (Burdige et al., 2001). We have also examined DOC, DON and fluorescence benthic fluxes at two of these sites (M3 and S3). Analytical and sampling methodologies are described in these papers and will not be repeated here. In this paper I will also present new data on pore water dissolved urea concentrations and urea benthic fluxes. Urea concentrations were measured colorimetrically using diacetyl monoxime (Rahmatullah and Boyde, 1980).

3. The composition of Chesapeake Bay pore water DOM

3.1. General trends

Pore water DOM concentrations at these sites are elevated over bottom water values, and generally increase with sediment depth (Fig. 2). Concentrations of DOC and DON are higher at site M3 than they are at the other two sites (Table 1). At site M3 DOM concentrations increase in an exponential-like fashion with depth and show the largest concentration gradients; much smaller concentration gradients are seen at sites S3 and N3. The C/N ratio of pore water DOM ($[\text{DOC}]/[\text{DON}] = C/N_{\text{pDOM}}$) is generally higher at site N3 than at the other two sites, which could reflect the source of organic matter to these upper Bay sediments (i.e. nitrogen-poor, terrestrially-derived material).

At site M3 pore water DOM concentrations (both DOC and DON) grow in and out seasonally, presumably in response to sediment temperatures and rates of sediment POM remineralization (Burdige and Zheng,

1998). This suggests that on seasonal time scales DOM concentrations in these sediments are controlled by a balance between DOM production and consumption (see similar discussions in Alperin et al., 1994). Average C/N_{pDOM} values at this site also vary seasonally and are out of phase with changes in DOM concentrations. Summer/fall cores with higher DOM pore water concentrations show lower C/N_{pDOM} values (less than ~ 14), while winter cores with lower DOM concentrations have higher average elemental ratios (greater than ~ 16). This inverse relationship between average pore water DOM concentrations at site M3 and C/N_{pDOM} values (also see Fig. 3) suggests that the net “selectivity” of DOM remineralization processes in these sediment varies with the overall rates of sediment POM remineralization. During periods of low remineralization, DOM consumption appears to be more selective, leading to the preferential net utilization of N-rich DOM (and thus to an increase in values of C/N_{pDOM}). In contrast, the opposite appears to be the case during periods when remineralization rates are more rapid, leading to the accumulation of higher concentrations of N-rich DOM.

Compared to site M3, DOM concentrations at site S3 are lower, show much smaller concentration gradients with depth and no obvious seasonal variability (Fig. 4). In individual cores the small-scale variability in DOM concentrations with depth may be a function of the heterogeneous distribution of macrofauna within the sediments. Values of C/N_{pDOM} at site S3 also show little

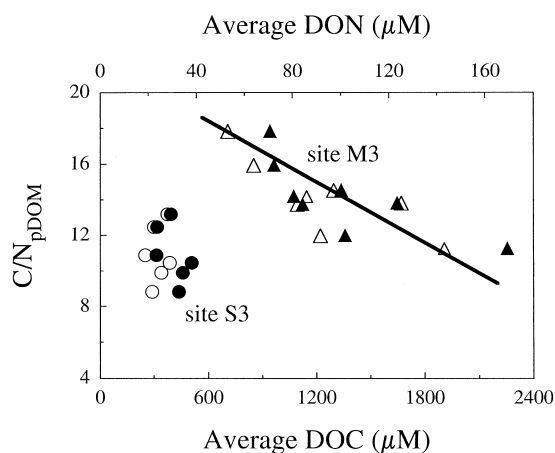


Fig. 3. Depth-weighted average DOC and DON concentrations versus depth-weighted average values of C/N_{pDOM} , all for the upper 20 cm of sites M3 and S3 sediments (data from Burdige and Zheng, 1998, and recent unpublished results from these sites). The line shown here through the site M3 results is meant to indicate the inverse relationship between average DOM concentrations and the average value of C/N_{pDOM} . Symbols: ○ = site S3 pore water DOC; ● = site S3 pore water DON; △ = site M3 pore water DOC; ▲ = site M3 pore water DON.

coherent spatial or temporal variability, and (within a broad envelope) are similar to those of bottom water DOM.

At site N3, pore water DOC profiles show variability in the upper ~ 5 – 10 cm of sediment (Fig. 5) that may be related to the bioturbation of these surficial sediments. Below these depths there is some evidence of seasonal variations that are consistent with the trends seen at site M3 (i.e. higher DOC concentrations when sediment temperatures are warmer). Unfortunately, the limited number of pore water DOC profiles at site N3 precludes a more detailed seasonal analysis of these results. Values of C/N_{pDOM} increase with depth in these sediments from ~ 6 to 15 near the sediment surface to ~ 18 – 27 below 20 cm (e.g. see Fig. 2). While this was initially interpreted as being due to the accumulation of refractory DOM with an increasing terrestrial signature (Burdige and Zheng, 1998) recent pore water DOM fluorescence studies at this site do not necessarily support this suggestion (Burdige et al., 2001). Given this observation, and evidence for non steady-state deposition of organic matter to these sediments discussed in Section 2, more detailed comparative analyses of site N3 results do not seem appropriate here.

Finally, DOM molecular weight studies show that the vast majority (~ 80 – 90%) of the DOC and DON in these sediment pore waters has a molecular weight less than ~ 3 kDa, and that this low molecular weight material (also referred to as DOC_3) accumulates in an absolute sense with sediment depth (Burdige and Gardner, 1998; Burdige and Zheng, 1998). Therefore, the accumulation of pore water DOM with depth in these sediments results from the net production of refractory *low*, and not high, molecular weight DOM. In these Chesapeake Bay sediments as well as other coastal marine sediments (Chen et al., 1993; Skoog et al., 1996; Burdige et al., 2001), DOM “humic”-like fluorescence is also strongly correlated with total pore water DOC (also see Section 3.3). Given that the properties of DOC_3 appear to be consistent with what is referred to as pLMW-DOM (see Burdige and Gardner, 1998, for further details), and that DOC_3 represents the vast majority of the bulk DOC in sediment pore waters, these observations support the notion that pLMW-DOM is likely what is often referred to as dissolved humic substances.

3.2. Dissolved carbohydrates

Concentrations of dissolved carbohydrates (DCHOs) in these sediment pore waters range from ~ 30 to 150 μM (Table 1), and increase with depth in a manner similar to total DOC (Burdige et al., 2000). Relative DCHO concentrations (DCHOs as a percentage of total DOC) range from 5 and 20% and decrease slightly with depth. These percentages may be slightly higher in site

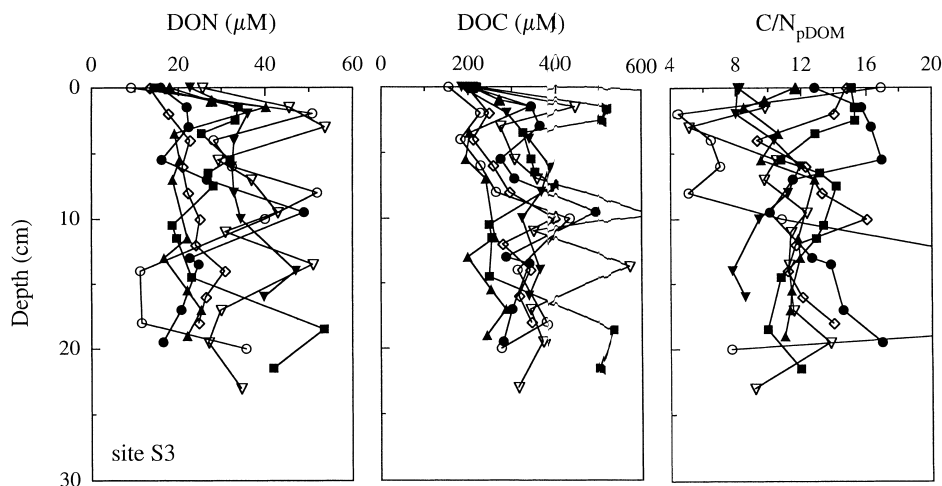


Fig. 4. Pore water DOM profiles at site S3 (data from Burdige and Zheng, 1998, and recent unpublished results). Cores were collected in 6/95 (●), 10/95 (◇), 3/96 (■), 8/96 (▲), 10/96 (▽), 8/97 (▼), and 11/97 (○). Symbols on the upper x-axes represent bottom water samples collected by hydrocasts.

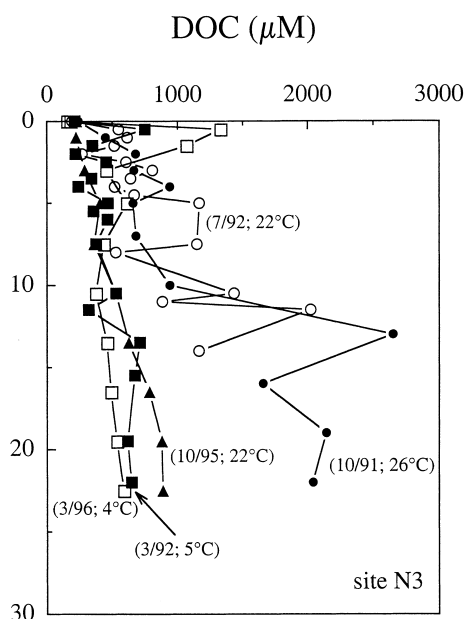


Fig. 5. Pore water DOC profiles at site N3. Cores were collected in 10/91 (●), 3/92 (■), 7/92 (○), 10/95 (▲), and 3/96 (□). Symbols on the upper x-axes represent bottom water samples collected by hydrocasts.

S3 sediments (Table 2) although the limited number of samples analyzed at this site (in comparison to site M3) makes such a comparison equivocal. In the analysis of a selected number of samples, individual aldoses (neutral sugars) were observed to account for ~30–50% of the total DCHOs. Dissolved glucose was the predominant aldose in these samples (29%), with the following order

Table 2
Distribution of DOC in Chesapeake Bay sediment pore waters

Parameter/site	N3	M3	S3
[DCHO] ^a	9±4%	8±2%	17±7%
[DOC _{amide}] ^{a,b}	20±4%	28±3%	40±10%
	(22±9%)	(29±4%)	(38±6%)
[DOC _{other}] ^a	71±8%	65±3%	46±14%
Number of samples ^c	3	29	12
Number of cores ^c	1	3	2

^a All as a percentage of [DOC]_{total} in the pore waters.

^b The absolute concentration of DOC_{amide} was calculated using the formula [DON]_{total} × (C/N)_{DON} (see the text for further details). The values in parentheses were determined using the larger set of DOC and DON pore water concentration measurements reported in Burdige and Zheng (1998).

^c The numbers of cores/samples in which DOC, DON and DCHOs were all determined on the same samples.

of abundance for the remaining aldoses: xylose (16%); fucose, rhamnose and galactose (each average value between 12 and 14%); mannose and arabinose (each average value between 8 and 9%).

3.3. DOM fluorescence

Using fluorescence excitation-emission matrix spectroscopy, 3-dimensional spectra of fluorescence intensity versus excitation and emission wavelengths can be used to examine some of the characteristics of DOM found in natural waters (e.g. see most recently Coble, 1996). Applying this technique to the study of Chesapeake Bay sediment pore waters the fluorescence peaks observed in these pore waters were similar to those observed in the

water column, and include peaks ascribed to the fluorescence of humic-like materials as well as protein-like peaks that appear to result from the fluorescence of the aromatic amino acids tryptophan and tyrosine (Burdige et al., 2001). Humic-like fluorescence generally increased with sediment depth and, as noted above, was closely correlated with pore water total DOC concentrations (i.e. DOC-normalized humic-like fluorescence intensities were roughly constant with sediment depth). At site M3, humic-like fluorescence was sufficiently strong that protein-like fluorescence peaks were often obscured by the larger and broader humic-like peaks. At site S3, where humic-like fluorescence was lower, protein-like fluorescence was easier to observe. In benthic flux studies at these sites, fluxes of both humic-like and tryptophan, protein-like fluorescent DOM components were observed. Thus, while pore water profiles at both sites show equivocal evidence of tryptophan fluorescence, benthic flux studies demonstrated that compounds with

this type of protein fluorescence are indeed produced in the sediments.

3.4. DOM benthic fluxes

Measured DOC fluxes from site M3 sediments range from ~ 0.7 to $3 \text{ mmol/m}^2/\text{d}$, and from essentially zero to $0.9 \text{ mmol/m}^2/\text{d}$ at site S3. Values of measured DON fluxes at these sites range from ~ 0.08 to 0.2 and essentially zero to $0.4 \text{ mmol/m}^2/\text{d}$, respectively (Burdige and Homstead, 1994; Burdige and Zheng, 1998; Burdige et al., 2001). Both sets of fluxes vary seasonally along with temperature and rates of overall sediment POM remineralization. The C/N ratio of the DOM leaving these sediments as a benthic flux generally ranges from ~ 4 to 6 at site M3, and ~ 2 to 5 at site S3 (Burdige and Zheng, 1998; also see Table 4). These values are substantially lower than C/N_{pDOM} values in the pore waters at these sites (which are greater than ~ 10). This implies that

Table 3
Pore water urea and DOM concentrations in Chesapeake Bay sediments

Date	Urea (μM)	Urea-N (% of DON)	Urea-C (% of DOC)	C/N_{pDOM}^c (mol/mol)	C/N (non-urea DOM) (mol/mol)
<i>Site M3</i>					
Aug 97 ^a	<0.2–2.7	$2.4 \pm 2.9\%$	$0.1 \pm 0.1\%$	14.2	14.5
Nov 97	0.3–3.1	$1.7 \pm 1.1\%$	$0.1 \pm 0.04\%$	11.3	11.5
<i>Site S3</i>					
Oct 95–Oct 96 ^b				10.1–12.7	9.6–12.0
Aug 97	0.5–1.5	$5.6 \pm 1.9\%$	$0.33 \pm 0.1\%$	7.9	8.3
Nov 97 ^a	<0.2	$1.7 \pm 1.1\%$	<0.04%	10.6	10.7

^a In these cores, pore water urea concentrations in several samples were below detection ($\sim 0.2 \mu\text{M}$). Relative urea concentrations were therefore calculated assuming that these samples had urea concentrations equal to $0.2 \mu\text{M}$. Thus these average relative concentrations are upper limits of the actual value.

^b Results from several cruises, reported in Burdige and Zheng (1998). The C/N ratio of the non-urea DOM was estimated by assuming that Urea-C was 0.33% of the pore water DOC and Urea-N was 5.6% of the DON. This calculated range is therefore an upper limit of its true value.

^c The C/N ratio of the total DOM pool.

Table 4
Urea and DOM benthic fluxes from Chesapeake Bay sediments

Date	DOC ^b	DON ^b	C/N ^c (total DOM)	Urea ^b	Urea (% of DON)	Urea (% of DOC)	C/N ^c (non-urea DOM)
<i>Site S3</i>							
Aug 96 ^a	0.85 ± 0.15	0.18 ± 0.08	4.7 ± 2.2	49 ± 15	$54 \pm 29\%$	$6 \pm 2\%$	9.6 ± 10.1
Oct 96 ^a	0.34 ± 0.32	0.42 ± 0.13	0.9 ± 0.8	26 ± 19	$13 \pm 10\%$	$7 \pm 8\%$	1.0 ± 1.0
Nov 97	0.25 ± 0.04	0.13 ± 0.04	1.9 ± 0.6	11 ± 10	$17 \pm 16\%$	$5 \pm 4\%$	2.2 ± 0.9
<i>Site M3</i>							
Nov 97	1.1 ± 0.4	0.18 ± 0.05	6.3 ± 2.8	2 ± 5	$2 \pm 5\%$	$0.1 \pm 0.4\%$	6.4 ± 2.9

^a DOC and DON benthic fluxes from Burdige and Zheng (1988).

^b DOC and DON fluxes are $\text{mmol/m}^2/\text{d}$ and urea fluxes are $\mu\text{mol urea/m}^2/\text{d}$. Positive fluxes are out of the sediments.

^c mol/mol.

DOM accumulating in these sediment pore waters is carbon-rich relative to 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 sediment POM undergoing remineralization in the surface sediments is close to the Redfield ratio, 6.6; e.g. Burdige, 1991a).

At site M3 most calculated, diffusive DOC benthic fluxes were equivalent to measured benthic fluxes on any given sampling date (ratio=1 in the upper panel of Fig. 6), and the average value of their ratio for the time period shown here was 1.1 ± 0.2 . In contrast, on all sampling dates the ratio of measured to calculated DON

benthic fluxes was greater than 1, and was greater than that for the DOC benthic flux on each date. The average value of this DON flux ratio at site M3 for the entire data set in Fig. 6 was also slightly greater than 1 (2.4 ± 0.7).

These observations imply that either pore water DON concentration gradients near the sediment–water interface are steeper than those predicted by the resolution of our sampling techniques (generally 0.5–1 cm resolution), or that there is DON production at the sediment surface in addition to within the sediments. Regardless of which phenomena explains these observations they are consistent with the observed differences discussed above

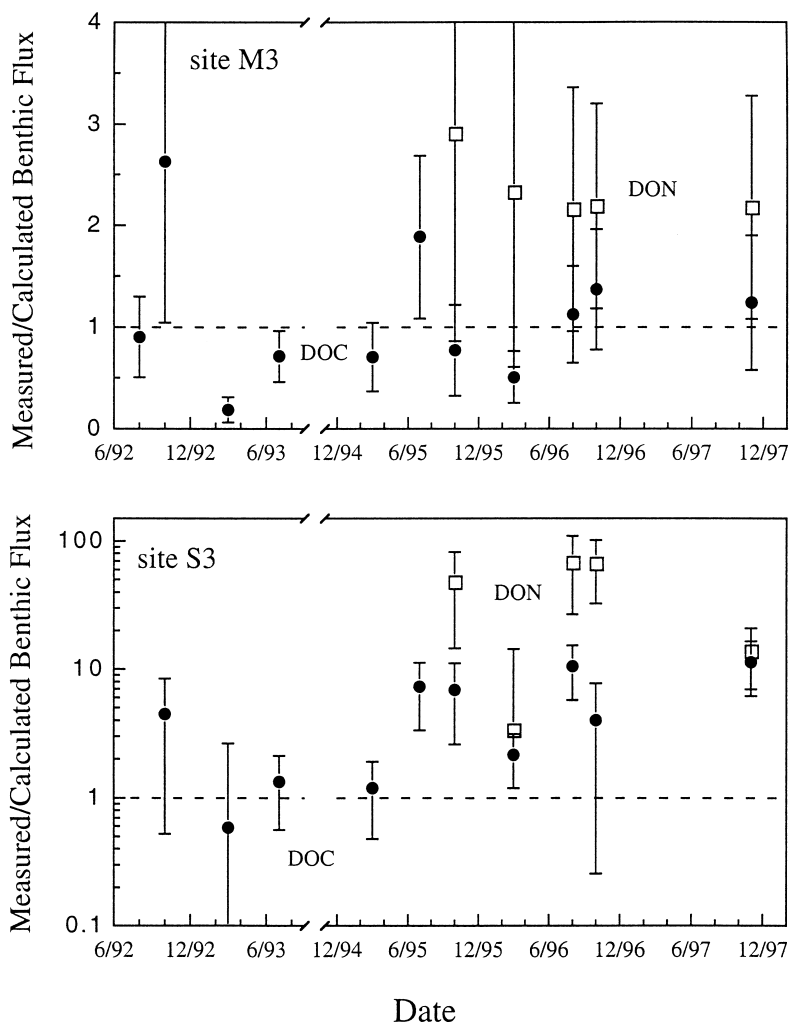


Fig. 6. The ratio of measured to calculated, diffusive benthic DOC (●) and DON (□) fluxes versus time at sites M3 (top panel) and S3 (bottom panel). Also shown in each panel is the 1:1 line (---) for these flux ratios. Note the logarithmic y-axis for the site S3 results. Calculated diffusive fluxes were determined as discussed previously (Burdige et al., 1995; Burdige and Zheng, 1998) and measured fluxes come from these references and recent unpublished results. For DON fluxes the ratios shown here differ slightly from the values originally reported in Burdige and Zheng (1998) due to an error in the choice of diffusion coefficients used in these earlier calculations.

between C/N ratios in DOM benthic fluxes and bulk pore waters, and imply that there is enhanced production of N-rich DOM at or near the sediment-water interface (see Blackburn et al., 1996, and Landén et al., in press, for similar results from other sediments).

At site S3, measured DOM benthic fluxes were generally greater than calculated, diffusive benthic fluxes (Fig. 6), consistent with the fact that these sediments are bioturbated/bioirrigated. The ratios of measured to calculated benthic fluxes were also larger for DON than they were for DOC (average values of 40 ± 13 and 5 ± 1 , respectively), implying preferential production of N-rich DOM in the upper sediments at site S3 as well.

A comparison of benthic DOM fluxes with inorganic nitrogen and carbon fluxes shows that benthic DOM fluxes are a small fraction (less than 10%) of sediment carbon oxidation and nitrogen remineralization in these Chesapeake Bay sediments (Burdige and Zheng, 1998; also see Burdige et al., 1999, for a more global perspective of this problem). These observations imply that *net* sediment DOM production is small in comparison to gross DOM production, since under steady state conditions the former is balanced by the benthic DOM flux (e.g. Berner, 1980), and the latter is approximately equal to gross DOM consumption or inorganic nutrient production (which then results in inorganic nutrient benthic fluxes). These trends are consistent with discussions in Section 1.1 regarding carbon and nitrogen flow through DOM intermediates during sediment POM remineralization and the role of different types of DOM compounds as intermediates in the remineralization process.

3.5. Dissolved urea and urea benthic fluxes

In past work (Burdige and Zheng, 1998), we suggested that urea cycling could be an important component of carbon and nitrogen cycling in the bioturbated site S3 sediments, and might help explain the observed discrepancy between values of C/N_{pDOM} in the pore waters and the C/N ratio of DOM benthic fluxes at this site (also see discussions in Lomstein et al., 1989). To examine this suggestion pore water urea concentrations and benthic urea fluxes at both sites S3 and M3 were determined using archived samples from the studies described in Burdige and Zheng (1998) and samples collected in subsequent studies at these sites (Burdige et al., 2001).

These results are summarized in Tables 3 and 4. In sediment pore waters at both sites urea concentrations ranged from below detection ($0.2 \mu\text{M}$) to $\sim 3 \mu\text{M}$, and constituted a small fraction of the total pore water DOC and DON (less than 0.3 and 6% respectively). Similarly, benthic urea fluxes were an insignificant component of the DOM fluxes at site M3. At site S3 benthic urea fluxes constituted higher percentages of both the DOC and DON benthic fluxes, with perhaps some seasonal

variability. However, urea benthic fluxes did not appear to substantially alter the C/N ratio of the DOM benthic fluxes at this site.

3.6. Other components of the DOM pool

Much of the biologically-produced organic matter in natural systems can (at least somewhat operationally) be categorized as carbohydrates, proteins (amino acids), lipids or hydrocarbons. In the water column, however, such an approach accounts for less than 15% of the measured DOC (e.g. Williams and Druffel, 1988; Bauer et al., 1992). Furthermore, traditional techniques used to isolate humic substance generally do not account for this large component of uncharacterized material.

To examine this problem in Chesapeake Bay sediment pore waters I have estimated the concentration of uncharacterized DOC with our data using the following equation,

$$[\text{DOC}]_{\text{unc}} = [\text{DOC}]_{\text{total}} - [\text{DCHO}] - [\text{DON}]_{\text{total}} \times (C/N)_{\text{DON}} \quad (1)$$

where $[\text{DOC}]_{\text{total}}$ and $[\text{DON}]_{\text{total}}$ are the total pore water DOC and DON concentrations, $[\text{DCHO}]$ is the concentration of dissolved carbohydrates (on a per-mole-carbon basis) and $(C/N)_{\text{DON}}$ is the C/N ratio of the specific organic compounds in the DON pool.

There are several assumptions made in this calculation. The first is that by analogy to water column studies (e.g. Thurman, 1985; Williams and Druffel, 1988), pore water concentrations of dissolved lipids are low in comparison to those of other DOM pools. A second assumption is that the concentrations of low molecular weight organic acids such as acetate or propionate are also low, since given the way this calculation is carried out these compounds are accounted for as $[\text{DOC}]_{\text{unc}}$. In most sediments these compounds generally represent a small percentage of the total DOC pool (Michelson et al., 1989; Alperin et al., 1994; Albert and Martens, 1997; Simjouw and Burdige, unpub. data), suggesting that this assumption may not be inappropriate. Furthermore, in anoxic, organic-rich sediment where these organic acids are a major fraction of the DOC pool this usually occurs in the region of these sediments where there is a transition from sulfate reduction to methanogenesis (Alperin et al., 1994; Albert and Martens, 1997). This might be expected to occur at depth at site M3 (e.g. see Fig. 2), although for the most part in our work we sampled the upper sediments where dissolved sulfate was still present and sulfate reduction therefore dominated. Finally, in assigning a C/N ratio to the material in the DON pool it was assumed that most of this nitrogen is amide nitrogen, based on studies of DON in the water column (McCarthy et al., 1996) and particulate organic nitrogen

in recent marine sediment (Patience et al., 1992). A C/N ratio of 4 was, therefore, used here, based on past studies of sediment pore water amino acids (Henrichs and Farrington, 1987; Burdige and Martens, 1990; Lomstein et al., 1998).

The results of these calculations are shown in Table 2, where it can be seen that DOC_{unc} represents ~50–70% of the total DOC in these sediment pore waters. Depth profiles of DOC_{unc} are similar in shape to those of total DOC, consistent with the fact that the percentages in this table show no depth trends (data not plotted here). At two of the three site (M3 and N3) the percentage of DOC_{unc} (~70%) is similar to, though slightly lower than, the percentage of the DOC_3 in the pore waters (~80–90%; Burdige and Gardner, 1998). This similarity is consistent with recent thoughts about humification, in which it is now thought that humification initially leads to the production of increasingly oxidized, low molecular weight DOM molecules (i.e. pLMW-DOM) from sediment POM (Hatcher and Spiker, 1988; Amon and Benner, 1996). This pLMW-DOM is presumably refractory because, as a result of how it is produced during sediment POM remineralization, it now contains carbon structures that are not recognizable by the degrading biota (see discussions in Amon and Benner, 1996, for further details). The fact that relative concentrations of DOC_{unc} are slightly lower than those of DOC_3 may be due to the fact that not all of material found in the DON or DCHO pools represents “original”, sediment POM-derived biochemicals such as free monomeric amino acids or sugars, or peptides or polysaccharides. Thus some fraction of the chemically-measured DON or DCHOs is likely to be found in the pLMW-DOM (humic) pool, leading to this possible underestimation of DOC_{unc} concentrations.

The results of these calculations also show that relative concentrations of DOC_{unc} at site S3 are lower than those observed at the other two sites, while relative concentrations of $\text{DOC}_{\text{amide}}$ are slightly higher (Table 2). Higher levels of $\text{DOC}_{\text{amide}}$ at site S3 may be related to an increasing importance of bacterial sources of organic matter to the pore water DOM pool in these sediments. Lower relative concentrations of DOC_{unc} at site S3 could imply that there is less effective preservation of refractory DOM in the bioturbated/bioirrigated sediments at site S3, depending on what DOC_{unc} represents and its relationship to pLMW-DOM and/or dissolved humic substances. Both of these suggestions will be further discussed in later sections.

Finally, the results of DOC_{unc} calculations at sites M3 and S3 are consistent with results presented by Otsuki and Hanya (1972a,b) in which they examined DOM production from decaying algal cells under aerobic and anaerobic conditions. In their studies they observed that what they termed “other” DOC (i.e., non-protein and non-carbohydrate DOC, roughly equal to the quantity

$[\text{DOC}]_{\text{unc}}$ calculated here) was higher in anaerobic experiments than it was in aerobic experiments (~60–80% versus <35%, respectively). They also observed that total DOC concentrations were higher in anaerobic experiments (as is seen in the pore water data from these sites).

4. The role of sediment redox conditions in controlling pore water DOM concentrations and cycling

It is well documented that macrofaunal activity in estuarine sediments can have a significant impact on sediment biogeochemical processes (see, for example, discussions in Rhoads, 1974; Aller, 1982, 1988; Berner and Westrich, 1985; Kristensen, 1988). Many past studies have focussed on the effects that bioturbation and bioirrigation can have on benthic fluxes of inorganic constituents. However recent studies have also examined the effects of benthic macrofauna on sediment redox conditions, with an emphasis on better understanding the role that sediment redox conditions may have on the “efficiency” of sediment POM remineralization (see the references cited above as well as Aller, 1978; Kristensen and Blackburn, 1987; Aller and Aller, 1998; Hulthe et al., 1998; Hedges et al., 1999).

In this section I will use our Chesapeake Bay results to examine the effects of sediment redox conditions on DOM cycling in estuarine sediments. This effort will focus on data collected at sites M3 and S3, in part because several lines of evidence suggest that similar types of organic matter are undergoing remineralization in the sediments at these two sites. This evidence includes similarities in the C/N ratio of the sediment POM that has been remineralized (based on pore water modeling and the results of long-term sediment decomposition experiments; Burdige, 1991a, and unpub. data) along with similarities in the relative carbohydrate content of the remineralized sediment organic matter at both sites (Burdige et al., 2000). Stable carbon isotope values also suggest that there are similar, predominantly phytoplankton sources for the sediment POM at the two sites (J. Cornwell, unpub. isotope data cited in Marvin-DiPasquale and Capone, 1998). Thus in comparing the effects that anoxic (site M3) vs. mixed redox (site S3) conditions have on sediment DOM cycling factors related to differences in the “quality” of the organic matter undergoing remineralization at the two sites should be minimized.

In beginning this discussion, I note that the results of past studies suggest that molecular diffusion and sediment remineralization processes control pore water DOM concentrations and DOM benthic fluxes at site M3 (see discussions in Burdige and Homstead, 1994, and Burdige and Zheng, 1998). In contrast, bioturbation and bioirrigation, along with sediment remineralization

processes, play the dominant roles in controlling sediment DOM cycling at site S3. In the former case, this occurs as a result of the mixing of bottom waters into the pore waters due to macrofaunal processes. In the latter case at least three lines of evidence support this observation. First, although gradients are small, concentrations of DOC, DON, DCHOs and humic-like fluorescence are all slightly higher in site S3 pore waters than they are in bottom waters (e.g. see Fig. 4). Second, benthic flux studies show that there are generally non-zero fluxes of DOC, DON and humic- and protein-like fluorescent material out of these sediments. And finally, DOC-normalized humic-like fluorescence values are slightly higher in site S3 pore waters than they are in bottom waters. All of these observations imply that there is net DOM production in site S3 sediments, presumably due to sediment remineralization processes.

4.1. Bulk DOM concentration differences

Pore water DOM concentrations are higher at site M3 than they are at site S3 (e.g. see Fig. 2), and based on observations in the literature (Otsuki and Hanya, 1972a,b; Hansen and Blackburn, 1991; Enoksson, 1993; Sloth et al., 1995). Burdige and Zheng (1998) suggested that higher inputs of organic matter to site M3 sediments or a greater degree of sediment anoxia at this site could explain these observations (as discussed above, a third possible explanation, differences in the “quality” of the organic matter undergoing remineralization in these sediments, appears to be of secondary importance). The extent to which reactive organic matter quantity versus sediment oxic/anoxic effects explain these differences in pore water DOM concentrations will be examined here with the model shown in Fig. 7. Parameters used in the model are defined in this figure and in Table 5. This effort will take a box-model approach to sediment DOM dynamics, and assume uniform concentrations in this surface sediment box. I will also assume that under steady-state conditions net pore water DOM production in the sediment box is balanced by its benthic flux out of the sediments (e.g. Berner, 1980). Although this approach neglects other sediment and pore water transport processes, it allows for a slightly easier examination of sediment DOM dynamics.

Given available information on the composition and reactivity of these different DOM pools in sediments, several other simplifying assumptions have been made here regarding the quantification of processes in the model. The first is that the production and consumption of HMW-DOM (=J) is relatively rapid and tightly coupled, and that the rate of POM loss (= HMW-DOM production) approximates the rate of HMW-DOM consumption. This assumption is based on arguments presented elsewhere (Burdige and Gardner, 1998; Burdige et al., 2000) that in estuarine sediments fer-

mentative or perhaps respiratory processes affecting lower molecular weight DOM intermediates appear to exert a greater overall control on sediment carbon remineralization than do hydrolytic, oxidative or fermentative processes affecting higher molecular weight intermediates (also see discussions in Arnosti et al., 1994; Kristensen et al., 1995). A second assumption made here is that remineralization processes through mLMW-DOM intermediates are more rapid than those through pLMW-DOM components, and can be quantified as a fraction (=α) of the total POM remineralization rate.

Based on these assumptions, the equation for the time rate of change of pLMW-DOM in the sediment box is given by,

$$\frac{dP}{dt} = \alpha J - \phi L k P - B_P \quad (2)$$

where P is the concentration of pLMW-DOM, k is the first order rate constant for pLMW-DOM consumption, ϕ is the sediment porosity, L is the thickness of the sediment box and B_P is the benthic flux of pLMW-DOM out of the sediments. Assuming that pLMW-DOM is a constant fraction (=f) of the total DOC in sediment pore waters (D_t), the steady state solution of Eq. (2) expressed in terms of total DOC concentrations is,

$$D_t = \frac{\alpha J - B_P}{\phi L k f} \quad (3)$$

In working with this equation I assume that B_P can be expressed as a fraction (γ) of the total DOC benthic flux, which is itself a fraction (β) of the total, depth-integrated sediment carbon oxidation rate. This then implies that B_P equals $\gamma\beta J$. This formalism is based in part on our recent results (Burdige et al., 1999) which show that there a positive, but non-linear relationship between total benthic DOC fluxes and sediment carbon oxidation rates (based on a compilation of benthic DOC fluxes and sediment carbon oxidation rates from more than 20 coastal and continental margin sediments, including sites S3 and M3). In the context of this model, this then implies that β is a non-linear function of J . This observation and past work at sites M3 and S3 then allows me to estimate values of β at these two sites. Constraining values of γ at the two sites will be discussed below.

Based on this discussion, Eq. (3) can be re-written as,

$$D_t = \frac{\alpha J - \gamma\beta J}{\phi L k f} = \frac{AJ}{\phi L k f} \quad (4)$$

where $A = \alpha - \gamma\beta$. With this equation, the ratio of average DOC concentrations in bioturbated (B; i.e. site

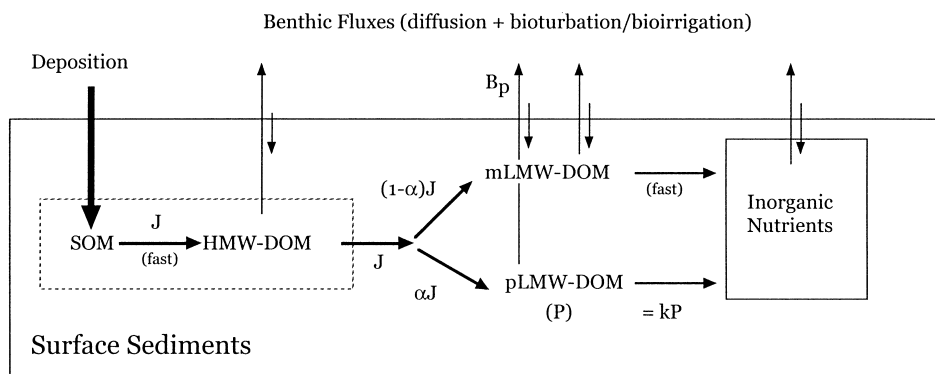


Fig. 7. A schematic box model of DOM remineralization in estuarine sediments based on the PWSR model. See the text and Table 5 for the definitions of these symbols.

Table 5
Parameters used in the sediment DOM box model

Parameter	Description
P	the concentration of pLMW-DOM
J	total POM remineralization rate (= production rate of HMW-DOM)
α	fraction of HMW-DOM remineralization that passes through pLMW-DOM intermediates
B_p	the benthic flux of pLMW-DOM out of the sediments
f	the ratio of pore water concentrations of pLMW-DOM to total DOC
k	the first-order rate constant for pLMW-DOM consumption
ϕ	sediment porosity
L	the thickness of the sediment box
D_t	the concentration of total DOC in the sediment pore waters
β	the ratio of the total benthic DOC flux to the sediment carbon oxidation rate
γ	the ratio of the pLMW-DOM benthic flux to the total DOC benthic flux
A	$= \alpha - \beta\gamma$ (see the text for further details)
R (subscript)	the ratio of a given parameter in bioturbated (B) versus non-bioturbated (N) sediments (i.e. $k_R = k_B/k_N$)

S3) versus non-bioturbated sediments (N; i.e. site M3) can then be expressed as,

$$\frac{D_{t,B}}{D_{t,N}} = \frac{J_B}{J_N} \left(\frac{A_B/A_N}{(k_B/k_N)(f_B/f_N)(\phi_B/\phi_N)} \right) \quad (5)$$

where the two equivalent values of L (=20 cm; see below) cancel one another out. Using the subscript “R” to define each of these ratios (e.g. $J_R = J_B/J_N$) allows Eq. (5) to be re-written as,

$$\frac{\phi_R D_R}{J_R} = \frac{A_R}{k_R f_R} \quad (6)$$

Pore water and benthic flux data from these sites can then be used to define several of these ratios, to begin to examine the relative values of the rate parameters in these two sediment types.

Before continuing though, I note that strictly speaking this model applies only to pore water DOM that is produced and consumed during sediment remineralization processes. However, the DOM found in sediment pore waters originates from both this source, as well as bottom waters entrained in the sediments during sediment deposition and also transported into the sediments by benthic macrofaunal processes. If we assume that this bottom water DOM component is “inert” in sediments on early diagenesis time scales, then the value of D_t in Eq. (6) should actually be the average pore water DOC concentration minus the bottom water concentration.

Taking all of this into account, depth-integrated average DOC concentrations in the upper 20 cm of these two sediments (corrected for bottom water concentrations) yield a D_R value that ranges from ~0.05 to 0.3, with an average value of 0.13 (based on a site M3 pore water DOC concentration range of ~900 to 2000 μM , a site S3 range of 250 to 400 μM , and bottom water DOC concentrations at both sites of ~150–200 μM). Without this bottom water correction D_R is slightly larger, ranging from 0.13 to 0.4 with an average value of 0.24. Assuming that J_R can be obtained from measurements of depth-integrated sediment carbon oxidation rates (Burdige and Homstead, 1994; Burdige and Zheng, 1998), this ratio then varies from ~0.4 to 0.8, while ϕ_R varies between ~0.5 and 0.7 (based on a site M3 ϕ range of 0.9–0.95 and a site S3 ϕ range of 0.5–0.6). Thus, a reasonable estimate of $\phi_R D_R / J_R$ is ~0.03–0.5 (or 0.1–0.6 without the above-discussed bottom water correction to D_R). However, in the rest of this discussion it will simply

be assumed that these results imply that this ratio (and therefore the ratio $A_R/k_R f_R$ as well) is less than 1.

In a broad sense, these results imply that the presence/absence of bioturbation and bioirrigation and/or differences in sediment redox conditions are more important than reactive organic matter quantity in explaining these differences in pore water DOM concentrations. Given these differences in sediment carbon oxidation rates, if organic matter quantity alone explained the differences in DOC concentrations, the ratio $\phi_R D_R/J_R$ would be expected to be essentially equal to one, which does not appear to be the case.

These results therefore indicate that changes in sediment redox conditions alter the pathways of sediment DOM remineralization and lead to the enhanced buildup of DOC under anoxic conditions. A further examination of how this anoxic build-up of DOC might occur can be done by looking at the inequality

$$A_R/k_R f_R [= {}_R D_R/J_R] < 1 \quad (7)$$

in slightly greater detail. In doing so, I first take the observation that DOC_3 is a near constant fraction of the total pore water DOC pool in both sediments (Burdige and Gardner, 1998) to imply that the value of f is similar in both sediments, and that $f_R = 1$. At the same time though, the results in Section 3.6 might lead one to conclude that $f_R \approx 0.7$ (based on the relative concentrations of $[DOC]_{unc}$ in Table 2). However, regardless of which value of f_R is more appropriate, both imply that the ratio A_R/k_R is also less than 1.

This analysis next requires evaluating the parameters γ and β . Based on directly measured benthic DOC fluxes and sediment carbon oxidation rates at these two sites (Burdige and Zheng, 1998) values of β are 0.04 ± 0.01 at site S3 and 0.05 ± 0.01 at site M3, leading to a β_R value of 0.75 ± 0.24 . Similarly, an initial estimate of γ might be that it is equal to the relative amount of pLMW-DOM in the pore waters ($=f$), implying that γ_r (along with f_R) might range from 0.7 to 1. Overall then, these observations imply that $\beta_R \gamma_R \leq 1$.

In examining the ways in which the ratio A_R/k_R can be less than 1, two end-member situations can be considered. In the first case we assume that α_R equals 1, which would imply that carbon flow through mLMW-DOM intermediates is unaffected by sediment redox conditions (consistent with the results of water column studies of these processes reported by Lee, 1992). As is shown in the Appendix this then leads to k_R being greater than 1, implying that k_B must be greater than k_N . Therefore in this case refractory pLMW-DOM is less effectively decomposed under anoxic conditions, leading to both its higher absolute concentrations as well as that of total DOC.

In the second end-member situation it is assumed that k_R is equal to one, implying that pLMW-DOM

consumption is unaffected by sediment redox conditions. In this case, results in the Appendix show that here α_R must be less than 1 and that $\alpha_N > \alpha_B$. Looking at this inequality from the standpoint of how it effects carbon flow through mLMW-DOM intermediates, this implies that $1-\alpha_{BT}$ is greater than $1-\alpha_{NBT}$. The inference here is that a greater percentage of carbon flow occurs through mLMW-DOM intermediates under oxic conditions, and that pLMW-DOM (or total DOC) concentrations increase under anoxic conditions because of a change in the relative importance of these two general remineralization pathways.

Regardless of which of these end-member situations exists (or more likely, that there is some continuum of the two), these results suggest that changes in sediment redox conditions alter the pathways of sediment DOM remineralization, leading to the buildup of refractory low molecular weight pLMW-DOM ($\approx [DOC]_t$) under anoxic conditions. It also seems likely that these differences in k or α might actually lead to β_B being less than β_N (and β_R then being less than 1), consistent with the $[DOC]_{unc}$ calculations in Table 2. These phenomena may also play a role in how sediment redox conditions possibly affect overall sediment carbon remineralization and preservation (e.g. see discussions in Aller, 1994; Cowie et al., 1995; Hedges et al., 1999). In the latter case this could be particularly important if pore water DOM is indeed an important intermediate in sediment carbon preservation (see recent discussions in Mayer, 1994; Hedges and Keil, 1995; Burdige et al., 1999). However more work will be needed to understand how (or even if) this occurs.

4.2. Differences in DOM elemental (C/N) ratios

In examining C/N_{pDOM} values at sites M3 and S3 Burdige and Zheng (1998) observed that DOM at site S3 is generally enriched in nitrogen as compared to that at site M3. These data are plotted in Fig. 3 along with more recent data from these sites. Assuming that the data from site S3 should fall along the site M3 trend line shown here, these results clearly show an apparent nitrogen enrichment in site S3 pore water DOM, given its relatively low concentrations.

To explain these data Burdige and Zheng (1998) suggested that the occurrence of benthic macrofauna might lead to the presence (production) of specific low C/N ratio organic compounds such as urea ($C/N=0.5$); also see similar discussions in Lomstein et al., 1989). However the results discussed in Section 3.5 (Table 3) suggest that urea is not a significant component of the DOM pool in these Chesapeake Bay sediment pore waters.

In addition to macrofaunal sources of low C/N ratio pore water DOM compounds, another possibility not originally considered by Burdige and Zheng (1998) is

bacterial sources. Bacteria have C/N ratios that range from ~ 3 to 5 (Saunders et al., 1983; Fenchel et al., 1998) and grazing of bacteria by higher organisms (Kemp, 1990; Lee, 1992) could lead to the production of low C/N ratio DOM in bioturbated/bioirrigated sediments. The absence of such bacterial grazing in anoxic sediments such as those at site M3 would then explain the observed differences in C/N_{pDOM} values among the two sites (see discussions in Lee, 1992, for further details).

To examine such possible bacterial sources of DOM to site S3 sediment pore waters a simple mass balance model was constructed. In this model pore water DOM at the site was assumed to have three potential components: a bottom water component, input to the sediments by macrofaunal irrigation and/or bioturbation; a sediment “remineralization” component that has a relatively “high” C/N ratio (similar to that of site M3 pore waters; $C/N_H = 13–18$); a “low” C/N ratio component, consistent with either a urea or bacterial source (i.e. $C/N_L = 0.5–6$).

The results of these calculations are shown in Fig. 8. Consistent with the observed urea concentrations in site S3 sediment pore waters (Table 3), these results further show that urea alone cannot likely explain the observed C/N_{pDOM} values in site S3 sediment pore waters. At the

same time model results could explain the site S3 C/N_{pDOM} values if $\sim 2–10\%$ of the pore water DOM at this site was material with a C/N ratio consistent with a bacterial source. Since much of this low C/N ratio bacterial material would likely be composed of amino acids, comparative studies of amino acids in strictly anoxic versus mixed redox sediments might prove useful in further examining this suggestion. Similarly, if some significant fraction of the pore water DOM at site S3 is indeed derived from such bacterial sources, it might then also explain why the relative concentrations of DOC_{amide} in Table 2 are slightly higher at site S3 than they are at site M3.

4.3. Relationship between the composition of pore water DOM and DOM benthic fluxes

At both sites S3 and M3 there is an apparent uncoupling between the chemical composition of the DOM that escapes the sediments as a benthic flux and that of the DOM in the pore waters. The causes of this appear to differ slightly at each site, further indicating the effects of sediment redox conditions on sediment DOM cycling.

As discussed in Section 3.4, DOM accumulating in these sediment pore waters is carbon-rich ($C/N_{pDOM} > 10$)

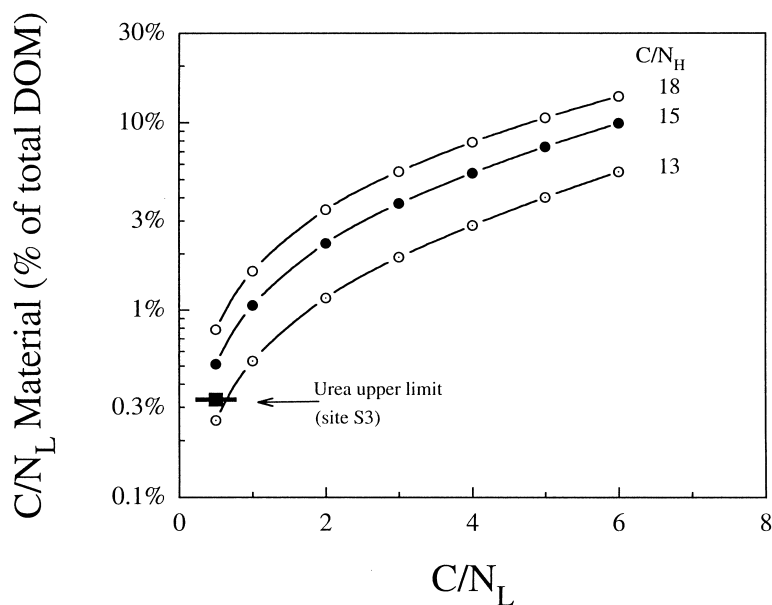


Fig. 8. Results of a three component pore water DOM mixing model for site S3 sediment pore waters. Shown here are the relative concentration of the low C/N ratio DOM component (i.e. urea or bacterial DOM) as a function of its C/N ratio, for three different values of the C/N ratio of the high C/N ratio component (i.e. site M3-like DOM). As discussed in the text, bottom water DOM is the third component in this model. In the results shown here the total pore water and bottom water DOC concentrations and DOM C/N ratios are fixed, and mass balance equations are then used to determine the curves shown here for the differing values of the C/N ratio of the site M3-like DOM component. For the results shown here it was assumed that bulk pore water had a DOC concentration of 330 μM and a DOM C/N ratio of 10.9 (based on results shown in Fig. 3). The analogous bottom water values were 170 μM and 10.4 (D. Burdige, unpub. data). Also shown here is the upper limit for the relative concentration of urea ($C/N = 0.5$) in site S3 pore waters, taken from Table 3.

relative to the more N-rich DOM that either escapes the sediments as a benthic flux (generally ~ 4 – 6 at site M3, and ~ 2 – 4 at site S3). At the same time, there is evidence of benthic fluxes of both humic-like and tryptophan, protein-like fluorescent material at both sites, in spite of the lack of strong evidence for the occurrence of tryptophan-like fluorescent material in the bulk pore waters (Burdige et al., 2001).

Similar trends in DOM elemental ratios have been observed in other sediments (Blackburn et al., 1996; Landén et al., in press), and were explained as being due to 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 explanation is consistent with the comparison of measured versus calculated DOC and DON benthic fluxes at these sites (particularly site M3; see Fig. 6) and with the fluorescence data discussed above, since several lines of evidence suggest that tryptophan-like fluorescence can be considered a tracer for relatively “fresh” (or “reactive”) dissolved proteinaceous-like material (Lakowicz, 1983; Mayer et al., 1999; Burdige et al., 2001).

All of these observations also further reinforce discussions in Burdige and Gardner (1998) regarding the

spatial separation in sediments between hydrolytic or oxidative processes that produce the initial high molecular weight intermediates of sediment POM remineralization, and processes responsible for the production of refractory DOM in sediment pore waters (i.e. pLMW-DOM). Building on these observations, Burdige et al. (2001) modified an advection/diffusion/reaction model for dissolved amino acid cycling in sediments (Burdige and Martens, 1990) to begin to quantify the cycling of the different DOM pools defined in the PWSR model (also see Burdige, 2001, for a discussion of this model). This model was then used to produce pore water representative profiles of these DOM pools, and model results were also linked to observed sediment distributions of pore water DOC and DOM fluorescence.

Model-derived profiles were similar in shape to those seen for sediment pore water profiles of total DOC as well humic-like and protein-like fluorescent DOM (see Fig. 9). In this analysis it was assumed that humic-like fluorescence is a tracer for the refractory pLMW-DOM, while protein-like, tryptophan fluorescence represents a component of the reactive HMW-DOM pool. Model results also demonstrated that net production rates of HMW-DOM and pLMW-DOM have different depth

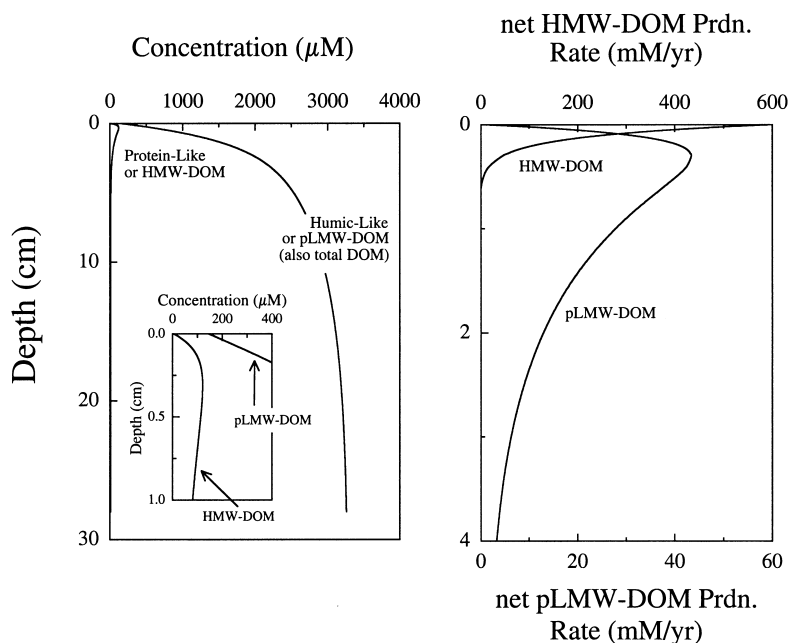


Fig. 9. The results of an advection/diffusion/reaction model for HMW-DOM and pLMW-DOM cycling in sediments. The model is described in Burdige et al. (in press) along with the rate parameters used in these calculations (also see Burdige, 2001, for a description of the model). [Left panel] Pore water profiles for protein-like (or HMW-) DOM and humic-like (or pLMW-) DOM predicted by the model equations. Shown as an insert are the same curves on an expanded scale, indicating the similarity in concentration gradients for both types of DOM near the sediment-water interface. [Right panel] Net production rates of HMW-DOM and pLMW-DOM versus depth in these model calculations. Note the expanded depth scale in this figure and the different rate scales for each type of DOM.

distributions. Net production of HMW-DOM was highest at the sediment-water interface and decreased very rapidly with depth. In contrast, net production rates of pLMW-DOM, while lower than those of HMW-DOM, initially increased with sediment depth, reached a maximum just below the sediment surface and then decreased slowly with depth. Interestingly, in spite of the fact that concentrations of HMW-DOM were significantly lower than those of pLMW-DOM, their pore water gradients near the sediment surface were similar in magnitude (see the insert to Fig. 9). In sediments where benthic fluxes are controlled by molecular diffusion, this would then lead to fluxes of these two types of DOM that are similar in magnitude.

Relating these model results back to our pore water data, they show that if production and consumption rates of different DOM fractions are balanced in such a way as to lead to low concentrations of HMW-DOM (or protein-like tryptophan fluorescence) as compared to pLMW-DOM (or humic-like fluorescence), one could have difficulty observing protein-like fluorescent DOM in pore waters, in spite of an observed benthic flux of this material (as is seen at Chesapeake Bay site M3). Furthermore, this spatial separation of HMW-DOM and pLMW-DOM net remineralization rates can also explain the uncoupling between DOM that effluxes from sediments and that which accumulates in pore waters if one assumes that the *C/N* ratio of humic-like, pLMW-DOM is greater (i.e. more carbon-rich) than that of this reactive HMW-DOM (which does not appear to be an unreasonable assumption).

The spatial separation of sediment remineralization processes predicted by these model results explains many of the site M3 results and, to some extent, explains some of the results at site S3. At the same time however, the very low *C/N* ratios (~2–4) of site S3 DOM benthic fluxes requires additional examination. Such low ratios could occur if sediment macrofauna excrete low *C/N* compounds such as urea directly into the overlying bottom waters bypassing the pore water DOM pool, or if production of these compounds occurs in such a way that they are input into the waters these organisms use to irrigate their burrows, again bypassing the pore waters. The results in Tables 3 and 4 provide some evidence for such processes in that urea as percentage of either the pore water DOC or DON pools (>0.1 and ~2% respectively) is lower than its similar percentage of either the DOC and DON benthic fluxes (~6 and ~10–50% respectively). However, the results in Table 4 also suggest that the importance of benthic urea fluxes in explaining these low *C/N* ratios are equivocal (i.e. compare the *C/N* ratios for the benthic flux of total DOM versus non-urea DOM). Thus as described above, bacterial sources of DOM (i.e. as a result of bacterial grazing by higher organisms) may also play some role in explaining low *C/N* ratios of the DOM escaping site S3

sediments as a benthic flux. Again, however, such inputs of bacterially-derived DOM must at least partially bypass the sediment pore waters to explain these observations.

5. Closing thoughts

It goes without saying that this summary leads to as many new questions for future research as it does provide answers to the questions posed here. The fact that much of the DOM in sediment pore waters appears to be refractory and is uncharacterized to date (at least in terms of known biochemicals) suggests that “structural” approaches, similar to those used in water column DOM studies, may prove useful here as well.

Implicit in much of the discussion here is that the *C/N* ratio of pore water DOM is not necessarily a good indicator of its reactivity (also see Kristensen and Blackburn, 1987, for similar discussions regarding sediment POM reactivity and its *C/N* ratio). Thus, further studies linking DOM composition and reactivity will clearly be required to further examine such problems. It is also interesting to note that many of these questions could be addressed in carefully conducted sediment incubation experiments (e.g. Burdige, 1991a,b; Pease et al., 1999).

Another observation that comes out of this work is the fact that studies at site N3 in the northern Bay have provided us with equivocal results on the effects of terrestrial sediment POM sources on sediment DOM composition and cycling. Since both terrestrial and marine POM sources play roles in sediment DOM cycling in all estuarine sediments (as well as in coastal and continental margin sediments in general), studies of DOM cycling in such an “end-member” sediments would be of great use.

Comparative analyses of data from sites S3 and M3 indicate that differences in the physical and biogeochemical processes in anoxic vs. bioturbated/bioirrigated sediments lead to distinct differences in the composition of the pore water DOM found in these sediments. In part this may result from the presence of macrofauna in the sediments, although it also appears that differences in sediment redox conditions (e.g. strictly anoxic vs. mixed redox conditions) are also important. As discussed above, DOM compounds are important intermediates in sediment carbon remineralization and perhaps sediment carbon preservation as well. Therefore, these observations suggest that differences in DOM composition and reactivity due to differences in sediment redox conditions might play a role in how sediment redox conditions affect overall sediment carbon preservation in these different sediment types (e.g. see discussions in Aller, 1994; Kristensen et al., 1995; Hulthe et al., 1998; Hedges et al., 1999). Again,

however, future studies will be needed to examine how (or even if) this occurs.

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Appendix. Derivation of the inequalities in the sediment model

If $\beta_R \gamma_R \leq 1$ then

$$\beta_N \gamma_N \geq \beta_B \gamma_B \quad (\text{A1})$$

and

$$\beta_N \gamma_N - \beta_B \gamma_B \geq 0 \quad (\text{A2})$$

In the first case discussed in the text it is assumed that $\alpha_R = 1$, or $\alpha_B = \alpha_N$. Multiplying Eq. (A1) by -1 switches the inequality sign, and then adding these α 's to both sides of the equation leads to $A_B \geq A_N$ or

$$A_R \geq 1 \quad (\text{A3})$$

Since $A_R/k_R < 1$ [see Eq. (7) in the text] this implies that

$$k_R > A_R \quad (\text{A4})$$

and combining Eqs. (A3) and (A4) leads to $k_R > 1$.

In the second case discussed in the text I assume that $k_R = 1$. Combining this with Eq. (A4) implies that $A_R < 1$ or

$$A_B < A_N \quad (\text{A5})$$

This can be re-expressed as

$$\alpha_B - \beta_B \gamma_B < \alpha_N - \beta_N \gamma_N \quad (\text{A6})$$

or

$$\alpha_N - \alpha_B > \beta_N \gamma_N - \beta_B \gamma_B \quad (\text{A7})$$

Combining Eq. (A7) with Eq. (A2) implies that $\alpha_N - \alpha_B > 0$ or,

$$\alpha_N > \alpha_B \quad (\text{A8})$$

and $\alpha_R < 1$.

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